Towards an artificial Leaf

–

Development of immobilizable Photocatalysts

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Für meine Eltern Beate und Hans
Modern society is confronted with two major challenges: energy supply and prevention of environmental pollution. The development of a novel energetic scenario based on the direct conversion of solar energy to storable solar fuels is one promising means of providing for long-term, ecologically friendly energy supply. Based on the use of two renewable and unarguably the largest exploitable resources, water and sunlight, the light-driven water splitting indeed generates the environmentally benign oxygen gas and hydrogen, a carbon-free fuel with the highest energy output relative to molecular weight. Inspired by natural photosynthesis and the architecture of dye-sensitized solar cells (DSSCs), dye-sensitized photoelectrochemical cells (DSPECs) are now being designed and tested as auspicious approaches to generate hydrogen via solar-driven water splitting. In these devices, metal oxide semiconductors such as NiO are functionalized with molecular sensitizers in association with hydrogen evolving catalysts (HECs). Especially, intramolecular photocatalysts are interesting candidates within this context, since they comprise all necessary modules in a single photochemical molecular device (PMD). The photocenter and catalytic unit are chemically connected by a bridging ligand. This intramolecular approach and modular composition allows one-step integration into DSPECs and at the same time specific analyses and separate tuning of the different subunits.

The main focus of this thesis was the optimization of an immobilizable PMD for visible light-induced hydrogen production based on a ruthenium-polypyridyl-platinum sensitizer-catalyst dyad. The PMD is equipped with potent phosphonate anchoring groups at its peripheral bipyridine (bpy) ligands to guarantee efficient binding on semiconducting metal oxides. Its general eligibility as hydrogen evolving photocatalyst was examined by homogenous catalysis experiments in the master thesis of the PhD candidate. In a first step of this work the hydrolysis and immobilization was optimized towards a facile processability of the PMD. Preliminary measurements in DSPEC setup lead to visible light-induced photocurrents, suggesting that hydrogen production in such a system is possible.

To optimize the photocatalyst with regard to long charge-separated lifetimes and improved photon absorption characteristics a modular synthesis concept for elongated bipyridines was established. The distance between anchoring group and bpy core was increased by introduction of phenylene and triazole building blocks, generated by modern transition metal catalyzed coupling reactions. The distance adjustability, which was monitored by X-ray crystallography, should lead to improved cell efficiency, as it will allow tuning of charge carrier recombination and dye aggregation. Application of the new bpy derivatives in ruthenium(II)- and rhenium(I)-complexes revealed enhanced performance of the corresponding chromophores with regard to their solar light-harvesting ability. Resonance Raman
experiments supported by theoretical calculations were conducted to further explore the effects of triazole and phenylene substitution.

Additional investigation of the luminescence properties of this series of complexes lead to a surprising observation. Contrary to conventional rutheniumpolypyridyl-complexes the triazole containing compounds showed a solvent dependent light switch effect. Certain water content in solution quenches the luminescence of these complexes. The light-switch behavior could clearly be correlated to the presence and number of triazole subunits. Theoretical studies helped finding possible explanations concerning the origin of the observed light-switch effect. Metal complexes incorporating triazole subunits have a wide scope of applications since they can connect important function-owning molecular building blocks and are easy to generate via CLICK chemistry. The presented findings are highly relevant because they suggest a major restriction concerning the utilization of such complexes in DSPECs with aqueous electrolytes. Opening additional deactivation pathways by triazole introduction might reduce charge separated lifetimes and therewith diminish catalytic turnover.

The combined research efforts of this thesis will further promote the targeted design of so-called artificial leafs for solar fuel production.
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1.) Introduction

The continuing revolution of civilization is linked to the history of energy transitions - from wood to coal and from coal to oil as well as natural gas. As economies develop and become more complex, the energy demand increases exceedingly. Therefore it is not surprising that Nobel prize laureate Richard E. Smalley and others list energy at the top of critical problems we are confronted with in this century.\textsuperscript{1,2} Energy is the key for the prosperity of any society. Other problems like water and food supply, quality of environment and poverty directly or indirectly depend on energy. Today the global energy needs are overwhelmingly dependent on fossil fuels, which account for about 86% of the used energy (Figure 1).\textsuperscript{3}

![Energy Consumption Chart](image)

**Figure 1: Global energy consumption 2015.**\textsuperscript{3}

However, the fossil resources are dwindling. Both oil and natural gas will be used up in the foreseeable future.\textsuperscript{4} The two so called “oil shocks” triggered by an OAPEC (Organization of Arab Petroleum Exporting Countries) oil embargo in response to the american and european involvement in the Yom Kippur war in 1973 and the decrease of oil output in the wake of the Iranian revolution in 1979, demonstrated the effects of an oil supply shortfall on modern society. As short-run consequences of the gasoline deficit, the prices per barrel oil quadrupled in 1973 or doubled in 1979, respectively, with high impact on global politics and the societies normal course of life (cf. Figure 2).\textsuperscript{5}
Introduction

Figure 2: Aftermath of the “oil shocks”: Line at a gas station in Maryland, United States, June 15, 1979. Reprinted from the U.S. Library of Congress (digital ID ppmsca.03433).

Rich nations or regions consume 10-20-fold more energy per capita compared to poor ones.\(^4\) It is unfeasible to bring over three billion people, belonging to the lower half of the economic ladder of human civilization, up to a modern way of life without low-cost and abundant energy.\(^{1}\) Although fossil fuels are cheap the emission of CO\(_2\) as a result of using them has been discussed as the dominating factor behind global warming. The vast upswing in temperature during the 20\(^{th}\) century has been accompanied by a rise of CO\(_2\) level in the atmosphere (Figure 3).

![Temperature Departure from 1961 to 1990 Average Temperature Departure from 1961 to 1990 Average K](image)

**Figure 3:** Global warming over the past millennium, by temperature and CO\(_2\) level.\(^1\) Reprinted with permission from ref. 1. Copyright 2005 Cambridge University Press.

A society based on polluting and depleted fossil energy is impossible in a longer time perspective. Fortunately, the 21\(^{st}\) century already undergoes the next major transition in energy production - away from fossil towards renewable sources. Even with respect to the enormous global energy consumption, there is no lack of renewable energy as supplies are continually replenished through natural processes. The largest and most abundant renewable resource is solar energy. Wind, hydropower and biomass are just secondary sources of energy provided by the sun. In one hour similar amounts of solar energy are falling on earth as the annual energy consumption of mankind (Figure 4), in other words, harvesting less than 0.02% of this solar energy would satisfy our present needs.\(^6\)^7
Figure 4: Solar irradiation versus established global energy resources. Fossil fuels are expressed with regard to their total reserves while renewable energies to their yearly potential.\textsuperscript{9}

This tremendous potential, by far, has not been yet fully exploited. In 2014 only one percent of the world electricity demand was covered by solar power.\textsuperscript{9}

Solar energy is available in almost any location but obviously there is more sunshine in some places and times of the year than in others. To build an energy dependent society on the pervasive, but not always flowing, solar energy we have to store this energy efficiently to provide it on demand. Current photovoltaic approaches based on inorganic semiconductor materials are costly and have a theoretical efficiency limit of 33.7%.\textsuperscript{10} We are used to living in a world where energy is cheap. But storage of the produced electricity again leads to increasing costs and to a significant loss of energy upon its conversion into potential, kinetic or chemical energy.\textsuperscript{11}

The state of the art storage techniques and mediums, including batteries, have modest capacities compared to liquid or gaseous fuels (Table 1).\textsuperscript{11,12}

<table>
<thead>
<tr>
<th>Storage method/medium</th>
<th>Energy density [MJ/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressed air</td>
<td>0.5 at 300 atm</td>
</tr>
<tr>
<td>Flywheels</td>
<td>0.5</td>
</tr>
<tr>
<td>Supercapacitors</td>
<td>0.01</td>
</tr>
<tr>
<td>Pumped water</td>
<td>0.001 at 100m</td>
</tr>
<tr>
<td>Batteries</td>
<td>0.1-0.5</td>
</tr>
<tr>
<td>Oil</td>
<td>40</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>140</td>
</tr>
</tbody>
</table>

Table 1: Approximate energy densities of different storage techniques and media.\textsuperscript{11,12}

A promising approach to overcome these drawbacks is the direct conversion of solar to chemical energy by energy storage in chemical bonds. The avoidance of multiple energy conversion steps will minimize energy loss and thereby reduce renewable energy costs in the long run. Hydrogen is considered as one of the most auspicious so-called “solar fuels” because it has a huge energy density (cf. Table1) and can be made from an inexhaustible, low-cost and widely available raw material – water. The release of chemical energy from hydrogen again leads to water as a waste product without emission of polluting greenhouse gases.
The research in this field is often named “artificial photosynthesis”, “solar-hydrogen research” or “the artificial leaf”. A Web of Science search under the key words “solar fuel hydrogen” proofs that this issue has become a major topic in the last decade. From 1990 to 2005 there were only few publications per year. Then, the number of publications under respective key words has risen rapidly and continuously and will likely continue to do so (Figure 5).

![Graph showing the increase in publications from 1990 to 2015.](image)

*Figure 5: Development of scientific research addressing hydrogen as a solar fuel.*
2.) Theoretical Fundamentals

2.1.) Natural photosynthesis

Nature is a great source of inspiration for the scientific community, especially when it comes to solar-to-chemical energy conversion. Natural photosynthesis (NPS) is the origin of all of our food and most of our energy resources. There is suggestive evidence that the evolution of photosynthesis started early in earth's history, approximately 3.2-3.5 billion years ago. Today, bacteria, algae, and plants use light to extract electrons from water, whereby molecular oxygen is liberated. By most organisms, energy-rich carbohydrates are subsequently produced by the photogenerated electrons from atmospheric carbon dioxide. To fuel this transformation known as the CALVIN cycle, the light reaction of photosynthesis in plants generates the organic hydride carrier NADPH$_2^+$.

\[
2 \text{H}_2\text{O} + 2 \text{NADP}^+ + 4 \text{photons} \rightarrow 2 \text{O}_2 + 2 \text{NADPH}_2^+
\]

This relatively simple chemical redox-reaction is realized in a fascinating biologic machinery. It consists of two large protein complexes, the photosystem I (PS I) and photosystem II (PS II), assisted by various redox cofactors and located in the thylakoid membrane of the chloroplast, which guarantees a highly organized composition. The photosynthetic process in this system, also known as “Z-scheme” according to the shape of the energy diagram, is depicted in Figure 6.

**Figure 6: Schematic representation of the photosynthetic chain in the NPS**

It can be divided in three main steps: (i) light absorption and local ultrafast charge separation in the photosystems I/II; (ii) further spatial charge separation by an electron transfer cascade between redox cofactors; (iii) multielectron catalytic oxidation and reduction processes at the
Theoretical Fundamentals

oxygen evolving complex (OEC) of PS II and the ferredoxin-NADP\(^+\) reductase (FNR) of PS I. First the reaction center of PS II a tetrameric chlorophyll molecule (phorphyryne derivatives with magnesium as central metal ion) P680 \((\lambda_{\text{max}} = 680 \text{ nm})\) is photoexcited with the help of nearby antenna pigments to yield P680\(^*\). The latter pumps electrons in multiple steps over the primary electron acceptor phoephitin (Pheo, a chlorophyll molecule void of the Mg center) and several plastoquinones \((Q_{A,B,C})\) to the cytochrome-b\(_6\f\)-complex (Cytb\(_6\f\)), incorporating cytochrome f, two cytochrome b\(_6\) molecules and an iron sulphur protein. The resulting oxidized P680\(^+\) has a highly oxidizing potential close to 1.2 V vs. NHE and drives the tyrosine (Tyr)-mediated water oxidation \((E^{0}_{\text{H}_{2}O/\text{H}_{2}O^{2+}} = 0.81\text{V vs. NHE, at pH=7})\) at the OEC, a multiple reducible CaMn\(_4\) cluster.\(^7,16\) This complex sequentially extracts four electrons from water and evolves oxygen and four protons. These electrons replenish the photooxidized P680\(^+\) by single electron transfer steps via Tyr. Simultaneously, pigment P700 (chlorophyll molecules with \(\lambda_{\text{max}} = 700 \text{ nm}\)) is excited by absorption of additional photon energy in a similar manner as P680 and passes an electron to \(A_0\) (a chlorophyll-a molecule) the primary electron acceptor of PS I. Via several other intermediates, including iron sulphur proteins (FeS) and the redox shuttle ferredoxin (Fd), the electron is ultimately transferred to the FNR, where formation of nature’s form of hydrogen, NADPH\(_2\)\(^+\) takes place under sequestration of two protons. P700\(^+\) becomes reoxidized by a copper(II) complex, the plastocyanine (Pc) which has previously received an electron from Cytb\(_6\f\) and therewith through the redox gradient originating in PS II.\(^16\) In summary, the highly organized structure of the photosynthetic apparatus pre-defines a directed electron transfer. The importance of rapid forward electron transfer between the single components to suppress charge recombination is one principle to be learned from nature, when we derive mimicking artificial concepts. The primary reactions in natural photosynthesis have close to 100% quantum efficiency (i.e. one quantum of light leads to one electron). However, due to losses at all transfer steps, the energy-conversion efficiency of most agricultural crops is less than 1%.\(^16\) Artificial photosynthesis, emulating nature by using much simpler man-made materials might potentially yield more controlled technologies for the solar-to-chemical-energy-conversion process.

2.2.) Artificial photosynthesis

Already over one century ago, the production of fuels by non-biological photochemical reactions (artificial photosynthesis) was anticipated by Giacomo Ciamician, an important pioneer of photochemistry research.\(^17\) Most studies on artificial photosynthesis are currently concentrated on using sunlight to split water into molecular hydrogen and molecular oxygen.\(^18\)

\[
2 \text{H}_2\text{O} + 4 \text{photons} \rightarrow 2 \text{O}_2 + 2 \text{H}_2
\]
Direct dissociation of water by solar irradiation is not possible because the electronic absorption spectrum of water and the emission spectrum of the sun do not overlap.\textsuperscript{19} Hence, photosensitizers qualified to absorb sunlight and use it for the desired reaction must be employed. Currently, research is focused on the independent development of the two half-reactions, by combination of such a photosensitizer with a suitable catalyst (water oxidation catalyst WOC or hydrogen evolving catalyst HEC) for either the oxidation or the reduction of water. Keeping natures principles for an efficient charge separation and unidirectional electron transfer in mind, the electronic interplay between sensitizer and respective catalyst should be mediated by additional electron relays. Furthermore, sacrificial electron acceptors or donors are needed to regenerate the chromophore. In principle these sacrificial agents may also be viewed as quenchers of the excited state to increase the efficiency of the electron transfer by hindering possible charge recombination. The main components of artificial photosynthetic systems, their function and equivalents in nature are summarized in Table 2 and displayed in Figure 7.

<table>
<thead>
<tr>
<th>component</th>
<th>function</th>
<th>NPS equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>photosensitizer (PS)</td>
<td>light absorption,</td>
<td>photosystems I/II</td>
</tr>
<tr>
<td></td>
<td>directional energy propagation</td>
<td></td>
</tr>
<tr>
<td>electron relay (R)</td>
<td>irreversible charge separation,</td>
<td>Tyr, Fd etc.</td>
</tr>
<tr>
<td></td>
<td>electron transfer between PS and C</td>
<td></td>
</tr>
<tr>
<td>catalyst (WOC/HEC)</td>
<td>center for redox reaction,</td>
<td>OEC, FNR</td>
</tr>
<tr>
<td></td>
<td>substrate binding, product release</td>
<td></td>
</tr>
<tr>
<td>sacrificial substrate,</td>
<td>regeneration of the photosensitizer,</td>
<td>water</td>
</tr>
<tr>
<td>donor (D) acceptor (A)</td>
<td>excited state quencher</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Important components of photosynthetic systems according to functionality
Figure 7: Artificial photosynthesis for light-driven water splitting.

In general there are two main approaches towards artificial light-driven water splitting: (i) homogenous and (ii) heterogenous systems. Most likely the homogenous systems in which the appropriate components for water reduction or oxidation are dissolved in a solvent will be less useful than heterogenous ones for practical applications. But they offer the opportunity to probe specific properties of photosensitizer, relay and catalyst and therefore to get information which may also be useful to improve heterogenous systems. Molecule-based photosystems have been extensively investigated, since the late 1970s. Since that time excellent studies have covered the field of intermolecular, homogenous water reduction or oxidation catalysis in particular. In these multicomponent systems each task: light absorption, electron transfer and catalytic turnover is fulfilled by non-covalently bound separate molecular units (PS, R, WOC or HEC). According to literature, intermolecular systems are expected to be disadvantageous because they are naturally dependent on diffusion and collision processes, which might limit the efficiency of the essential photoelectron transfer. Therefore continuous efforts have been made to develop organized systems (cf. Figure 8). In such intramolecular arrays a bridging unit (or in the case of coordination compounds a bridging ligand, BL) adopts the role of the electron relay and at the same time stably connects the light-harvesting and catalytic unit. Intramolecular photocatalysts are anticipated to become much higher in the overall catalytic efficiency than the corresponding multi-component systems.
Figure 8: Schematic comparison of inter- and intramolecular systems for water reduction.

Within this context a review on the studies of intramolecular systems coupling Ru-polypyrrolidyl chromophores with Pt-, Rh- or Pd-based hydrogen evolving catalysts will be presented in chapter 3.1.) Artificial Photosynthesis by homogenous catalysis: Tuning photochemical molecular devices for hydrogen evolution of this thesis. For future commercial water splitting devices it is now believed that photoactivation of solid-state semiconductor materials, according to the concept of dye sensitized solar cells (DSSCs, cf. chapter 2.3.) Solar Cells), is an auspicious approach. Therefore, systems optimized in homogenous catalysis experiments are immobilized on electrodes by incorporated anchoring groups to yield so-called dye sensitized photoelectrochemical cells (DSPECs) for heterogenous catalysis. This should lead to a similarly organized composition as in nature, since the absorption of light and transport of charge carriers are spatially separated by fixation of the photosynthetic devices on surfaces (cf. Figure 9). Anchoring group elongation might even further suppress charge recombination (cf. chapter 2.3.4.) Anchoring groups). The heterogenous approach has benefits for industrial processes or commercial applications since the immobilized systems can be separated from the reaction mixture in a straightforward manner. In this way expensive photocatalysts can be easily recovered. One additional striking advantage of DSPECs in comparison to homogenous systems is that the sacrificial electron donor or acceptor, required for chromophore regeneration, is not necessary any more. The electrodes in DSPECs restore PS1/PS2 and water itself ensures electron supply. For homogenous water reduction commonly used sacrificial donors are tertiary amines like triethylamine (TEA) or triethanolamine (TEOA). The main drawback concerning TEA and TEOA is their degradation pathway. Upon oxidation a positively charged aminyl radical is formed, which could in principle react with any reduced species in the homogenous system and therefore lead to counter-productive back electron transfer. Therefore sacrificial agents limit the sustainability of the catalytic process, either by side reactions or simply once they are used up because they need to be employed stoichiometrically. This shortcoming is eliminated in DSPECs.
2.3.) Solar Cells

The general functionality of a photovoltaic or solar cell (PV) is based on a charge separated state which is generated by the absorption of sunlight. If this state is sufficiently long-living it can be utilized to produce electrical from solar energy. Besides the conventional solar cells adapted from highly pure semiconducting materials as the silicon p-n-junction cells, there are multiple other approaches like hybrid organic-inorganic-perovskite solar cells, quantum dot solar cells, conducting polymer solar cells or dye-sensitized solar cells (DSSCs). In this work I will focus on the latter because the configuration of DSSCs is the bases for the construction of dye sensitized photoelectrochemical cells (DSPECs) for water splitting. DSSCs are basically constructed on a dyad model which separates the responsibilities of light harvesting and charge carrier transport. This is in contrast to conventional cells where the semiconductor (SC) takes both duties. Instead of smooth surfaces, mesoporous membrane type semiconductor films with huge internal interfaces and without strict demands on the purity.
of the material are employed in DSSCs.\textsuperscript{33,34} Low production costs of the materials are a convincing advantage of the DSSC systems. Others are ease of fabrication, light weight and flexibility in the design.\textsuperscript{34} Efficient light absorption is performed by a monolayer of sensitziers attached to these films. The roughness of the SC should be high to adsorb a large number of dyes. The requirements of a photosensitizer are (i) intense absorption in the visible region, (ii) photo- and electrochemical stability and (iii) strong adsorption on and (iv) efficient charge injection in the SC. Many different compounds have been investigated to fulfill these demands, such as polymeric films and organic dyes derived from natural products like porphyrine, phtalocyanine and coumarine. But transition metal complexes have been the best photosensitizers so far.\textsuperscript{33} The energies of their MLCT absorption can be systematically tuned by modification of their anchoring and ancillary ligands.

2.3.1. n-Type DSSCs.

DSSCs were drastically improved by O’Reagen and Grätzel in 1991.\textsuperscript{35} The Grätzel-cell is a n-type DSSC utilizing TiO\textsubscript{2} as a wide-band-gap SC and a ruthenium complex sensitizer. Titania is very cheap and widely used as pigment. Ruthenium(II) polypyrindyl complexes have shown outstanding solar-to-electricity power conversion efficiency (PCE), due to their appropriate redox, spectroscopic, and excited-state properties.\textsuperscript{33} The highest certified PCE of a ruthenium(II)-based DSSC to date is 11.9\% under full sun illumination.\textsuperscript{36,37} A schematic presentation of the working principle of a typical n-Type DSSC and an example based on the industry standard dye N719 is shown in Figure 10. It consists of three major components: (i) a working electrode (typically TiO\textsubscript{2} deposited on a transparent conducting oxide like FTO) onto which sensitizer molecules are immobilized. (ii) a redox electrolyte like the commonly used I\textsubscript{3} /I\textsubscript{2} couple which closes the electron flux cycle by contact with (iii) a counter electrode, often coated with platinum particles. Upon solar photoexcitation of the dye (PS1) an electron is injected to the conduction band (CB) of the TiO\textsubscript{2}. Regeneration of the oxidized sensitizer is secured by the reduced component of the redox mediator (Red). The injected electron in the CB migrates through an external circuit to the counter electrode where the regenerative cycle is completed by electron transfer to reduce the oxidized component (Ox) of the redox mediator. The regeneration of the sensitizer must be fast to avoid electron recombination processes. To guarantee a down-hill process from an energy point of view, a functioning device must employ a stable photosensitizer with a LUMO level more negative than the CB edge of the n-type SC to facilitate electron injection from the excited state. On the other hand, the HOMO level of the sensitizer should be positive compared to the redox potential of the mediator (cf. Figure 10).
Figure 10: Working principle of a n-type DSSCs (top). PS1: photosensitizer 1; Red/Ox: redox mediator. Standard dye N719 as exemplary photosensitizer (bottom).

2.3.2) p-Type and tandem-DSSCs

As presented in Figure 11 the p-type DSSCs operate in an inverse fashion compared to classical n-type DSSCs.

Figure 11: Working principle of a p-type DSSCs (top). PS2: photosensitizer 2; Red/Ox: redox mediator. A Ru photosensitizer presented by Odobel and coworkers as example (bottom).
After solar photoexcitation, the excited state of the dye (PS2) injects a hole into the valence band (VB) of a p-type SC (or, in other words, an electron in the VB of the SC is transferred to the HOMO level of the dye). The reduced sensitizer PS2- reduces in turn the redox couple which completes the circuit by passing the electron to the counter electrode. The specific electronic properties of the ideal sensitizer for p-SCs significantly differ from those designed for conventional Grätzel cells. In the latter case, the dye must be a strong reducer in its excited state to inject an electron in the conduction band of the n-SC. On the contrary the excited dye in p-type DSSCs must be an oxidant for the VB of the p-SC (cf. Figure 11). Actually, the electronic requirements of the sensitizers for p-SCs are just the opposite of those for n-SCs.\textsuperscript{36} Therefore it might be surprising that in both cases ruthenium(II) polypyridyl complexes are applied. But as mentioned before their energy levels (LUMO, HOMO) can be easily fine-tuned by specific modification of their molecular structures. Because of its convenient band structure transparent NiO is the most typically used SC in p-type cells. But as a consequence of its intrinsic characteristics and poor electronic properties,\textsuperscript{39,40} the efficiency of p-type DSSCs did not surpass 1.3% so far.\textsuperscript{41} An auspicious concept to boost the overall efficiency of DSSCs is to make both electrodes of one cell photoactive. The resulting tandem-DSSCs consist of a dye sensitized TiO\textsubscript{2} photoanode, a redox electrolyte and a dye sensitized NiO photocathode. The operating principle is a combination of both n-type and p-type DSSCs (Figure 12). The theoretical efficiency limit is 43%,\textsuperscript{42} which is comparable to leading-edge technology solar cells based on expensive III/V semiconductors.\textsuperscript{43} However, a system presented by Bach et al. (cf. Figure 12) reached only 1.91% because of the limited hole transporting ability of NiO.\textsuperscript{44} An efficient p-type photocathode is the missing key part towards highly productive tandem-DSSCs. A lot future effort has to be addressed to this much younger research field compared to the well-established area of n-type DSSCs.\textsuperscript{45}

Figure 12: Working principles of a tandem-DSSCs (top). PS1 and PS2: photosensitizers; Red/Ox: redox mediator. A tandem-DSSC presented by Bach et al. as example (bottom).\textsuperscript{44}
2.3.3.) DSPECs

To provide the electric energy generated by solar cells on demand it has to be stored. An exceptionally attractive approach is the conversion to energy rich compounds (solar fuels).\(^7\) One possibility is the indirect conversion of solar to storable energy. Here electricity is first produced in a stand-alone photovoltaic cell. Instead of being used directly, the electricity is used by an electrolyzer coupled to the PV to make hydrogen from water.\(^4\) This detour around electricity will always result in the loss of already gained energy since the overall solar-to-hydrogen efficiency in these devices is the product of the efficiencies of both the PV and the electrolyzer. To produce carbon-based fuels from hydrogen an additional process (e.g. Fischer-Tropsch-synthesis) must be coupled to the other conversion steps. Hence, every single process has to be optimized on its own (Figure 13).

Much more auspicious is to integrate the functions of light-harvesting, electrolysis and catalytic processes into a single photocatalyst chemistry cell (PEC). This artificial photosynthesis approach resembles the photosynthesis in nature. The sole role of the device is to harvest the solar energy and convert this into a fuel that can be stored and transported. This direct process has the opportunity to become more efficient as compared to indirect methods. Furthermore it is potentially cheaper because of the avoidance of unnecessary steps and machines.\(^4\)

![Diagram](image)

**Figure 13:** Comparison of indirect and direct processes for solar fuel generation.

In 1972 Fujishima and Honda reported in *Nature* on a PEC which proved the feasibility of water splitting under UV irradiation.\(^{46}\) It consists of a TiO\(_2\) anode coupled with a Pt cathode. The photogenerated electrons in the CB of the anode migrate through an external circuit to the cathode, where water is reduced to form hydrogen. The positive holes in the valence band in turn oxidize water to oxygen. The required potential for water splitting is 1.23 eV. This means that the minimum band gap of a suitable SC has to be at least larger than this value to drive the redox process and to avoid the use of additional undesirable external bias, which can influence band bending in a semiconductor electrode and thereby move the band edges.
Moreover the band gap should be smaller than the one of TiO₂ (3.0 eV) to use the visible region of sunlight.² It has been proven difficult to prepare SC materials with adequate characteristics.⁴⁷ Therefore the concept of dye sensitization is very promising in processing photo-electrodes that exhibit an increased energy conversion by visible light absorption.⁴⁸ The resulting so called dye sensitized photoelectrochemical cells (DSPECs) are based on the working principles and materials of DSSCs and share similar requirements on the dye characteristics. In tandem-DSPECs the redox mediators are replaced by water oxidation (WOC) or hydrogen evolving catalysts (HEC), which are coupled to the photosensitizers and act as electron donors or acceptors, respectively (Figure 14).

![Diagram](image)

Figure 14: Working principle of a tandem-DSPEC (top); PS1 and PS2: photosensitizers; WOC: water oxidation catalyst; HEC: hydrogen evolving catalyst; PEM: proton exchange membrane. A tandem-DSPEC (bottom) presented by Sun et al. (bottom).⁴⁹

Both electrodes are photoactive and the catalyst can either be covalently connected to the PS, co-adsorbed on the SC electrode, or just be dissolved in the electrolyte.⁴⁹⁻⁵² The water oxidation half reaction should be separated from the reduction half reaction by a proton exchange membrane (PEM) to guarantee oxygen free conditions at the HEC and to avoid local pH changes which can cause dye degradation and desorption, thus limiting the stability of the system.⁵³ Similar to DSSCs, n-type or p-type DSPECs are also possible in conjunction with a passive platinum electrode (cf. Figure 15 A&B).
2.3.4.) Anchoring groups

A crucial factor for the durability of DSSCs and DSPECs is the binding of the chromophore or photocatalyst on the semiconductor. The photosensitizer should have anchoring groups to strongly bind the dye onto the SC surface and to facilitate the charge carrier injection into the SC. The most studied class of surface binding groups in DSSCs and DSPECs are carboxylates and phosphonates. Both are utilized on n-type SCs like TiO₂ as well as on p-type SCs like NiO. Most often phosphonate binding groups guarantee a chemically more stable link-up to semiconducting surfaces than carboxylates and other anchoring groups. Its adsorption strength onto metal oxide surfaces was estimated to be approximately 80 times higher than that of the carboxylic acid, and desorption in the presence of water was negligible. Odobel and coworkers compared DSSCs based on differently functionalized [Ru²⁺(bpy)₃]²⁺ on nanocrystalline NiO. Methyl phosphonic acid and carboxylic acid displayed the highest affinity and monolayer coverage for NiO. They demonstrated that higher solar energy conversion efficiencies are obtained in the following order: -CH₂PO₃H₂ >> -COOH >> -catechol >> -CSSH (Figure 16).
A possible reason for the improved photoconversion efficiency might be that the methyl spacer hinders charge carrier annihilation in p-type SCs. In a recently published article on hole injection dynamics of ruthenium polypyridyl complexes into NiO, it was suggested, that the -1 effect of the carboxylic anchoring groups (without linkers between chromophore and NiO) might inhibit hole injection.\(^5\) The CH\(_2\)-spacer in methyl phosphonic acid might prevent such an effect, since the electronic interaction between the bipyridine and anchoring groups is significantly reduced by the CH\(_2\) group between them.\(^6\) Within this context T.J. Meyer et al. presented a structure-property relationship study for [Ru\(^{II}\)(bpy)\(_3\)]\(^{2+}\)-derivatives differing in the quantity of phosphonate functionalized bpy ligands and in the presence or absence of a CH\(_2\)- spacer between the aromatic ring and -PO\(_3\)H\(_2\) anchor. They compared properties of these [Ru\(^{II}\)(bpy)\(_3\)]\(^{2+}\)-derivatives in solution and chemically bound on TiO\(_2\) or ZrO\(_2\), respectively.\(^7\) They found that electron injection yields decreased with increased number of phosphonate substituents or the addition of a methylene spacer. But electro- and photochemical stabilities on TiO\(_2\) are enhanced with an increasing number of phosphonate groups. In addition the binding constants for -CH\(_2\)PO\(_3\)H\(_2\) are higher compared with -PO\(_3\)H\(_2\). However, they discovered a major drawback of the methylene spacer containing complexes. Under oxidizing conditions, as may be encountered in n-type cells, a conversion of the methyl phosphonic acid groups to carboxylate groups was witnessed, caused by oxidation of the CH\(_2\)-spacer. Nevertheless, methyl phosphonic acid anchoring groups are still promising candidates for p-type cells.

Besides stable binding and charge carrier injection the anchoring group, as a connecting module between SC surface and chromophore, can fulfill multiple other tasks which govern the photovoltaic characteristics of the corresponding solar cells. For instance, anchoring group elongation controls efficiency determining factors of a cell, since charge carrier recombination processes and aggregation of the chromophores on the SC surface can be inhibited.\(^{45,65}\) Distance increase between dye and surface potentially increases the lifetime of the excited states by effective charge separation and thereby guarantees an efficient and directional electron transfer. Furthermore, in order to enhance the application potential the properties of the dye should be tuned for a good light harvesting ability, e.g. by extension of its \(\pi\)-conjugated system. In studies of dyes attached to surfaces through flexible saturated linkers it has been observed that the electronic coupling is weakened and that charge carrier injection rates slow down with increased bridge length.\(^{65}\) For these reasons synthetic efforts to introduce rigid and aromatic linkers like phenyl-groups have been followed. For instance, Galoppini et al. have shown, that the extinction coefficient of pyrene increases and the long-wavelength absorbance is shifted to the red, when it is attached to fully conjugated rods.\(^{66}\) Similar effects were described for typical solar cell sensitizers like organic donor-acceptor dyes or transition metal complexes.\(^{44,59,67,68}\) Nattlestadt et al. increased the performance of p-type DSSCs by systematic
variation of the distance between the hole in NiO and an excited push-pull triphenylamine (TPA)-perylene monoimide (PMI) dye, by a variable-length oligothiophene bridge (Figure 17).\textsuperscript{44}

![Figure 17: p-type DSSC photosensitizer presented by Nattestadt and coworkers.\textsuperscript{44}](image)

Wu and coworkers conducted structure–property relationship studies for Ru-[(bpy)_2(C'N)]\textsuperscript{+} -derivatives where C'N represents bidentate phenyl/pyridine derivatives with carboxylate anchoring groups for their application on NiO in p-type DSSCs. They differ in the number of phenylene spacer units between the Ru-[(bpy)_2(C'N)]\textsuperscript{+} core and the anchoring group.\textsuperscript{58} With increasing number of phenylene units in the linker, the interfacial charge recombination rate decreased, and the efficiency of the solar cells was enhanced (Figure 18).

<p>| | | |</p>
<table>
<thead>
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<tbody>
<tr>
<td>![Image of Ru-[(bpy)_2(C'N)]\textsuperscript{+} complexes]</td>
<td>![Image of Ru-[(bpy)_2(C'N)]\textsuperscript{+} complexes]</td>
<td>![Image of Ru-[(bpy)_2(C'N)]\textsuperscript{+} complexes]</td>
</tr>
<tr>
<td>η [%]</td>
<td>0.009</td>
<td>0.033</td>
</tr>
<tr>
<td>τ\textsubscript{1} [ps]</td>
<td>8.92</td>
<td>24.12</td>
</tr>
<tr>
<td>τ\textsubscript{2} [ps]</td>
<td>248.4</td>
<td>629.4</td>
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![Figure 18: Ruthenium complexes with variable-length anchoring groups presented by Wu et al. η=photoconversion efficiency. τ\textsubscript{1}, τ\textsubscript{2} = time constants assigned to charge recombination processes.\textsuperscript{58}](image)

Similarly, Housecroft \textit{et al.} increased the performance of copper(I) dyes with phosphonic acid group functionalized 6,6'-dimethyl-2,2'-bipyridine in \textit{n}-type DSSCs.\textsuperscript{59} The presence of a phenylene spacer resulted in improved efficiencies compared to dyes without this spacer between the bpy core and the phosphonic acid group.

These studies highlight the importance of the nature and the dimensions of the anchoring group. Therefore, modification of this moiety is a valuable strategy to improve solar cell performances.
2.4.) Photophysics

2.4.1.) Photophysical Fundamentals

The general processes occurring upon visible light excitation of a chromophore are summarized in the Jablonski diagram (see Figure 19). This scheme illustrates the involved states and the transitions between them in a simplified and therefore easily understandable manner.

![Jablonski diagram](image)

**Figure 19:** The Jablonski scheme summarizes processes which are associated with the absorption of a photon by a molecular chromophore.

After absorption of a photon, excitation of the ground state $S_0$ results in transfer of a valence electron to energetically higher lying singlet-excited state $S_n$ ($n = 1, 2, 3...$). According to Kasha’s rule, the excited states with $n > 1$ non-radiatively decay, into the lowest vibrational level of excited state $S_1$ via internal conversions (IC), ultimately transferring heat to the surrounding environment. Depending on the molecular structure, radiative depopulation of $S_1 \rightarrow S_0$ might occur by spontaneous emission of a photon. This event is called fluorescence. Due to the decay processes $S_n \rightarrow S_1$ whereupon several vibronic sub-states are involved, the energy of the fluorescence is shifted with respect to the initial excitation wavelength (Stokes shift). According to quantum mechanics and the general conservation of spin, only transitions between states of the same multiplicity are allowed. Nevertheless a so-called intersystem crossing (ISC) is possible where the $S_1$ state converts into the respective $T_1$ triplet state via spin flip of an unpaired electron due to spin-orbit coupling processes. This effect is most prominently observed when heavy elements with high spin-orbit coupling constants are involved. Direct relaxation of the $T_1$ state into the $S_0$ ground state can occur upon radiative emission, but this process called phosphorescence is generally much slower as compared to fluorescence.
In case that reaction partners with suitable energetic requirements are present, nature has proven that light excitation can easily cause redox reactions. Compared to the ground state, electronically excited molecules are both better electron donors and better electron acceptors. Qualitatively, this can be understood from Scheme 1.

Scheme 1: Orbital Scheme useful for understanding why an excited state is both a better electron donor and a better electron acceptor than the ground-state species.

The electron which has been promoted within the molecule (M) can be more easily removed by an acceptor reactant (A). At the same time, the promotion of an electron leaves behind a low-lying vacancy that can accept an electron from a donor (D). Generating species by light which are capable of performing as both an oxidant and a reductant, is essential for photocatalytic processes. Any approach towards artificial photosynthesis is therefore in need of suitable synthesizable chromophores. Basic requirements are (photo-)chemical stability, fitting redox properties, high molar extinction coefficients (ε) and long excited state lifetimes to facilitate the desired reactivity.

2.4.2.) Photophysics of ruthenium polypyridyl complexes

Besides organic molecules possessing highly delocalized π-systems, metal complexes have been scrutinized with great interest. Particularly, Ru(II) polypyridine complexes, are the class of transition metal complexes which has been most deeply investigated from a photochemical viewpoint. They feature the unique combination of the aforementioned requirements since they are indeed good visible light absorbers with long-lived excited states (up to several microseconds). Ru(II) polypyridine complexes can undergo reversible redox processes in the ground as well as in the excited state. These properties can be easily tuned by substitution of the ligand sphere. But for a general discussion of the properties of these complexes, it is convenient to refer to the archetype, that is, [Ru(bpy)₃]²⁺.

Ru²⁺ is a d⁶ system and the bpy ligands are colorless molecules possessing σ donor orbitals localized on the nitrogen atoms and π donor and π* acceptor orbitals more or less delocalized on aromatic rings. The absorption spectrum [Ru(bpy)₃]²⁺ is shown in Figure 20 with the proposed assignments. There are mainly three transition processes to be distinguished. (i)
metal centered transitions (MC), (ii) ligand centered transitions (LC) and (iii) charge transfer (CT) between both components. Depending on the direction of CT the latter are either metal-to-ligand-charge-transfers (MLCT) or ligand-to-metal-charge transfers (LMCT). Considering the molecular orbital energy scheme of octahedral [Ru(bpy)₃]²⁺ (Figure 20) it becomes clearly visible that the excited ligand orbital π⁺ is localized energetically lower than the corresponding metal orbital σ⁺(eg). Accordingly the least energy demanding transition in [Ru(bpy)₃]²⁺ (λₘₐₓ=450 nm, εₘₐₓ= 14600 M⁻¹cm⁻¹) is a ¹MLCT from the highest occupied molecular orbital (HOMO) πₘ(2g) to the lowest unoccupied molecular orbital (LUMO) π⁺. Promotion of an electron from πₘ(2g) to σ⁺(eg) orbitals gives rise to MC excited states (λₘₐₓ=350 nm). LC excited states (λₘₐₓ=285 nm) can be obtained by transferring an electron from πₐ to π⁺.

Figure 20: Absorbance spectrum, emission spectrum and schematic energy-level diagram for octahedral [Ru(bpy)₃]²⁺. The various kind of electronic transitions are also indicated.⁷³,⁷⁴

The singlet excited ¹MLCT state (¹[Ru(bpy)₃]²⁺) relaxes with quantum efficiency of unity (ηₛᴄ = 1) into the ³MLCT state (³[Ru(bpy)₃]²⁺) by ISC (cf. Figure 21).

Figure 21: Photophysical, electrochemical properties and Jablonski diagram of [Ru(bpy)₃]²⁺

This formally forbidden process with such high efficiency proceeds due to the high degree of spin orbit coupling. This excited triplet state lives long enough (τ=0.6 μs) to encounter other
solute molecules before undergoing radiationless or radiative deactivation to the ground state (GS) which can be detected as emission at around 610 nm.\textsuperscript{29}

In general it is also possible to depopulate the \(^3\text{MLCT}\) by IC to an energetically close lying \(^3\text{MC}\) from which radiationless deactivation can occur. In order to perform photochemical reactions with \(^*\text{[Ru(bpy)]_3}^{2+}\) this process should be inhibited. The energy gap between \(^3\text{MC}\) and \(^3\text{MLCT}\) can therefore be increased by proper ligand substitutions. \(^*\text{[Ru(bpy)]_3}^{2+}\) possesses an energy excess of 2.12 eV relative to the ground state, and its reduction and oxidation potentials are \(+0.84\text{ V and } -0.86\text{ V vs. NHE in water (cf. Figure 21, left).}\textsuperscript{29}\) Consequently, \(^*\text{[Ru(bpy)]_3}^{2+}\) is a good electron donor and a good electron acceptor at the same time. Electron transfer from a donor molecule D to \(^*\text{[Ru(bpy)]_3}^{2+}\) is referred to as reductive quenching. Contrariwise, oxidative quenching is observed if the excited electron of \(^*\text{[Ru(bpy)]_3}^{2+}\) is given to an acceptor molecule A. The two processes are potentially in competition, but usually only one is thermodynamically allowed for a given reaction partner. When both are thermodynamically allowed, kinetic factors establish which process is in favor.\textsuperscript{75}\n
In summary a Jablonski diagram for \([\text{Ru(bpy)}_3]^{2+}\) can be drawn (Figure 21, right).

As mentioned before, for most Ru(II) polypyridine complexes, the lowest excited state is a \(^3\text{MLCT}\) level which undergoes relatively slow radiationless transitions and thus exhibits relatively long lifetime and intense luminescence emission.\textsuperscript{71}\n
This picture can change if a conventional polypyridine ligand can be viewed as being made of two separated subunits. Examples for such ligands are dipyrido[3,2-a:2',3'-c]phenazine (dppz) and tetrapyrido[3,2-a:2',3'-c:3'',2'',h:2'',3''-j]phenazine (tpphz) (Figure 22).

![Diagram showing MLCT transitions in ruthenium complexes](image)

**Figure 22:** Structural formula of dppz and tpphz and two possible MLCT transitions in ruthenium complexes with these ligands.
These ligands can be seen as combinations of bpy units and a phenazine (pz) moiety. In these species there are several triplet excited states quite close in energy: (i) a $^3\text{MLCT}_0$ state with the excited state located on the LUMO which is centered on the pz-like portion of the ligand (ii) a $^3\text{MLCT}_1$ state where the electron resides in the higher lying orbital LUMO+1 centered on the chelating bpy-like portion and (iii) a ligand centered excited state.\textsuperscript{71} The energy gap and order of these three low-lying excited states can be modulated by various parameters, including solvent dielectrics, protic ability of the solvent and hydrophobic interactions.\textsuperscript{71} Indeed, [Ru(bpy)$_2$(dppz)]$^{2+}$ and [Ru(bpy)$_2$(tpphz)]$^{2+}$ derivatives show an environmentally sensitive “light switch” behavior. They are weakly or non-luminescent in aqueous solution but brightly emit in non-polar aprotic solvents. Three main possibilities were reported to be potential causes of this behavior: (i) the mentioned presence of two types of $^3\text{MLCT}$ states on different portions of the dppz ligand. A bright one localized on the bpy moiety ($^3\text{MLCT}_1$) and a non-luminescent or weakly emissive dark state mainly localized on the pz portion ($^3\text{MLCT}_0$). The light switch effect is a result of competition between energetic factors that favor the population of the dark state and the entropically favored bright state.\textsuperscript{76,77} Brenneman et al. suggest the dark state is always lower in energy than the bright one, but in some environments the bright state is within thermal energy of the dark state, leading to the environmentally sensitive light switch.\textsuperscript{76–78} (ii) The presence of other triplet states e.g. intraligand charge transfers (ILCT) near to the lowest/emissive $^3\text{MLCT}$ state may quench luminescence and lead to other deactivation processes.\textsuperscript{79,80} (iii) Hydrogen bonding interactions between the pz nitrogen atoms and solvent lower the energy of the dark state and thereby quench luminescence.\textsuperscript{77,81–83} Dppz and tpphz are almost planar ligands and the pz moiety is located at the periphery of the octahedral complex-sphere, facilitating interactions between it and the surrounding environment. These structural properties enable the intercalation of dppz or tpphz into DNA. Therefore ruthenium complexes based on these ligands are useful as selective probes for DNA because they can utilize the light-switch effect to detect DNA in aqueous solution upon intercalation.\textsuperscript{81,84–85} When the complex interacts with DNA, the MLCT state involving the bpy-like subunit becomes dominant, and since such a state has better luminescent properties, the luminescence of the complex is switched on.

Besides sensor applications, Ru(II) polypyridine complexes are predestined to develop systems for supramolecular photochemistry. In particular, in view of their convenient qualification related to photoinduced electron and energy transfer processes within multicomponent (supramolecular) assemblies.\textsuperscript{71} Replacing single bipyridine units by polypyridyl type bridging ligands like tpphz opens the possibility to synthesize multinuclear complexes which couple Ru-polypyridyl chromophores with catalytic metal centers. A review on such intramolecular photocatalysts with Pt-, Rh- or Pd-based catalytic units is given in the next chapter.
3.) State of the Art

3.1.) Artificial Photosynthesis by homogenous catalysis: Tuning photochemical molecular devices for hydrogen evolution

This chapter was written by Simon Kaufhold (chapter 3.1.1. and 3.1.2.3.), Markus Braumüller (abstract, chapter 3.1.2., 3.1.2.1. and 3.1.4.), Katharina Ritter (chapter 3.1.2.2.), Lydia Petermann (chapter 3.1.3., 3.1.3.1. and 3.1.3.2.) and Alexander Mengele (chapter 3.1.3.3.) as an invited contribution to a special issue of Coordination Chemistry reviews. The corresponding manuscript is still in preparation.

Abbreviations within this chapter:

\[[\text{Pd}] = \text{PdCl}_2\]
\[[\text{Pd}^{\text{bpy}}] = \text{Pd(bpy)}\]
\[[\text{Pd}^{\text{Cl}}] = \text{PdCl}\]
\[[\text{Pt}] = \text{PtCl}_2\]
\[[\text{Pt}^{\text{t}}] = \text{PtI}_2\]
\[[\text{Pt}^{\text{t}_2}] = \text{pivalamidato bridged Pt-dimer}\]
\[[\text{Rh}] = \text{Rh(bpy)}_2\]
\[[\text{Rh}^{\text{I}}] = \text{Rh(I)}\]
\[[\text{Rh}^{\text{II}-\text{H}}] = \text{Rh(II)-hydride}\]
\[[\text{Rh}^{\text{I}']} = \text{Rh(cod)Cl}\]
\[[\text{Rh}^{\text{I}+}] = \text{RhCl(Cp}^+)\]
\[[\text{Rh}^{\text{COD}}] = \text{Rh(cod)}\]
\[[\text{Ru}] = \text{Ru(bpy)}_2\]
\[[\text{Ru}^{\text{I}}] = \text{Ru(tbbpy)}_2\]
\[[\text{Ru}^{\text{dcepby}}] = \text{Ru(dcepby)}_2\]
\[[\text{Ru}^{\text{phi phen}}] = \text{Ru(Ph}_2\text{phen)}_2\]
\[[\text{Ru}^{\text{phen}}] = \text{Ru(phen)}_2\]
\[[\text{Ru}^{\text{terpy}}] = \text{Ru(terpy)}\]
\[[\text{Ru}^{\text{dmbpy}}] = \text{Ru(dmbpy)}_2\]

BL – bridging ligand
BL1 = 2,2'-bipyridine

BL2a = 1,2-bis[4-(4'-methyl-2,2'-bipyridinyl)]ethane

BL2b = similar to BL2a, but containing a central dimethoxybenzene moiety

BL3 = 4'-((3,4-dioxo-)phenyl-terpy

BL4a = phen-NHCO-bpyCOOH,

BL4a' = bpyCOOH-CONH-phen

BL4b = phen-NHCO-bpyCOOEt,

BL4c = phen-NHCO-bpyCH₃

BL4d = (phen-NHCO)₂-bpy

BL4e = bridged dimer of BL4

BL5a-f = BL based on tpPhz

BL6 = PHAT = phenanthroline-HAT = 9,10,19,20,29,30-hexazahexapyrido[3,2-a:2',3'-c:3'',2''-k:2'',3'''-m:3'''',2''''-u:2'''',3'''''-x]trinaphthylene

BL7 = 2,5-bis(2-pyridyl)pyrazine

BL8a = 2,3-bis(2-pyridyl)pyrazine

BL8b = 2,3-bis(2-pyridyl)quinoxaline

BL9 = 4,4'-bis(N-(3-aminopropyl)-carbamoyl)-2,2'-bipyridine

BL10 = 4,4'-bis(N-(4-pyridyl)methyl-carbamoyl)-2,2'-bipyridine

bpy = 2,2'-bipyridine

bpyCH₃ = 4-methyl-2,2'-bipyridine

bpyCOOH = 4-carboxylic acid-2,2'-bipyridine

bpyCOOEt = 4-carboxylic acid ethyl ester-2,2'-bipyridine

CC = catalytic center

Cp = Cyclopentadienyl

CS = charge separated state

dcebpby = 4,4'-dicarboxyethyl-2,2'-bipyridine

dmbpy=4,4'-dimethyl-2,2'-bipyridine

DMA = N,N-dimethylaniline

DMF = N,N-dimethylformamide
ECEC = electron transfer-chemical reaction-electron transfer-chemical reaction cascade
EECC = electron transfer-electron transfer-chemical reaction-chemical reaction cascade
EDTA = ethylenediaminetetraacetic acid
HAT = 1,4,5,8,9,12-hexaazatriphenylene
HEPMD = hydrogen evolving PMD
LF = ligand field
MLCT = metal to ligand charge transfer
MV$^{2+}$ = methyl viologen
NHC = N-heterocyclic carbene
phen = 1,10-phenanthroline
Ph$_2$phen = 4,7-diphenyl-1,10-phenanthroline
PMD = photochemical molecular device
PS = photosensitizer
tbbpy = 4,4'--di-tert-butyl-2,2'-bipyridine
TEA = triethylamine
TEOA = triethanolamine
terpy = 2,2':6',2''-terpyridine
TON = turnover number
TOF = turnover frequency
tpphz = tetrapyrido[3,2-a:2',3'c:3'',2'',-h:2'',3''-j]phenazine
Abstract

This review summarizes the studies of supramolecular systems coupling Ru-polypyridyl chromophores with Pt-, Rh- or Pd-based hydrogen evolving catalysts to highlight design criteria for the optimization of these photochemical molecular devices (PMD). Catalytic activities and stability of a PMD can be tuned by modification of its components, i.e. variation of the peripheral and bridging ligands as well as optimization of the catalytic center can lead to increased performance of intramolecular photocatalysts and make them superior to intermolecular systems. To get a better understanding of the underlying principles driving functioning HEPMDs, the impact of structural modifications will be discussed.

3.1.1.) Introduction

Climate and environmental issues connected to the production and usage of fossil and nuclear fuels as well as their finite nature have led to the necessity to seek for alternative energy carriers to cover the energy demand of mankind in the future. Ideally these energy carriers should be producible in a renewable manner from abundant resources and have low or no environmental impact upon usage in order to provide a sustainable source of energy. In the quest for finding such an energy carrier the conversion of sunlight into more useful form of energy is a big topic as the power of light energy irradiated to the earth’s surface is 750-fold higher than the average human consumption. The crux, however, is to efficiently convert and store the sun’s energy to make it fit for human use. Photovoltaic devices have become a large scale product within the past decades and now play a significant role in electricity production in a growing number of countries. Electricity has the disadvantage of being a non-storable form of energy that can only be used the moment it is produced. Nature, in contrast, has developed a method of converting light energy into storable, chemical energy in form of simple hydrocarbons, using abundant resources – water and carbon dioxide – as feedstock. Natural photosynthesis has been an inspiration for scientists for decades and an intensively discussed strategy for the utilization of sunlight is artificial photosynthesis. Of particular interest is the photocatalytic reduction of water to produce hydrogen gas (H₂) as a high energy chemical.

Besides heterogeneous and intermolecular multicomponent systems to achieve efficient production of H₂ the use of supramolecular photocatalysts has a particular appeal. A catalyst of this type can also be seen as a photochemical molecular device (PMD) which is composed of different subunits that perform a certain task. Three main components are essential in this type of device: i) a photosensitizer (PS) which absorbs light i.e. takes up energy and provides it to ii) a bridging ligand (BL) that is able to transport the energy or electrons directionally to iii) a catalytic center (CC) that is able to carry out the desired reaction (Figure 23).
Figure 23: Schematic presentation of a HEPMD comprised of photosensitizer (PS), bridging ligand (BL) and catalytic center (CC) using an artificial electron donor (D) for reduction of protons.

One advantage of PMDs over intermolecular systems is the potential of higher efficiency. In intermolecular systems each task is carried out by a separate molecule, thus the energy or electron transport from the PS to the CC, often via an electron relay, depends on the probability of collision processes between these molecules. This is in contrast to supramolecular assemblies, where a directional energy / electron transport from PS via BL to the CC can be achieved.\textsuperscript{100,101}

Usually the single subunits of a PMD are fused together synthetically in a step-by-step manner which enables the selective manipulation of each subunit to alter the overall properties of the photocatalyst, this is a significant advantage of supramolecular systems. The higher synthetic effort for the assembly of such a system in comparison to an intermolecular one is justified by the structure-property-correlation that can be drawn from these supramolecular systems by investigating their characteristics in detail. Distinct changes to the single subunits can be made and the effect can be visualized by comparing the compound’s properties like optical and electrochemical characteristics, the localization and lifetime of the excited states or simply the reaction outcome. In that way a library of information can be established and their interpretation will yield important information as to which manipulation has to be performed in order to tune a certain property. Ideally this leads to systematic improvement of the performance of the catalytic system.

In this review we aim to collect examples of this process of investigation and alteration of PMDs that subsequently led to changes in stability and performance of the catalytic system. However, it is still a point of discussion which way is the most straightforward to well working catalysts (compare Figure 24).
Figure 24: Different approaches to get the best performing catalyst.

Here we will focus on PMDs for the generation of hydrogen gas from water that are comprised of a ruthenium PS connected to a palladium, platinum or rhodium CC. The true nature (molecular vs. colloidal) of the active species has often been point of contention in the past and needs to be addressed carefully. Brewer et al. have reported on the tuning of Ru/Os-Rh PMDs for hydrogen evolution elsewhere. Rhodium-based catalysts have also recently been reviewed by Fortage and Collomb and co-workers. Manipulation strategies on Ru/Ir-Co systems have been investigated by Artero et al.,

3.1.2.) The role of the bridging ligand

The nature of the bridging ligand, which not only acts as passive spacer to provide chemical connection, but rather mediates the electronic interplay between the involved substructures (PS and CC) at the same time is of great importance. It can affect the overall catalytic performance and stability of the PMD. For an effective electronic communication between chromophore and catalyst the molecular structure of the bridging ligand can be fine-tuned by changing its spatial dimension and rigidity to control the distance between the metal centers and by introducing functional groups. The latter determine the intracomponent HOMO and LUMO energies and electron withdrawing or releasing capacity as well as intracomponent redox potentials. In order to obtain highly stable and effective intramolecular photocatalysts, the bridge has to fulfill several requirements: (i) having suitable intracomponent HOMO and LUMO energies (redox-, ground state- and excited state potentials) to allow unidirectional electron transfer from the excited state to the catalytic center, (ii) the ability to stabilize the charge separated intermediates and/or electron storage capacity in order to prevent recombination and allow additional electron transfer steps to occur, (iii) featuring intrinsic and intercomponent stability towards thermal, photo- and electrochemical decomposition and reaction products or intermediates and (iv) the ability to bind PS and CC in various oxidation states in a stable manner. Nevertheless, because of the complex interdependences and interactions in a supramolecule it is difficult to predict its overall properties by only designing
an optimized BL, without considering the other components of the PMD. To date, many chromophore or catalytic subunits of PMDs utilize rare metals such as ruthenium or palladium, rhodium, and platinum, respectively. It is self-explanatory that the use of noble metals, to overcome the global energy problems is counterproductive. However, their photo- and electrochemistry are well investigated and therefore they contribute to a better understanding of the underlying principles driving functional PMDs. In the following the role of the BL in photocatalytic proton reduction and its interplay with the other parts of the supramolecular assembly, based on the low abundant metals given above, will be discussed. Figure 25 gives an overview of the presented BLs.

![BL1](image1) ![BL2a](image2) ![BL3](image3) ![BL4](image4)

![BL5](image5) ![BL6](image6) ![BL7](image7) ![BL8a](image8) ![BL8b](image9)

![BL9](image10) ![BL10](image11) ![BL11](image12) ![BL12-H](image13)

Figure 25: Overview of presented bridging ligands in order of appearance.

3.1.2.1.) N- or O-donor bridging ligands

In the late 1980s and early 1990s the working groups of Rillema, Petersen and Ward presented the first PMDs made up of a polypyridyl Ru(II) photosensitizer and a Pt(II), Rh(III) or Pd(II) unit,
respectively (see Figure 26). Although these complexes showed potential application as hydrogen evolving photocatalysts they did not investigate catalytic activity.\textsuperscript{112–115}

![Chemical structures](image)

**Figure 26:** Structures of the first PMDs utilizing Ru-Pt/Rh/Pd-systems.

It took almost 2 decades from these initial reports until the first catalytically active system of a hydrogen evolving PMD [Ru(bpy)\textsubscript{2}(phen-NHCO-bpyCOOH)PtCl\textsubscript{4}]\textsuperscript{2+} ([RuBL4a[Pt]) was presented by Sakai and co-workers in 2006 (Figure 27).\textsuperscript{116} [RuBL4a[Pt] consists of a heterodinuclear ruthenium platinum complex bridged by amide linked phen and bpy coordination spheres. Although the amide linkage preserves the aromaticity, BL4a represents a flexible bridge which may flip back and forth. The authors could show that the complex is capable of producing hydrogen under irradiation with visible light in water using EDTA as electron donor (TON = 2.4, TON = turnover number = n(H\textsubscript{2})/n(catalyst)\textsuperscript{1}). To clarify the working principle of this active system, BL4a was manipulated in different ways and in the end a structure-property-correlation could be derived.

\textsuperscript{1}When considering the TONs in this review, it must be taken into account that the catalytic conditions (i.e. different solvents, electron donors, irradiation times/intensities/wavelengths and technical setups) of the presented systems may differ to a great extent. Thus, great care must be taken when comparing the values.
At first they synthesized \([\text{Ru}]\text{BL4a}^{*}[\text{Pt}]\), where \text{BL4a} is bound to the metal centers in a reversed manner compared to \([\text{Ru}]\text{BL4a}[\text{Pt}]\) (Figure 27).\(^{117}\)

![Complexes based on BL4 investigated by the group of Sakai.](image)

Figure 27: Complexes based on BL4 investigated by the group of Sakai.

As a simple tool to predict catalytic activity in Ru-Pt assemblies, Sakai et al. correlated the Pt-induced luminescence quenching (compared to the non-platinated “Ru-only” precursor compound) to the electron transfer efficiency in catalytic direction.\(^{118}\) It was found that the catalytic activity of \([\text{Ru}]\text{BL4a}^{*}[\text{Pt}]\) is about 50% lower than that of \([\text{Ru}]\text{BL4a}[\text{Pt}]\) and the luminescent quenching upon platination for \([\text{Ru}]\text{BL4a}^{*}[\text{Pt}]\) is less than that of \([\text{Ru}]\text{BL4a}[\text{Pt}]\) (28% vs. 70%), which is in agreement with the proposed tendency.\(^{117}\) The emissive \(3^\text{MLCT}\) of the PS part should be quenched by electron transfer to a lower lying state at the CC part of the PMD to render catalytic activity. This low lying state can be called charge separated state (CS). The driving-force of electron transfer to the CS is given by the difference in energy between other excited states and the CS. Taking the example of the emissive \(3^\text{MLCT}\) state into consideration following picture evolved: the emission energy of \([\text{Ru}]\text{BL4a}^{*}[\text{Pt}]\) is lower than that of \([\text{Ru}]\text{BL4a}[\text{Pt}]\) (\(\lambda_{\text{max}}=670\) nm vs. \(\lambda_{\text{max}}=610\) nm).\(^{116,117}\) Accordingly, the driving force for electron transfer to the CS is higher for \([\text{Ru}]\text{BL4a}[\text{Pt}]\). Additionally, electrochemical measurements showed that the first reduction of \([\text{Ru}]\text{BL4a}[\text{Pt}]\) occurs at the bpy ligand bound to the CC, whereas that of \([\text{Ru}]\text{BL4a}^{*}[\text{Pt}]\) is found at either the bpy ligand bound to the PS or the phen ligand bound to the CC.\(^{20,119,120}\) DFT investigations support these findings, since the LUMO of \([\text{Ru}]\text{BL4a}[\text{Pt}]\) and \([\text{Ru}]\text{BL4a}^{*}[\text{Pt}]\) were located on the bpy parts of the bridges (bpy-\(\pi^*\) orbital) and therefore an efficient intramolecular electron transfer to the CC is only possible for \([\text{Ru}]\text{BL4a}[\text{Pt}]\).

Since the energy level of the \(\pi^*\) orbital of the bpy ligand should have a major effect on this electron transfer, Sakai et al. substituted the carboxyl group of \([\text{Ru}]\text{BL4a}[\text{Pt}]\) by the more electron donating groups ethoxycarbonyl and methyl. This modification of \text{BL4a} led to the complexes \([\text{Ru}]\text{BL4b}[\text{Pt}]\) and \([\text{Ru}]\text{BL4c}[\text{Pt}]\) (Figure 27).\(^{119}\) With increased electron donating character of the bpy substituent, a destabilization of the Pt(bpyR) based \(\pi^*\) orbital was observed (R=CH\(_3\), COOH, COOEt). The driving forces for the charge transfer from the Ru*-phen based \(3^\text{MLCT}\) state to the Pt(bpyR)-based CS were estimated as -0.16 eV for
[Ru]BL4a[Pt], -0.09 eV for [Ru]BL4b[Pt] and +0.03 eV for [Ru]BL4c[Pt], using the Rehm-Weller equation. These findings were supported by transient absorption spectroscopy, showing that this electron transfer takes place in the picosecond timescale for [Ru]BL4a[Pt] and [Ru]BL4b[Pt] but is way slower for [Ru]BL4c[Pt] (>10 ns). In accordance with these results [Ru]BL4c[Pt] did not show any catalytic activity, since electron transfer to the CS is an uphill process and [Ru]BL4a[Pt] is performing approximately twice as good as [Ru]BL4b[Pt].

BL4 was also used to generate tri- ([Ru]BL4d[Pt]) and tetranuclear complexes (([Ru]BL4a)2[Pt]2, ([Ru]BL4e[Pt])2), derived from the archetype complex [Ru]BL4a[Pt] (Figure 27 and Figure 28). These multinuclear complexes showed strong platination-induced emission quenching. However, [Ru]BL4d[Pt] and ([(Ru]BL4a)2[Pt]2 were found to be inactive as HEPMDs. As a possible reason for their inactivity it was suggested that intramolecular energy transfer quenching among the two Ru-PS moieties results in deactivation of the 3MLCT excited state.

![Figure 28: Structures of multinuclear PMDs presented by Sakai et al.](image)

Similarly, for the homodinuclear ruthenium complex [Ru']BL5[Ru'] (Figure 29) a so called triplet-triplet annihilation has been observed. It was discussed that this opens a deactivation channel for excited states in multi-chromophoric PMDs like [Ru']BL5[Ru']. As one example
of such a PMD Rau and coworkers presented \([\text{Ru}']_2\text{BL6}[\text{Pd}]\), where \text{BL6} is used to connect two ruthenium centers and a \text{PdCl}_2 unit, combining multichromophore and multielectron storage strategies (Figure 29).\(^{123}\)

![Figure 29: Structures of PMDs developed in the Rau group.](image)

This promising system did not produce hydrogen. For this outcome, two possible explanations can be considered: (i) The electron transfer from the Ru\(^{II}\) chromophores towards BL6 is not localized on the phenazine-type moiety, but rather delocalized over the whole \(\pi\)-accepting HAT core. This delocalization of negative charges will lower the driving force for the reduction of the Pd-CC, inducing complete loss of catalytic activity. (ii) The before mentioned triplet-triplet annihilation between the two Ru-moieties leads to deactivation of the exited states.

In case of Sakai’s tetranuclear complex \([\text{Ru}][\text{BL4a}[\text{Pt}]]_2\) a Pt-to-Pt charge transfer resulting in a fast decay of the \(^3\text{MLCT}\) of the Ru(bpy)_3-like unit, has also been discussed.\(^{121}\) Such Pt-to-Pt charge transfer bands were reported for the analogous Pt\(^{II}\)-dimer \([\text{Pt}_2(bpy)_2(\mu-\text{pivalamidato})_2]^{2+}\).\(^{124}\) For the alkyl-chain linked complex \([\text{Ru}][\text{BL4e}[\text{Pt}]]_2\) no unfavorable electronic coupling between the two Ru-PS or Pt-CC moieties respectively, could be observed. The catalytic mechanism of \([\text{Ru}][\text{BL4a}[\text{Pt}]]\) was proposed to be bimolecular. One \([\text{Ru}][\text{BL4a}[\text{Pt}]]^+\) reacts with another \([\text{Ru}][\text{BL4a}[\text{Pt}]]\) in the groundstate (see also chapter 3.1.3.2.) Systems based on BL4.\(^{20,120}\) \([\text{Ru}][\text{BL4e}[\text{Pt}]]_2\) can be seen as linked dimer of \([\text{Ru}][\text{BL4a}[\text{Pt}]]\) where the two Ru\(^{II}\)-Pt\(^{II}\)-fragments can interact with each other without diffusion. Consequently, \([\text{Ru}][\text{BL4e}[\text{Pt}]]_2\) showed considerably enhanced catalytic performance compared to \([\text{Ru}][\text{BL4a}[\text{Pt}]]\), under conditions where the total contents of the dimeric Ru\(^{II}\)-Pt\(^{II}\)moiety were adjusted as equal.\(^{120}\) The presented systems, utilizing the different variations of BL4 give proof that modifications of the BL can have major effects on the catalytic activity of a system.

In further studies Sakai and co-workers investigated fully aromatic and planar bridges BL7 and BL8a as well as bridges with aliphatic spacers BL9 and BL10, leading to the RuPt-systems \([\text{Ru}][\text{BL7}[\text{Pt}]]\), \([\text{Ru}][\text{BL8a}[\text{Pt}]]\), \([\text{Ru}][\text{BL9}[\text{Pt}]]\) and \([\text{Ru}][\text{BL10}[\text{Pt}]]\) (Figure 30).\(^{116,125}\)
Figure 30: Structures of PMDs utilizing BL7, BL8a, BL9 and BL10.

It was found that these compounds did not show any strong platination-induced emission quenching or catalytic activity for hydrogen evolution.121 To get further insights, [Ru]BL8a[Pt], [Ru]BL9[Pt] and [Ru]BL10[Pt] were tested in a three component system (EDTA/[Ru(bpy)]3+/methylviologene and [Ru]BL8a[Pt] or [Ru]BL9[Pt] or [Ru]BL10[Pt]) for H2-evolving activity of their Pt-catalyst moiety.20,119 Within this intermolecular approach [Ru]BL8a[Pt] and [Ru]BL9[Pt] proved to be active, but [Ru]BL10[Pt] did not evolve any hydrogen. This outcome suggests that [Ru]BL8a[Pt] and [Ru]BL9[Pt] are inactive as HEPMDs because of an inefficient intramolecular photoinduced electron transfer or insufficient stabilization of CS, whereas for [Ru]BL10[Pt] another reason must be considered. The ineffectiveness of its Pt moiety in the three component system was suggested to be due to sterical hindrance of a proton approaching the axial Pt(\(d_2^2\)) orbital by the hydrogen atoms on the 2-position of the (not freely rotating) coordinating pyridyl rings.113 On the contrary, the planar geometries around the Pt units of [Ru]BL7[Pt], [Ru]BL8a[Pt] and [Ru]BL9[Pt] sterically allow this proton migration and thus are an explanation for their catalytic activity in the three component mixtures. The Pt(\(d_2^2\)) is expected to play an important role in the mechanism for H2 evolution (cf. 3.1.3.2.) Systems based on BL4). The complexes [Ru]BL7[Pt]
and [Ru]BL8a[Pt] with their rather small aromatic bridges BL7 and BL8a show additional features which are in strong contrast to the above discussed complexes based on BL4. In [Ru]BL8a[Pt] the MLCT absorption band is significantly red-shifted and electrochemical properties are altered compared to the non-platinated mononuclear complex, reflecting the extensive hybridization of the Pt-based orbitals over BL8a. Similar strong electronic coupling was found for complex [Ru]BL7[Pt] that is also inactive as photocatalyst, as mentioned above. Strong electronic coupling between two metal centers over a bridge is presumed to have a negative effect on the lifetime of the excited-state, which then might not be sufficiently long-lived to conduct the H₂-evolving process.

However, Brewer and co-workers have presented functional hydrogen evolving trinuclear (Ru)₄Rh₃PMDs ([(Ru]BL8a)₂[RhX₂], X=Cl, Br) based on BL8a (Figure 30), Similarly to [Ru]BL8a[Pt], BL8a induces a strong electronic coupling between the Ru unit(s) and the CC in [Ru]BL8a₂[RhX₂]. This is reflected by the red-shift of the absorption and emission bands upon coordination of the Rh III center. Electrochemical investigations in MeCN have shown an overlapping ruthenium based oxidation (Ru[III]) which indicates that inter-ruthenium coupling is absent. As the first reduction process, an irreversible wave attributed to a two-electron rhodium based reduction (Rh[II/III]) was observed. This is in contrast to [Ru]BL8a[Pt], where the first reduction is located on the bridge BL8a. In [(Ru]BL8a)₂[RhX₂] the rhodium reduction is followed by the loss of a halide. At more negative potentials two reversible reduction waves were found, each corresponding to a single electron reduction of the two BL8a bridging ligands. The facile reduction of Rh[III] to Rh[I] and the different catalytic mechanism (halide loss at the CC) in comparison to the RuPt-systems ([Ru]BL8a[Pt]) of Sakai et al. are the reasons for the photocatalytic activity of [(Ru]BL8a)₂[RhX₂] (cf. chapter 3.1.3.3.) Systems based on BL8a. BL8a proves the statement given above, that the catalytic activity or inactivity of a PMD does not rely on a single subunit like the BL. Instead all components of the supramolecule must be taken into consideration. After optimization of the catalytic conditions the Rh-catalyst based PMDs ([(Ru]BL8a)₂[RhX₂] are indeed very efficient HEPMDs, whereas [Ru]BL8a[Pt] with its Pt-CC is inactive (with X = Br, in DMF/H₂O (0.62M) solution with DMA as electron donor, ((Ru]BL8a)₂[RhX₂], exhibits a TON of 820 under monochromatic irradiation (λ = 460-470nm)).

Brewer’s group succeeded also in generating active Ru₅-Pt-HEPMDs by the use of BL8a and BL8b (Figure 31). In their studies they presented four Ru III, Pt II tetrametallic complexes ([(Ru²⁺]BL8a)₂RuBL8a[Pt], [(Ru²⁺][²]BL8a)₂RuBL8a[Pt], [(Ru²⁺][²]BL8a)₂RuBL8b[Pt] and [(Ru²⁺][²]BL8a)₂RuBL8b[Pt], which are utilizing either phen or Ph₂phen as terminal Ru-ligands and BL8a or BL8b to connect the trinmetallic Ru₅-lightabsorber to the cis-PtCl₂ moiety.
Figure 31: Structures of tetrametallic complexes presented by Brewer et al.\textsuperscript{128,129}

Electrochemistry, steady-state and time-resolved emission studies as well as emission excitation profiles predicted that a lowest-lying CS excited state, with oxidized terminal Ru (localization of the HOMOs) and reduced bridging ligands between central Ru and Pt (localization of the LUMO), is realized by intramolecular electron transfer. Accordingly, each tetrametallic complex is an active photocatalyst for H\textsubscript{2} production. No detectable H\textsubscript{2} production with the trinuclear “Ru-only” synthons and cis-[PtCl\textsubscript{2}(DMSO)\textsubscript{2}] as well as insensitivity to the mercury poisoning experiment (cf. 3.1.3.1.) Systems based on BL5) were taken as proofs that an intact supramolecule functions as the photocatalyst. A system containing 50 \mu M Ru\textsubscript{3}Pt-complex, 0.62 M H\textsubscript{2}O, 1.5 M DMA as sacrificial electron donor and 110 \mu M [DMAH\textsuperscript{+}][CF\textsubscript{3}SO\textsubscript{3}] irradiated at 470 nm produced hydrogen from H\textsubscript{2}O. ([Ru\textsuperscript{Ph2phen}BL8a\textsubscript{2}]RuBL8b[Pt]) gave the highest TON of 94 compared to the BL8a analogue ([Ru\textsuperscript{Ph2phen}BL8a\textsubscript{2}]RuBL8a[Pt]) with a TON of 23. The same trend was observed for the phen analogues ([Ru\textsuperscript{phen}BL8a\textsubscript{2}]RuBL8b[Pt]) and ([Ru\textsuperscript{phen}BL8a\textsubscript{2}]RuBL8a[Pt]) with TONs of 66 and 18, respectively.\textsuperscript{129} Hence, the nature of the bridging ligand had a significant impact on the catalyst activity. Variation of the BL from BL8a to BL8b results in a more stabilized LUMO and lowest-lying CS excited state and consequently in enhanced driving force for intramolecular electron transfer toward the reactive Pt center. Upon platination of the “Ru-only” precursor compounds, there is a quenching of emission of about 70\% for the BL8b containing complexes compared to about 30\% emission quenching for the BL8a analogues. The emissive state of these systems is populated with unequal efficiency as a result of competitive population of the CS state. The identity of the BL has the largest impact on the emissive state population, with near unity population for “only”-BL8a containing Ru\textsubscript{3}Pt-PMDs and greatly decreased population for the BL8b containing Ru3Pt-systems. Brewer et al. suggest that a higher-lying excited state, likely the central Ru to BL CT state, directly populates the CS state when BL = BL8b.

Besides the presented tetrametallic complexes, Brewer et al. recently reported on trinuclear analogues [Ru\textsuperscript{Ph2phen}BL8aRu(bpy)BL8a[Pt] and [Ru\textsuperscript{Ph2phen}BL8aRu(bpy)BL8b[Pt], where
one [Ru\textsuperscript{Ph2phen}]BL8a/b is replaced by bpy, resulting in a reduced number of light absorbing units and enhanced stability (Figure 32).

![Chemical structures]  

Figure 32: Presentation of trimetallic (Ru)2-Pt-complexes utilizing BL8a or BL8b.

The redox and photophysical behavior of these trimetallic RuRuPt-supramolecules are similar to those of the Ru2RuPt-architecture. Accordingly, the same trend regarding the catalytic activity could be observed when BL8b instead of BL8a is employed as BL (TON=230 vs. TON=130, 50 µM RuRuPt-complex, 0.62 M H\textsubscript{2}O, 1.5 M DMA and 110 µM [DMAH\textsuperscript{+}][CF\textsubscript{3}SO\textsubscript{3}\textsuperscript{-}], λ\textsubscript{ex} = 470 nm). In agreement with the trend observed in the analogous Ru2RuPt-systems the enhancement of hydrogen production is related to the enhanced CS state population. Interestingly, despite the lower molar absorptivity owing to the reduced number of light absorbing units the photocatalytic activity of the RuRuPt-complexes is higher than the Ru2RuPt analogue. As possible reasons the varied distribution of geometric isomers (16 vs. 32) and steric factors are mentioned. In the proximity of the cis-PtCl\textsubscript{2} site, the RuRuPt-architecture is expected to be sterically less demanding because one bulky [Ru\textsuperscript{Ph2phen}]BL8a/b unit which may hinder interactions between the substrate and the CC is absent. In contrast to Sakai’s Ru-Pt complex [Ru]BL8a[Pt], the relatively long-lived excited states in the tri- and tetrametallic architecture of Brewer’s RuPt-systems arising from spatial separation of the PS and CC might be an explanation for photocatalytic activity.

For the tetrametallic complexes the choice of terminal ligand (phen or Ph\textsubscript{2}phen) affects visible light absorption but had a minor influence on photocatalytic H\textsubscript{2} production from H\textsubscript{2}O.\textsuperscript{129} In contrast, Vos \textit{et al.} introduced the effective Ru-Pd photocatalyst [Ru\textsuperscript{dcebp}][BL7[Pd] where the catalytic activity strongly depends on terminal ligands.\textsuperscript{131} In agreement with the platinum analogue ([Ru]BL7[Pt]), [Ru]BL7[Pd] (with terminal bpy ligands) does not produce hydrogen (Figure 30). But [Ru\textsuperscript{dcebp}][BL7[Pd] with peripheral dicarboxyethyl substituted bpy ligands generates hydrogen with high turnover numbers, although BL7 is known to facilitate strong electronic coupling between the metal centers, leading to very short excited state lifetimes for
these complexes.\textsuperscript{28,131} The investigations concerning BL7 again highlight the considerable influence of all subunits of a PMD (the terminal ligands in this case) on the catalytic activity in general.

The presented bridges BL1 and BL3-BL8 are spacers, which preserve aromaticity. As pointed out before, these conjugated links can alter the electronic properties of each component of a PMD, thus making the comparison with isolated components unsuitable.\textsuperscript{108} Recently, Collomb and co-workers reported on a trinuclear, active Ru\textsubscript{2}Rh-HEPMD (\{(Ru)BL2a\textsubscript{2}(RhCl\textsubscript{2})\}) utilizing the non-conjugated bridge, which Rilema et al. first introduced in heterodinuclear RuPt-complex [Ru]BL2a[Pt] (BL2a, see Figure 25 and Figure 33).\textsuperscript{113,132}

Figure 33: Structures of \{(Ru)BL2a\textsubscript{2}(RhCl\textsubscript{2})\} and [Ru]BL2b[Pd].

Non-conjugated BL2a was chosen in order to maintain the photophysical and catalytic properties of each unit. Within \{(Ru)BL2a\textsubscript{2}(RhCl\textsubscript{2})\}, the Rh-CC is based on [Rh\textsuperscript{III}(dmbpy)\textsubscript{2}Cl\textsubscript{2}]Cl, which was found to be an efficient hydrogen producing catalyst in a three component system in pure water (ascorbate/[Ru(bpy)\textsubscript{3}]\textsuperscript{2+}/[Rh\textsuperscript{III}(dmbpy)\textsubscript{2}Cl\textsubscript{2}]Cl).\textsuperscript{133} The cyclic voltammogram and UV-vis absorption spectrum of \{(Ru)BL2a\textsubscript{2}(RhCl\textsubscript{2})\} correspond exactly to the superposition of those of the individual mononuclear species from a three-component system in their respective proportions. This superposition confirms that the three metal centers of \{(Ru)BL2a\textsubscript{2}(RhCl\textsubscript{2})\} are largely electronically decoupled.

In the investigated concentration range (\(1 \times 10^{-5} - 1 \times 10^{-4}\)M) the hydrogen evolution during catalysis with \{(Ru)BL2a\textsubscript{2}(RhCl\textsubscript{2})\} increased almost linearly, indicating that it is not limited by diffusion and that efficient intramolecular electron transfer takes place. Furthermore, the efficiency of the trinuclear system \{(Ru)BL2a\textsubscript{2}(RhCl\textsubscript{2})\} is much higher compared to the corresponding mixture of [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} and [Rh\textsuperscript{III}(dmbpy)\textsubscript{2}Cl\textsubscript{2}]Cl (TON = 310 vs. 150 at a concentration of \(1 \times 10^{-5}\)M and TON = 280 vs. 28 at \(1 \times 10^{-6}\)M), which has been related to its higher temporal stability (more than 12h compared to 0.5h - 5h, depending on the concentration).\textsuperscript{108} No decrease in H\textsubscript{2} evolution and no induction period were observed during mercury poisoning experiments with \{(Ru)BL2a\textsubscript{2}(RhCl\textsubscript{2})\}, suggesting that formation of rhodium colloids during catalysis can be excluded (cf. 3.1.3.1.) Systems based on BL5). Time resolved
photophysical studies showed, that the photocatalytic mechanism follows mainly a reductive quenching of the Ru subunit and electron transfer between the active components is much faster in \([\text{RuBL2a}]_2\text{[RhCl}]\) (subnanosecond compared to microsecond time scale in the mixture).\(^{108}\) This fast consumption of the reduced Ru species in \([\text{RuBL2a}]_2\text{[RhCl}]\) has been proposed as a reason for the improved stability, since it limits its degradation by the loss of one bpy ligand.

The presented PMDs demonstrate that conjugated bridges (BL1 and BL3-BL8), which enable coupling between the metals of PS and CC, as well as non-conjugated spacers (BL2a, BL9 and BL10) that prevent a significant coupling, gave both active and inactive PMDs. Accordingly, no generalized conclusion can be drawn which relates the photocatalytic activity to the aromaticity of the bridge.

Hammarström and coworkers described a heterodinuclear Ru-BL-Pd photocatalyst \([\text{RuBL2b}[\text{Pd}]]\) with BL2b as BL (similar to BL2a, but containing a central dimethoxybenzene moiety, Figure 33).\(^{134}\) During 8 h a maximum TON of 30 was observed upon irradiation with visible light (\(\lambda \geq 475\) nm) in MeCN/TEA (2:1, v/v) solution. But the main focus of this study was the potential formation of colloidal palladium during catalysis. With the help of TEM and XPS experiments they could show that photo-reduction upon visible light irradiation in the presence of TEA as sacrificial substrate and proton source leads to the cleavage of the N-donor-stabilized palladium metal from the supramolecular array. Furthermore, appearance of palladium colloids, known to be catalytically active themselves, strongly correlated in time with the formation of hydrogen. Hydrogen production by homogeneous catalysis could not be excluded, but the Pd-colloids had a major contribution to the observed \(\text{H}_2\) formation. The proven formation of colloidal palladium emphasizes the main drawback of the use of the presented N-donor ligands (BL1, BL2 and BL4-BL10) to link low valent catalyst centers, since they result in relatively weak interactions between the components in a supramolecular system.\(^{111}\) Hence, these findings reopen the important question of the true nature of the catalyst in all supramolecular assemblies. Therefore, an improved design of the BL and the coordination sphere around the CC is of great importance to assure the stability of the scaffold during the high energy photocatalysis processes. Promising candidates are N-heterocyclic carbene ligands (NHC, chapter 3.1.2.3.) NHC bridging ligands which can be adapted from low valent metalorganic catalysis (e.g. the Nobel-prize-winning olefin metathesis reaction).

3.1.2.2. Tetrpyridophenazine based bridging ligands

Rau et al. examined numerous RuPd photocatalysts bridged by the tetrpyrido[3,2-a:2',3'-c:3'',2''-h:2'',3''-j]phenazine (tpphz) ligand, BL5, and studied to a great extent which influence different substituents in different positions of BL5 have on their photocatalytic activity. This ligand class features several advantageous properties like (i) the defined length that induces spatial separation between the two ligated metal centers leading to rather low charge
recombination (ii) the conjugated character to facilitate electron transfer along the BL (iii) the rigidity, to avoid conformational variety and (iv) the property to act as an electron reservoir.

It is known that the phenazine part of BL5 is electronically decoupled from the phenanthroline parts and that an electron located at the phenazine subunit can reduce an adjacent metal center. BL5 can be substituted at various positions without changing the general function of the photocatalyst. An overview of RuPd complexes with modified BL5 ligands is given in Figure 34.

Figure 34: Structures of complexes based on BL5 investigated by Rau et al.

The first application of [Ru']BL5[Pd] as photocatalyst for water reduction was reported in 2006 by Rau et al. Photocatalytic hydrogen evolution with a TON of 56 was first performed in pure acetonitrile with TEA as sacrificial electron donor and blue light excitation ($\lambda = 470$ nm). Optimization of the catalytic conditions (e.g. reactor setup, intensity and wavelength of the light source, water content of the catalytic mixture) yielded an improved TON up to 238. Although an induction period of roughly 2 hours and colloid formation during catalysis are observed, the actual role of colloids remains unclear. Photocatalytic reduction of tolane with [Ru']BL5[Pd] lead to selective formation of cis-stilbene suggesting a molecular mechanism for the reduction mechanism.

An interesting correlation between the $^1$MLCT-excitation wavelength and the initial localization of the $^1$MLCT (either on the peripheral tbppy ligands or on the phenanthroline part of BL5) and the produced amount of hydrogen was observed for [Ru']BL5[Pd] by means of Resonance Raman spectroscopy and photocatalytic studies. These investigations showed that the $\pi^*$ orbitals of the phenanthroline moiety of BL5 are energetically lower than the $\pi^*$ orbitals of the tbppy sphere in the ruthenium complexes. Enhanced localization of the initial excited state on the BL is accompanied by proportionally higher catalytic activity (depicted in Figure 35).
Figure 35: At the top: Absorption spectrum of [Ru\(^{+}\)BL5[Pd] in MeCN (----) and TON spectrum (+). At the bottom: Efficiency spectrum \(\Phi(\lambda)\) of the photon-to-hydrogen conversion of the catalytic process calculated as the ratio of TON values and the extinction coefficient, normalized to a constant photon flux.\(^{142}\) Reprinted with permission from ref. 142. Copyright 2010 John Wiley and Sons.

Electrochemical investigations of [Ru\(^{+}\)]BL5 and [Ru\(^{+}\)]BL5[Pd] show several related aspects: A first reduction of the phenazine moiety is observed, followed by two reductions of the two peripheral ligands and a final reduction of the phenanthroline moiety of tpphz that is bound to Ru.\(^{139,145}\) For [Ru\(^{+}\)]BL5[Pd] an irreversible reduction at potentials very similar to the phenazine redox couple occurs which has been assigned to the formation of Pd\(^{1}\). This indicates suitable intracomponent energy levels and allows directional electron transfer from the PS to the CC. To understand the ongoing electron transfer mechanism for [Ru\(^{+}\)]BL5[Pd] upon light absorption in the spectral range of 400 to 550 nm, the photocatalyst was investigated in more detail by ultrafast time-resolved absorption spectroscopy.\(^{100}\) [Ru\(^{+}\)]BL5[Pd] shows a multistep electron transfer from the ruthenium to the palladium center upon photoexcitation of visible light on a subnanosecond timescale (see Scheme 2 and Table 3). Photoexcitation leads to a \(^{1}\)MLCT within 20 fs, located on either one of the tbppy ligands or the phenanthroline part of BL5 attached to the ruthenium center. Within 1 ps these states transform to a \(^{3}\)MLCT located on the ruthenium ligated phenanthroline sphere of BL5. While [Ru\(^{+}\)]BL5 shows emissive decay from this state very weak emission is found for [Ru\(^{+}\)]BL5[Pd] indicating a more efficient non-radiative deactivation route in this case. Here, an intraligand charge transfer (ILCT) from the phenanthroline based \(^{3}\)MLCT state to the phenazine moiety of BL5 can occur (5–20 ps, depending on the solvent). Finally the electron can be transferred from the ligand to the catalytic subunit in [Ru\(^{+}\)]BL5[Pd]. This last step is the slowest (310–850 ps) and is considered to occur accompanied by chloride dissociation from Pd.\(^{100,143}\) However, it is still faster than diffusion-dependent steps like the re-reduction of the Ru\(^{III}\) center by TEA. The decay from this
electronic state occurs after 30 ns or more and competes directly with catalytic turnover for which the charge localization on the CC is crucial.\textsuperscript{100}

Scheme 2: Light-induced electron transfer processes in [Ru']BL5[Pd]. Localization of the photoexcited electron within the supramolecular unit is schematically highlighted by shaded areas.\textsuperscript{100,143}

<table>
<thead>
<tr>
<th></th>
<th>solvent</th>
<th>$T_1$ [ps]</th>
<th>$T_2$ [ps]</th>
<th>$T_3$ [ps]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru']BL5[Pd]</td>
<td>ACN</td>
<td>0.8</td>
<td>5</td>
<td>310</td>
</tr>
<tr>
<td></td>
<td>DCM</td>
<td>1.0</td>
<td>19</td>
<td>740</td>
</tr>
<tr>
<td></td>
<td>ACN/H$_2$O(10%)</td>
<td>1.2</td>
<td>6.1</td>
<td>850</td>
</tr>
<tr>
<td>[Ru']BL5a[Pd]</td>
<td>ACN</td>
<td>1.1</td>
<td>8.2</td>
<td>580</td>
</tr>
<tr>
<td></td>
<td>DCM</td>
<td>2.8</td>
<td>52</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>ACN/H$_2$O(10%)</td>
<td>1</td>
<td>10.5</td>
<td>800</td>
</tr>
<tr>
<td>[Ru']BL5d[Pd]</td>
<td>ACN</td>
<td>4.4</td>
<td></td>
<td>580</td>
</tr>
</tbody>
</table>
Table 3: Characteristic time constants ($\tau_{1,3}$) for the kinetic processes observed in photo-excited [Ru']BL5[Pd], [Ru']BL5a[Pd] and [Ru']BL5d[Pd].

<table>
<thead>
<tr>
<th></th>
<th>Probably faster than 500 fs</th>
<th>42</th>
<th>1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ACN/H$_2$O(10%)</td>
<td></td>
<td>5.5</td>
<td>340</td>
</tr>
</tbody>
</table>

The solvent has a significant influence on the time constant of these processes (see [Ru']BL5[Pd] Table 3),$^{100,101,136–138,142–144,146,147}$ as seen by the longer time constants in DCM compared to MeCN. This effect can be explained by the decreased solvent polarity in DCM, which favors the population of the emissive phenanthroline-centered $^3$MLCT. In contrast the population of the dark phenazine centered $^3$MLCT will increase the dipole moment of the complex and is enhanced in the polar solvent MeCN.$^{148}$

In order to promote photocatalytic hydrogen production, favored localization of the excited state on the BL would be advantageous and therefore different substituents were introduced in 3,16-position of BL5. Electron withdrawing bromine substituents yielding BL5a or enlargement of the aromatic system by introduction of tert-butyl phenyl groups yielding BL5b (structures of BL5a and BL5b see Figure 34) were assumed as two examples decreasing the phenazine-based energy levels in comparison to the tbbpy-based energy states for the corresponding ruthenium complexes.$^{145,149}$

For both Ru chromophores, [Ru']BL5a and [Ru']BL5b, absorption and emission, lifetime and electrochemical experiments demonstrate stabilized $^1$MLCT and $^3$MLCT states localized at the phenanthroline part of the BL coordinated to ruthenium in comparison to [Ru']BL5. Furthermore, even the phenanzine-based reduction occurs at remarkable less cathodic potentials after substitution of BL5 due to the more pronounced π-acceptance by the substituted tpphz ligand.$^{143,145,149}$ This stabilization effect is sustained for the corresponding photocatalyst [Ru']BL5a[Pd] (see Figure 34).$^{143}$ However, the catalytic activity of [Ru']BL5a[Pd] (TON = 94) was found to be lower compared to [Ru']BL5[Pd] (TON = 238) under the same catalytic conditions. It seems that stabilization decelerate the ILCT to the phenazine part of the BL and also the charge transfer to the CC (see [Ru']BL5a[Pd] Table 3). Furthermore it was found that charge recombination from the CC located state occurs faster (7 ns for [Ru']BL5[Pd] vs. > 30 ns [Ru']BL5a[Pd]) upon introduction of heavy halogen atoms into the BL structure. Alternatively, processes associated with the second electron transfer might be slowed down by bromine substitution.$^{100,143}$ These measurements illustrate that the bromine substituents influence the electron transfer gradient across the entire supramolecular framework.$^{143}$ Unfortunately, no photocatalytically active complexes were reported for BL5b so far.

Komatsuzaki et al. achieved another manipulation of BL5 by introduction of methyl groups in 4,15-position resulting in the BL5e and the corresponding ruthenium complex [Ru]BL5e depicted in Figure 36.$^{150}$ Its absorption and emission properties are almost unaffected,
however, the lifetime of the excited state is increased considerably and the sensitivity towards protic environments is reduced. Obviously a steric shielding effect hinders H-bonding to the phenazine nitrogen atoms and thereby stabilizing the phenazine centered state. Unfortunately, no catalytically active complexes were reported for this ligand.

![Structure of [Ru]BL5e.](image)

**Figure 36: Structure of [Ru]BL5e.**

Another approach to improve the photocatalytic system is to stabilize the CC and at the same time push electron density into its direction. This was attempted by introduction of 4-methoxyphenyl substitution in position 2 and 17 of BL5 resulting in ligand BL5c. The corresponding RuPd complex is depicted in Figure 37.\(^{151,152}\) BL5c shows interesting optical properties as it features an intense absorption band at 416 nm, assigned to the excitation of an electron from a 4-metoxy-phenyl substituent to the phenazine moiety.\(^{152}\) This enhanced absorption is also observed for the corresponding heterodinuclear complex [Ru']BL5c[Pd\(^{0}\)]. However, [Ru']BL5c[Pd\(^{0}\)] only reaches a TON of 50 in 64h in comparison to a TON of 187 in 24h for [Ru']BL5[Pd] under the selected catalytic conditions. An explanation could be that the electron density at the CC is actually decreased upon photo excitation as an electron could be transferred from the 4-metoxy-phenyl substituent to the tpfhz core. Furthermore Pd is coordinated in a tridentate NNC-coordination sphere in [Ru']BL5c[Pd\(^{0}\)]. This leads to enhanced stability of the palladium center compared to [Ru']BL5[Pd] as proved by stirring the dissolved complex in the presence of mercury whereby the latter decompose to [Ru']BL5 but [Ru']BL5c[Pd\(^{0}\)] remains untouched. But as mercury poisoning eliminated hydrogen production under catalytic conditions the substitution seems to not sufficiently stabilize the palladium center under catalytic conditions.\(^{152}\) Additionally, the changed coordination sphere might influence the catalytic performance by altering the energy levels of the charge transfer states or by steric shielding of the CC trough the substituents.
Figure 37: Structure of [Ru']BL5c[PdCl] and UV/Vis absorption spectra of BL5c (dotted), [Ru']BL5c (dashed) and [Ru']BL5c[PdCl] (solid) in MeCN. Reprinted with permission from ref. 152. Copyright 2014 The Royal Society of Chemistry.

A further variation of BL5 is BL5d where one nitrogen atom of the phenazine unit is "exchanged" for a carbon atom (see Figure 34). The idea behind this was to investigate the role of this phenazine nitrogen atom on the passing electron. The absorption spectra of [Ru']BL5d and [Ru']BL5d[Pd] indicate alteration of the states of the phenazine moiety as a hypsochromic shift (ca. 15 nm) of the bands at around 350 nm is observed. These bands are assigned to ligand based \( \pi-\pi^* \) transitions in [Ru']BL5-like complexes. Two characteristic time constants are detected for the electron transfer along BL5d in [Ru']BL5d[Pd] after photoexcitation (4.4 ps, 580 ps). These constants are assigned to the ILCT and charge transfer to the catalytic center in analogy to the discussed behavior of [Ru']BL5[Pd] in Scheme 2 and [Ru']BL5d[Pd] in Table 3. The transitions \(^1\)MLCT-phen and \(^3\)MLCT-phen were not detected probably because they were very fast processes and that they were associated with very little spectral changes. However, less catalytic activity with a TON of 139 (vs. 238 for [Ru']BL5[Pd]) under the chosen conditions was observed pointing out that a phenazine moiety (e.g. in BL5) facilitates electron transfer and thus hydrogen production occurs much better compared to the acridine moiety in BL5d.

Addition of water to the acetonitrile solvent system shows an unexpected slight increase of emission lifetime (MeCN: 153 ns; MeCN/H\(_2\)O(10%): 162 ns) for [Ru']BL5d which shows that the acridine moiety is less prone to interact with the solvent water by forming hydrogen bonds in contrast to the phenazine unit in BL5. On the contrary, [Ru']BL5d[Pd] exhibits an emission lifetime decrease through water addition (MeCN: 180 ns; MeCN/H\(_2\)O (9:1): 90 ns). Furthermore the addition of water to MeCN as a solvent leads to a deceleration of all electron transfer steps in [Ru']BL5[Pd], [Ru']BL5a[Pd] and [Ru']BL5d[Pd] with the exception of the final charge transfer step in [Ru']BL5d[Pd] which is accelerated compared to pure MeCN. The other time constants are influenced much less by water addition for any of the three complexes.
Supported by the facts that there is i) no significant change of the ILCT time constant, ii) an
deceleration or an acceleration of the charge transfer to the metal center and iii) a decrease in
emission lifetime for $[\text{Ru}^\text{II}]\text{BL5d}[\text{Pd}]$ by water addition, it is concluded that the interaction of
water is rather based on the Pd-center than on the BL.

Another interesting variation of the tpphz skeleton is the introduction of nitrogen atoms instead
of carbon atoms in position 4 and 15 (see Figure 38). BL5f is asymmetric and two isomeric
compounds were synthesized the $[\text{Ru}^\text{phen}]\text{BL5f}$ and $[\text{Ru}^\text{phen}]\text{BL5f'}$.

$[\text{Ru}^\text{phen}]\text{BL5f}$ shows besides the bright $^3\text{MLCT}$ state located at the phenanthroline portion two
further states: one bright $^3\text{MLCT}$ located at the HAT portion and exhibiting lower energy
compared to $^3\text{MLCT}$-phen state and a dark state that seems to be located also at the HAT
portion being even lower in energy. The lifetimes of the first two states amount to 407 ns and
348 ns at room temperature. $[\text{Ru}^\text{phen}]\text{BL5f}$ seems to exhibit an energetic decay of the electronic
states along the BL from the phen moiety to the HAT moiety.$^{153}$

Figure 38: Structure of BL5f and the dinuclear $[\text{Ru}^\text{phen}]\text{BL5f}[\text{Ru}^\text{phen}]$; BL5f = Ru complexation
at 1; BL5f' = Ru complexation at 2.

In the dinuclear $[\text{Ru}^\text{phen}]\text{BL5f}[\text{Ru}^\text{phen}]$ complex the redox potentials of the differently
surrounded Ru centers vary by 200 mV ($\text{Ru}^\text{phen}: + 1.34 \text{ V}; \text{Ru}^\text{HAT}: + 1.55 \text{ V}$) indicating a strong
stabilization of the $\sigma\tau$ orbital involving the Ru$^{II}$ chelated on the HAT side.$^{154}$ If the electron
withdrawing feature of the HAT part of that ligand is not too strong this ligand might be an
interesting candidate for a hydrogen production catalyst. However, no photocatalyst based on
BL5f was realized yet.

Metal complexes with large aromatic ligands like BL5 show concentration dependent signals
in $^1\text{H}$-NMR experiments. This is explained by intermolecular $\pi-\pi$ aggregation of the ligands
and is also confirmed by solid state structures where complexes with one large aromatic ligand,
e.g. BL5, appear in a dimer formation.$^{139,145,148,149}$ In X-ray crystallographic investigations
$[\text{Ru}]\text{BL5[Pd]}$ also showed aggregation in a dimeric manner. To disturb the dimer-formation
during the catalysis planar aromatic molecules anthracene and pyrene were added to the
catalytic mixture of the $[\text{Ru}]\text{BL5[Pd]}$ system. Thereby a significant acceleration of the
photocatalytic hydrogen production and a shortening of the induction phase from ca. 2 to 1 h
was observed. The overall TON remained unchanged by the additives. A potential reason for
the catalytic activation in the initial phase through anthracene or pyrene could be the breakup of [Ru']BL5[Pd] aggregates due to the interaction with the polyaromatic compounds, as shown in Figure 39, resulting in a faster generation of the reactive species under photocatalytic conditions.\textsuperscript{155}

![Chemical structure](image)

**Figure 39:** Schematic display of π-attraction between pyrene and [Ru']BL5[Pd].

The biggest challenge in the design of BLs is to facilitate the desired electron transfer along the BL, i.e. to introduce a gradient of the energetic states from the PS along the BL to the CC. Thereby, fine tuning of the BL is of importance as a too strong stabilization of the first states diminishes the electron transfer (cf. [Ru']BL5a[Pd]) yet a moderate stabilization could channel the electron stream to the desired direction (cf. [Ru']BL5b). A good positioning of electron withdrawing nitrogen atoms seems to be a tool for the optimal design (cf. [Ru']BL5d[Pd] and [Ru']BL5f). However, unforeseen effects were found (and will further appear) during the search for the optimal design of BLs like heavy atom effect (cf. bromine substitution in [Ru']BL5a[Pd]) and competing ligand based photoinduced electron transfers (cf. [Ru']BL5c[Pd]).
3.1.2.3.) *NHC bridging ligands*

As mentioned above, purely N-donor based polypyridyl bridging ligands can suffer from insufficient binding of the CC in all redox states occurring during catalytic turnover, leading to decomposition of the catalyst. Similar demands to a catalyst are made in organometallic reactions such as coupling reactions. Here the use of *N*-heterocyclic carbene ligands (NHCs) has prospered significantly during the past decade or so due to the extraordinary binding properties of NHCs.\textsuperscript{156} Their strong σ-donor character and the possibility to act as π-donors as well as π-acceptors renders them ideal to stabilize metal centers during catalysis.\textsuperscript{157,158} In order to keep the light absorbing properties of the PS in place and at the same time stabilize the CC, a polypyridyl moiety on one side of the BL and the NHC moiety on the other side is a feasible concept. 1,3-(Dibenzyl)-1*H*-imidazo[4,5-*f*][1,10]phenanthroline(Bl12-H) is a precursor for such a ligand as it fuses together a phenanthroline moiety and a disubstituted imidazolium unit that can be deprotonated to form a carbene. The synthesis of the ligand is straightforward in many cases but can be challenging for smaller alkyl substituents like methyl or ethyl.\textsuperscript{159} The first report on this class of compounds appeared in 2012.\textsuperscript{160} So far several aspects have been published like synthesis and characterization of heterodinuclear complexes comprising RRip systems as a bridging ligand.\textsuperscript{160–162} Photocatalytic hydrogen evolution in molecular, homogenous systems has been investigated for selected combinations of PS and CC.\textsuperscript{162} Chung and co-workers used a system consisting of [Ru]mmip-H or [Ruphen]mmip-H as PS (and electron mediator) and (NHC)$_2$Pdl$_2$ as a catalyst precursor as an intermolecular system to generate a TON of 16 under optimized conditions.\textsuperscript{163}

![Figure 40: Investigated heterodinuclear complexes featuring BL12.](image-url)
In the investigation of Rau et al. the three complexes depicted in Figure 40 [Ru']BL12[Ag], [Ru']BL12[Rh'] and [Ru']BL12[Pd'] were characterized in detail. As [Ru']BL12[Ag] and its precursor [Ru']BL12-H were reduced more easily than the [Ru']phen reference in cyclic voltammetry measurements, it was postulated that the lowest energy 3MLCT state is based on the BL. Absorption and emission of the complexes are similar to that of [Ru(bpy)3]2+ but a red shift of the emission of up to 60 nm was observed which is in line with the electrochemical data and supports the assumption of the emissive 3MLCT state being located on the BL. Furthermore an increased emission intensity compared to [Ru(bpy)3]2+ was found for all complexes. Time correlated measurements revealed two lifetimes for all three compounds which can be explained by the presence of two emissive states: a shorter lifetime (220-1447 ns) based on one of the tbppy ligands and a longer lifetime component based on BL12 ligand (1096 – 2309 ns).

The complexes were tested as catalysts in a 6:3:1 MeCN/TEA/H2O mixture with 0.25 mM catalyst concentration and all of them showed catalytic activity upon irradiation with a 470 nm LED light source, yet with quite different outcomes ([Ru']BL12[Ag] TON = 4, [Ru']BL12[Rh'] TON = 16, [Ru']BL12[Pd'] TON = 36 after 5h). Out of these three unsurprisingly [Ru']BL12[Ag] performed the worst and DLS measurements revealed the formation and growth of particles during the irradiation time. This can be explained by agglomeration of silver halogenido species that may be formed during the synthesis or photodecomposition of the complex or by formation of elemental silver from AgCl by the photophysical effect. The DLS investigations did not give clear results in the case of [Ru']BL12[Pd'], however, the lack of an induction period and constant TOF are indicative for a stable molecular catalyst. An explanation for the unclear results could be small amounts of particles formed from silver halogenido impurities stemming from the synthesis of the complexes similar as explained for [Ru']BL12[Ag]. These first results look quite promising and further investigations on this kind of complexes are carried out in the group of Rau. The fact that not only the nature of the substituents at the BL can be varied but also different metals can be employed as CCs opens a vast area of potential applications for this type of complex.

3.1.3.) The role of the catalytic center

Beside the right choice of the BL the metal of the CC has an obvious high influence on the catalytic mechanism and the activity of the photocatalyst. For driving intramolecular, homogeneous photocatalysis a stable linkage between BL and CC is necessary. As mentioned before and described by Hammarström et al. 102 as well as Eisenberg et al. 103 in 2008, the formation of metal colloids always needs to be considered under photocatalytic conditions as they may serve as the actual catalysts.

In the case of proton reduction to form molecular hydrogen the catalytic center needs to be considered carefully and need to fulfill certain tasks: (i) The metal center should be able to
reduce protons to molecular hydrogen. (ii) The HOMO and LUMO properties compared to the 
photo center and BL should ideally follow a downhill process starting at the photo center and 
ending at the CC to avoid back electron transfer. (iii) The CC should be able to exist in various 
oxidation states during photocatalysis. An essential component to influence the activity and 
stability of the CC is the choice of co-ligands coordinated to it.

Within this context this chapter will give insight into the influence of the variations of the CC on 
catalytic activity, correlations between its redox properties and the influence of coordinated co-
ligands on catalytic activity will be visible. Here we will focus on two selected cases of BL.
Some examples have already been discussed in the previous chapters under a different point 
of view and hence will be discussed here in more detail.

3.1.3.1.) Systems based on BL5

![Complexes based on BL5 of Rau et al. discussed upon their varying CC.](image)

First investigations into [Ru']BL5[Pd] (see Figure 41), as intramolecular photocatalyst, as one 
of the first HEPMDs involved in intramolecular photocatalysis by Rau et al., suggested that it 
may drive photocatalytic water reduction as molecular catalyst. This was concluded by indirect 
approaches, i.e. the highly selective hydrogenation of diphenylalkyne to cis-stilbene. This 
strong selectivity is a strong indication for a molecular nature of the active catalyst.\textsuperscript{136}

Further investigations were carried out under more optimized catalytic conditions with a water 
content of 10 %. However, a significant induction period of roughly 2 hours was observed for 
[Ru']BL5[Pd] illustrated by a time dependent TOF. This indicates that the catalytically active 
species is not [Ru']BL5[Pd] but formed \textit{in situ}. Additionally, X-ray absorption spectroscopy 
(XAS) showed a fast and significant accumulation of Pd\textsuperscript{0} with a metal like environment as a 
function of irradiation time. So far it is not fully clarified whether the Pd\textsuperscript{0} colloids function as an 
essential intermediate in the catalytic cycle, or as the catalyst themselves or just a catalytically 
inactive decomposition product.\textsuperscript{144,152}

To elucidate the role of colloidal palladium during catalysis, mercury tests were further 
applied,\textsuperscript{164} as mercury reacts with metal colloids and particles forming amalgams.\textsuperscript{164} However,
elemental Hg is able to decompose the photocatalyst already in pure solvent under non-catalytic conditions as recently observed for structurally related RuPd photocatalysts.\textsuperscript{131,152,165} Comparable tests were also carried out for [Ru']BL5[Pd] and \textsuperscript{1}H-NMR studies. revealed decomposition to [Ru']BL5 in the presence of Hg even under non-catalytic conditions and exclusion of light, in pure MeCN.\textsuperscript{152}

In general, the formation of colloidal palladium takes place if the stability of the zero valent metal center in the corresponding ligand sphere is too low. As described above, BL5 was manipulated by introduction of 4-methoxyphenyl substituents leading to BL5c and the corresponding [Ru']BL5c[Pd\textsuperscript{6}]. Here the Pd center is ligated by a tridentate NNC-sphere compared to the bidentate NN-sphere in BL5. [Ru']BL5c[Pd\textsuperscript{6}] does not decompose in the presence of Hg in pure solvent, verifying a higher stability. The catalytic activity was lowered by this manipulation, possibly due to a changed catalytic reaction mechanism. However, complete loss of catalytic activity occurred upon addition of elemental mercury.\textsuperscript{152}

A different approach to modify the catalytic activity is the change of the catalytically active metal instead of changing the coordination environment (Structures of [Ru']BL5[CC] with varying CC are depicted in Figure 41). Rau et al. therefore exchanged the Pd to Pt in the [Ru']BL5[CC] system.\textsuperscript{144} The two photocatalysts [Ru']BL5[Pd] and [Ru']BL5[Pt], differing only in the catalytically active metal center, allow a detailed investigation into the influence of the CC on the overall photocatalytic activity. UV/Vis spectroscopy and ultrafast time-resolved transient absorption experiments state that the nature of the second metal center has neither significant influence on photophysical properties of the chromophore nor on the photophysical processes in the subnanosecond region. However, the catalytic activity of [Ru']BL5[Pt] (TON = 7) is strongly decreased in comparison to [Ru']BL5[Pd] (TON = 161) after 10 hours irradiation under identical catalytic conditions.\textsuperscript{142,144} However, the lack of an induction phase and the constant TOF of 0.7 h\textsuperscript{-1} in the case of [Ru']BL5[Pt] illustrate an improvement in stability and suggest for a different reaction mechanism. Some experiments to investigate the ongoing mechanism were performed\textsuperscript{144}: (i) Addition of high excess of Cl-ions to the photocatalytic solutions of [Ru']BL5[Pd] and [Ru']BL5[Pt] yielded complete deactivation of hydrogen formation for the former, and no influence on the latter. This is in agreement with the already proposed reaction pathway relying on the dissociation of a chloride ligand for [Ru']BL5[Pd].\textsuperscript{136} A different mechanism without ligand dissociation is proposed for [Ru']BL5[Pt].\textsuperscript{144} (ii) Simultaneous X-ray absorption near-edge structure (XANES) measurements for both photocatalysts were performed under photocatalytic conditions to obtain information about the oxidation states and ligand environment of the CCs. It became obvious that after 35 min irradiation under catalytic conditions [Ru']BL5[Pd] started to decompose to palladium particles as the XANES spectrum changed from matching the molecular to matching the metallic references. In contrast the spectrum of [Ru']BL5[Pt] did not change even after 6 hours upon
irradiation under catalytic conditions proving the high stability of the complex during catalysis.\textsuperscript{144} (iii) This was also confirmed by mercury poisoning experiments as [Ru\textsuperscript{IV}]BL5[Pt\textsuperscript{IV}] remains stable under non-reductive conditions in pure MeCN under exclusion of light and retains catalytically active in the presence of Hg under catalytic conditions.\textsuperscript{144}

A drastic effect on catalytic activity was described by Rau \textit{et al.} by the replacement of the terminal ligands on the CC.\textsuperscript{101} The substitution of the chlorido by iodido ligands forming [Ru\textsuperscript{IV}]BL5[Pt\textsuperscript{IV}] as depicted in Figure 41 lead to a drastic enhancement of the maximal TON from 7 to 276, maintaining a relative constant TOF. This means an overall increase of the maximal TON by the factor of almost 40 compared to [Ru\textsuperscript{IV}]BL5[Pt\textsuperscript{II}]. Furthermore, the TON and TOF can be improved significantly by increasing light intensity. A maximal TON of 465 was reached after 48 hours with an overall TOF = 9.9 h\textsuperscript{-1} using 4 LED arrays (30–40 mW/cm\textsuperscript{2}) vs. a maximal TON of 276 and a TOF of 6 h\textsuperscript{-1} for 2 LED arrays (30–40 mW/cm\textsuperscript{2}).\textsuperscript{101}

The higher activity of [Ru\textsuperscript{IV}]BL5[Pt\textsuperscript{IV}] in comparison to [Ru\textsuperscript{IV}]BL5[Pt\textsuperscript{II}] can be explained by the increased electron density at the Pt center because of the stronger π-donor nature of the iodido ligand.\textsuperscript{101} To determine the influence of the terminal iodido ligands on intramolecular electron transfer processes or the catalytic mechanism at the platinum center in comparison to the chloride containing related Pd and Pt catalysts ([Ru\textsuperscript{IV}]BL5[Pd\textsuperscript{II}] and [Ru\textsuperscript{IV}]BL5[Pt\textsuperscript{II}]), steady state UV/Vis, transient absorption spectroscopy and positive excited state absorption (ESA) measurements were performed. The obtained results are similar for all three complexes. These observations indicate that the ultrafast photoinduced electron transfer processes are not affected by the exchange of the terminal Pt bound anions.\textsuperscript{101}

For [Ru\textsuperscript{IV}]BL5[Pt\textsuperscript{IV}] the activity was unaltered upon addition of excess chloride and iodide ions, demonstrating that no iodido dissociation occurs during catalysis.\textsuperscript{101} Unfortunately, the mercury test turned out to be not applicable for [Ru\textsuperscript{IV}]BL5[Pt\textsuperscript{IV}], as the catalyst reacts with elemental mercury in the dark in pure DMSO already. Nevertheless, significant photocatalytic activity is still observed even under the presence of elemental mercury which excludes the presence of colloidal Pt under photocatalytic conditions.\textsuperscript{101}

DFT calculations as well as \textsuperscript{195}Pt NMR studies show an increase in electron density essentially induced by the iodido ligands. As suggested by Sakai \textit{et al.} on a related RuPt HEPMD the d\textsubscript{2} orbital of the Pt center plays a major role in the bond formation with the proton source (water).\textsuperscript{165} Additional electrochemical investigations do not state significant changes in the reduction potentials upon substitution of chloride to iodide ligands. The replacement of chlorido to iodido ligands is a first example for targeted co-ligand optimization of the catalytic metal center, without modification of the photophysical properties.\textsuperscript{101}

Photocatalytic activity was also strongly affected upon introduction of [Rh\textsuperscript{III}] as the CC unit. First irradiation experiments proved [Ru\textsuperscript{IV}]BL5[Rh\textsuperscript{III}] to serve as an active photocatalyst for hydrogen production with a maximum TON of 17 after 670 hours. It is remarkable to see
hydrogen evolution for such a long irradiation time. Mercury poisoning experiments in darkness in pure MeCN lead only to a small amount of decomposition and did not have any effect on the rate of photocatalytic hydrogen formation. Further optimization to enhance catalytic activity and studies into the photocatalytic mechanism are under way.\textsuperscript{167}

In summary these findings by Rau \textit{et al.} indicate stable catalysts in the case of [Ru\textsuperscript{II}BL5[Pt]], [Ru\textsuperscript{II}BL5[Pt\textsuperscript{II}]] and [Ru\textsuperscript{II}BL5[Rh\textsuperscript{II}]]. The obtained results show that the exchange of the catalytically active metal center as well as the co-ligands has major effect on ongoing catalytic activity, even though the photophysical processes of the compounds in pure solvents may remain largely unaltered.

\textit{3.1.3.2.) Systems based on BL4}

Sakai \textit{et al.} presented the first homogeneous photocatalyst for hydrogen evolution, i. e. [Ru]BL4a[Pt].\textsuperscript{116} Detailed information on photocatalytic activity, ongoing catalytic reaction mechanisms and modifications on the BL were given in chapter \textit{3.1.2.1.) N- or O-donor bridging ligands}.

For a better understanding of the mechanistic processes on the CC, Sakai \textit{et al.} set focus on the investigation of the mere catalytic [Pt] center. Therefore, photocatalytic studies on the intramolecular systems were compared to intermolecular set-ups consisting of [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} as the PS, MV\textsuperscript{2+} serving as an electron relay and the different [Ru][Pt] photocatalysts serving potentially only as CC, amongst others [Ru]BL4a[Pt] and [Ru]BL10[Pt] (cf. Figure 27 and Figure 30). It was observed that the former was active for hydrogen evolution under intra- as well as intermolecular catalytic conditions. However [Ru]BL10[Pt] was not active in any case.\textsuperscript{166}

As mentioned before spectroscopic studies on [Ru]BL10[Pt] revealed only weak platination-induced emission quenching. Furthermore, the hindered rotation of the 4-substituted pyridine donors might result in a sterical hindrance of H\textsuperscript{+} attack on the [Pt] CC during catalytic turnover.\textsuperscript{166} It is further important to mention that a structural analog to [Ru]BL10[Pt], cis-PtCl\textsubscript{2}(4-methylpyridine)\textsubscript{2}, which possesses freely rotating pyridyl rings about the Pt-N bond axis in solution, applied in intermolecular photocatalysis showed relatively high H\textsubscript{2}-evolving activity. It was concluded, that the hydrogenic activation at the axial site of the Pt may be allowed for the more flexible cis-PtCl\textsubscript{2}(4-methylpyridine)\textsubscript{2} complex, in contrast to the rigid catalytic unit in [Ru]BL10[Pt].\textsuperscript{166} These results suggest that the ineffectiveness of [Ru]BL10[Pt] as a photocatalyst for hydrogen evolution is ascribable to the ineffectiveness of the Pt unit and the poor efficiency in the intramolecular electron transfer from the \textsuperscript{3}MLCT excited state of the Ru\textsuperscript{II} moiety to the Pt\textsuperscript{II} catalyst.

Detailed studies of Sakai \textit{et al.} of mononuclear Pt\textsuperscript{II} complexes in intermolecular systems revealed that hydrogen evolving catalytic activity is enhanced for mononuclear Pt CC consisting of amine type ligands in comparison to pyridyl type ligands. This is in contrast to
catalytic activity observed for the dinuclear [Ru]BL8a[Pt] and [Ru]BL9[Pt]. Cis-coordinated chlorido ligands containing Pt CCs yield higher catalytic activity.\textsuperscript{20,121,166} Especially, shorter bridged Pt-Pt distances seem to enhance catalytic activity. The authors suggest destabilization of the HOMO due to a strong Pt\textsuperscript{ll}-Pt\textsuperscript{lll} interaction to be relevant for the higher catalytic activity (see Figure 42) or the ligation of negatively charged chloride ions in the cis-PtCl\textsubscript{2} complexes are responsible for the destabilization of the HOMO corresponding to the filled Pt(d\textsubscript{z\textsuperscript{2}}) orbital. This leads to higher activity in the hydrogenic activation at the axial site of the Pt. The energy level of the Pt d\textsubscript{z\textsuperscript{2}} orbital greatly affects the H\textsubscript{2}-evolving activity of the Pt.\textsuperscript{166}

![Molecular orbital diagrams of cis-[Pt(NH\textsubscript{3})\textsubscript{2} (H\textsubscript{2}O)\textsubscript{2}]\textsuperscript{2+} and [Pt\textsubscript{2}(NH\textsubscript{3})\textsubscript{4} (\mu-amidato)\textsubscript{2}]\textsuperscript{2+}.](image)

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To gain an advantage of favored Pt-Pt interactions, covalently linked RuPt fragments were to be considered to exhibit higher photocatalytic activity towards hydrogen formation, because the two RuPt fragments can interact with each other without diffusion. Therefore, [Ru\textsubscript{2}BL4e[Pt]\textsubscript{2}, a dimer of [Ru]BL4a[Pt], was prepared and tested to ascertain the validity of the bimolecular mechanism (cf. Figure 27&Figure 28).\textsuperscript{20,120} Unfavorable electronic coupling between the two Ru moieties, i.e. excited state quenching of one Ru\textsuperscript{*} with the other Ru in the ground state, were not observed and quite strong platination-induced emission quenching (approximately 90\%) proved to be in consistence with the almost doubled initial rate of H\textsubscript{2} formation for [Ru\textsubscript{2}BL4e[Pt]\textsubscript{2} (\(\Phi_{\text{H}_2} = 1.4\%\)) in comparison to [Ru]BL4a[Pt] (\(\Phi_{\text{H}_2} = 0.6\%\)).\textsuperscript{20,120}

The following reaction pathways can be postulated based on DFT calculations for mononuclear Pt-catalysts for H\textsubscript{2} production (see Figure 43). An uphill process by initial proton coupled electron transfer occurs where two Pt\textsuperscript{lll} centers, a proton and an electron forming a Pt\textsuperscript{lll}Pt\textsuperscript{lllH} intermediate. It is proposed to be followed either by a homolytic (route III; a bimolecular path) or heterolytic coupling (route II, unimolecular path) with respect to the Pt\textsubscript{2} intermediate under elimination of H\textsubscript{2}.\textsuperscript{20,168}
Figure 43: Postulated reaction pathways for H₂ production catalyzed by Pt CCs based on Pt-Pt interaction. Reprinted with permission from ref. 20. Copyright 2012 The Royal Society of Chemistry.

Sakai et al. also discussed optimized photocatalytic hydrogen evolution activity by optimizing the ratio between Ru PS and the number of Pt CC. This is achieved by the addition of one and two corresponding BL4[Pt] units coordinated to the Ru PS yielding \([\text{Ru}]\{\text{BL4a}[\text{Pt}]\}_2\) and \([\text{Ru}]\{\text{BL4a}[\text{Pt}]\}_3\) (see Figure 44). 169

Figure 44: Structures of dyad \([\text{Ru}]\{\text{BL4a}[\text{Pt}]\}_2\) and dyad \([\text{Ru}]\{\text{BL4a}[\text{Pt}]\}_3\).

Photocatalytic hydrogen evolving experiments showed an increase of produced hydrogen yielding TONs of 6.9 after 5 hours irradiation for \([\text{Ru}]\{\text{BL4a}[\text{Pt}]\}_2\) and 7.4 after 12 hours irradiation for \([\text{Ru}]\{\text{BL4a}[\text{Pt}]\}_3\). However, the apparent photocatalytic efficiency does not linearly correlate with the number of catalytic sites per molecule (Ru-Pt << Ru-Pt₂ < Ru-Pt₃). Commonly, the photocatalytically active [Ru]Pt-based compounds (\([\text{Ru}]\{\text{BL4a}[\text{Pt}]\]), \([\text{Ru}]\{\text{BL4a}[\text{Pt}]\}_2\) and \([\text{Ru}]\{\text{BL4a}[\text{Pt}]\}_3\) showed a rapid decay in the transient absorption spectroscopy. This is in contrast to \([\text{Ru}]\{\text{Pt}\}\)-based compounds, which are inactive for photocatalytic hydrogen formation and do not exhibit rapid intramolecular electron
Electron transfer kinetics and electrochemical data are consistent with the dinuclear [Ru]BL4a[Pt] analog.\textsuperscript{169}

In summary, the presented findings show that a huge influence on catalytic activity can be exerted by altering the CC. Not only the choice of the metal for the CC but also the co-ligands at that moiety have an influence and can be used to tune the activity. Interestingly, these changes do not necessarily alter the photophysical properties, meaning that the general function of the catalyst stays intact after manipulation. This also leads to the conclusion that the rate-determining step could be based on the CC and more effort should be put in designing CCs that facilitate the proton reduction step itself. As shown, this can be achieved by tuning steric factors or optimizing ligand architectures to change orbital energies.

### 3.1.3.3.) Systems based on BL8a

In 1977 Lehnh and Sauvage reported a multicomponent system for the light driven hydrogen generation, using a rhodium-polypyrrole complex as integral part of the whole process.\textsuperscript{171} In 1979 Kirch et al. showed that the luminescence of [Ru(bpy)\textsubscript{3}]\textsuperscript{2\textsuperscript{+}} can be quenched by various rhodium-based coordination compounds such as [Rh(bpy)\textsubscript{3}]\textsuperscript{2\textsuperscript{+}} or [Rh(bpy)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{2}]\textsuperscript{2\textsuperscript{+}}.\textsuperscript{172}

Furthermore, Kalynasundaram et al. investigated the luminescence quenching behavior by intramolecular electron-transfer in [Ru]BL8a[Rh].\textsuperscript{173} Based on these promising results, Brewer et al. started to examine similar systems as electron collectors and HEPMDs. First results indicated that a well-balanced combination of BL and CC could open the possibility of generating metal-based electron collectors in trinetallic supramolecular systems, which may serve as HEPMDs under proper conditions.\textsuperscript{174–176}

The first working HEPMD based on BL8a was presented by Brewer and coworkers in 2007.\textsuperscript{126} ([Ru]BL8a)\textsubscript{2}[RhCl\textsubscript{2}] was able to reach a TON of H\textsubscript{2} formation per photocatalyst of 30 after 4 hours of irradiation with 470 nm in presence of DMA as sacrificial electron donor in a solvent mixture consisting of CH\textsubscript{3}CN and water. Addition of HCl as the proton source instead of CF\textsubscript{3}SO\textsubscript{2}H reduced the amount of produced hydrogen, indicating a Cl\textsuperscript{−} loss as an important step in the photocatalysis. The combination of electrochemical and spectroscopic data indicated, that the threefold reduced species [Ru][BL8a][Rh][BL8a][Ru] is the active catalyst, generated by three visible light-driven oxidations of DMA concomitant with the loss of two chloride ligands.

Interestingly, the supramolecular system was much more efficient than the combination of the corresponding monometallic compounds, which was ascribed to the steric protection of the reduced rhodium center against dimerization. Exchange of the Cl\textsuperscript{−} ligands by Br\textsuperscript{−} ligands generated the trinetallic complex ([Ru]BL8a)\textsubscript{3}[RhBr\textsubscript{2}].\textsuperscript{177} Although the absorption spectra of the chloride and bromide derivative were identical, the reduced \(\sigma\)-donating ability of the Br ligands versus the Cl\textsuperscript{−} ligands resulted in a 40 mV cathodic shift of the irreversible two-electron reduction of the rhodium center in the cyclic voltammogram. As the energy of the emission did not change upon halide exchange, the easier reduction of the bromide derivative resulted in
lower excited state lifetimes, which was assigned to a faster population of the $^3_{\text{MMCT}}$ state from the emissive $^3_{\text{MLCT}}$ state due to the higher driving force for intramolecular electron transfer. Consequently, ((Ru)BL8a)$_2$[RhBr$_2$] achieved a TON of 38 under the same catalytic conditions and therefore higher activity than the chloride derivative$^{177}$ As a halide loss has been shown to be part of the catalytic cycle, the enhanced TON for the bromide derivative has also been attributed to a faster dissociation of the bromide in the reduced rhodium intermediates$^{105,177}$ which could be proven in later studies$^{179}$ By anion metathesis it was possible to convert the PF$_6$ salt of ((Ru)BL8a)$_2$[RhBr$_2$] to the bromide salt and making the trimetallic architecture water soluble$^{180}$ This complex was the first molecular system capable of evolving hydrogen in pure aqueous media. In contrast to the previous obtained TON of 38 in MeCN, they obtained values between 1 and 3, though mainly caused by changing the electron donor from DMA to TEOA. Interestingly they found out, that the presence of coordinating anions such as CF$_3$SO$_3$ and Br results in lower TONs with respect to PO$_4^{3-}$, further indicating halide loss as important step in catalysis.

The TON enhancement in ((Ru)BL8a)$_2$[RhX$_2$] systems going from $X = \text{Cl}$ to $X = \text{Br}$ is also observed in related systems such as (Ru$^{\text{Phen}}$)BL8a)$_2$[RhX$_2$] and (Ru$^{\text{Phzphen}}$)BL8a)$_2$[RhX$_2$] and seems to be a general trend in those trimetallic systems$^{178,181}$ Changing the Cl$^-$ ligands to Br$^-$ ligands leads in all cases to an easier rhodium based reduction, more efficient luminescence quenching relative to the model systems [Ru$^{\text{phen}}$]BL8a and [Ru$^{\text{Phzphen}}$]BL8a, smaller excited state lifetimes and increased rates for intramolecular electron transfer as well as higher TONs for hydrogen evolution. Applying the previously optimized catalytic conditions for those systems (120 µM of catalyst, 0.62 M of water, 3.1 M of DMA in 24.5 mL DMF solution with a headspace of 25 mL)$^{127}$ resulted in a TON in H$_2$ formation of 870 per catalyst (Ru$^{\text{Phzphen}}$)BL8a)$_2$[RhBr$_2$] after 46 hours and 1300 after prolonged irradiation. TONs for (Ru$^{\text{Phzphen}}$)BL8a)$_2$[RhCl$_2$] under these conditions were not reported. Further electrochemical and kinetic studies revealed that upon changing of $X = \text{Cl}$ to $X = \text{Br}$ in all systems ((Ru)BL8a)$_2$[RhX$_2$], ([Ru$^{\text{phen}}$]BL8a)$_2$[RhX$_2$] and (Ru$^{\text{Phzphen}}$)BL8a)$_2$[RhX$_2$] leads to an increased thermodynamic driving force and rate constants for the reductive quenching of the $^3_{\text{MLCT}}$ and $^3_{\text{MMCT}}$ states by DMA$^{182}$ Alongside with these potential positive results for photocatalytic hydrogen evolution they also obtained increasing rate constants for bimolecular deactivation of the excited states through interaction with DMA when changing the Cl$^-$ ligands to Br$^-$ ligands. For all complexes regardless of $X = \text{Cl}$ or Br the photoreduction occurs primarily from the $^3_{\text{MLCT}}$ rather than from the $^3_{\text{MMCT}}$ state. Detailed electrochemical studies of (Ru$^{\text{Phzphen}}$)BL8a)$_2$[RhX$_2$] showed, that upon changing $X = \text{Cl}$ to $X = \text{Br}$ the current enhancement in presence of an acid as well as the TOF for H$_2$ evolution increases$^{183}$ Furthermore they identified a solvent dependent speciation of the complexes upon two-electron reduction. As the Br$^-$ anion is well soluble in dry and wet CH$_3$CN, as well as in DMF
the rhodium based reduction always leads to \([(Ru^{\text{Ph2phen}})BL8a]_2[Rh^+]\). Due to the lower solubility of the Cl\(^-\) anion in dry CH\(_3\)CN a breakup \([(Ru^{\text{Ph2phen}})BL8a]_2[RhCl_2]\) into \([Ru^{\text{Ph2phen}}]BL8a[RhCl_2]\) and \([Ru^{\text{Ph2phen}}]BL8a\) occurs. The Cl\(^-\) dissociation is facilitated in wet CH\(_3\)CN and DMF leading to the intact trimetallic architecture upon two-electron reduction under these conditions. For both halide derivatives the catalyst activation proceeds therefore by an ECEC mechanism in DMF and the true working catalyst has been assigned as the four times reduced \([Ru^{\text{Ph2phen}}](BL8a)[(Ru^{\text{Ph2phen}})BL8a][Ru^{\text{Ph2phen}}]\). Changing X = Cl or Br to X = OH in \([(Ru)BL8a]_2[RhX_2]\) leads to a more difficult reduction of the rhodium based LUMO with concomitant decrease of the intramolecular electron transfer rate.\(^{184}\) Interestingly the TONs for hydrogen evolution in DMF increases in the order X = Cl, Br, OH against the expectations from the photophysical data, whereas in pure water the TONs are nearly identical. Brewer and coworkers suggested an ion pairing of the dissociated anions with the reduced rhodium center having a negatively impact on H\(_2\) formation rate by hindering interactions with the substrate. Using water as solvent, which exhibits a higher dielectric constant than DMF, leads to a better separation of the ions in all cases and therefore to similar TONs. The increased TON of the hydroxide derivative in the lower dielectric constant solvent DMF is also explained by this ion pairing mechanism. The catalytic mixtures pH value of 9 leads to almost complete protonation of the dissociated OH\(^-\) ions resulting in no ion pairing with the activated catalyst, whereas Cl\(^-\) and Br remain anionic and active for coulombic interactions due to the low pK\(_a\) value of the corresponding acids, showing again the feasible tuning of photocatalytic activity by changing of terminal ligands.

After work from MacQueen et al. which showed reductive elimination of hydrogen upon irradiation of \([Ru]BL8a[Rh^{\text{PPP3}2H_2}]\) by a possible energy transfer from a Ru based \(^3\)MLCT to a rhodium centered \(^3\)LF excited state,\(^{115}\) the first binuclear system based on BL8a for the intended photocatalytic generation of hydrogen under irradiation with light was reported in 2007 from Sakai and coworkers.\(^{118}\) Due to the extensive hybridization of the Pt\(^{\text{II}}\)-based orbitals over BL8a a very easy first reduction localized on the bridge in \([Ru]BL8a[Pt]\) occurs, leading to inactivity in hydrogen evolution. Control experiments with added \([Ru(bpy)_3]^{2+}\) as PS and MV\(^{2+}\) as electron relay showed, that the Pt center in \([Ru]BL8a[Pt]\) is able of proton reduction catalysis and intramolecular electron transfer seems to be the bottleneck for this system.
State of the Art

Figure 45: Structures of dyad [RuBL8a[Rh\textsubscript{BppyCl}\textsubscript{2}], [Ru\textsuperscript{Ph2phen}\textsubscript{B}][BL8a[Rh\textsuperscript{Ph2phen}Cl\textsubscript{2}], [Ru\textsuperscript{Ph2phen}\textsubscript{B}][BL8a[Rh\textsuperscript{Ph2phen}Br\textsubscript{2}], [RuBL8a[Rh\textsubscript{COD}], [Ru\textsuperscript{CH3bpy}\textsubscript{B}][BL8a[Rh\textsubscript{COD}], [Ru\textsuperscript{phen}\textsubscript{B}][BL8a[Rh\textsuperscript{bpy}Cl\textsubscript{2}] and dyad [RuBL4a[Rh\textsuperscript{bpy}Cl\textsubscript{2}].

After evaluation of synthetic procedures and design principles for electron collection on the CC,\textsuperscript{185} Brewer and coworkers presented in 2011 another inactive bimetallic BL8a based supramolecular architecture towards hydrogen production.\textsuperscript{186} Despite the favorable energetics of [Ru\textsuperscript{phen}\textsubscript{B}][BL8a[Rh\textsuperscript{bpy}Cl\textsubscript{2}] (see Figure 45) with a Ru based HOMO and a Rh based LUMO as well as a concomitant efficient luminescence quenching compared to the system [Ru\textsuperscript{phen}\textsubscript{B}][BL8a due to intramolecular electron transfer, the catalytic inactivity of this system was ascribed to a Rh\textsuperscript{1},Rh\textsuperscript{1} dimer formation of the photochemically reduced bimetallic complex. In order to circumvent this effective inactivation process, steric shielding of the reduced rhodium center was intended by introduction of larger terminal ligands at the CC mimicking the trimetallic systems, which do not exhibit dimerization.\textsuperscript{187} Due to the closeness of the BL8a(\pi\textsuperscript{+}) and the Rh(\sigma\textsuperscript{+}) energy, minor changes on the terminal ligands affected the sequence of orbital energies. Because of the electron donating effect of the tert-butyl groups in
[Ru]BL8a[Rh\textsuperscript{bbpy}Cl\textsubscript{2}] ligand, the CC becomes harder to reduce than BL8a with the LUMO localized on the BL, probably preventing an efficient intramolecular electron transfer to the rhodium center. Using [Ru\textsuperscript{Ph2phen}]BL8a[Rh\textsuperscript{ppy}Cl\textsubscript{2}] steric protection as well as a Rh based LUMO could be obtained. The TONs of this bimetallic complex were approximately 50% of the trimetallic system ([Ru\textsuperscript{Ph2phen}]BL8a)\textsubscript{2}[RhCl\textsubscript{2}], well in agreement with the 50% absorptivity due to only one PS.

Further studies on the functionality of bimetallic BL8a based complexes lead to the Rh\textsuperscript{i} complexes [Ru]BL8a[Rh\textsuperscript{COD}] and [Ru\textsuperscript{dbppy}]BL8a[Rh\textsuperscript{COD}] as electronic analogs of photocatalytic intermediates.\textsuperscript{186} Electrochemical investigations revealed that in the Ru\textsuperscript{II}-Rh\textsuperscript{i} bimetallics the HOMO is Ru based whereas the LUMO is localized on BL8a. Large emission quantum yields and excited state lifetimes in those architectures indicate efficient luminescence quenching of analogous Ru\textsuperscript{II}-Rh\textsuperscript{III} complexes by intramolecular electron transfer from a \textsuperscript{3}MLCT to a \textsuperscript{3}MMCT state. Additionally the authors described a CH\textsubscript{3}CN induced decomplexation of the CC due to steric interactions between BL8a and COD leading to [Ru]BL8a or [Ru\textsuperscript{dbppy}]BL8a and [Rh(CH\textsubscript{3}CN)\textsubscript{2}(COD)]\textsuperscript{+}. Therefore photocatalysis was performed in the weaker ligating solvent acetone, where decomplexation does not occur. In presence of DMA as electron donor TONs of 170 and 60 were obtained for [Ru]BL8a[Rh\textsuperscript{COD}] and [Ru\textsuperscript{dbppy}]BL8a[Rh\textsuperscript{COD}] after 20 hours of irradiation with 470 nm, indicating that the COD ligand also acts as a steric protector for the reduced CC inhibiting Rh\textsuperscript{i}-Rh\textsuperscript{i}-dimerization. However both Rh\textsuperscript{i} complexes were not able to stoichiometrically reduce protons in absence of sacrificial electron donor even in acidified water. The authors conclude the necessity of further activation for catalysis, as they also have this described for their trimetallic systems.\textsuperscript{183} Detailed electrochemical investigations were undertaken using the systems [Ru\textsuperscript{Ph2phen}]BL8a[Rh\textsuperscript{Ph2phen}X\textsubscript{2}] with X = Cl, Br and [Ru]BL8a[Rh\textsuperscript{bbpy}Cl\textsubscript{2}].\textsuperscript{179} Comparison of the chloro and the bromo derivative under different scan rates in the cyclic voltammograms revealed an easier dissociation of the Br ligand versus the Cl ligand, resulting that the ECEC mechanism for the generation of the doubly rhodium centered reduction is more preferred for X = Br than for X = Cl, whereas the EECC mechanism is rather favored for the Cl derivative than for the Br derivative. For the generation of the catalytic active species [Ru]BL8a[Rh\textsuperscript{bbpy}Cl\textsubscript{2}] needs in contrast to the above discussed systems a further electron transfer step from BL8a to the CC in addition, due to its BL localized LUMO.

Upon introduction of the terpy ligand to the rhodium center, photocatalytic activity of [Ru]BL8a[Rh\textsuperscript{terpy}Cl] indicated, that there is no need of bearing two labile halide ligands on a rhodium based CC.\textsuperscript{189} Due to the easier CC based two-electron reduction compared to [Ru]BL8a[Rh\textsuperscript{bbpy}Cl\textsubscript{2}] the emission quantum yield compared to the model compound [Ru\textsubscript{2}]BL8a and the excited state lifetime are lowered due to the enhanced driving force for intramolecular electron transfer. Consistent with the obtained photophysical and electrochemical data the
achieved TON was higher for [Ru]BL8a[Rh^II/III] (TON = 58 after 10 hours of irradiation with 470 nm in deaerated DMF) as for [Ru]BL8a[Rh^II/III] (TON = 33, same conditions). It seems therefore that the η^2 coordination of the terpy ligand induces steric shielding of the reduced CC, preventing dimerization and inactivation of the catalyst. Additionally η^1-η^2 cycling is suggested to assist catalysis through secondary coordination sphere effects.

In conclusion, BL8a based supramolecular architectures can be used as HEPMDs. In contrast to the Pt derivatives which are inactive for hydrogen evolution, the rhodium systems are active when an optimized ligand environment is chosen. Key factors for the CC design are the securing of a high driving force for the Rh^III→Rh^I reduction by a Rh based LUMO as well as the existence of easy dissociable co-ligands.

3.1.4.) Conclusion

This article describes extensive challenges made in the field of artificial photosynthesis, with special attention paid to the development of PMDs capable of driving catalysis of hydrogen evolution. Moreover, this article provides valuable guidelines towards the development of more active photocatalysts based on the covalent linkage of Ru-polypyridyl derived photosensitizing components and Pt-, Rh- or Pd-based hydrogen evolving catalysts. Variation of the peripheral and bridging ligands as well as optimization of the catalytic center can lead to increased performance for each single HEPMD. However, no universally valid conclusion for design strategies towards the optimal intramolecular photocatalyst can be drawn yet. Therefore, we need to get a better mechanistic understanding of the underlying principles driving functioning HEPMDs (cf. Figure 46). Reducing protons to molecular hydrogen is a two electron process. Especially the second electron transfer step is expected to play a crucial role in determining the overall efficiency.\textsuperscript{150}

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**Figure 46:** A better mechanistic understanding is needed to gain more general optimization strategies for photocatalysts.

The development of catalysts that enable two-electron transfer from the same molecule will allow for kinetically more efficient reduction. Furthermore present need for the usage of sacrificial donors such as TEA, TEOA or EDTA in the catalytic hydrogen production is a
fundamental problem.⁲⁸ These donors have to be replaced by others such as water to gain a sustainable future energy economy.⁹¹ To fulfill this task immobilization of the catalyst on electrode surfaces and their utilization in DSPECs should be targeted (cf. chapter 2.2.) Artificial photosynthesis.

3.2.) Artificial Photosynthesis by heterogeneous catalysis: DSPECs for hydrogen evolution.

As shown in the last chapter a great number of HEPMDs have been designed and studied for proton reductions in homogenous systems. In this chapter I will focus on (inter- and intramolecular) hydrogen evolving systems incorporated in p-type and tandem-DSPECs to yield heterogeneous approaches with photoactive cathodes. Currently photocathodes limit the achievable photocurrents for tandem-DSPECs because they are the lower current-producing electrode. Photocurrent is generated by a light induced electron transfer cascade from the semiconductor over the sensitizer to the catalyst to perform redox reactions. Its magnitude therefore correlates to catalytic activity. Photocurrent densities for photocathodes, in the commonly used pH 7 buffer solution, range from 10-45 μA/cm², which pales in comparison to the 1.7 mA/cm² so far reached by the photoanode side.⁴⁹-⁵²,⁴⁹,¹⁹²,¹⁹³ Therefore, it is reasonable to invest more research effort in the field of dye sensitized photocathodes.

In 2012, the working group of Sun reported on the first example of a hydrogen producing photocathode.⁵⁴ It was based on a nanostructured NiO electrode immobilized with a push-pull triphenylamine (TPA) organic dye, P1, which was used before in a p-type DSSC with an incident photon to current conversion efficiency (IPCE) of 64%.³⁹

![Diagram](image)

Figure 47: DSPEC presented by Sun et al. in 2012.⁵⁴ Transient photocurrent responses to on-off cycles of illumination at an applied bias of -0.4 V vs. Ag/AgCl. Reprinted with permission from ref. 54. Copyright 2012 The Royal Society of Chemistry.

The incident photon to current conversion efficiency (IPCE) is defined as the ratio of collected charges to the number of incident photons, depending on the wavelength. After deposition of the HEC, a cobaloxime catalyst Co1, and connection to a Pt wire anode (Figure 47, left), this
DSPEC initially produced a photocurrent of 20 $\mu$Acm$^{-2}$. This measurement was performed under illumination with a visible light emitting diode with a light intensity of 250 Wm$^{-2}$, by applying a -0.4 V bias potential vs. Ag/AgCl in an aqueous pH 7.0 phosphate buffer solution. The three component homogenous system P1 as a photosensitizer, Co1 as a proton reduction catalyst, and triethanolamine (TEOA) as a sacrificial electron donor showed catalytic activity. Light-driven hydrogen production could also be confirmed for the cathode (NiO−P1−Co1), by applying a modified Clark electrode. However, pronounced photocurrent decay was observed under illumination with time, most likely due to leaching of the non-covalent bound catalyst or the organic dye from the electrode surface or decomposition of the system (Figure 47, right).

In 2013 Wu and co-workers published an intramolecular sensitizer-catalyst dyad, O22-CodmgBF2, in which the Ru polypyridyl sensitizer is connected via a polypyridyl bridging unit to a cobaloxime HEC, very similar to Co1 (Figure 48).\textsuperscript{50}

![Figure 48: Left: DSPEC presented by Wu et al. in 2013.\textsuperscript{50} Right: Transient photocurrent responses to on-off cycles of illumination at an applied bias of 0.1 V vs. NHE. Reprinted with permission from ref. 50. Copyright 2013 American Chemical Society.](image)

However, the assembly process of the functional photocatalyst is sequential, i.e. first the photoredoxactive ruthenium was bound to the surface and then the catalytic active cobalt unit had to be bound to the already immobilized photocenter. Hence it was not possible to correlate the photocatalytic properties of the assembled photocatalyst on the surface with those of a molecular Ru−Co catalyst in solution. O22 was covalently attached on alumina coated NiO by an elongated carboxylate unit. Wu and his group showed before that this elongation by an additional phenylene unit had positive effects on the efficiency of related p-type DSSCs.\textsuperscript{68} They also found that the alumina coating can enhance the magnitude of photocurrent. In connection with a Pt counter electrode, irradiation of the alumina coated NiO-O22-CodmgBF2 working electrode gave a stable photocurrent density of 9 $\mu$Acm$^{-2}$ over a period of one hour at a bias potential of 0.1 V vs. NHE. The experiment was conducted in aqueous pH 7.0 phosphate buffer solution and irradiation was supplied by a 300 W xenon lamp with a 420 nm cut off filter. H$_2$ generation was confirmed by gas chromatography after 2.5 hours, with a Faradic efficiency of 68% and a bias potential of 0.1 V vs. NHE.
In a recent publication the same group presented the first acidically stable p-type DSPEC with average photocurrents of 186 ± 36 μAcm⁻² over 16h at an applied bias of 0 V vs. NHE and pH 0 or as high as 300 μAcm⁻² at an bias of -0.2 V vs. NHE, again by illumination with a 300 W xenon lamp. The acid stability on NiO in the highly protic aqueous electrolyte (1 M HCl) was achieved by hydrophobic hexyl substituents incorporated in the organic push-double-pull dye (BH4), since they hinder interaction of the electrolyte with NiO. BH4 consists of a TPA donor moiety and two perylenemonoimide (PMI) acceptor groups. Charge recombination processes were slowed down by oligothiophene π-conjugated linkers between TPA and PMI moieties. The excited electron can interact with the hydrophilic electrolyte, which contains the catalyst, because the PMI groups are located above the canopy of the hexyl groups. The low pH electrolyte rendered the utilization of a [Mo₆S₄]⁴⁺ cluster as the catalyst possible. In contrast to cobaloxime, Mo₆S₄ clusters are stable and soluble in acidic aqueous solution and exhibit optimal activity. Hydrogen evolution was verified by GC in a cell with a platinum mesh counter electrode connected to the working cathode (described above) and 5mM catalyst in pH 0 with an applied bias of -0.3 V (Figure 49). However, an additional chemical bias is supplied by the acidic electrolyte compared to the pH 7 conditions in the aforementioned examples. The rather low faradaic efficiency of 49±11% was attributed to decomposition of the catalyst over time. Nevertheless, the high and stable photocurrents obtained in this system give rise to optimism (Figure 49, right), since they better match to the performance of photoanodes, allowing for more efficient tandem cells to be developed.

Figure 49: Left: DSPEC presented by Wu et al. in 2016. Right: Transient photocurrent responses to on-off cycles of illumination at an applied bias of 0 V vs. NHE and different pH values. Reprinted with permission from ref. 53. Copyright 2016 American Chemical Society.

The groups of Collomb and Odobel examined several cobalt and rhodium HECs in a p-type DSPEC with a ruthenium complex (RuP) sensitized photocathode and a platinum anode (Figure 50). To guarantee conductivity and solubility of the catalysts the experiments were performed in 0.1M [Bu₄N]ClO₄ acetonitrile solution with formic acid as a proton source. At a 1.5 mM catalyst concentration, illumination of the photocathode by visible light (λ = 400–700
nm, I = 350 mW) at an applied bias of -0.45 V vs. Ag/AgNO₃ generated almost no photocurrent in the case of the Co catalysts. In contrast, in the presence of the Rh catalysts an increase in photocurrent was observed (32 \, \mu \text{Acm}^{-2} for the [Rh^{III}(dbm)₂Cl₂]⁺ complex and up to ca. 80 \, \mu \text{Acm}^{-2} for the [Rh^{III}(tbppy)₂Cl₂]⁺ derivative), as a consequence of the electron transfer from NiO to RuP⁺ and from RuP⁺ to the Rh catalyst. Increasing the formic acid concentration from 1mM to 3mM resulted in a photocurrent increase of ca. 26% for [Rh^{III}(tbppy)₂Cl₂]⁺. Unfortunately, they only could observe the generation of the Rh^{III}-H hydride species, most likely due to the low reduction potential of RuP. This Rh^{III}-H hydride slowly reacts with formic acid to produce hydrogen. However, this process was not catalytic.

![Image](image.png)

Figure 50: Left: DSPECs presented by Collomb et al. in 2015.⁵¹ Right: Transient photocurrent responses to on-off cycles of illumination at an applied bias of -0.45 V vs. Ag/AgNO₃. Without catalyst (blue) and with [Rh(R₂bpy)₂Cl₂]⁺ (R= Me: green, R= tBu: red). Reprinted with permission from ref. 51. Copyright 2015 American Chemical Society.

Another example of dye sensitized photocathode was presented by Mozer and coworkers.⁵² Again a TPA-PMI donor-acceptor dye connected by an oligothiophene linker (PMI–6T–TPA) was employed as a sensitizer on NiO. Intriguingly, no HEC was involved in this system. Protons were directly reduced by photogenerated dye anions. Connection of the photocathode with a Pt wire anode in an aqueous pH=7 Na₂SO₄ buffer solution yielded the p-type DSPEC shown in Figure 51. Illumination with a 300 W Xe lamp with a λ > 420 nm long pass filter resulted in a photocurrent density of initially only 1.7 \, \mu \text{Acm}^{-2} which increased to 3.9 \, \mu \text{Acm}^{-2} over a period of 4h at zero bias potential. The Faradic efficiency for H₂ generation was calculated to be ca. 97%. A tandem DSSC was also realized by combination of this photocathode with a BiVO₄ photoanode. Under the same operating conditions an initial photocurrent of 1.8 \, \mu \text{Acm}^{-2} was obtained, which increased to 2.7 \, \mu \text{Acm}^{-2}. Unfortunately, O₂ production could not be verified due to sensitivity limits of the GC. Nonetheless, H₂ was detected with a Faradic efficiency of ca. 80% without any external bias in this tandem cell setup.
Figure 51: Left: DSPEC presented by Mozer et al. in 2012. Right: Chronoamperogram at an applied bias of 0 V vs. Ag/AgCl. Reprinted with permission from ref. 52. Copyright 2012 The Royal Society of Chemistry.

The first example of a potentially water splitting tandem cell with both electrodes photoactivated by dye sensitization was introduced by Sun et al. in 2014. For the photoanode, Ru based photosensitizer (RuP$'$) and water oxidation catalyst (RuOEC) were co-adsorbed onto TiO$_2$. The same photosensitizer was used for the NiO photocathode together with a co-grafted cobaloxime (CoHEC). Both catalyst were equipped with a pyridine-2,6-dicarboxylic acid anchoring group. A photocurrent density of 25 $\mu$Acm$^{-2}$ was obtained under 300 mWcm$^{-2}$ illumination in an aqueous phosphate buffer (pH=7) without any external bias. A cut off filter with $\lambda > 400$ nm was used to obtain the visible light illumination. Neither hydrogen nor oxygen evolution was investigated, questioning the origin of the photocurrent (illustrated by a question mark in Figure 52). Possibly, no detection was feasible because they did not use a two compartment cell, separating the two half-reactions. Once water is oxidized at the photoanode the oxidized product species might just be re-reduced at the photocathode, resulting in a self-destructive catalytic cycle.

Figure 52: Left: DSPEC presented by Sun et al. in 2014. Right: Transient photocurrent responses to on-off cycles of illumination without external bias but different light intensities. Reprinted with permission from ref. 192. Copyright 2014 The Royal Society of Chemistry.

One year later Sun’s group did present the first tandem-DSPEC with a dye sensitized photoanode and cathode, for which water splitting into oxygen and hydrogen could be demonstrated. For both electrodes organic TPA dyes (L0', P1) were applied. The water oxidation catalyst on TiO$_2$ was the same as in their last-mentioned system (RuOEC). The
cobaloxime hydrogen evolving catalyst (Co1\(^+\)) was attached on NiO by an elongated phosphonic acid anchoring group. Indeed, phosphonic acids are known to provide a more stable bonding to metal oxide than carboxylic acid (cf. chapter 2.3.4.) Anchoring groups.

Using a two compartment cell by dividing this photoanode and cathode by a glass frit, 0.33 μmol of H\(_2\) was produced without external bias after 100 min illumination with a white LED lamp (100mWcm\(^{-2}\), λ > 400 nm) in aqueous pH 7 phosphate buffer solution. This corresponds to 55% Faradic efficiency. Although a two compartment setup was employed, this low value was explained by diffusion of hydrogen or oxygen to the other compartment for respective reduction and oxidation. The amount of produced oxygen in this tandem DSPEC was not mentioned, although it was determined for the corresponding n-type DSPEC with Pt as counter electrode. The tandem-cell displayed a photocurrent of 70 μAcm\(^{-2}\). But notable decay was observed in that only ~60% of this photocurrent remained after the first 10 min of illumination, indicating instability of the system (Figure 49).

Figure 53: Left: DSPEC presented by Sun et al. in 2015. Right: Transient photocurrent responses to on−off cycles and fulltime photocurrent of illumination without external bias. Reprinted with permission from ref. 49. Copyright 2015 American Chemical Society.

For practical use, the photosensitizer and catalyst should be active for at least millions of cycles. From the practical application point of view the lifetime of current-state systems is thus far from ideal. But DSSCs with long operating durability have been commercialized successfully. Therefore future work should be focused on developing robust individual components for DSPECs based on their DSSC counterparts.
4.) Scope of the thesis

The present work was focused on the design and optimization of new immobilizable photocatalysts and their potential application in DSPECs for hydrogen generation following examples set by Wu et al.\textsuperscript{50,53,68} and Sun et al.\textsuperscript{49,54,192} Based on previous studies by the groups of Eisenberg\textsuperscript{196} and Rau\textsuperscript{144} and the master thesis of the PhD candidate\textsuperscript{197}, an intramolecular photochemical molecular device (PMD) (4) served as starting system for optimization (Figure 54).

![Intramolecular photocatalyst (4).](image)

The PMD is equipped with potent anchoring groups (anchor) and incorporates both a photoactive (PS) and a catalytic center (HEC) connected by a bridging ligand (BL) (Figure 55).

![DSPEC for light induced proton reduction. The photocatalyst consists of a photoactive Ru(bpy)$_2$-unit with variable-length phosphonate anchoring groups, a tpphz BL as suitable electron transfer mediator and PtCl$_2$ as a catalytically active metal center for hydrogen production.](image)
The intramolecular approach allows one-step immobilization of the PMD on semiconducting surfaces such as NiO and therefore easy integration into photoelectrochemical cells. Furthermore it should guarantee an efficient electron transfer cascade from NiO to the PS and from the PS over the BL to the HEC. This process can be optimized by specific modifications of the PMD. For instance, distance elongation between anchoring groups and PS by π-conjugated linkers (X) should prevent efficiency limiting factors like fast charge carrier recombination processes and aggregation of the chromophores on the SC surface. In addition extension of the aromatic system might have positive effects on molar absorbptivities and excitation energies of the corresponding dye. However, great care must be taken to choose appropriate spacer moieties X.

The particular aspects to be investigated comprise four main topics:

- **Optimization of the processability of the PMD with regard to facile integration in a DSPEC.**
  - Improvement of the hydrolysis strategy of (4).
  - Immobilization of the photocatalyst on NiO.
- **Examination of the immobilized system in DSPECs.**
  - NiO binding affinity studies.
  - Optimization of the DSPEC setup.
  - Photocurrent measurements.
- **Implementation of a modular synthesis concept for anchor elongation as a possible optimization strategy for PMDs in DSPECs**
  - Synthesis and characterization of bipyridine derivatives elongated by phenylene and triazole building blocks, using modern methods such as palladium catalyzed cross coupling and copper catalyzed CLICK reactions.
  - Sythesis of new metal complexes utilizing elongated bipyridine derivatives.
  - Photophysical studies of all new ligands and complexes.
- **Investigation of the new complexes with regard to possible utilization restrictions in DSPECs.**
  - Characterization of the nature and origin of a light-switch effect witnessed in triazole containing ruthenium complexes.
5.) Results and Discussion

5.1.) Designing a photochemical molecular device for $H_2$-generation in DSPECs

This chapter summarizes manuscript [MB1] and therefore contains parts of the master thesis of the PhD candidate. This includes the synthesis, preliminary characterization and determination of the photocatalytic activity of the novel intramolecular photocatalyst (4) in homogenous solution. More detailed photophysical studies, improvement of the hydrolysis strategy, immobilization experiments and writing of the publication [MB1] (cf. chapter 8.) were performed during the course of the PhD thesis. Below, the combined research efforts are presented.

![Figure 56: Retrosynthesis of [Ru^4(L0)CltpphzPtCl2]^{2+} (4). R = Cl, DMSO.](image)

The photocatalyst (4) incorporates phosphonic ester groups as precursors for potent phosphonate anchoring groups, which enable the immobilization of the catalyst on semiconducting electrode surfaces (cf. chapter 2.3.4.) Anchoring groups) and therby its utilization in DSPECs (Figure 56). The photocatalyst is based on a related complex [Ru^4(tbbpy)CltpphzPtCl2]^{2+} (6) with tbutyl groups instead of methyl phosphonic ester substituents, which has been reported by Eisenberg et al. as early as 1998. But the utilization of this functional unit as intramolecular photocatalyst for hydrogen production has been achieved only recently. For an effective fixation of the complex to a commonly used semiconductor like NiO, L0 (4,4'-bis(diethyl-(methylene)-phosphonate)-2,2'-bipyridine) was synthesized by slight modification of a five step route reported by the group of Odobel (Figure 57).

![Figure 57: Five steps synthesis of L0.](image)
A one step approach with N-bromosuccinimide is not productive since it leads to multi-
halogenation of the methyl groups of 4,4’-dimethyl-2,2’-bipyridine.\textsuperscript{198} For the first time single
crystals of L0 suitable for X-ray diffractometry could be obtained (Figure 58). The same was
achieved for the model complex $[\text{Ru}^{II}(\text{tbbpy})_2(\text{L0})]^{2+}$ (M) which was obtained by reaction of
$[\text{Ru}^{II}(\text{tbbpy})_2\text{Cl}_2]$ with one equivalent of L0.\textsuperscript{200}

![Diagram of molecular structure](image)

**Figure 58:** Solid-state structures of L0 and (M) (ball and stick depiction, Hydrogen atoms are
omitted for clarity).

Upon coordination phosphonic ester groups of L0 are turned into cis configuration with respect
to the C2-C2’-bond of the bipyridine. In comparison to related compounds no conspicuous
features were observed considering the pyridine-C-methylene-C bond, the methylene-C-P
bond, or the respective angle $<$(CCP). Neither hydrogen bonding nor $\pi$-$\pi$-stacking were found
within the structures. But packing patterns reveal positive polarization of the methylene and
ethyl moieties of L0 according to short contact interactions with oxygen atoms of the
neighboring phosphonate groups. The introduction of one L0 ligand to a Ru$^{2+}$ was already
described in aforementioned publication by Odobel and coworkers.\textsuperscript{199} For this work the crux
however was to find a synthesis strategy to coordinate two phosphonate bipyridines,
providing four anchoring groups per ruthenium complex for stable binding on semiconducting
surfaces. The preparation of Ru$^{II}$(L0)$_2$Cl$_2$ from ruthenium trichloride had indeed been presented
by Fitzmaurice et al.\textsuperscript{201} However, only moderate yields of 32% were reported. In addition, L0
proved to be instable in a microwave-assisted reaction with Ru[(COD)Cl]$_n$ which is usually
used for the efficient synthesis of Ru(bpy)$_2$Cl$_2$-derivatives.\textsuperscript{200} Hence, we presented a synthetic
route under mild conditions, i.e. reflux in methanol, starting with Ru[DMSO]$_4$Cl$_2$ as a precursor.
Looking at previous publications, DMSO as well as Cl could be replaced bpy-like ligands,
leading to ruthenium complexes with different substitution patterns.\textsuperscript{202,203} Nonetheless,
independent from the extant monodentate ligands of this raw product, coordination of a third
N$^4$N-coordinating ligand will lead to the desired complex. Actually, introduction of phen(O)$_2$
(1,10-phenantrolinene-5,6-dione) to the crude Ru(L0)$_2$Cl$_2$-DMSO$_x$-complexes (1) gave an overall yield of (2) of 86%, starting with
Ru[DMSO]$_4$Cl$_2$ (Figure 59). Therefore, this strategy turned out to be a high-yielding method to
generate ruthenium complexes with two L0 ligands. By condensation of complex-bound phen(O)₂ and phen(NH₂)₂ (1,10-phenanthroline-5,6-diamine) we obtained the bridging ligand tpphpz and complex (3). In principle, direct complexation of tpphpz to Ru(bpy)₂Cl₂-derivatives is possible. But due to thermal instability of L0 we avoided the high-temperature conditions which are necessary for solvation of the poorly soluble tpphpz. In the last step (3) and Pt[DMSO]₂Cl₂ were refluxed in ethanol to gain the novel photocatalyst (4) in 82% yield. (3) and (4) have been fully characterized by NMR-spectroscopy, high-resolution mass spectrometry (HRMS) and elemental analysis.

Figure 59: Synthesis route to (4).

Additionally, differences in ¹H-NMR spectra of (3) and (4) proved the introduction of the PtCl₂-catalytic unit successful.

Figure 60: Comparison of ¹H-NMR spectra of (3) and (4). Signal shifts for protons a’ and b’ are evident.
The deshielding by platinum has a particular strong effect on the tpphz protons in close proximity (a', b'; cf. Figure 60). For this investigation it must be guaranteed that the spectra are measured at equivalent concentrations, since $^1H$-NMR signal shifts of (3), (4) and similar ruthenium complexes are concentration dependent.\textsuperscript{155,204,205} Another strong indication for the coordination of platinum to the free phenanthroline sphere of tpphz is given by absorption and emission spectroscopy. In (4) as well as in structurally related Ru-tpphz-Pt complexes we observe loss of the pronounced absorption band at 380 nm, which is typical for the phenazine based $\pi$-$\pi^*$-transitions of mononuclear Ru-tpphz.\textsuperscript{147} Furthermore, quenching of the emitting excited state upon Pt introduction could be seen (Figure 61).\textsuperscript{196} Other features like intense $\pi$-$\pi^*$-absorption below 350 nm and metal-to-ligand charge-transfers centered around 450 nm are usual for ruthenium polypyridyl complexes (cf. chapter 2.4.2.) Photophysics of ruthenium polypyridyl complexes).

Figure 61: UV/Vis (solid lines) and emission spectra (dashed lines) of (3) and (4) in MeCN.

A more electron-withdrawing substitution effect of the methyl phosphonic ester groups of (3) compared to tbutyl-groups became visible by comparison with the photophysics of $[\text{Ru}^{\text{II}}(\text{tbbpy})_2\text{tpphz}]^{2+}$ (5). At the same time we witnessed a pronounced maximum at the low energy part of the MLCT absorption band (bathochromic shift of 0.08 eV compared to (5)) and a slight hypsochromic shift in emission (0.084 eV compared to (5)). This antipodal behavior might be attributed to lowered $\pi^*$-levels on L0 compared to tbbpy and reduced electron density at the Ru center of (3) relative to (5), caused by an electron-pull of the methyl phosphonic ester substituents. The latter was confirmed by studying the oxidation potential for the Ru$^{\text{III}}$ couple in (3) and (5). In MeCN and 0.1 M NBu$_4$PF$_6$ as supporting electrolyte Ru$^{\text{III}}$ oxidation is easier accessible for (5) (0.86 V vs. Fc/Fc$^+$) as to
(3) (1.02 V vs. Fc/Fc⁺). Importantly, (3) also showed the light switch effect, i.e. luminescence quenching upon addition of water to the MeCN dye solution (cf. 2.4.2.) *Photophysics of ruthenium polypyridyl complexes*, which suggest that the methyl phosphonic ester groups do not change the emission behavior compared to similar compounds without anchoring groups.²⁰⁶²⁰⁷ Related Ru-dppz complexes with dicarboxylated bipyridines, which represent another popular anchoring group for semiconduction surfaces (cf. chapter 2.3.4.) *Anchoring groups*, did not show a light switch behavior, implying fundamentally different excited state relaxation pathways than those typically observed.²⁰⁸ Having in mind that [Ru²⁺(tbppy)₂tpphzPtCl₂]²⁺ (6) represents an active photocatalyst for hydrogen production it is promising that methylene phosphonic ester derivatives do not change the photophysical properties significantly. This trend could further be supported by Resonance Raman experiments. As has been shown before for the ruthenium/palladium catalyst [Ru²⁺(tbppy)₂tpphzPdCl₂]²⁺, the localization of the initially excited state is highly important for the catalytic process.²⁰⁹ This is independent of the nature of the catalytic center (palladium or platinum). From the comparison of Resonance-Raman spectra of (3) and (4) with [Ru²⁺(tbppy)₂tpphzPdCl₂]²⁺ we could conclude that changing the peripheral ligands did not alter the localization of the initially photoexcited states. Hence electron transfer in the direction of catalysis (GS→¹MLCTₜₚₚₜₚ) is likely. In this process the methylene spacer between bpy and the anchoring moiety might be crucial, since the extent of the aromatic system of bpy is not altered by introducing tbutyl- or methyl phosphonic ester groups. The photocatalytic activity of (4) was indeed superior to (6) (cf. Figure 62).

![Figure 62: Photocatalytic activity of (4) and (6).](image)

In a MeCN:H₂O (9:1) mixture and in the presence of TEA as sacrificial electron donor, (4) showed prolonged catalytic lifetimes (48h vs. 10h) and raised turnover numbers (37 vs. 7).¹⁰⁴ One possible reason is the aforementioned increased energy of the luminescent state detected for (3) if compared to (5), since this excited state relaxation pathway is more difficult to reach.
Moreover, the polarity of the phosphonate ester units in (4) is higher in comparison to tbutyl-groups of (6). As a consequence they may lead to different aggregation of the catalyst thus providing more optimal conditions for proton migration and activation.

Although PtCl₂ as catalytic center displays lower catalytic turnover than similar complexes with PdCl₂, its utilization in an intramolecular photocatalyst seems more appropriate, since loss of the intramolecular character as result of colloid formation can be excluded. Additionally, just a slight modification of the co-ligands of (6) from chloride to iodide lead to an boost of catalytic activity by a factor of 40, from 7 to 276. ¹⁰¹ Hence an immobilizable photocatalyst based on (4) seems to be very attractive.

To investigate its principle applicability in dye sensitized cells, tests into hydrolysis and immobilization of (M), (3) and (4) were conducted. For this purpose, the ester groups of L0 need to be deprotected to generate free phosphonate anchoring groups. This was accomplished by refluxing the corresponding complex in half-concentrated HCl as described by Odobel et al. ¹⁹⁹ To regain solubility in organic solvents [Ru⁴(tbbpy)₂(bpy(CH₂PO₃H₂)₂)]Cl₂ (Mₜₜₜₜ) was reprecipitated in water as PF₆ salt. Interestingly, deprotection of (3) and (4) with half-concentrated HCl yielded completely insoluble products. However, addition of NaOH rendered the deprotected species water-soluble, most likely as a consequence of phosphonate group deprotonation (hydrolysis procedure 1). Unfortunately the ¹H-NMR spectra of these complexes in D₂O + 4% NaOD show complicatedly shaped signals compared to the protected species which were not straightforward to interpret. To improve the processability of the complexes, solubility in organic solvents should be restored. Therefore the hydrolysis strategy was altered. In this case hydrolysis of (3) and (4) was accomplished by reaction with Me₃SiBr as reported for similar ruthenium complexes (cf. chapter 9.). ²¹⁰ Solubility of (3ₜₜₜₜ) in MeOH was restored by treatment with the lipophilic cation tetrabutylammonium (tBu₄N+) and by deprotonation with tetrabutylammonium hydroxide (TBAOH) as Grätzel et al. applied for the famous dye N719 (cf. Figure 10). ²¹¹ This hydrolysis procedure 2 yielded a uniformly deprotected species of (3ₜₜₜₜ) which could be characterized by ¹H-NMR- and ³¹P-NMR spectroscopy. The ethylgroups were completely removed as expected (Figure 63).
Results and Discussion

Figure 63: \(^1\)H-NMR spectra of (3) in MeCN [D3] and (3_hydrolyzed) in MeOD [D4].

Independent of the hydrolysis procedure, signals can be found at 14-15 ppm in the \(^{31}\)P-NMR spectra which might be explained by differing degrees of deprotonation at the hydroxide groups connected to the phosphorous atoms (Figure 64). The utilization of hydrolysis procedure 1 gave rise to an additional signal at ca. 5.5 ppm for (3_hydrolyzed). One possible explanation of its appearance is the coordination of Na\(^+\)-ions at the phosphonate groups, resulting in an downfield shift as similarly observed for (benzoxazol-2-ylmethyl)phosphonic acid for instance.\(^{212}\) No such signal was obtained after the use of hydrolysis procedure 2.

hydrolysis procedure 1:
• deprotection with 18% HCl.
• treatment with NaOH to restore solubility in H\(_2\)O.

Figure 64: \(^{31}\)P-NMR spectra of (3_hydrolyzed) deprotected by different hydrolysis procedures. Recorded in D\(_2\)O + 4% NaOD for the product of hydrolysis procedure 1 (top) and in MeOD [D4] for the product of hydrolysis procedure 2 (bottom).

hydrolysis procedure 2:
• deprotection with Me\(_2\)SiBr.
• treatment with TBAOH to restore solubility in and MeOH.
Altogether, hydrolysis procedure 2 provides a more uniform product compared to hydrolysis procedure 1. Furthermore, solubility in organic solvents like methanol is enabled which is advantageous for the immobilization of the corresponding complex. The complexes ($M_{\text{hydrolyzed}}$), ($3_{\text{hydrolyzed}}$) and ($4_{\text{hydrolyzed}}$) were immobilized on NiO which is deposited on a FTO glass substrate. The sensitized films were analyzed by UV/vis (reflection) spectroscopy, showing no significant changes to the protected or hydrolyzed analogues in solution (Figure 65). From these spectra we even could derive the hint that platinum is still stably connected to (4) after hydrolysis and immobilization. The mononuclear complex ($3@\text{NiO}$) shows the phenazine based $\pi-\pi^*$-transitions band at 380 nm whereas ($4@\text{NiO}$) has the characteristic unstructured absorbance of a dinuclear RutpphzhPt-species in this region, as described before. This indicates the preservation of the principle functional capability as intramolecular photocatalyst.

![Absorption spectra of (3), (4) and (M) in acetonitrile, ($3_{\text{hydrolyzed}}$), ($4_{\text{hydrolyzed}}$) and ($M_{\text{hydrolyzed}}$) in water + 4% NaOH and ($3@\text{NiO}$), ($4@\text{NiO}$) and ($M@\text{NiO}$).]

Figure 65: Absorption spectra of (3), (4) and (M) in acetonitrile, ($3_{\text{hydrolyzed}}$), ($4_{\text{hydrolyzed}}$) and ($M_{\text{hydrolyzed}}$) in water + 4% NaOH and ($3@\text{NiO}$), ($4@\text{NiO}$) and ($M@\text{NiO}$).

The combined research efforts of this study showed that the detailed analysis and understanding of photocatalytic activity of the presented novel system is possible and will enable the design of photoelectrochemical cells for overall water splitting with molecular building blocks similar to (4).
5.2.) Preliminary results in DSPEC setup

An important property for a viable photocatalyst in a DSPEC is its strong attachment to the semiconductor surface as it governs the stability of the binding and the electronic coupling with the semiconductor. The affinity of the binding groups in the mononuclear complex (\(3_{\text{hydrolyzed}}\)) was assessed by determination of the binding constant with NiO by recording the Langmuir adsorption isotherm in methanol, according to literature.\(^{38}\) Table 4 lists the values of the binding constants \(K\) as well as the surface concentration at monolayer full coverage \(\Gamma_{\text{max}}\) compared to Ru(bpy)\(_2\)(L\(_0\)\(_{\text{hydrolyzed}}\)) as a model complex from literature.\(^{38}\)

<table>
<thead>
<tr>
<th>complex</th>
<th>(K (M^{-1}))</th>
<th>(\Gamma_{\text{max}} ) ((\mu\text{mol} \cdot m^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ru(bpy)}(L_0_{\text{hydrolyzed}}))</td>
<td>(1.7 \times 10^4)</td>
<td>(1.2)</td>
</tr>
<tr>
<td>((3_{\text{hydrolyzed}})\text{CN}^+)</td>
<td>(1.2 \times 10^6)</td>
<td>(0.43)</td>
</tr>
</tbody>
</table>

\(\text{[a]}\) determined from MeCN solution
\(\text{[b]}\) determined from MeOH solution

Table 4: Adsorbance data for (\(3_{\text{hydrolyzed}}\)) and Ru(bpy)\(_2\)(L\(_0\)\(_{\text{hydrolyzed}}\)).\(^{38}\)

According to binding constants the affinity of (\(3_{\text{hydrolyzed}}\)) towards NiO is about two orders of magnitude stronger than for Ru(bpy)\(_2\)(L\(_0\)\(_{\text{hydrolyzed}}\)). This can be simply explained by the quantity of anchoring groups per complex, which is four compared to two. However, the surface coverage is not proportional to the binding constant. Indeed, the surface coverage for (\(3_{\text{hydrolyzed}}\)) at NiO is only about one third of the value obtained for Ru(bpy)\(_2\)(L\(_0\)\(_{\text{hydrolyzed}}\)) at NiO. Besides sterical factors, molar coverage is probably related to the overall charge of the complex which will be inevitably changed upon deprotonation of the complex. Upon full deprotonation (\(3_{\text{hydrolyzed}}\)) is a 6-fold negatively charged complex, whereas Ru(bpy)\(_2\)(L\(_0\)\(_{\text{hydrolyzed}}\)) is only 2-fold negatively charged. The mean distance between each complex on the surface is therefore controlled by its charge owing to the electrostatic repulsions.\(^{38}\)
Results and Discussion

Figure 66: HRMS spectrum of (4_{hydrolyzed}) (at the top). Calculated Spectrum for [(4_{hydrolyzed}) - 4H^+]^{2-} (at the bottom). (4_{hydrolyzed}) was obtained according to hydrolysis procedure 2. The main peak cluster appearing in the high-resolution ESI-mass spectrum of (4_{hydrolyzed}) was consistent with the formula of the four-fold deprotonated complex [(4_{hydrolyzed}) - 4H^+]^{2-} (m/z = 717.9769) (Figure 66). Two additional peak clusters suggest that partial chloride-bromide co-ligand substitution at the Pt center took place, most probably due to the use of Me_3SiBr as hydrolysis agent (Figure 67).

Figure 67: HRMS spectrum of (4_{hydrolyzed}).
As mentioned before, in case of [RuII(tbbpy)$_2$tpphzPtCl$_2$]$^{2+}$ the exchange of chlorido by iodido ligands at the platinum center lead to a drastic enhancement of the maximal TON in homogeneous catalysis by a factor of 40, presumably as consequence of an increased electron density at the Pt center (cf. chapter 3.1.3.) The role of the catalytic center.$^{101}$ Compared to chloride, bromide co-ligands should improve the catalytic activity in a similar positive fashion. Therefore we decided not to alter the hydrolysis agent to the corresponding Me$_3$SiCl.

But to further maximize the performance in DSPECs, efforts were made to substitute the chloride co-ligands of (4) by iodide. Unfortunately, during hydrolysis and workup with TBAOH to regain solubility in MeOH, the iodide ligands in the respective PtI$_2$-complex (4') seem to be more labile compared to chloride. Its better ability to stabilize the negative charge makes iodide a superior leaving group to chloride which in turn makes (4') prone to nucleophilic attack by hydroxide from TBAOH (Figure 68).

![Hydroxide-iodide substitution at the Pt center of (4') hydrolyzed) upon workup with TBAOH.](image-url)

After hydrolysis of (4') with Me$_3$Si multiple peak clusters appeared in the high-resolution ESI-mass spectrum, suggesting that hydroxide ions replaced iodide (Figure 69). For this reason we decided to further investigate the more stable complex (4$_{\text{hydrolyzed}}$) for which no such hydroxide-halogenide co-ligand substitution could be observed.
First measurements in a DSPEC were performed during a research visit in the working group of Prof. Dr. Anders Hagfeldt in Uppsala. The NiO electrodes were prepared according to literature.\(^\text{39}\) (4\textsuperscript{hydrolyzed}) was immobilized by dipping the NiO substrate for 2 days into a 0.2 mM dye solution. A beaker served as compartment for a standard three-electrode cell where the reference electrode is Ag/AgCl in 0.1M degassed phosphate buffer and the counter electrode is a platinum wire (setup 1, see Figure 70). A potential of -0.4 V vs. Ag/AgCl was applied as approximately equal to the position of the conduction band of TiO\(_2\), which is essential to facilitate future studies in combination with a TiO\(_2\) based photoanode to achieve visible light-driven total water splitting.\(^\text{54}\)

![DSPEC setup in Uppsala (setup 1).](image)
Results and Discussion

Figure 71 shows the transient short-circuit photocurrent generated by light chopping under illumination with a light emitting diode with a light intensity density of 250 Wm\(^{-2}\) and a 450 nm cut off filter.

![Graph of transient photocurrent responses](image)

**Figure 71**: Transient photocurrent responses to on–off cycles of illumination in setup 1 with an applied bias of -0.4 V vs. Ag/AgCl and 0.1M phosphate buffer solution as electrolyte. (4)@NiO as working electrode (black), bare NiO as working electrode (red).

An initial photocurrent density of 25 μA/cm\(^2\) was generated. However, decay upon multiple on-off-cycles of illumination was observed, which might be due to catalyst decomposition or leaching from the electrode surface to the solution. Indeed, UV/vis-experiments of electrode films sensitized with (3\(_{\text{hydrolyzed}}\)) indicated that dye anchorage is prone to the phosphate buffer solution (cf. Figure 72).

![Absorption spectrum](image)

**Figure 72**: Absorption spectrum of (3)@NiO before and after 2 days in phosphate buffer (0.1M). After 2 days in 0.1M phosphate buffer the well-structured MLCT and the phenazine based π-π*-transitions band vanished. Most probably, the phosphonate anchoring groups and the phosphonate anions from the buffer solution are in competition for binding positions at the NiO surface. Bound photocatalyst detaches from the surface until equilibrium is reached (Figure 73).
Results and Discussion

Figure 73: Competition for binding positions at NiO between complex $3_{\text{hydrolyzed}}$ and phosphonate anions from the electrolyte.

Since phosphate buffer solutions are most commonly used for DSPECs for hydrogen evolution (cf. chapter 3.2.) Artificial Photosynthesis by heterogenous catalysis: DSPECs for hydrogen evolution.) this finding might imply a severe limitation for the utilization of phosphonate anchoring groups in these devices.

Additionally, the beaker-setup (setup 1) is exposed to ambient atmosphere. The obtained photocurrents might therefore originate from oxygen instead of proton reduction. In homogenous catalysis experiments in the presence of oxygen, Dr. Michael Pfeffer could show that the related complex $\text{[Ru}^{II}(tbbpy)_{2}pophzPtI}_{2}^{2+}$ first reduces oxygen before hydrogen formation takes place. Not until the oxygen concentration in the headspace of the reaction vessel levelled below 5 volume %, the photocatalyst started to produce molecular hydrogen.$^{213}$ Hence, we decided to design an improved DSPEC setup (setup 2, Figure 74), which was realized in cooperation with the research group of Prof. Dr. Jacob at the institute for electrochemistry at the university of Ulm.

Figure 74: Schematic illustration of the DSPEC setup in Ulm (setup2). Inset: photo of the illuminated cell.
The presence of oxygen close to the working electrode was avoided by a continuous nitrogen flux atop the head space of the electrolyte during measurement. A pore 5 glass frit, separating the DSPEC in two half-cells, should slow down diffusion of potentially generated oxygen from the counter electrode compartment to the working electrode. The NiO electrodes were prepared according to a slight modification of the literature method used for the electrodes in Uppsala (cf. chapter 9.).NiO was immobilized by dipping the NiO substrate for 2 days into a 0.2 mM dye solution (cf. Figure 75).

![Figure 75: NiO electrodes used in setup 1 (active area 0.32 cm²) before (A) and after (B) immobilization of (4hydrolyzed) and NiO electrodes used in setup 2 (active area 1 cm²) before (C) and after (D) immobilization of (4hydrolyzed).](image)

The photocathode in the new DSPEC setup 2 was illuminated by a blue LED lamp (I = 100 mWcm⁻², λ = 470 nm). To stabilize the baseline and minimize the impact of background, the on–off cycles of illumination were carried out at 400 seconds after the application of -0.4 V vs. Ag/AgCl. Since the aforementioned results indicated instability of the surface binding in phosphate buffer, the measurements were also performed in a 0.1M Na₂SO₄ solution (cf. Figure 76). Most obviously, the results from the light chopping measurements show a dramatic diminution of the obtained photocurrents compared to the DSPEC setup 1. The sharp transient photocurrent spikes observed should be a result of accumulation of charge carriers at the NiO/electrolyte interface due to either the trap of holes in the bulk of NiO or slow kinetics of proton reduction until an equilibrium is reached between proton reduction, charge recombination, and charge extraction.₅₀,₂₁⁴
Results and Discussion

Figure 76: Transient photocurrent responses to on-off cycles of illumination in setup 2 with an applied bias of -0.4 V vs. Ag/AgCl. (4)@NiO as working electrode (black), bare NiO as working electrode (red). In phosphate buffer (0.1M) (left), in Na$_2$SO$_4$ (0.1M) (right).

After equilibration the extant photocurrents are a consequence of the electron transfer cascade from the VB of NiO to (4$_{hydrolized}$) to perform reduction reactions. In comparison, bare NiO films did not show any photocurrents upon irradiation with visible light. In the oxygen free setup 2 photocurrents of only 3 μA/cm$^2$ in 0.1M phosphate buffer or 4 μA/cm$^2$ in 0.1M Na$_2$SO$_4$ solution were obtained. This finding is a clear hint that most of the 25 μA/cm$^2$ photocurrent observed in setup 1 was caused by oxygen reduction processes. Nevertheless, great care must be taken when considering these results as exact values. Photocurrents are influenced by multiple operating conditions like pH, electrolyte, electrodes, light intensity and applied bias. Since the cell setups 1 and 2 differ in some of these factors, the preliminary results should be interpreted rather qualitatively.

Figure 77: Chronoamperogram of (4)@NiO in setup 2 with an applied bias of -0.4 V vs. Ag/AgCl. First 10 minutes of chopped measurement omitted for clarity. In phosphate buffer (0.1M) (left), in Na$_2$SO$_4$ (0.1M) (right).

Chronoamperometry studies suggest that binding stability of (4)@NiO in Na$_2$SO$_4$ solution is increased compared to the phosphate buffer solution (Figure 77). Whereas fast photocurrent
decay within the first 5 minutes can be observed for the measurement in phosphate buffer a prolonged decay time is obtained for the Na$_2$SO$_4$ electrolyte.

In conclusion, utilization of (4) in DSPECs did lead to visible light-induced photocurrents, which suggest that hydrogen production with such a system is possible. However, its stability still needs to be improved and the cell setup must be optimized to detect actual hydrogen formation e.g. by gaschromatography.

5.3.) Optimization of immobilizable photocatalyst by anchoring group elongation

Aim of these studies ([MB2]$_{216}$ and [MB3]$_{216}$, cf. chapter 8.) was to find viable routes to improve the photovoltaic performance of polypyridyl metal-complexes in solar- or photosynthesis cell. A promising approach is to introduce π-conjugated spacers between chromophores and electrode surfaces. Based on the knowledge of organic and metallorganic dyes, such elongated linkers provide for long charge separated state life times, hinder aggregation and have positive effects on molar absorptivities and excitation energies of the corresponding dye (see chapter 2.3.4.) Anchoring groups.$^{44,50,65-68}$ In a first step a modular synthesis concept for distance control between phosphonate anchoring unit and bipyridine was established using building blocks (BB) in modern methods such as palladium catalyzed cross coupling and copper catalyzed azide-alkyne coupling (CuAAC). The resulting phenylene and triazole units were utilized to prepare elongated ligands L1–L3 based on the original bipyridine L0 (cf. Figure 78).

![Diagram of linker elongation](image)

Figure 78: Starting materials for modular synthesis of elongated bipyridines L1-L3.

In a second step we coordinated this series of new ligands to rhenium and ruthenium metal centers to study the effect of linker elongation on the properties of the resulting homo- and heteroleptic complexes. Previous examples of the groups of Wu and Ishitani showed that the application of Re- or Ru-polypyridyl complexes on p-type SCs like TaON or NiO is very
desirable because of their photocatalytic activity in cells for CO₂ reduction or hydrogen evolution.²⁰,²¹⁷,²¹⁸ In order to further develop this potential, it is necessary to tune the properties of the dye for an effective directional electron transfer and a good light-harvesting ability with respect to the solar irradiation spectrum, since especially the excitation of rheniumbipyridyl complexes is typically only achieved under UV-light irradiation with low molar absorbivities. Suzuki coupling between (4-hydroxymethylphenyl)boronic acid (BB1) and 4,4’-dibromo-2,2'-bipyridine (bpyBr₂), followed by two subsequent substitution reactions (OH→Br, Br→PO(OEt)₂) were used to prepare ligand L1. Numerous attempts to introduce a second phenylene unit by adaption of literature methods failed.²¹⁹-²²⁶ An obvious candidate to replace phenylene as second spacer unit is triazole. Along with also being rigid and aromatic, triazoles are easy to generate via “CuAAC-CLICK-reaction”. According to Karl B. Sharpless’ definition of “CLICK-chemistry” it is straightforward to perform under mild reaction conditions, efficient, selective and insensitive towards many functional groups.²²⁷ To employ CuAAC for the synthesis of L2, diethyl-4-aminobenzylphosphonate (BB2) was transferred to the corresponding azide and bpyBr₂ was converted to 4,4’-Bis(ethynyl)-2,2'-bipyridine by Sonogashira coupling.²²⁸,²²⁹ The resulting azide and acetylene functionalities cyclize to triazole during the copper catalyzed reaction (Figure 79).

![Click reaction mechanism](image)

**Figure 79: CuAAC click reaction to yield L2 and mechanism of triazole cyclization.**

In order to insert more phenylene units between anchoring group and bpy core by CLICK-reaction, a new building block (BB5) needed to be synthesized. Suzuki coupling of diethyl-4-bromobenzylphosphonate (BB3) and 3-aminophenylboronic acid (BB4) and subsequent treatment with NaNO₂ and NaN₃ yielded BB5. Afterwards, according to the L2 synthesis route, L3 was created by CuAAC (Figure 80).
Figure 80: Synthesis of L3.

All new ligands were characterized by $^1$H, $^{13}$C-, $^{31}$P-NMR spectroscopy and HRMS. Additionally, crystals suitable for X-ray analysis were obtained for L1, L2 and for the amine intermediate BB5'.

The corresponding rhenium complexes were obtained by equimolar reaction of a Re(CO)$_3$Cl-precursor with the bpy derivatives (L0-L3) in toluene or methanol respectively. The synthesis of the trishomoleptic Ru-complex analogues was achieved in two steps according to the high-yielding procedure described in the last chapter for the generation of photocatalyst (4). Initially two equivalents of the bpy derivative are coordinated to Ru[DMSO]$_4$Cl$_2$ by refluxing in methanol. Then the third equivalent is introduced to the crude product of the first reaction by refluxing in an ethanol/water mixture (3:1). $^1$H, $^{13}$C-NMR and HRMS data were consistent with the desired product for each new Re- and Ru-complex (Figure 81). The structures of Re(L0), Re(L1) and Re(L2) were confirmed by X-ray crystallography.
Figure 81: Structures of Re- and Ru-complexes Re(L0)-Re(L3) and Ru(L0)₃-Ru(L3)₃.

The obtained ligand and Re-complex crystal structures enabled the determination of bpy-core to anchoring group lengths, making them a useful tool to estimate charge carrier injection distances between semiconductor and immobilized complex (Figure 82). A direct identification of the metal–surface distance depends on the binding mode of the immobilized complex towards the semiconductor, which is unknown at this point. Nevertheless, a comparative investigation of distances between pyridine nitrogen and the calculated centroid of the phosphonate oxygen atoms was carried out. The results show that the presented modular synthesis strategy proved itself as a valuable approach to increase the length of a bipyridine with phosphonate anchors stepwise by about 3–4 Å. All bond length and angles of the rhenium coordination polyhedrons for Re(L0)-Re(L2) are in agreement with respect to the data obtained for 62 structures of Re(CO)₃Cl(bpy)-derivatives in the CCDC database. Furthermore the complex structures support the trend that the distance is increased by about 4 Å by phenylene and by additional 3.4 Å through the introduction of the triazole spacer.
Results and Discussion

Figure 82: Solid state structures of L0-L2 and Re(L0)-Re(L2). Distances are displayed for the pyridine nitrogen atom (N1) and the calculated centroid between the phosphonate oxygen atoms (O3). A superposition of the solid-state structures of BBS (red) and L2 (blue) is depicted in order to estimate the O3-N1 distance for L3. Hydrogen atoms are omitted for clarity.

It is also worth noting that Re(L1) and Re(L2) both form dimers in the solid state with the chloride oriented in between the spacers groups of the opposite complex (Figure 83).

Figure 83: Ball and stick depiction of Re(L1) and Re(L2) dimers in the solid state. Hydrogen atoms are omitted for clarity.

In Re(L2) the triazole-C-H hydrogen atoms point to the chloride ligand, whereas the triazole nitrogen atoms on the outer rim of the scaffold establish short contacts with protons of the adjacent phenyl spacer. Triazoles have been suggested as versatile sensing tools because of this amphoteric behavior. 230–232

The photophysical studies of the free ligands as well as of the complexes revealed pronounced effects of the aryl substitution. Relative to L0 all three new ligands L1, L2 and L3 display broadened absorption bands and raised extinction coefficients (cf. Figure 85). While the absorption maximum of L1 is almost unchanged compared to the long wavelength maximum of L0, a shift to lower energies (0.12 eV and 0.18 eV) was observed for the triazole-containing
ligands L2 and L3. Bunz and coworkers proposed electron delocalization in pyridyltriazenes, displayed by mesomeric structures I and II, to be the reason for this energetic stabilization (cf. Figure 84).²³³

![Figure 84: Resonance structures I and II of pyridyltriazenes in L2 and L3.](image)

As a general and important trend a shift of absorbance to lower energies and an increase in molar absorptivities can also be observed for the MLCT absorbance in the complexes bearing elongated bpy derivatives compared to the complexes without π-extended ligands.

![Figure 85: Absorption (solid lines) and emission (dashed lines) spectra of L0-L3 and the respective rhenium and ruthenium complexes.](image)

It is known that ruthenium complexes with triazole or phenyl-substituted bipyridines show much stronger visible light absorption than the parent bipyridine complex.²³⁴,²³⁵ Furthermore, Hupp et al. witnessed an energy decrease of the MLCT excited states of phenyl- or ethynyl-substituted Re bipyridine complexes due to increased intraligand electron delocalization.²³⁵ In the series Re(L0) or Ru(L0)₃ to Re(L3) or Ru(L3)₃, the extinction coefficients were approximately doubled (3.4 vs. 7.1 or 17.6 vs. 29.5 [10²⁴ x M⁻¹ cm⁻¹]) and the MLCT maxima were red-shifted by 15 nm (i.e. 0.14 eV) or 20 nm (i.e. 0.11 eV), respectively. Time-dependent density functional theory calculations performed on Ru(L1)₃ and Ru(L2)₃ supported the experimental findings. Two main and one weaker MLCT states with calculated wavelengths of
454, 475 and 505 nm were predicted for Ru(L1)_3. The same was the case for Ru(L2)_3 at 456, 477 and 508 nm. The presence of these lower energy states also contributes to the increased absorption in the red part of the MLCT band. With the ultimate goal of efficient sunlight harvesting by enhancing the molar extinction coefficients and shifting the MLCT absorption bathochromically, metal complexes based on L1-L3 represent auspicious aspirants for sensitizers in photovoltaic cells. Within this context, another advantageous characteristic of L1-L3 can be derived from a phenomenon visible in the ligand emission spectra. With increasing number of aromatic substituents at the bpy an increase in individually distinguishable emission bands could be observed. This speaks for weak electronic coupling within the single molecule subunits, which in turn might impair charge carrier recombination processes in DSSCs or DSPECs. An impact of bpy elongation could also be observed for the emission maxima of the complexes. They slightly shift from the L0 containing complexes to lower energies for the L1–L3 containing ones. A conceivable reason for this bathochromic shift in emission might be a higher electron density at the respective metal center because of the more electron donating capability of triazole or phenyl substituents at the bpy in comparison to directly bound methyl phosphonic ester groups.

This explanatory approach was promoted by electrochemical studies. For instance, the redox potential for the Ru^III/II couple in Ru(L0)_3 occurs at more positive potential than that of Ru(L1)_3. The reversible one-electron reductions obtained for the Re(L0)-Re(L3) series showed rather modest shifts of the bpyR → bpyR^− potentials. Nevertheless L1-L3 were easier to reduce than L0. Although the emission behavior of the free ligands indicated weak electron coupling, this still suggests increased π-conjugation, as derived from the trends in the absorption spectra.

To further examine this putatively contradicting tendencies within the elongated ligands, resonance raman experiments were conducted. In order to elucidate the localization of the initially excited states and its dependence on phenylene and triazole units, three additional ruthenium complexes Ru(tbbpy)_3, Ru(tbbpy)(L1) and Ru(tbbpy)(L2) with more or less elongated bipyridine ligands were synthesized and compared to the Raman spectra of homoleptic complexes Ru(L1)_3 and Ru(L2)_3. Spectra were recorded at the high and low energy flank of the MLCT absorption band at 457 and 488 nm respectively. Quantum chemical calculations aided the assignment of the Raman bands. The combined methods revealed a stronger population of tbbpy upon excitation at 457 nm than at 488 nm, whereas L1 is almost equally strong populated by excitation at both wavelengths. This suggests that the introduction of a phenylene moiety to bpy (L1) lead to an energetic stabilization of the metal to ligand excitation. The experiments also exposed that tuning excited states by insertion of a triazole unit (L2) is not straightforward. Excitation with higher energy (λ_ex = 457nm) populates a state with contributions of the triazole while a low-energy state
\( \lambda_{\text{ex}} = 488 \text{nm} \) is dominated by the bpy portion of L2. Based on these findings, the excited state encompasses the whole bpy-triazole scaffold and \( \pi \)-conjugation is not disrupted.

Preliminary Investigations in deprotection and immobilization were performed, in order to investigate the principle suitability of the presented compounds for dye sensitized cells. As a result of these efforts the structure of Re(L0\text{hydrolyzed}) with free phosphonate anchoring groups could be obtained. According to CCDC database only one other solid state structure of a metal complex with phosphonic acid substituents at a pyridyl ligand is known.\(^{237}\) The axial labile chloride ligand of Re(L0) was substituted by bromide, due to hydrolysis with excess trimethylsilyl bromide (Me\(_3\)SiBr). Re(L0\text{hydrolyzed}), in contrast to its protected ester analogues, showed an extended hydrogen bond framework in the crystal packing, which is capped by bridging methanol molecules (Figure 86).

![Figure 86: Solid-state structure and crystal packing of Re(L0\text{hydrolyzed}).](image)

Concerning the PO\(_3\)-group it was found that the difference between single and double bond is significantly longer in the phosphonic ester complexes (0.09 Å) as in the phosphonic acid complex Re(L0\text{hydrolyzed}) (0.027 Å), indicating enhanced delocalization in the latter, as would be expected. To examine the chemical stability of triazole towards harsh hydrolysis conditions Re(L2) was chosen as another more challenging reference probe for deprotection. After treatment with Me\(_3\)SiBr Re(L2\text{hydrolyzed}) was rendered soluble in MeOH and H\(_2\)O by addition of TBAOH. The successful hydrolysis could be confirmed by \(^1\text{H}-\text{NMR} \) spectroscopy and HRMS. With the latter method the lability of the axial chloride ligand was proven, since species consistent with the formula of the respective bromo- or hydroxo ligand were detected. As similarly witnessed by Daniel and coworkers, this ligand substitution might also be a reason for the bathochromic shift of MLCT absorption maxima when comparing Re(L2) to its hydrolyzed analogue Re(L2\text{hydrolyzed}) in MeOH (Figure 87).\(^{238}\) However it was demonstrated that the triazole unit of Re(L2\text{hydrolyzed}) is not decomposed during hydrolysis. After immobilization, followed by subsequent washing steps, the sensitized films were analyzed by UV/vis spectroscopy. The resulting spectrum validated the successful fixation of Re(L2\text{hydrolyzed}) on NiO. The MLCT absorption band could be observed, but it was red-shifted compared to the analogue complexes in solution. A more detailed investigation exposed that the MLCT
absorption band of Re(L2) is shifted to lower energies in the following solvent order: DCM>DMF>MeOH, i.e. the higher the solvent polarity, the higher the energy for MLCT excitation (Figure 87). We concluded that the surrounding of the immobilized Re(L2_{hydrolyzed})@NiO might be nonpolar, since the maximum MLCT absorbance at 415 nm is red-shifted by 31 nm (0.24 eV) in comparison to Re(L2_{hydrolyzed}) in MeOH. Re(L2_{hydrolyzed})@NiO exhibits an absorbance maximum at the edge of the visible region of solar irradiation spectrum.

Figure 87: Absorbance spectra at the MLCT absorption band of Re(L2) in DCM, DMF and MeOH and of its hydrolyzed analogue Re(L2_{hydrolyzed}) in MeOH and immobilized on NiO.

In summary, these studies reported the first modular synthetic approach towards phosphonated bipyridine ligands with tunable distances between the phosphonate and the bipyridine nitrogen. The huge potential of CLICK chemistry should provide manifold possibilities to employ different building blocks for modifying the extent of linkage and thereby the photophysical properties of bipyridines and their metal complexes. The photophysical investigations in these contributions supported the assumption that the presented linkers enhance the performance of the corresponding chromophores by shifting the absorption to lower energies and increasing their molar extinction coefficients and π-conjugation. These effects were further investigated with resonance Raman experiments and supported by theoretical calculations. After hydrolysis the triazole containing Re(L2) was successfully immobilized on NiO, suggesting that its application in photovoltaic cells is feasible. The reported solid state structures of ligands and complexes enabled the exact determination of linker lengths. Charge carrier recombination processes and aggregation of the chromophores on the SC surface might be inhibited because of the rigid and elongated spacers. Therefore the new bpy derivatives (L1-L3) meet the requirements to improve the photovoltaic performance of polymeric metal-complexes in photovoltaic cells, which is currently under investigation.
5.4.) Possible restriction for the utilization of CLICK chemistry towards the overall function of photocatalysts

A more detailed investigation ([MB4] \textsuperscript{1239}, cf. chapter 8.) concerning the luminescence properties of the new elongated complexes lead to a surprising observation which might infer a limitation for CLICK chemistry as universal tool for construction of functional photomolecular devices. In contrast to conventional Ru\textsuperscript{II}-trisbipyridyl complexes, the triazole containing complexes Ru(L2)\textsubscript{3} and Ru(L3)\textsubscript{3} showed a solvent dependent light switch effect. This environment dependent fluorescence quenching was studied thoroughly in a set of ruthenium complexes incorporating different numbers of triazoles (Ru(tbbpy)\textsubscript{2}(L2), Ru(tbbpy)(L2)\textsubscript{2}, Ru(L2)\textsubscript{3}) or a different triazole substituent Ru(L4)\textsubscript{3} (Figure 88). L4 with benzyl was chosen to disrupt the π-conjugation over the whole complex.

![Figure 88: Structures of Ru-complexes Ru(tbbpy)\textsubscript{2}(L2), Ru(tbbpy) (L2)\textsubscript{2}, Ru(L2)\textsubscript{3} and Ru(L4)\textsubscript{3}. Triazole moieties highlighted in blue.]

While Ru(bpy)\textsubscript{3}, Ru(L0)\textsubscript{3} and Ru(L1)\textsubscript{3} displayed an increasing fluorescence intensity by increasing the content of water in acetonitrile, the emission intensity of Ru(L2)\textsubscript{3} initially also follows this tendency but drops drastically in a MeCN: \textsubscript{H2}O (1:9) mixture (Figure 89). All spectra (Figure 89-Figure 91, Figure 93) were measured at the same optical density at the corresponding MLCT maxima.
Results and Discussion

Figure 89: Emission spectra of Ru(bpy)$_3$, Ru(L0)$_3$, Ru(L1)$_3$ and Ru(L2)$_3$ in MeCN with differing water content. Identical excitation conditions for measuring the emission spectra at identical optical density at the corresponding MLCT.

This behavior could be clearly correlated to the triazole subunit. The magnitude of quenching increased with the quantity of triazole rings per Ru-complex and was generally independent of the substitution at the triazoles. However, Ru(L4)$_3$ with its benzyl unit showed a pronounced light switch effect compared to the phenyl (L2) substituted complexes (cf. Figure 90 and Table 5).

Figure 90: Emission spectra of L2 and L4 containing complexes in different MeCN:H$_2$O mixtures. Identical excitation conditions for measuring the emission spectra at identical optical density at the corresponding MLCT.
Because of that, Ru(L4)₃ was chosen to conduct more photoluminescence analysis in different solvents (Figure 91). In aprotic solvents the intensity decreased in the following order DCM > DMF > THF > MeCN. Almost a complete loss of emission was witnessed in the protic solvent mixtures THF:H₂O (1:9) and MeCN: H₂O (1:9). These findings suggest that the character of the solvent has major influence on the emission behavior.

![Emission spectra of Ru(L4)₃ in different solvents. Identical excitation conditions for measuring the emission spectra at identical optical density at the corresponding MLCT.](image)

Table 5: Emission data of L2 and L4 containing complexes.

<table>
<thead>
<tr>
<th>Substance</th>
<th>λₑₓₜ [a] [nm]</th>
<th>λₑₜ [b] [nm]</th>
<th>quenching [c] [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(tbbpy)(L2)</td>
<td>648</td>
<td>652</td>
<td>9.7</td>
</tr>
<tr>
<td>Ru(tbbpy)(L2)₂</td>
<td>636</td>
<td>645</td>
<td>45.1</td>
</tr>
<tr>
<td>Ru(L2)₃</td>
<td>627</td>
<td>639</td>
<td>58.6</td>
</tr>
<tr>
<td>Ru(L4)₃</td>
<td>828</td>
<td>634</td>
<td>79.6</td>
</tr>
</tbody>
</table>

[a] measured in MeCN  
[b] measured in MeCN:H₂O (1:9)  
[c] luminescence intensity quenching in MeCN:H₂O (1:9) vs. pure MeCN

With the aim of determining the origin of the solvent dependent light switch effect, TDDFT calculations were performed. To identify the excited states playing a role in the emission properties of triazole containing ruthenium complexes in general and to reduce computational cost, a model complex was simulated. This complex Ru(Me bpy)₂(L5) was derived from (Ru(tbbpy)₂(L2) but simplified by replacing the tert-butyl and P(O)(OEt)₂ groups by methyl groups (cf. Figure 92). The solvent effects were considered using the polarizable continuum model (PCM). According to the excited states energies calculations in acetonitrile the lowest triplet state (T₁) is mainly of MLCT character, with the LUMO localized on the bpy portion of ligand L5 (cf. Figure 94). The second triplet state (T₂) was found about 0.2 eV higher and corresponds to a mixing of MLCT and IL contributions, with charge transfer on the ligand L5 (MLCTₕ₉ + ILₕ₉). Surprisingly, the results obtained in water featured very small differences in comparison to water with T2 also very close in energy to T1 (Table 6). Nevertheless calculations of the adiabatic emission wavelengths including zero-point vibrational corrections were in nice agreement with the experimental values (649.3 in MeCN and 652.7 in water, cf.
Table 5). This emission occurred from the lowest triplet state T1. The archetype ruthenium complex, showing an solvent-dependent light switch effect is [Ru(bpy)2(dppz)] (cf. chapter 2.4.2.) *Photophysics of ruthenium polypyridyl complexes*). A proposed model to explain this phenomenon is the presence of other dark triplet states (e.g., 3ILCT) near to the lowest/emissive 3MLCT. If the dark state is within thermal energy of the bright state it may quench luminescence.\(^{77-80}\) This thermally activated competition can be tuned by the environment. Because T2 in Ru(Me(bpy))\(_2\)(L5) is only about 0.2 eV above T1 and displays a significant contribution of ILCT, it was deduced that it is less emissive than T1 and therefore might be responsible for the emission quenching in water. Another explanation for the light switch of [Ru(bpy)2(dppz)] related compounds is that the formation of hydrogen bonding interactions between the phenazine nitrogen atoms of dppz and solvent molecules lowers the excited states and thereby quenches luminescence (Scheme 3).\(^{77,80-83,240}\)

Scheme 3: Schematic explanation for the light switch effect in [Ru(bpy)2(dppz)] based on a publication by Olofsson and coworkers.\(^{240}\) Upon excitation of an electron from a d-orbital in ruthenium (ground state) the negative charge from the excited electron is distributed over the three ligands and forms state A. The A state converts to state B (no hydrogen bond) where the electron is localized on the dppz ligand. Only after hydrogen-bond formation and conversion to state C, non-radiative relaxation occurs.

By including a cluster of six water molecules in close proximity of the triazole rings, the hydrogen bond formation was studied for Ru(Me(bpy))\(_2\)(L5) (Figure 92).
Results and Discussion

Figure 92: Calculated structure of Ru(Mebpy)$_2$(L5) with six water molecules.

Again no considerable changes in comparison to the calculations in acetonitrile were found. Despite its IL character only a slight stabilization of T2 by about 0.01 eV took place. The calculations in MeCN, water and in the hydrogen-bond scenario are summarized in Table 6.

<table>
<thead>
<tr>
<th>State number and main character</th>
<th>Transitions$^{[a]}$</th>
<th>Weights [%]$^{[a]}$</th>
<th>Energy [eV]$^{[b]}$ MeCN$^{[c]}$</th>
<th>Energy [eV]$^{[b]}$ Water$^{[c]}$</th>
<th>Energy [eV]$^{[b]}$ Water$^{[c]} + 6H_2O$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T$<em>1$ (MLCT$</em>{L5}$)</td>
<td>HOMO $\rightarrow$ LUMO</td>
<td>91</td>
<td>1.80 (689)</td>
<td>1.79 (690)</td>
<td>1.77 (699)</td>
</tr>
<tr>
<td>T$<em>2$ (MLCT$</em>{L5}$+IL$_{L5}$)</td>
<td>HOMO-1 $\rightarrow$ LUMO</td>
<td>91</td>
<td>2.00 (618)</td>
<td>2.00 (619)</td>
<td>1.99 (622)</td>
</tr>
</tbody>
</table>

$^{[a]}$ The reported transitions and weights are for the cluster with six water molecules, the weights for the other environments differ by less than 1% $^{[b]}$ Corresponding wavelengths (in nm) are given in parentheses. $^{[c]}$ Indicates the solvent described with PCM.

Table 6: TDDFT vertical excitation energies of the five lowest triplet states of Ru(Mebpy)$_2$(L5) in different environments. The calculations are performed at the T$_1$ geometry.

Since the emission loss was discovered in protic solvent mixtures, the influence of proton concentration on the light switch behavior was further investigated by addition of HCl to THF or THF:H$_2$O (1:9), respectively. These experiments were conducted with Ru(L3)$_3$ and showed that the emission intensities are even more diminished compared to the untreated solvents (Figure 93).

Figure 93: Emission spectra of Ru(L4)$_3$ in THF:H$_2$O (1:9) or THF upon addition with aliquots of conc. HCl. Identical excitation conditions ($\lambda_{ex} = 480$ nm) for measuring the emission spectra at identical optical density at the corresponding MLCT.
As a consequence we decided to simulate the excited state energies for a protonated version of Ru(Me bpy)$_2$(L5) as an extreme scenario. Two protons were bound to the nitrogens N1 and N4 (cf. Figure 92).

<table>
<thead>
<tr>
<th>State number and main character</th>
<th>Transitions</th>
<th>Weights [%]</th>
<th>Energy [eV][a] Water[b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>T$<em>1$ (MLCT$</em>{1S}$)</td>
<td>HOMO $\rightarrow$ LUMO</td>
<td>94</td>
<td>1.53 (811)</td>
</tr>
<tr>
<td>T$<em>2$ (MLCT$</em>{1S}$+IL$_{1S}$)</td>
<td>HOMO-2 $\rightarrow$ LUMO</td>
<td>95</td>
<td>1.74 (713)</td>
</tr>
</tbody>
</table>

[a] Corresponding wavelengths (in nm) are given in parentheses. [b] Indicates the solvent described with PCM.

Table 7: TDDFT vertical excitation energies of the two lowest triplet states of the protonated Ru(Me bpy)$_2$(L4) complex in water. The calculations are performed at the T$_1$ geometry.

This modification lead to a significant stabilization of T1 and T2 with predicted emission wavelengths higher than the measured ones and more charge transfer to the triazoles (Table 7, Figure 94).

![LUMO](image1.png)

![HOMO](image2.png)

Figure 94: Main orbitals of Ru(Me bpy)$_2$(L5) and the protonated complex Ru(Me bpy)$_2$(L5)(H$^+$)$_2$.

The calculated MLCT states were now lower in energy than the emissive state and were therefore proposed to be dark and responsible for opening radiationless relaxation pathways. According to these findings a light-initiated proton transfer from water to triazole was suggested to be the origin of the light-switch effect (Scheme 4 and Scheme 5).
Results and Discussion

Scheme 4: Depiction of the localized charge excitation: i) electron transfer Ru$^{II}$→MLCT, resulting in Ru$^{III}$, ii) proton movement H$_2$O→triazole(H). $R^2$=CH$_3$, $R^1$=C$_6$H$_5$-C$_2$H$_5$.

A similar effect was reported for a trisheteroleptic ruthenium complex comprising dppz and 5,6,5’,6’-tetramethyl-2,2’-bibenzimidazole subunits.$^{241}$

Scheme 5: Schematic explanation for the light switch effect in Ru(Mebpy)$_2$(L5) (cf. Scheme 3). Hydrogen bond formation (state B) still leads to radiative decay in the case of Ru(Mebpy)$_2$(L5). Only upon protonation non-radiative relaxation occurs (from state C).

In conclusion this study discussed the effect of triazole moieties on the luminescence intensity of corresponding ruthenium complexes. It was clearly shown that the presence of a triazole subunit leads to enhanced sensitivity of the emissive properties towards solvent nature or apparent proton concentration. The increase of the water content of a solvent mixture leads via a maximum always to a significantly lower emission intensity at high water contents. This later behavior is reminiscent of the famous light switch effect. For the investigated class of metal complexes its magnitude correlates obviously with the number of triazole moieties. Rational explanations of the observed effect were proposed based on theoretical
investigations. They comprise either radiationless decay from a second, energetically close lying triplet state with a MLCT/IL character or a light-initiated protonation. This protonation stabilizes potentially dark excited states.

The study revealed a major restriction for the utilization of CLICK chemistry. CuAAc is indeed suitable to connect important function-owning molecular building blocks but the resulting triazoles are by no means innocent with respect to desired overall function of the target devices. For instance triazole units in Ru-polypyridyl sensitizers might reduce the charge separated lifetimes in dye sensitized cells by opening additional deactivation pathways.
6.) Summary and Outlook

The studies performed within this thesis describe the development of an advanced photocatalyst for visible light-driven hydrogen generation in dye-sensitized photoelectrochemical cells (DSPECs) based on (4) (cf. Figure 54). The photochemical molecular device (PMD) consists of an anchoring group, a rutheniumpolypyrpidyl photocenter, an electron relaying bridging ligand and a platinum catalytic center. The PMD therefore contains every module necessary to construct the photoactive cathode of a so-called artificial leaf for solar fuel production (Figure 95).

Figure 95: From the natural to the artificial leaf with a hydrogen-evolving PMD.
In detail, the following results were achieved:

- Advanced photophysical, hydrolysis and immobilization studies for (4). In contrast to similar dicarboxylated ruthenium complexes detailed photophysical studies, including Resonance Raman spectroscopy revealed that methyl phosphonic ester groups of (4) do not change the photophysical properties significantly compared to related active photocatalysts. Therefore electron transfer in the direction of catalysis is guaranteed. The principle applicability of the novel photocatalyst (4) in dye-sensitized cells was further supported by successful hydrolysis experiments and immobilization studies on NiO. The hydrolysis conditions were optimized to gain a chemically stable and active photocatalyst \((4_{hydrolized})\) and to enable its solubility in organic solvents. The immobilization experiments revealed improved binding affinity of (4) compared to the model complex \([\text{Ru}^{II}(\text{bpy})_2\text{L}_{0_{hydrolized}}]^2+\).

- Integration of \((4_{hydrolized})\) in a DSPEC and optimization of the operating conditions. Photoelectrocatalytic measurements lead to visible light-induced photocurrents, which suggest that hydrogen production with such a system is possible (Figure 96).

![Figure 96: Schematic illustration of a DSPEC with (4)@NiO.](image)

However, the observed photocurrents under oxygen-free conditions are rather small which hampers proof for actual hydrogen formation by gas chromatography due to detection limits. Additionally, chronoamperometry and UV/vis absorbance studies of the NiO electrodes revealed binding stability limitations of the system, in particular in the commonly used phosphonate buffer electrolyte.
Potential improvement of the system by implementation of a modular synthesis concept for anchor elongation.

Figure 97: Table of content graphics of manuscripts [MB2] and [MB3].

Suzuki coupling and CuAAC-CLICK reactions were used to introduce triazole and phenylene π-conjugated building blocks between bpy core and methyl phosphonic acid anchoring group. The building block-concept enables specific distance adjustability between NiO surface and immobilized chromophore. This allows tuning of cell efficiency limiting factors like charge carrier recombination and dye aggregation. The distance elongation could be determined by solid state structures of the respective ligands or building blocks (Figure 98).

Figure 98: Distance determination between pyridine nitrogen atom (N1) and the calculated centroid between the phosphonate oxygen atoms for L0-L3 by solid state structures.

The new bpy derivatives were applied in ruthenium(II)- and rhenium(I)-complexes. Photophysical studies revealed enhanced performance of these chromophores with regard to their photon absorption characteristics. In order to elucidate the localization of the initially excited states and its dependence on phenylene and triazole units.
resonance Raman spectroscopy and theoretical calculations were conducted. They suggest that introduction of a phenylene moiety (L1) to the original bipyridine ligand lead to an energetic stabilization of the metal to ligand excitation. Furthermore, addition of a triazole unit (L2) did not lead to a disruption of the π-conjugation over the whole bpy ligand. Therefore fast electron injection from NiO to chromophores using these elongated bpy derivatives should be possible. But at the same time counterproductive charge recombination processes might be facilitated. To ascertain which of these antagonistic effects is in favor metal-complexes equipped with ligands L1-L3 are currently investigated in p-Type DSSCs. Preliminary experiments with selected rhenium complexes already showed that triazole units withstand the harsh hydrolysis conditions and that immobilization on NiO is possible.

- Revelation of a possible utilization restriction for CLICK chemistry as universal tool for construction of functional photomolecular devices.

![Figure 99: Table of content graphic of manuscript MB4.](image)

A thorough investigation of a set of ruthenium complexes incorporating triazole rings in their peripheral bpy ligands showed a solvent dependent light switch effect. Just like conventional rutheniumpolypyridyl-complexes they brightly emit in aprotic solvents. But from certain water content on luminescence of the triazole containing complexes is quenched. It was demonstrated that the magnitude of luminescence quenching is dependent on the number of triazole units and its substitution pattern.

TDDFT calculations helped finding two potential explanations for the observed light-switch effect:
(1) Radiationless decay from a second, triplet state which is energetically close lying to the emissive state. This state is accessible by thermal activation in particular environments such as water.

(2) Light-initiated protonation of the triazole unit in aqueous solution stabilizes potentially dark excited states.

The latter explanation was supported by experimental evidence, showing that treatment with HCl further diminishes luminescence of these complexes in solution. The additional deactivation pathways in aqueous solution limit the application potential of such complexes in DSPECs for water splitting.

The combined results of this thesis will further promote the systematic design of DSPECs for hydrogen production. Nevertheless optimizations will be required to improve the efficiency of the systems. Two key aspects should be addressed in future studies: activity and stability of the system (cf. Figure 100).

![Figure 100: Schematic illustration of an optimized DSPEC based on (4)@NiO. Optimization strategies highlighted in yellow.](image)

According to previous studies in the working group of Rau one promising approach to boost the catalytic activity of (4) would be substitution of the chloride co-ligands at the catalytic platinum center by iodide. For this purpose the hydrolysis strategy has to be modified, since the route adapted from (4) did lead to hydroxide-iodide substitution in case of the RuPtI$_2$-photocatalyst. Furthermore the effect of the presented anchoring group elongation should be investigated. Referring to the obtained results especially, phenylene spacers should have positive effects on cell performance. To increase the binding stability of (4)@NiO a concept inspired by a publication of Wu et al. might be auspicious. Hydrophobic hexyl substituents
incorporated in an immobilized organic dye hindered interaction of the electrolyte with NiO. After immobilization of (4), co-adsorption of alkyl-chain substituted carboxylic acids should lead to the same effect. The phosphonate anchoring groups might be protected from protic electrolyte. Additionally excited state quenching in triazole containing photocatalysts based on (4) should be inhibited by this hydrophobic protection layer, since the aqueous electrolyte might not reach the triazole moiety.

Alternatively to the aspired hydrogen production, the future application of DSPECs to generate reduced nicotinamide cofactors as nature’s hydrogen equivalents would be highly attractive. NADH$_2^+$ and NADPH$_2^+$ can easily be detected by sensitive methods like UV/vis absorption or fluorescence spectroscopy.$^{242-244}$ As an integral part of his PhD thesis Alexander Mengele could show that a related [Ru(tbpy)$_2$tpphzRh(Cp*)Cl]$_n^+$ photocatalyst was able reduce NAD$^+$ to NADH$_2^+$ in homogenous catalysis experiments. This conversion could be coupled to an enzymatic reaction, more precisely the biocatalyzed transformation of pyruvate to lactate.$^{245}$ Depending on the used enzyme also transformations of CO$_2$ or carbonates to produce formates, formaldehyde, and/or methanol, are possible.$^{246-250}$ Designing interconnected light and dark reactions like natural photosynthesis could therefore enable sustainable and highly efficient photobiocatalytic redox reactions. Exchange of PtCl$_2$ with a Rh(Cp*)Cl catalytic center in (4) would facilitate heterogenous nicotinamide cofactor conversions in DSPECs. The resulting artificial leaf would generate the same products as the light reaction of the natural role model (Figure 101).

Figure 101: Illustration of an artificial leaf for NADP$^+$ reduction based on (4)@NiO.
7. References


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8.) Publications

Parts of this thesis were already published in the following manuscripts. Reprints of the manuscripts are presented in the appendix. The reprints were made with permission of the respective journal. The permission by the publisher and a short description of the individual contribution by the authors is given below.

8.1) [MB1] Synthesis and characterization of an immobilizable photochemical molecular device for H₂-generation

Markus Braumüller, Martin Schulz, Dieter Sorsche, Michael Pfeffer, Markus Schaub, Jürgen Popp, Byung-Wook Park, Anders Hagfeldt*, Benjamin Dietzkek* and Sven Rau*.

* corresponding authors

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Author contributions:
M. Braumüller: Synthesis and complete characterization of the ligands and the ruthenium complexes, photophysical, electrochemical, catalysis and immobilization studies, and writing of the manuscript (except “Resonance Raman experiments” part).
M. Schulz: Resonance Raman experiments, writing of the corresponding chapter, discussion and revision of the manuscript.
D. Sorsche: Measurement and refinement of the X-ray structures, discussion of the manuscript.
M. Pfeffer: Supported the catalysis experiments.
M. Schaub: Supported the electrochemical measurements.
B. Park: Supported the immobilization experiments.
J. Popp: Revision of the manuscript.
A. Hagfeldt: Discussion and revision of the manuscript.
B. Dietzkek: Discussion and revision of the manuscript.
S. Rau: Discussion and revision of the manuscript, concept and results discussion.

8.2) [MB2] Modular Synthesis of Elongated Phosphonate Bipyridines

Markus Braumüller, Dieter Sorsche, Markus Wunderlin and Sven Rau*.

* corresponding authors

Published in: European Journal of Organic Chemistry, 2015, 5987-5994. DOI: 10.1002/ejoc.201500641
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Author contributions:
M. Braumüller: Synthesis and complete characterization of the ligands, photophysical studies, and writing of the manuscript.
D. Sorsche: Measurement and refinement of the X-ray structures, discussion of the manuscript.

M. Wunderlin: Mass spectrometry measurements.

S. Rau: Discussion and revision of the manuscript, concept and results discussion.

8.3) [MB3] Synthesis and characterization of ruthenium and rhenium dyes with phosphonate anchoring groups

Markus Braumüller, Martin Schulz, Magdalena Staniszewska, Dieter Sorsche, Markus Wunderlin, Jürgen Popp, Julien Guthmuller, Benjamin Dietzek* and Sven Rau*.

* corresponding authors

Published in: Dalton Transactions, 2016, 45, 9216-9228. DOI: 10.1039/C6DT01047D

Permission: Reproduced by permission of The Royal Society of Chemistry.

Author contributions:

M. Braumüller: Synthesis and complete characterization of the rhenium and the ruthenium complexes, photophysical, electrochemical and immobilization studies, and writing of the manuscript (except Crystal structures chapter, Resonance Raman experiments chapter).

M. Schulz: Resonance Raman experiments, writing of the corresponding chapter, discussion and revision of the manuscript.

M. Staniszewska: Theoretical calculations.

D. Sorsche: Measurement and refinement of the X-ray structures, writing of the corresponding chapter, discussion of the manuscript.

M. Wunderlin: Mass spectrometry measurements.

J. Popp: Revision of the manuscript.

J. Guthmuller: Theoretical calculations. Discussion and revision of the manuscript.

B. Dietzek: Discussion and revision of the manuscript.

S. Rau: Discussion and revision of the manuscript, concept and results discussion.

8.4) [MB4] CLICK N’ Sleep: Light-Switch Behavior of Triazole-Containing Tris(bipyridyl)ruthenium Complexes

Markus Braumüller, Magdalena Staniszewska, Julien Guthmuller and Sven Rau*.

* corresponding authors

Published in: European Journal of Inorganic Chemistry, 2016, 4958–4963. DOI: 10.1002/ejic.201600964

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Author contributions:

M. Braumüller: Synthesis and complete characterization of the ruthenium complexes, photophysical studies, and writing of the manuscript.

M. Staniszewska: Theoretical calculations.

J. Guthmuller: Theoretical calculations, writing of the corresponding chapter. Discussion and revision of the manuscript.

S. Rau: Discussion and revision of the manuscript, concept and results discussion.
9.) Experimental Part (not covered in the publications)

Preparation of porous NiO film
The NiO film was prepared by a modified literature procedure. Standard precursor solution of NiO was prepared by dissolving anhydrous NiCl₂ (1 g) and the triblock co-polymer F108 (1 g) into a mixture of water (3 g) and ethanol (6 g). The solution was stirred for 3 days at 25 °C. The films were made by doctor-blading the precursor solution onto conducting glass substrates (Fluorine doped tin oxide coated glass slide, sheet resistance 7 Ω/square) using Scotch tape as a spacer (1 cm² active area), followed by sintering in an oven at 420 °C for 30 min. The film was prepared in two steps using one layer of tape and sintering in between applications.

General hydrolysis procedure
In order to hydrolyze the ester groups, the complex ((3) (4) or (4')) (0.025 mmol) was dissolved in anhydrous MeCN (30 mL) under argon atmosphere. Bromo- or iodo(trimethyl)silane was added (15equiv.). The reaction was stirred at 85°C for 18 h, after which water (15 mL) was added and the reaction was stirred for additional 30 min at room temperature. After removal of MeCN at the rotary evaporator an excess of tetrabutylammonium chloride or iodide was added and the pH of the aqueous solution was adjusted to 7 by treatment with tetrabutylammonium hydroxide (0.1M). The solvent was evaporated and the residue was dissolved in MeOH. By addition of excess EtOAc the hydrolysed product was precipitated from solution.

(3hydrolyzed)

(3hydrolyzed) was synthesized according to the general hydrolysis procedure. Due to an excess of TBA ions in the product no yields can be given.

\(^1H\-NMR\ ((D3)MeOD, 400 MHz): \delta [ppm] = 9.84 (s, 2H), 9.82 (s, 2H), 9.11 (s, 2H), 8.65 (s, 2H), 8.60 (s, 2H), 8.44 (d, 2H), \text{J} (H,H) = 5.3 Hz), 8.00 (m, 2H), 7.92 (m, 2H), 7.73 (d, 2H), \text{J} (H,H) = 5.9 Hz), 7.52 (m, 2H), 7.47 (m, 2H), 7.26 (m, 2H), 3.09 (d, 4H), \text{J} (H,P) = 20.1 Hz), 3.01 (d, 4H), \text{J} (H,P) = 20.3 Hz).

\(^31P\-NMR\ ((D3)MeOD, 162 MHz): \delta [ppm] = 14.05, 13.72.

HRMS (m/z (ESI, MeOH)): m/z calcd. for [M/2]^2⁺: 585.0266; found = 585.0273; M = C₄₇H₆₅N₁₇O₁₂P₄Ru.
Experimental Part (not covered in the publications)

(4_{hydrolyzed}) was synthesized according to the general hydrolysis procedure. Due to an excess of TBA ions in the product no yields can be given.

NMR: No interpretable NMR spectra could be obtained. Multiple species were present in solution since partial chloride-bromide substitution took place which could be proven by HRMS.

**HRMS** (m/z (ESI, MeOH)): m/z calcd. for [M/2]$^{2+}$ = 717.9772; found = 717.9769; m/z calcd. for [(M-Cl+Br)/2]$^{2+}$ = 739.9517; found = 739.9515; m/z calcd. for [(M-2Cl+2Br)/2]$^{2+}$ = 762.4266; found = 762.4266; M = C_{68}H_{36}Cl_{6}N_{10}O_{12}P_{4}PtRu.

**A**

A red solution of (4) (30 mg, 15.4 μmol) and potassium iodide (294 mg, 1.77 mmol) were refluxed in 25 mL EtOH for 18h. The solvent was evaporated and the residue was dissolved in MeCN. After filtration over a pore 4 frit, an excess of aqueous solution of NH_{4}PF_{6} was added. The precipitate was washed with water and dried in vacuo to yield 33 mg of dark red (4') (quantitative yield).

$^{1}$H-NMR ([D3]MeCN, 400 MHz): δ [ppm] = 9.91 (d, 2H), 9.81 (s, 2H), 9.57 (d, 2H), 8.51 (s, 2H), 8.48 (s, 2H), 8.35 (d, 2H), 8.08 (m, 2H), 7.97 (m, 2H), 7.88 (m, 2H), 7.78 (d, 2H), 7.45 (d, 2H), 7.32 (d, 2H), 4.12-3.95 (m, 16H), 3.47 (d, 4H), 3.38 (d, 4H), 1.26-1.10 (m, 24H);

$^{31}$P-NMR ([D3]MeCN, 162 MHz): δ [ppm] = 22.83;

**HRMS** (m/z (ESI, MeCN)): m/z calcd. for [M/2]$^{2+}$ = 923.5526; found = 923.5524; M = C_{68}H_{72}I_{2}N_{10}O_{12}P_{4}PtRu.

(4'_{hydrolyzed})
(4′hydrolyzed) was synthesized according to the general hydrolysis procedure. Due to an excess of TBA ions in the product no yields can be given.

**NMR:** No interpretable NMR spectra could be obtained. Multiple species were present in solution since partial iodide-hydroxide substitution took place which could be proven by HRMS.

**HRMS (m/z (ESI, MeOH/MeCN (1:1))):**
m/z calcd. for [M/2]$^{2-}$ = 809.4128; found = 809.4115;
m/z calcd. for [[M-I+OH]/2]$^{2-}$ = 754.4619; found = 754.4605;
m/z calcd. for [[M-2I+2OH+2MeCN]/2]$^{2-}$ = 740.5376; found = 740.5364;
M = C$_{49}$H$_{35}$I$_{2}$N$_{10}$O$_{15}$P$_{4}$PtRu.
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Scheme 1: Orbital Scheme useful for understanding why an excited state is both a better electron donor and a better electron acceptor than the ground-state species.

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List of abbreviations

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<thead>
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<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>$A_0$</td>
<td>chlorophyll a molecule</td>
</tr>
<tr>
<td>APS</td>
<td>artificial photosynthesis</td>
</tr>
<tr>
<td>a.u.</td>
<td>arbitrary units</td>
</tr>
<tr>
<td>BB</td>
<td>building block</td>
</tr>
<tr>
<td>BB1</td>
<td>(4-hydroxymethylphenyl)boronic acid</td>
</tr>
<tr>
<td>BB2</td>
<td>diethyl-4-aminobenzylphosphonate</td>
</tr>
<tr>
<td>BB3</td>
<td>diethyl-4-bromobenzylphosphonate</td>
</tr>
<tr>
<td>BB4</td>
<td>3-aminophenylboronic acid</td>
</tr>
<tr>
<td>BB5</td>
<td>diethyl-((3'-azido-[1,1'-biphenyl]-4-yl)methyl)phosphonate</td>
</tr>
<tr>
<td>BB5'</td>
<td>diethyl-((3'-amino-[1,1'-biphenyl]-4-yl)methyl)phosphonate</td>
</tr>
<tr>
<td>BL</td>
<td>bridging ligand</td>
</tr>
<tr>
<td>bpy</td>
<td>2,2'-bipyridine</td>
</tr>
<tr>
<td>bpyBr$_2$</td>
<td>4,4'-dibromo-2,2'-bipyridine</td>
</tr>
<tr>
<td>CB</td>
<td>conduction band</td>
</tr>
<tr>
<td>CT</td>
<td>charge transfer</td>
</tr>
<tr>
<td>Cytb$_{6f}$</td>
<td>cytochrome-b$_{6f}$-complex</td>
</tr>
<tr>
<td>dmbrpy</td>
<td>4,4'-dimethyl-2,2'-bipyridine</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide</td>
</tr>
<tr>
<td>DNA</td>
<td>deoxyribonucleic acid</td>
</tr>
<tr>
<td>dppz</td>
<td>dipyrido[3,2-a:2',3'-c]phenazine</td>
</tr>
<tr>
<td>DSPEC</td>
<td>dye-sensitized photoelectrochemical cells</td>
</tr>
<tr>
<td>DSSC</td>
<td>dye-sensitized solar cells</td>
</tr>
<tr>
<td>EDTA</td>
<td>ethylenediaminetetraacetic acid</td>
</tr>
<tr>
<td>ESI</td>
<td>electrospray ionization</td>
</tr>
<tr>
<td>Fc/Fc'</td>
<td>ferrocene/ferrocenium redox couple</td>
</tr>
<tr>
<td>Fd</td>
<td>ferredoxin</td>
</tr>
<tr>
<td>FNR</td>
<td>ferredoxin-NADP$^+$ reductase</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>HEC</td>
<td>hydrogen evolving catalyst</td>
</tr>
<tr>
<td>HEPMD</td>
<td>hydrogen evolving photochemical molecular device</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>HRMS</td>
<td>high-resolution mass spectrometry</td>
</tr>
<tr>
<td>$h\nu$</td>
<td>energy of a photon as characterized by the Planck constant $h$ and the frequency $\nu$</td>
</tr>
</tbody>
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List of abbreviations

ISC  intersystem crossing
L0  4,4’-bis(diethyl-(methylene)-phosphonate)-2,2’-bipyridine
L1  L0 elongated by a phenylene unit
L2  L0 elongated by a phenylene and a triazole unit
L3  L0 elongated by a two phenylene and a triazole unit
L4  4,4’-bis(1-benzyl-1H-1,2,3-triazol-4-yl)-2,2’-bipyridine
L5  4,4’-bis(1-(4-ethylphenyl)-1H-1,2,3-triazol-4-yl)-2,2’-bipyridine
LC  ligand-centered (also referring to ligand-centered state)
LED light emitting diode
LLCT ligand-to-ligand charge transfer (also referring to ligand-to-ligand charge transfer state)
LMCT ligand-to-metal charge transfer (also referring to ligand-to-metal charge transfer state)
LUMO lowest unoccupied molecular orbital
(M) [Ru(tbbpy)2(L0)]2+
MC  metal-centered (also referring to metal-centered state)
MeCN acetonitrile
MLCT metal-to-ligand charge transfer (also referring to metal-to-ligand charge transfer state)
NAD nicotinamide adenine dinucleotide
NADP nicotinamide adenine dinucleotide phosphate
NHE standard hydrogen electrode
NMR nuclear magnetic resonance (spectroscopy)
NPS natural photosynthesis
OEC oxygen evolving catalyst
Ox oxidized redox mediator
Pc plastocyanine
PCE power conversion efficiency
PEC photoelectrochemical cell
phen(NH2)2 1,10-phenantroline-5,6-diamine
phen(O2) 1,10-phenantrolene-5,6-dione
Pheo pheophytin
PMD photochemical molecular device
PS  photosensitizer
PS I/II photosystem I/II
PV photovoltaic device
List of abbreviations

pz: phenazine
$Q_{A,B,C}$: different plastoquinones
R: electron relay / substituent
Red: reduced redox mediator
SC: semiconductor
$S_n$: $n^{th}$ electronic singlet state
TBA: tetrabutylammonium
tbbpy: 4,4'-di-tert-butyl-2,2'-bipyridine
tbu$_4$N$^+$: tetra-n-butylammonium
TEA: triethylamine
TEOA: triethanolamine
THF: tetrahydrofuran
$T_n$: $n^{th}$ electronic triplet state
TON: turn-over-number, generated equivalents of hydrogen with respect to the catalyst concentration
TPA: triphenylamine
tpphz: tetrapyrido[3,2-a:2',3':3'',2''',h:2''',3''']-phenazine
Tyr: tyrosine
UV: ultraviolet
UV/vis: ultraviolet/visible light
WOC: water oxidation catalyst
XRD: X-ray diffractometry
(1) Ru(L0)$_2$Cl$_2$·2DMSO$_{2}$-complexes
(2) Ru(L0)$_2$phen(O$_2$)
(3) Ru(L0)$_2$tpphz
(4) Ru(L0)$_2$tpphzPtCl$_2$
(4′) Ru(L0)$_2$tpphzPtl$_2$
(5) Ru(tbbpy)$_2$tpphz
(6) Ru(tbbpy)$_2$tpphzPtCl$_2$
# Curriculum vitae

## General

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List of scientific contributions

Publications (first authorship)

+ Synthesis and characterization of Ruthenium and Rhenium dyes with phosphonate anchoring groups
  Dalton Transactions, 2016, 45, 9216-9228.
+ Modular synthesis of elongated phosphonate bipyridines
+ Synthesis and characterization of an immobilizable photochemical molecular device for \( \text{H}_2 \)-generation
  Dalton Transactions, 2015, 44, 5577-5586. DOI: 10.1039/C4DT03730H
+ Click N' Sleep: light switch behavior of triazole containing Ruthenium Complexes

Manuscripts (first authorship)

+ Tuning photochemical molecular devices for hydrogen evolution
  Review, invited publication: Coordination Chemistry Reviews
+ A dye-sensitized photoelectrochemical cell for \( \text{NAD}^+ \) reduction
  Manuscript in preparation

Publications (co-authorship)

+ Titania modification with a ruthenium(II) complex and gold nanoparticles for photocatalytic degradation of organic compounds
+ Mono- and dual-modified titania with a ruthenium(II) complex and silver nanoparticles for photocatalytic degradation of organic compounds
+ “CLICKable” azide-functionalized phosphonates for the surface-modification of molecular and solid-state metal oxides
  Short Communication, accepted by: Dalton Transactions, 2016, 45, 16121-16124,
  DOI: 10.1039/C6DT03370A

Conference Proceedings

+ COST Training School & WG Meetings in Tarragona (Spain)
  Oral presentation: Towards another artificial leaf
+ 21st ISPPCC in Krakow (Poland)
  Poster presentation: A new approach to the artificial leaf
+ 5th EuCheMS Chemistry Congress in Istanbul (Turkey)
  Poster presentation: On the way to the artificial leaf
+ JCF Frühjahrssymposium der GdCh 2014 in Jena (Germany)
  Poster presentation: Towards an artificial leaf
+ Energie Campus 2013 „Stiftung Energie und Klimaschutz in Ulm“ (Germany)
  Oral and poster presentation: The artificial leaf
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Danke Anna, dass du mir immer Rückhalt gibst und ich Teil deines Lebens sein darf!
15.) Declaration of honesty in academic work

Die vorliegende Arbeit entstand im Zeitraum von November 2012 bis Juli 2016 am Institut für Anorganische Chemie I (Materialien und Katalyse) der Universität Ulm im Arbeitskreis von Prof. Dr. Sven Rau. Hiermit erkläre ich, dass ich die vorliegende Arbeit selbstständig angefertigt und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt sowie die wörtlich oder inhaltlich übernommenen Stellen als solche kenntlich gemacht und die Satzung der Universität Ulm zur Sicherung guter wissenschaftlicher Praxis in der aktuell gültigen Fassung vom 08.03.2012 beachtet habe.

Ulm, 12.09.2016

Ort, Datum

Markus Braumüller
Appendix

Parts of this thesis were already published in the following scientific articles:
Manuscript [MB1]


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Title: Synthesis and characterization of an immobilizable photochemical molecular device for H₂-generation

Author(s): Markus Braumüller, Martin Schulz, Dieter Sorsche, Michael Pfeffer, Markus Schaub, Jürgen Popp, Byung-Wook Park, Anders Hagfeldt, Benjamin Dietzek and Sven Rau.

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Synthesis and characterization of an immobilizable photochemical molecular device for H₂-generation†

Markus Braunmüller,a Martin Schulz,b,c Dieter Sorsche,a Michael Pfeffer,a Markus Schaub,a Jürgen Popp,c Byung Wook Park,d Anders Hagfeldt,*e Benjamin Dietzkeke,b,f and Sven Rau*a

With [RuII(bpyMeP)tpphzPtCl]2+ (4) a molecular photocatalyst has been synthesized for visible-light-driven H₂-evolution. It contains the ligand bpyMeP (4,4’-bis(diethyl-(methylen)-phosphonate)-2,2’-bipyridine) with phosphate ester groups as precursors for the highly potent phosphonate anchoring groups, which can be utilized for immobilization of the catalyst on metal–oxide semiconductor surfaces. The synthesis was optimized with regard to high yields, bpyMeP was fully characterized and a solid-state structure could be obtained. Photophysical studies showed that the photophysical properties and the localization of the excited states are not altered compared to similar Ru-complexes without anchoring group precursors. (4) was even more active in homogenous catalysis experiments than [RuII(tbbpy)tpphzPtCl]2+ (6) with tbbpy (4,4’-bis(butyl)-2,2’-bipyridine) as peripheral ligands. After hydrolysis (4) was successfully immobilized on NiO, suggesting that an application in photoelectrosynthesis cells is feasible.

Introduction

The sensitization of semiconductors (SC) to prepare dye sensitized photoelectrosynthesis (DSPECs) or photovoltaic cells (DSSCs) is a research area with growing interest.1-3 Here immobilization of a suitable chromophore or photocatalyst on these semiconductors is a crucial factor. The photosensitizer should have anchoring groups to strongly bind the dye onto the SC surface and to facilitate the charge carrier injection into the SC.2 The most studied class of surface binding groups in DSSCs and DSPECs are carboxylates and phosphonates. Both are utilized on n-type SCs like TiO₂ as well as on p-type SCs like NiO. Comparisons of DSSCs based on differently functionalized [RuII(bpy)]²⁺ on nanocrystalline NiO demonstrate that higher solar energy conversion efficiencies are obtained in the following order –CH₂PO₂H₂ > –COOH > –catechol > –CSSH.4 Additionally, methyl phosphonic acid and carboxylic acid display the highest affinity and monolayer coverage for NiO, which can be monitored by resonance Raman microscopy that can also be used to assure the quality of dye sensitized NiO films.5 Recently it could be shown, that the conjugation of a molecular photocatalyst to a NiO surface did lead to electron transfer from the surface to the catalytic centre which in turn lead to hydrogen formation.6 Within the context of molecular photocatalysts, tpphz based multinuclear complexes are of great interest as it contains a redoxactive side which can store electrons more efficiently than e.g. bpy ligands (tpphz = tetrapyrido[3,2-a:2′,3′-c:3,2″-h:2″′,3″′-j]phenazine, bpy = 2,2’-bipyridine).7 The H₂-evolving activity of palladium(n)-based Ru²⁺-tpphz-Pd⁰ photocatalysts have been extensively investigated so far in our group.7-10 However the hydrogen production is accompanied with the formation of colloidal Pd⁰, since the stability of the zero valent metal centre is too low in the N,N’ chelating sphere of tpphz.11 A related complex [RuII(tbbpy)tpphzPtCl]²⁺ has been reported by Eisenberg et al. as early as 1998.12 The possible application of this
complex as intramolecular photocatalyst has recently been reported. In contrast to the analogous palladium catalyst reported high chemical stability under photocatalytic hydrogen evolving conditions was observed. However relatively low catalytic activity (max. turnover number of 7) was reported as well.

Homodinuclear Ru$_2$tphz complexes have already been bound via carboxylated bipyridine ligands to semiconducting TiO$_2$ electrodes. Here the favourable charge transfer properties of the tphz ligand proved useful. However, in a related study for a heteroleptic ruthenium complex with carboxylated bipyridine ligands and a structurally related dipyrudophenazine ligand a significant impact of the ligand composition on the photo- and electrochemistry could be observed. Most notably this complex show unexpected luminescence in water, i.e. a switch off of the known light switch effect, implying fundamentally different excited state relaxation pathways than those typically observed for complexes of this kind without anchoring groups. Carboxylate anchoring groups might even hinder hole injection into NiO as recently investigated for rutheniumpolypyridyl complexes.

Phosphonate binding groups guarantee a chemically more stable link-up to semiconducting surfaces than carboxylates. This general assumption has been investigated in detail in a recent publication resulting in a structure–property relationship study for [Ru$_3^2$(bpy)$_4$]F$_2$-derivatives differing in the quantity of phosphonate functionalized bpy ligands and the presence or absence of a CH$_2$-spacer between the aromatic ring and –PO$_2$H$_2$ anchor. T. J. Meyer et al. compared properties of these [Ru$_3^2$(bpy)$_4$]F$_2$-derivatives in solution and chemically bound on TiO$_2$ or ZrO$_2$, respectively. They found that electron injection yields decrease with increased number of phosphonate substituents or the addition of a methylene spacer. But electro- and photochemical stabilities on TiO$_2$ are enhanced with an increasing number of phosphonate groups. In addition the binding constants for –CH$_2$PO$_2$H$_2$ are higher compared with –PO$_2$H$_2$. Therefrom we chose to utilize two diphosphonated bipyridine ligands including a methylene spacer. [Ru$_3^2$(bpyMeP)$_2$tphzPtCl$_2$] (4) comprises all components of an intramolecular photocatalyst (bpyMeP = 4,4’-bis(diethyl-(methylene)phosphonate)-2,2’-bipyri-dine). A rutheniumpolypyridyl light harvesting unit, the bridging ligand tphpz as an electron transfer system and platinum as catalytic centre (Fig. 1). As will be shown, the methyl phosphonic ester groups can be deprotected to make this complex immobilizable on SC surfaces.

(4) would be one of the first functional units which consists of a photocentre intramolecularly connected via a bridging ligand to a catalyst, which could be utilized for H$_2$-generation on SC surfaces. To the best of our knowledge only one other system was published yet, in which an intramolecular photocatalyst is utilized on an electrode surface. However, there the assembly process of the functional catalyst is sequential, i.e. first the photoelectroactive ruthenium was bound to surface and then the catalytic active cobalt unit had to be bound to the already immobilized photocentre. Hence it was not possible to correlate the photocatalytic properties of the assembled photocatalyst on the surface with these of a molecular Ru–Co catalyst in solution. Target catalyst (4) would make this useful correlation feasible, since the intramolecularity of photo- and catalytic centre is given a priori. After hydrolysis of the ethyl ester groups (4) could be immobilized on electrode surfaces in one single step. In this contribution we describe the synthesis and photophysical and photocatalytical properties of complex (4). The hydrolysis and immobilization of (4) are presented at the stage of preliminary tests.

**Results and discussion**

**Ligand synthesis**

For the composition of supramolecular systems it is necessary to apply suitable ligands which guarantee a stable linkage between the single moieties. For water reduction in an electrochemical cell the immobilization of chromophores to the SC NiO is most commonly used. An effective fixation of metal complexes to NiO could be accomplished by bpyMeP as ligand. The desired ligand was synthesized according to Fig. S1† using modified literature methods. The proton signal splitting of the methylene group between bipyridine and bromine or phosphor respectively from a singlet in 4,4’-bis(bromomethyl)-2,2’-bipyridine to a broad doublet in bpyMeP is characteristic since it stems from the coupling of these protons with the phosphor atom. A broad coupling can also be found in $^{13}$C-NMR between the methylene carbon and the phosphor atom. The ligand bpyMeP could be fully characterised by $^1$H-, $^{13}$C- and $^{31}$P-NMR ([[D$_3$]MeCN, 162 MHz]: $\delta$ [ppm] = 24.35), mass spectrometry ($m/z$ (MALDI) = 457.4 [M + $^{1}$H$^+$]), 479.3 [M + $^{1}$Na$^+$]) and elemental analysis.

The structure was later confirmed by X-ray crystallography. The atom connectivity and atomic numbering scheme for bpyMeP are shown in Fig. 2. Selected bond lengths and angles are given in Table 1. The structure of bpyMeP exhibits an inversion symmetry centre located on the C2–C2’ bond.

![Fig. 1 Desired dinuclear photocatalyst (4).](image1)

![Fig. 2 Solid state structure of bpyMeP.](image2)
The C–N–C angle of 116.9° within the pyridine ring is similar to those for free pyridine (for example, about 117° in a pyridine derivative). The two pyridyl rings within bpyMeP are in anti conformation with no deviation from planarity.

The C1–P1 bond is turned out of the bipyridine plane with a torsion angle of 88.17°. The bond length between C4 in the pyridine ring and the methylene C1 is given as 1.507 Å and is therefore in the normal range of a sp³-C(sp³)-C single bond. Likewise the C1–P1 distance exhibits a standard value of 1.791 Å for a methylene C–phosphonate P–C bond. Neither hydrogen bonding nor π–π-stacking were found within the structure.

### Metal complex synthesis

Here we present the synthesis of the mono- and dinuclear target complexes [Ru⁹(bpyMeP)₂]tpphz⁶⁺ (3) and [Ru⁹(bpyMeP)₂]tphhzPtCl₂⁴⁺ (4) (Fig. 3).

The coordination of one bpyMeP-ligand to a Ru²⁺ core was already described by Odobel and coworkers in 2001 with the complex [Ru⁹(bpy)₂(bpyMeP)₂]⁻²¹. To assure comparability to complexes (3) and (4) within this contribution we synthesized [Ru⁹(tbbpy)₂(bpyMeP)²²⁺ (M) as a model complex with more electron-rich bipyridines. The synthesis of (M) was accomplished by reaction of [Ru⁹(tbbpy)₂Cl₂] with one equivalent of bpyMeP in an ethanol–water-mixture for 20 h. (M) was characterised by ¹H-, and ³¹P-NMR ([D₃]MeCN, 162 MHz): δ (ppm) = 23.00. The solid-state structure of (M) was derived from X-ray suitable single crystals which were grown by slow vapor diffusion of diethyl ether into a solution of the complex in acetone (Fig. 4).

Upon coordination phosphinic ester groups are turned into cis configuration with respect to the C₂–C₂'-bond of the bipyridine. No significant changes are observed concerning the pyridine–C–methylene-C bond, the methylene-C–P bond, or the respective angle <(CCP) (cf. Table 2).

The Ru–N bond lengths (2.051(3) Å–2.067(3) Å) and bite angles (78.5°–79.0°) of all bipyridine ligands are in the usual range.

The coordination of two bpyMeP-ligands to a Ru²⁺ core should provide four anchoring groups per ruthenium complex, ensuring stable binding on semiconductor-surfaces. The preparation of complex (1) with L₁L′ = Cl as a precursor is literature known. But the yields did not surpass 32%. Hence different preparation routes were investigated to optimize the yield of (1). bpyMeP turned out to be instable in a microwave-assisted reaction with Ru[[COD]Cl]₂, which is usually used for the efficient synthesis of [bpy]₂RuCl₂-derivatives. Also a two steps synthesis of (1), starting with refluxing Ru[[CO]₆]Cl₄ and one equivalent of bpyMeP in MeOH then introducing the second equivalent by lightdriven reaction failed. The coordination of two equivalents of bpyMeP to Ru finally was accomplished by using Ru(DMSO)₄Cl₂ as precursor in methanol with a reaction time of 20 h at reflux. Looking at previous results, the reaction of two bpy-like ligands with Ru(DMSO)₄Cl₂ might lead to Ru complexes with different substitution patterns. DMSO as well as Cl could be replaced by bpy. Since the substitution pattern of (1) (Cl or DMSO) is not important for the preparation of (2) or other [Ru⁹(bpyMeP)₂]Cl₂⁻²⁻ complexes the raw product was used directly without further purification for the next step (Fig. 5).

The Ru(bpyMeP)₂Cl₂–/DMSO-plexes are refluxed with an equimolar amount of phen(O)₃ (1,10-phenanthroline-5,6-dione) in an ethanol–water mixture for 20 h. Starting with Ru(DMSO)₄Cl₂ the overall yield of (2) is 86%. Hence this synthetic route proved itself as a high-yielding method to generate [Ru⁹(bpyMeP)₂]L₂⁻²⁻-plexes.

Recently T. J. Meyer et al. published another approach to synthesize [Ru⁹(bpyMeP)₂]L²⁺ with L = bpy²⁻. They applied a [Ru(n⁶-C₆H₆)₆]bpy[OTf]OTF precursor with two equivalents of bpyMeP in 1 : 1 (v/v) EtOH–H₂O under refluxing conditions to generate the hydrolyzed form of [Ru⁹(bpyMeP)₂]bpy in 62% yield. In other words, they first introduced bpy and in a

---

**Table 1** Selected bond length and angle of bpyMeP

<table>
<thead>
<tr>
<th></th>
<th>C1 P1</th>
<th>C1 C4</th>
<th>&lt;C4 C1 P1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distances/Å</td>
<td>1.791</td>
<td>1.507</td>
<td>1.791</td>
</tr>
<tr>
<td>Angle/°</td>
<td>115.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

**Table 2** Selected bond length and angle of (M)

<table>
<thead>
<tr>
<th></th>
<th>Cₜₜₑ P</th>
<th>Cₚₚₑ Cₜₜₑ</th>
<th>&lt;Cₚₚₑ Cₜₜₑ P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distances/Å</td>
<td>1.781</td>
<td>1.505</td>
<td>1.781</td>
</tr>
<tr>
<td>Angles/°</td>
<td>110.2</td>
<td>113.3</td>
<td></td>
</tr>
</tbody>
</table>

*With respect to the two phosphonate groups being symmetrically non equivalent in the complex.
second step two equivalents of bpyMeP to the Ru$^{2+}$ core. The preparation of (3) would therefore imply the generation of the precursor [Ru(n$^6$-C$_8$H$_8$)(tpphz)OTf]OTf. Since a successful synthesis of this precursor is intricate and the synthesis of (2) by our presented procedure is straightforward and high yielding, we decided to avoid this alternative strategy.

Beginning with (2) and phen(NH$_2$)$_2$ (1,10-phenanthroline-5,6-diamine) the synthesis of (4) is performed by two steps. At first the bridging ligand tpphz is synthesized by condensation of phen(NH$_2$)$_2$ and phen(O)$_2$ to yield (3). In principle this condensation in the presence of a coordinated Ru-complex is known to literature. A direct introduction of the poorly soluble tpphz to (1) was avoided because of the thermal instability of bpyMeP under high-temperature conditions needed for the introduction of tpphz. Our best results for the tpphz-condensation were obtained by working in an acetonitrile–glacial acetic acid mixture (4:1) under inert atmosphere. After work up by column chromatography and recrystallisation (3) was received in 57% yield and characterised by $^1$H-, $^{13}$C-, $^{31}$P-NMR ([D$_3$]MeCN, 162 MHz): $\delta$ [ppm] = 22.92, mass spectrometry (m/z (MALDI/TOF) = 699.50 [(M – 2PF$_6$)/2]$^{2+}$, 1543.42 [M – PF$_6$]$^{−}$) and elemental analysis. To complete the photocatalyst (4) Pt has to be coordinated to the free phenanthroline sphere of tpphz. For this purpose (3) and Pt(DMSO)$_2$Cl$_2$ are refluxed in ethanol for 5 h to gain (4) in 82% yield. The target complex (4) was characterised by $^1$H-, $^{31}$P-NMR ([D$_3$]MeCN, 162 MHz): $\delta$ [ppm] = 22.82, mass spectrometry (m/z (MALDI/TOF) = 832.65 [(M – 2PF$_6$)/2]$^{2+}$, 1809.28 [M – PF$_6$]$^{−}$) and elemental analysis. If one compares the $^{31}$P-NMR shifts of bpyMeP with (3) and (4) there is almost no difference, indicating that the coordination to mono- or dinuclear ruthenium complexes has minor electronic effects on the phosphor atoms of bpyMeP. The introduction of Pt to (3) tpphz could be observed by $^1$H-NMR-spectroscopy. As known from previous investigations the $^1$H-NMR signal shifts of similar Ru-complexes like (3) and (4) are concentration dependent. For comparison it must be guaranteed that the spectra are measured at equivalent concentrations. The presence of Pt leads to a decreasing electron density at the tpphz moiety. This deshielding has a particularly strong effect on the protons which are located in direct proximity of Pt. In comparison to (3) their signals are shifted to downfield (cf. protons a’ in Fig. S3 in the ESI$^\dagger$)

**Photophysics**

Absorption spectra for (3) and (4) in MeCN (measured at a concentration of $10^{-5}$ M) (Fig. 6) exhibit characteristic intense $\pi$–$\pi^*$ absorptions below 350 nm and metal-to-ligand charge-transfer (MLCT) absorptions from 400 to 500 nm as usual for ruthenium poly(pyridyl) complexes. Both compounds feature a similar MLCT absorption maximum ($\lambda_{max}$ ≈ 450 nm). Notably (4) does not reveal the pronounced absorption bands which (3) shows at 380 nm. These bands are assigned to phenazine based $\pi$–$\pi^*$-transitions. As previously shown, these absorptions features are also absent in structurally related Ru-tpphz-Pt complexes. Thus, the absorption spectrum presents a strong indication for the coordination of platinum on the free phenanthroline sphere of tpphz in (4). This is assured by the quenching of the emitting excited state by platinum as shown in the emission spectra (Fig. 6). Complex (3) shows the light switch effect. Typically the luminescent state is active in aprotic solvents whereas the non-luminescent state dominates in protic solvents such as water. As depicted in Fig. S4 in the ESI$^\dagger$ the luminescence of (3) is quenched by adding water to the MeCN dye solution. So (3) shows the expected photophysical properties of similar Ru-tpphz-complexes and the methyl phosphonic ester groups do not change the emission behavior compared to related compounds without anchoring groups. This is in contrast to related Ru-dpz complexes with dicarboxylated bipyridines for which no such light switch effect could be observed. From these results one can infer that the photophysical properties of (3) are not changed significantly if methyl phosphonic ester groups are utilized as anchoring groups.

Absorption and emission spectra of (3) and [Ru$^4$(tbbpy)$_2$]tpphz$^{2+}$ (5) after excitation within the range of the
MLCTs were recorded at a dye concentration of $5 \times 10^{-6}$ M. The comparison of (3) with (5), where the bpyMeP ligands are replaced by tbppy, shows different absorption and emission characteristics, which point to altered excited state properties upon introduction of the bpyMeP ligand (cf. Fig. S5 in the ESI†) (tbppy = 4,4′-bis(dbutyl)-2,2′-bipyridine). Concerning the absorption, (3) exhibits a pronounced maximum at low energy part of MLCT band (bathochromic shift of 646.4 cm$^{-1}$, i.e. 0.08 eV compared to (5)) whereas in the emission spectrum a slight hypsochromic shift could be observed (513.8 cm$^{-1}$, i.e. 0.064 eV compared to (5)). This antipodal behavior leads to a difference in Stokes shifts of (5) compared to (3) obviously caused by the exchange of bpy substituents. The bathochromic shift in absorption could be explained by the electron-withdrawing substituent effect of the methyl phosphonic ester groups in lowering the π* levels on bpyMeP with respect to tbppy as similarly described by T. J. Meyer et al.$^{29}$ This electron-pull induces also a lowered electron density at the Ru centre of (3) in comparison to the Ru centre of (5). This might be an explanation for the hypsochromic shift in emission. Important absorption and emission features of complexes (2)–(5) are summarized in Table 3.

### Electrochemical properties

In order to study the effect of the phosphonate ester moiety on the electronic properties of the Ru-centre, related mononuclear complexes are investigated. The redox potential for the Ru$^{III/II}$ couple in (3) occurs at more positive potential than that of the Ru$^{III/II}$ of (5) (cf. Table 4, Fig. S6 in the ESI†). The dbutyl-groups are more electron-donating compared to methyl phosphonic ester substituents, resulting in an eased oxidation of Ru$^{	ext{III}}$ in (5). If compared to [Ru$^{	ext{II}}$(bpy)$_2$tpphz]$^{2+}$ with unsubstituted and [Ru$^{	ext{II}}$(bpy$(\text{COOMe})_2$)$_2$dppz]$^{2+}$ with carboxylic ester substituted bpy ligands Ru$^{	ext{II}}$ oxidation becomes easier in the following order: [Ru$^{	ext{II}}$(bpy$(\text{COOMe})_2$)$_2$dppz]$^{2+}$ < (3) < [Ru$^{	ext{II}}$(bpy)$_2$tpphz]$^{2+}$ < (5).$^{16,37}$ In the same order the character of peripheral bpy substituent changes from electron withdrawing to electron donating.

### Resonance-Raman experiments

The localization of the initially excited state (Franck-Condon point) is highly important for the catalytic process as has been shown before for the ruthenium/palladium dyad [Ru(tbbpy)$_2$tpphzPdCl$_2$]$^{2+}$. For [Ru(tbbpy)$_2$tpphzPdCl$_2$]$^{2+}$ excitation of the red-edge of the 1MLCT absorption band – populates a mainly tpphz-based state which can be deactivated via vectorial electron transfer to the Pd centre.$^{8,9}$ The discussed electron-withdrawing properties (vide supra) of the bpyMeP ligands may, however, result in a different Franck-Condon point structure. It was therefore of immediate interest to determine the localization of the initially excited state on certain parts (bridge or periphery) of compound (4). Resonance-Raman spectroscopy is suited to investigate the localization of states shortly after excitation due to the enhancement of modes that display a large nuclear displacement from the equilibrium geometry at the Franck-Condon point.$^{39}$ We recorded resonance-Raman spectra of (3) and (4) in MeCN solution upon excitation at 458, 476 and 514 nm, i.e. in resonance with the 1MLCT-absorption of the complexes. Resonance-Raman spectra at 514 nm suffer from a strong luminescence background and are therefore not displayed. The resonance-Raman spectra obtained for excitation of (4) at 458 nm show modes from the peripheral bpyMeP ligands as well as from the tpphz-bridge (Fig. 7).

The spectrum of (4) closely resembles that of the previously reported [[tbbpy)$_2$RutpphzPdCl$_2$]$^{2+}$. Comparison between (4) and [Ru(tbbpy)$_2$tpphzPdCl$_2$]$^{2+}$ shows that the relative signal intensities are not changed significantly. Only two bands of (4) appear at different positions than those of

---

**Table 3** Absorption and emission data of complexes (2)–(5) measured in acetonitrile (MLCT absorption maxima $\lambda_{\text{MLCT}}$, phenazine based transition maxima $\lambda_{\text{phz}}$, emission maxima $\lambda_{\text{em}}$)

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\lambda_{\text{MLCT}}$ [nm]</th>
<th>$\lambda_{\text{phz}}$ [nm]</th>
<th>$\lambda_{\text{em}}$ [nm]</th>
</tr>
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<tbody>
<tr>
<td>(2)</td>
<td>443</td>
<td>614</td>
<td></td>
</tr>
<tr>
<td>(3)</td>
<td>455</td>
<td>381</td>
<td>614</td>
</tr>
<tr>
<td>(4)</td>
<td>445.5</td>
<td>381</td>
<td>624</td>
</tr>
<tr>
<td>(5)</td>
<td>442</td>
<td>381.5</td>
<td>635</td>
</tr>
</tbody>
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**Table 4** Electrochemical data for complexes of the types Rutpphz and Rudppz

<table>
<thead>
<tr>
<th>Substance</th>
<th>Half wave potentials $E$ (V) for the oxidation $E_{1/2}$ (Ru$^{0}$/Ru$^{II}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3)$_{a,b}$</td>
<td>1.02</td>
</tr>
<tr>
<td>[Ru$^{II}$(bpy)$<em>2$tpphz]$^{2+}$</em>{b,c}$</td>
<td>0.86</td>
</tr>
<tr>
<td>[Ru$^{II}$(bpy$^{(\text{COOMe})}_2$)$<em>2$dppz]$^{2+}$</em>{c,f}$</td>
<td>0.93</td>
</tr>
<tr>
<td>[Ru$^{II}$(bpy$^{(\text{COOMe})}_2$)$<em>2$dppz]$^{2+}$</em>{c,f}$</td>
<td>1.14</td>
</tr>
</tbody>
</table>

*a The electrochemical measurements were carried out in anhydrous and argon purged MeCN.  
*b 0.1 M NaN$_3$PF$_6$ as supporting electrolyte.  
*c 0.1 M NaN$_3$ClO$_4$ as supporting electrolyte.  
*d The oxidation potentials are given vs. Fe/Ce$.  
*e From ref. 37; Fe/Ce$^+ +0.40$ V vs. SCE in acetonitrile.  
*f From ref. 16; Fe/Ce$^+ +0.36$ V vs. Ag/AgCl in acetonitrile.
[Ru(tbbpy)$_2$tpphzPdCl$_2$]$^{2+}$ (4): 1549, 1275 cm$^{-1}$; [Ru(tbbpy)$_2$tpphzPdCl$_2$]$^{3+}$: 1539, 1282 cm$^{-1}$). The latter were previously assigned to the peripheral ligands, the structure of which is directly impacted by introduction of the anchoring group.\textsuperscript{9} Resonance-Raman experiments are suited to gain information about the energetic order of different electronic transitions that compose a UV/Vis band. This is achieved by a comparison of the resonance-Raman spectra obtained from excitation at different energies of the UV/Vis band. A comparison between the resonance-Raman spectra obtained by excitation of (4) at 458 nm and 476 nm respectively, reveals that the relative intensities of the bipyridine marker bands (at 1547, 1484, 1318 cm$^{-1}$) decrease compared to the tpphz bands when going from higher to lower energy (458 nm to 476 nm, Fig. S7, ESI$^{\dagger}$). The same observation was made for (3) (Fig. S8, ESI$^{\dagger}$). This indicates that the low energy flank of the $^1$MLCT absorption band is governed by $^1$MLCT$_{tphhza}$-GS charge transfer while the higher energy side is governed by $^1$MLCT$_{tpphzPdP}$-GS transitions (GS is ground state).

From this comparison we conclude that changing the peripheral ligands from 4,4’-bis[(butoxy)2,2’-bipyridine to 4,4’-bis-(diethyl(methylene)phosphonate)-2,2’-bipyridine does not alter the localization of the initially photexcited state. This is relevant for an efficient catalytic process, independent of the nature of the catalytic metal centre (palladium or platinum).

**Catalysis**

The new heterodinuclear ruthenium complex [Ru$^{II}$(bpyMeP)$_2$tpphzPtCl$_2$]$^{2+}$ (4) was investigated towards its catalytic activity for light-driven hydrogen production and compared to [Ru$^{II}$(tbbpy)$_2$tpphzPtCl$_2$]$^{3+}$ (6). Therefore commercially available LED sticks ($\lambda = 470$ nm, $P = 45$ mW) in combination with a specialized air-cooled photomicroreactor were used. Irradiation times of 72 h or 17 h, respectively, were recorded in the presence of triethylamine (TEA) acting as a sacrificial electron donor. For both complexes, the catalytic activity is higher in the presence of water (10 vol%). This is in accordance with similar RutpphzPd complexes where water has an optimal concentration range between 10 and 15 vol% and already minor amounts of water strongly increase catalytic activity up to a turnover number of 210 for [Ru$^{II}$(tbbpy)$_2$tpphzPdCl$_2$]$^{2+}$.8 Higher water concentrations are limiting the catalytic turnover. Possibly this is associated with the disadvantageous effect of water on the long-lived excited state in ruthenium complexes bearing a phenazine moiety.\textsuperscript{40} To ensure comparability the catalyst concentration ($c = 7 \times 10^{-5}$ mol L$^{-1}$) were kept constant. (4) and (6) show no induction phase, indicating that they are really the active catalyst. In contrast to RutpphzPd where an significant induction period was observed, suggested to be related to the photodecomposition and formation of colloidal intermediates.\textsuperscript{10} The period of active catalysis of the RutpphzPt catalyst is prolonged by replacing tbbpy with bpyMeP from 10 h for (6) to 48 h for (4). As can be seen, (4) displays a generally higher turnover number (TON) than (6) (37 vs. 7) (Fig. 8). One possible reason for the improved catalytic activity of (4) could be due to the increased energy of the luminescent state detected for (3) if compared to (5), as described above. Furthermore, the phosphonate moieties represent significantly more polar groups than the butyl-groups in (6). They may therefore lead to a different aggregation of the catalyst thus providing more optimal conditions for proton migration and activation. As shown for RutpphPzPd-complexes, optimization of the supramolecular aggregation in solution can have a significant effect on the catalytic activity.\textsuperscript{41} As described above (4) with PCl$_3$ as catalytic unit shows lower catalytic turnover than similar complexes with PdCl$_2$. However, its utilization as an intramolecular photocatalyst on semiconducting surfaces seems more appropriate, since colloid formation, which goes along with the loss of the intramolecular character, can be excluded.

**Hydrolysis and immobilization**

In order to investigate principle utilisability of the presented compounds (3) and (4) in dye sensitized cells, preliminary investigations into deprotection and immobilization were performed.

The methyl phosphonic ester groups of model complex [Ru$^{II}$(tbbpy)$_2$bpyMeP] $^+$ (M) were deprotected by reaction with half-concentrated HCl at reflux as reported for a similar complex by Odobel and coworkers.\textsuperscript{21} The loss of the ethylgroups of (M) can be traced by $^3$H-NMR spectroscopy (Fig. S10, ESI$^{\dagger}$). The deprotected species [Ru$^{II}$(tbbpy)$_2$(bpy(CH$_2$PO$_2$H)$_2$)]$^{2+}$ (M$_{\text{hydrolyzed}}$) is soluble in water (most probably as Cl$^-$salt) and can be reprecipitated as PF$_6$-salt to regain solubility in organic solvents. Comparison of the $^{31}$P-NMR-spectra in acetonitrile of (M) and its deprotected analogue (M$_{\text{hydrolyzed}}$) revealed only minor change in the chemical shift with $\delta$ [ppm] = 23.00 and $\delta$ [ppm] = 19.22, respectively. Notably, deprotection of (3) and (4) according to the above described procedure yielded completely insoluble products.

However, addition of NaOH rendered the deprotected compounds (3) and (4) water-soluble, most probably as 6-fold negatively charged species. Unfortunately the $^3$H-NMR spectra of these complexes in D$_2$O + 4% NaOD show complicated shapes compared to the protected species which were not straightforward to interpret. But in the $^{31}$P-NMR-spectra signals similar to the one for (M$_{\text{hydrolyzed}}$) in deuterated water could be found ($\delta$ [ppm] = 14.77 for (3) and (4) compared to $\delta$ [ppm] =
Methods and materials

Experimental

Methods and materials

$^1$H (400.13 MHz), $^{13}$C-NMR (101 MHz) and $^{31}$P (161.98 MHz) spectra were measured with a Bruker DRX 400 spectrometer. The NMR spectra were recorded in CD$_3$CN or CDCl$_3$ at 298 K. $^1$H-NMR chemical shifts were referenced to the solvent peak for acetonitrile (δ = 1.94 ppm) or chloroform (δ = 7.26 ppm).

MS analysis was performed on Bruker solariX (2010) Hybrid 7 T FT-ICR for MALDI and with a Bruker Ultraflex III MALDI TOF/TOF for MALDI/TOF measurements.

The crystal suitable for X-ray analysis was mounted using a MicroLoop and Fomblin oil. X-ray diffraction intensity data were measured at 180 K on a SuperNova (Dual Source) diffractometer, equipped with an ATLAS detector, from Agilent Technologies. The structures were solved by direct methods (SHELXS) and refined by full-matrix least squares techniques against Fo2 (SHELXL 2013). The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.

Electrochemical data were obtained by cyclic voltammetry using a conventional single-compartment three-electrode cell arrangement in combination with a “Parstat 2273 Princeton Applied Research” potentiostat. The measurements were carried out in 0.1 M solutions of Bu$_4$NPF$_6$ in dry and argon purged acetonitrile. All values were determined with a glassy carbon working electrode and platinum counter and reference electrodes. The measured values were referenced versus the redox couple Fe$^+/Fe$ at $E_{1/2} \approx 0$ V.

The hydrogen evolved was measured by headspace GC on a Bruker Scion GC/MS, with a thermal conductivity detector 15 (column: Mol. Sieve 5A 75 m × 0.53 mm I.D., oven temp. 70 °C, flow rate 22.5 ml min$^{-1}$, detector temp. 200 °C) with argon as carrier gas. The GC was calibrated by mixing different volumes of pure hydrogen together with argon into a schlenk vessel. The obtained signal was plotted against the calibration curve and 20 multiplied accordingly to receive the total produced hydrogen content in the headspace.

The UV/Vis-spectra were recorded with a JASCO Spectrometer V-670. Quartz cells with a 10 mm path length were used.

The emission-spectra were recorded with a JASCO 25 Spectrofluorometer FP-8500. Quartz cells with a 10 mm path length were used.

Immobilization of the hydrolyzed complexes on a NiO surface on a FTO glass carrier was accomplished by dipping the NiO substrate for 3 days at 20 °C into a 0.2 mM solution of [(3$_{\text{hydrolyzed}}$)NiO@FTO]. The dye in 0.1 M NaOH. After immobilization the dye sensitized NiO films were washed several times with water and then analyzed by UV/Vis (reflection spectroscopy) in the MLCT region. For all complexes no significant changes in absorption behavior were found when comparing the protected, the hydrolyzed and the immobilized species (cf. Fig. S12–S14 in the ESI†). (3)@NiO shows the phenazine based π-π*-transitions band at 370 nm (Fig. 9, cf. Fig. 6) whereas (4)@NiO still shows the characteristic unstructured absorption behavior typical for the RutphhzPt-species. For both films the MLCT absorption band ($\lambda_{\text{max}} \approx 450$ nm) of complexes (3) and (4) can be observed.

Starting materials

4,4'-Dimethyl-2,2'-bipyridine and ruthenium trichloride trihydrate (RuCl$_3$$\cdot$3H$_2$O) was purchased from commercial sources and used without further purification. Ru[DMSSO]$_2$Cl$_2$, [Ru($^\text{b}$(tbbpy)$_2$Cl$_2$, [Ru($^\text{t}$(tbbpy)$_2$(tpphz)]$^+$][PF$_6$]$_2$ (5) and [Ru($^\text{t}$](tbbpy)$_2$(tpphz)PtCl$_2$][PF$_6$]$_2$ (6) were prepared as reported elsewhere. 7,11,24,44

Ligand synthesis

4,4'-Dicarboxy-2,2'-bipyridine. This compound was prepared as previously reported. 45

4,4'-Diethoxycarbonyl-2,2'-bipyridine. This compound was prepared as previously reported. 21
4,4'-Dicarboxyethyl ester 2,2'-bipyridine. This compound was prepared by a modified literature procedure. An 5.5 g amount of sodium borohydride was added to a mixture of 4,4'-diethoxycarbonyl-2,2'-bipyridine (5.0 g, 16.7 mmol) in 400 mL of degassed isopropanol alcohol. The mixture was refluxed for 24 h and cooled to room temperature, and then another 5.5 g portion of sodium borohydride was added. After another 36 h heating at reflux the solvent was removed under vacuum and the residue was dissolved in a small amount of water. The resulting solution was extracted with ethyl acetate (3 × 200 mL), dried over magnesium sulfate, and the solvent was removed under vacuum. The desired solid was obtained in 86% yield. Characterization data match literature values.

4,4'-Bis(bromomethyl)-2,2'-bipyridine. This compound was prepared as previously reported.

4,4'-Bis(diethyl(methylene)phosphonate)-2,2'-bipyridine (bpyMeP). This compound was prepared as previously reported.

1H-NMR ([D3]MeCN, 400 MHz): \( \delta [ppm] = 8.59 \text{ (dd, 2H, } J(H,H) = 4.8 \text{ Hz)}, 8.31 \text{ (s, 2H)}, 7.30 \text{ (m, 2H)}, 4.05 \text{ (q, 8H, } J = 6.0 \text{ Hz)} \); C=N=P-Me-P: elemental analysis calcd (\%) for C64H38N8O2P2: C = 45.87, H = 4.25, N = 8.33; C=N=P-Me-P: δ (ppm) = 157.10, 156.19, 153.90, 153.69, 125.08, 124.72, 124.57, 62.52, 62.28, 33.22 (8/2) to acetonitrile, δ (ppm) = 9.81 (d, 2H, J(H,H) = 13.4 Hz), 16.36; δ (ppm) = 22.83, 22.74.

4,4'-Bis(diethyl(methylene)phosphonate)-2,2'-bipyridine (bpyMeP). This compound was prepared as previously reported.

1H-NMR ([D3]MeCN, 400 MHz): \( \delta [ppm] = 9.70 \text{ (d, 2H, } J(H,H) = 7.6 \text{ Hz)}, 9.46 \text{ (d, 2H, } J(H,H) = 8 \text{ Hz)} \); C=N=P-Me-P: elemental analysis calcd (\%) for C64H38N8O2P2: C = 45.87, H = 4.25, N = 8.33; C=N=P-Me-P: δ (ppm) = 157.10, 156.19, 153.90, 153.69, 125.08, 124.72, 124.57, 62.52, 62.28, 33.22 (8/2) to acetonitrile, δ (ppm) = 9.81 (d, 2H, J(H,H) = 13.4 Hz), 16.36; δ (ppm) = 22.83, 22.74.
(m, 2H), 8.02 (m, 2H), 7.94 (m, 2H), 7.76 (d, 2H, J(H,H) = 5.6 Hz), 7.45 (d, 2H, J(H,H) = 6 Hz), 7.26 (d, 2H, J(H,H) = 5.2 Hz), 4.04 (m, 316H), 3.47 (dd, 4H, J(H,P) = 22.8 Hz), 3.38 (dd, 4H, J(H,P) = 22.4 Hz), 1.25–1.11 (m, 24H); 31P-NMR ([D3]-

[RuII(tbbpy),bpyMeP][PF6]4− (M). A solution of [RuII-(tbbpy),Cl2]0.125 g, 176 µmol and bpyMeP (80.3 mg, 0.5 molecules of
the hydrolyzed product. One option to restore solubility in organic solvents might be treatment with a lipophilic cation like rbu4N+ as Grätzel et al. applied for the famous dye N719. In this contribution (4) was successfully immobilized on NiO from aqueous NaOH solution (0.1 mM) and the sensitized film was analyzed by UV/Vis (reflection) spectroscopy. Therefore a supramolecular building block approach towards photochemical molecular devices attached to electrode surfaces seems feasible.

Acknowledgements
This research was supported by the Studienstiftung des deutschen Volkes (MB), the German Research Association (DFG GRK 1626, MP), the Carl-Zeiss-Stiftung (DS), the CONCERT Japan and the COST Action CM1202, PERSPECT-H2O.

Notes and references


Figures and Tables.

Figure S1. Synthetic scheme for the preparation of bpyMeP.

Figure S2. $^1$H-NMR-spectrum of (3). By comparing the results for (3) with known Ru-tpphz-complexes the proton signals were assigned as depicted.
Figure S3. Comparison of $^1$H-NMR spectra of (3) and (4).

Figure S4. Emission quenching upon the addition of water to an acetonitrile solution of (3).*

*=excitation at identical optical density at 459 nm.
Figure S5. UV/vis and emission spectra of (3) and (5). *
*=excitation at a concentration of $5 \times 10^{-6}$ M at 450 nm.

Figure S6. Cyclovoltamogram of (3) and (5) (oxidation part).
**Figure S7.** Resonance-Raman spectra ($\lambda_{exc} = 458$ nm and 476 nm) of the Ru-complex (4)

**Figure S8.** Resonance-Raman spectra ($\lambda_{exc} = 458$ nm and 476 nm) of the Ru-complex (3)
Figure S10. $^1$H-NMR spectra of [Ru$^{	ext{II}}$(tbbpy)$_2$bpyMeP] (M) in [D3]MeCN (bottom) and [Ru$^{	ext{II}}$(tbbpy)$_2$(bpy(CH$_2$PO$_2$H$_2$)$_2$)] (M$_{	ext{hydrolyzed}}$) in D$_2$O (top). The protons of the ethyl groups (highlighted by red rectangles) disappear upon deprotection.

Figure S11. $^{31}$P-NMR spectra of (M$_{	ext{hydrolyzed}}$) in D2O and (3$_{	ext{hydrolyzed}}$) and (4$_{	ext{hydrolyzed}}$) in D2O + 4% NaOD.
Figure S12. Absorption spectra of (M) in acetonitrile, (M$_\text{hydrolyzed}$) in water and (M)$_\text{@NiO}$**

**= NiO and FTO glass background substracted

Figure S13. Absorption spectra of (3) in acetonitrile, (3$_\text{hydrolyzed}$) in water + 4% NaOH and (3)$_\text{@NiO}$**

**= NiO and FTO glass background substracted

Figure S14. Absorption spectra of (4) in acetonitrile, (4$_\text{hydrolyzed}$) in water + 4% NaOH and (4)$_\text{@NiO}$**

**= NiO and FTO glass background substracted
Table S1. Crystal data and structure refinement for 4,4'-bis(diethyl(methylene)phosphonate)-2,2'-bipyridine.

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<tr>
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<td>Largest diff. peak and hole</td>
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Figure S15. ORTEP depiction of 4,4′-bis(diethyl(methylene)phosphonate)-2,2′-bipyridine (bpyMeP) in the solid state (ellipsoids drawn at 50% probability).

Table S2. Crystal data and structure refinement for [Ru(bbbpy)₂(bpyMeP)][PF₆]₂ (M)

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<tbody>
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<td>Empirical formula</td>
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<td>Wavelength</td>
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</tr>
<tr>
<td></td>
<td>□ = 90°, □ = 121.496(3)°, □ = 90°</td>
</tr>
<tr>
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<td>Z</td>
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<tr>
<td>Density (calculated)</td>
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<td>F(000)</td>
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<tr>
<td>Crystal size</td>
<td>0.1211 x 0.0645 x 0.0487 mm³</td>
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</table>
Theta range for data collection: 7.517 to 73.818°.

Index ranges:
-57 ≤ h ≤ 40, -15 ≤ k ≤ 15, -35 ≤ l ≤ 36

Reflections collected: 44485

Independent reflections: 14953 [R(int) = 0.0384]

Completeness to theta = 67.679°: 99.5%

Refinement method: Full-matrix least-squares on F2

Data / restraints / parameters: 14953 / 70 / 864

Goodness-of-fit on F2: 1.034

Final R indices [I > 2σ(I)]: R1 = 0.0555, wR2 = 0.1549

R indices (all data): R1 = 0.0705, wR2 = 0.1662

Largest diff. peak and hole: 1.145 and -0.652 e Å⁻³

**Figure S16.** ORTEP depiction of [RuII(tbbpy)₂(bpyMeP)](PF₆)₂ (M) in the solid state (ellipsoids drawn at 50% probability).
Modular Synthesis of Elongated Phosphonate Bipyridines

Markus Braumüller,[a] Dieter Sorsche,[a] Markus Wunderlin,[b] and Sven Rauss[a]

Keywords: Ligand design / Linkers / Photochemistry / Anchoring groups / Nitrogen heterocycles

The synthesis and the photophysical properties of a series of bpy-R₃ derivatives L1–L3 (bpy = 2,2'-bipyridine, R represents the substitution at the 4- and 4'−positions of the bpy) are described. R includes phosphonic ester groups as precursors for potent phosphonate anchoring groups, which enable immobilization on transition metal oxide semiconductor surfaces for applications like dye-sensitized solar cells (DSSCs) or dye-sensitized photoelectrosynthesis cells (DSPECs). The ligands L1−L3 differ in the length of conjugated linker units between bpy core and anchoring groups. Phenylene and triazole moieties serve as building blocks for linker elongation. The resulting adjustability of the distance between semiconductor and chromophore represents a viable route to improve cell efficiency, as it will allow tuning of charge carrier recombination and dye aggregation. Furthermore, the photophysical studies of the free ligands reveal a pronounced effect of the ary1 substitution. The solid-state structures of L1 and L2 are reported within this contribution, enabling the determination of distances between bipyridine nitrogen donor and anchoring group.

Introduction

Metal−organic photosensitizers or photocatalysts anchored to semiconductor (SC) surfaces find important utilisation in DSSCs or DSPECs (dye-sensitized solar cells or dye-sensitized photoelectrosynthesis cells).[1−5] In particular, polypyridyl metal complexes have received extensive attention. They succeeded in converting light to electrical or chemical energy with good efficiency in n-type as well as in p-type cells.[6−8] For n-type DSSCs, the advantages of Ru-polypyridyl complexes are well known, whereas for p-type DSSCs, their use is still in its infancy.[6] The application of, e.g., Re- or Ru-polypyridyl complexes for photocatalytic CO₂ reduction or hydrogen evolution on p-type SCs like TaON or NiO seems very desirable.[3,4,6]

In order to further develop the application potential, it is necessary to tune the properties of the dye for a good light-harvesting ability and an effective directional electron transfer, to overcome fundamental obstacles like recombination processes and to prevent aggregation of the chromophores. For this aim, it is important to modify the linkage between the semiconductor and the sensitizer and to extend the n-conjugated system of the ligands.[7−10] Hence, peripheral substitution of the most commonly used original 2,2'-bipyridine ligand might be an auspicious concept. As anchoring groups, phosphonic acid derivatives have been shown to be chemically more stable than others, both on n-type SCs like TiO₂ and on p-type materials like NiO.[2,11−18] Methyl phosphonic acids display especially high affinities to these SCs. In a recently published article on hole injection dynamics of ruthenium polypyridyl complexes into NiO, it was suggested, that the −I effect of the carboxylic anchoring groups (without linkers between chromophore and NiO) might hinder hole injection.[19] The CH₃ spacer in methyl phosphonic acid might prevent such an effect, since the electronic interaction between the bipyridine and anchoring groups is significantly reduced by the CH₃ group between them.[20] It is noteworthy that phosphonic esters can also be used to modify TiO₂ or other inorganic substrates. Organic-soluble dialkyl phosphonates are useful coupling agent alternatives to phosphonic acids, which are often difficult to solubilize and must be generated under harsh conditions from the corresponding ester.[11,21−24]

To increase the distance of the dye from the semiconductor surface and thereby potentially increase the lifetime of the excited states and slow down unfavorable recombination, it is necessary to introduce linkers between the anchoring group and the ligand moiety. In studies of dyes attached through flexible saturated linkers, it has been observed that the electronic coupling is weakened, and that charge carrier injection rates slow down with increased bridge length.[7] For this reason, synthetic efforts to introduce rigid and aromatic linkers like phenyl groups have followed in this context. For instance, Galoppini et al. have shown that the extinction coefficient of pyrene increases and the long-wavelength absorbance is shifted to the red when it is attached to fully conjugated rods.[25] They also equipped Ru-bpy sensitizers with elongated linkers of this kind and immobilized them on TiO₂. Concerning charge carrier transport there...
was only weak linker–length dependency.\textsuperscript{[26,27]} They suggest that direct contacts of the Ru complex in the sponge-like environment of the mesoporous TiO$_2$ films may act as “short-circuits”, highlighting the importance of anchoring group design. However, structure–property relationship studies for Ru-[(N∧N)$_2$/(C∧N)]$^+$ derivatives, where N∧N represents 2,2′-bipyridine, and C∧N represents bidentate phenylpyridine derivatives with carboxylate anchoring groups, were performed by Wu et al. for their application on NiO in $p$-type DSSCs. They differ in the number of phenylene spacer units between the Ru-[(N∧N)$_2$/(C∧N)]$^+$ core and the anchoring group.\textsuperscript{[8]} They found that as the number of the phenylene units in the linker increases, the interfacial charge recombination rate decreases, and the efficiency of the solar cells increases. Similarly, Nattestadt et al. increased the performance of $p$-type DSSCs by systematic variation of the distance between the hole in the NiO and a perylene monoimide (PMI) acceptor dye.\textsuperscript{[28]} This might also be the case for molecularly sensitized semiconductors for photocatalytically active electrode materials in DSPECs, making distance control between semiconductor and sensitizer even more desirable, for example, to enhance the activity of an immobilized photocatalyst based on a hydrogen evolving photochemical molecular device.\textsuperscript{[29]}

Generally, for a more chemically stable linkage between dye and semiconductor, both positions 4 and 4′ of the bpy should be equipped with anchoring groups. The superior chemical stability of phosphonate anchoring groups on transition metal oxide semiconductor surfaces should increase overall stability further.

Taking all of this into consideration, we decided to develop strategies for the synthesis of 2,2′-bpy derivatives with

---

**Scheme 1.** Synthesis of ligand L1.

**Scheme 2.** Synthesis of ligand L2.
peripheral methyl phosphonic acid anchoring groups including aromatic linkers, such as phenylene and triazole units, for distance control in 4 and 4'-positions of the bpy (cf. Schemes 1, 2, and 3).

The phenylene group represents the archetype for a rigid and aromatic linker. Besides being aromatic and rigid units, triazoles can be synthesized by copper(I)-catalyzed azide–alkyne cycloaddition (CuAAC, well-known under the general term of “click chemistry”). By definition, “click chemistry” is straightforward to perform under mild conditions, insensitive towards many functional groups, efficient and selective.\[^{10}\]

With L1, L2, and L3 we have designed and synthesized three new bpy derivatives, which comprise the demands discussed above. Their phosphonic ester groups can easily be deprotected to generate the free acid functions, for their utilization as anchoring groups.\[^{29,31,32}\]

**Results and Discussion**

**Synthesis**

The new bpy derivative L1 has been prepared in three steps (cf. Scheme 1).

Suzuki coupling of 4-(hydroxymethyl)phenylboronic acid with 4,4'-dibromo-2,2'-bipyridine gave compound 1 in 82% yield.\[^{33}\]

In the last step, the bromine groups of 2 could be substituted by phosphonic ester groups via the Arbusov reaction with triethyl phosphite in 66% yield.\[^{31}\]

L1 was characterized by \(^1\)H, \(^13\)C and \(^{31}\)P NMR and high-resolution mass spectrometry (HRMS) (m/z (MALDI) = 609.22786). The structure was later confirmed by X-ray crystallography. A structurally closely related 6,6'-dimethyl-2,2'-bipyridine with phosphonic acid groups was reported by Housecroft et al. for its utilization as an anchoring ligand for copper(I) dyes in n-type DSSCs.\[^{15}\]

The presence of the phenylene spacer resulted in enhanced performances compared to dyes without this spacer between the bpy core and the phosphonic acid group. For this reason, we intended to get synthetic access to phosphonate bipyridine derivatives with even more aromatic spacer units. At first we tried to introduce another phenylene moiety, but the adaptation of numerous routes to prepare a suitable boronic acid coupling unit failed.\[^{34,41}\]

Therefore we inserted a triazole ring as an alternative since it is easy to generate via CuAAC (click) chemistry. This strategy allowed synthetic access to ligands L2 and L3 (cf. Scheme 2 and Scheme 3).

Azide 3 was generated from the corresponding amide (diethyl 4-aminobenzylphosphonate) using sodium nitrite and sodium azide (98% yield).\[^{42}\]

4,4'-Bis(ethylidene)-2,2'-bipyridine (4) was prepared according to literature methods.\[^{43}\]

L2 was synthesized by the click reaction between azide 3 and bipyridine 4 in 53% yield, with use of catalytic Cu\(^{11}\) in the presence of sodium ascorbate to generate Cu\(^{11}\) in situ.\[^{44}\]

L2 was characterized by \(^1\)H, \(^13\)C and \(^{31}\)P NMR, and HRMS [m/z (MALDI) = 743.26195]. Additionally, crystals suitable for X-ray analysis were obtained.

In order to insert more aromatic linkers between the bpy core and the anchoring unit by using bipyridine 4 and click chemistry, a new azide building block 8 needed to be generated. Compared to 3, the distance between the azide group and the methylphosphonic ester group was increased by the introduction of another phenylene unit via Suzuki coupling. The synthesis of 8 was accomplished in three steps (cf. Scheme 3).
First, compound 5 was prepared according to literature procedures (quantitative yield). Then, Suzuki coupling of 5 and 3-aminophenylboronic acid (6) gave compound 7 in 97% yield. The solid-state structure of 7 was derived from X-ray suitable single crystals (Figure S1 in the Supporting Information). Finally, compound 8 was generated from 7 using sodium nitrite and sodium azide (quantitative yield).

L3 was obtained by the click reaction of azide 8 and bisalkyne 4 in 30% yield, by using the same conditions as for the synthesis of L2. The complexation of CuI with bipyridine might be one reason for the modest yield. L3 was characterized by 1H, 13C and 31P NMR and HRMS [m/z (MALDI) = 895.32441].

Crystal Structures of L1 and L2

Solid-state structures of L1, L2, and the amine intermediate 7 of L3 were obtained and compared to the known 4,4′-bis[diethyl(methylene)phosphonate]-2,2′-bipyridine (L0), where methylphosphonic ester groups are directly bound to the 4- and 4′-position of the bpy core, in the absence of aromatic linker units in between (cf. Figure 1).

Accordingly, the increase in length for the respective ligands can be compared directly from the values obtained. A direct characterization of the metal–surface distance of an immobilized complex depends on its binding mode towards the surface, which is unknown at this point. However, a comparative investigation of N–O3 distances was carried out, and is reflected in Table 1 along with characteristic values of bond lengths and angles of the methylene-phosphonate moiety.

As proposed by Wu et al., a subsequent increase in anchor length may provide improved efficiencies for light-induced charge separation between a bipyridine-bound chromophore and an oxide surface. The results from the solid-state structures show that the presented synthetic structures are a valuable approach in order to increase the length of a bipyridine with phosphonate anchors stepwise by about 3–4 Å per step. The overall distance between the metal-bind-

Table 1. Characteristic lengths and angles.

<table>
<thead>
<tr>
<th></th>
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<th></th>
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<tbody>
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<td>1.791(1)</td>
<td>1.507(2)</td>
<td>115.7(1)</td>
</tr>
<tr>
<td>L1</td>
<td>9.807</td>
<td>1.794</td>
<td>1.509</td>
<td>112.09</td>
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<td>L2</td>
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<td>L3</td>
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<td>1.514(3)</td>
<td>112.2(1)</td>
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</tbody>
</table>

[a] Distance between pyridine nitrogen atom and the calculated centroid centered between the phosphonate oxygen atoms. [b] Ar refers to aryl, i.e. either pyridyl or phenyl. [c] From ref. [d] Median values from two molecules in the asymmetric unit. [e] Estimated value from the O3–N(amine) value of the intermediate structure 7 and the N(pyridine)–N(triazole) distance from L2 (for details see Figure S4 in the Supporting Information).
Modular Synthesis of Elongated Phosphonate Bipyridines

Figure 3. Absorption (top) and emission spectra (bottom) of ligands L0–L3.

Figure 4. Resonance structures I and II of triazole-pyridines in L2 and L3.

The existence of distinguishable emissive states speaks for weak electronic coupling within the single molecule moieties. This might be advantageous for the application of L1–L3 in DSSCs or DSPECs, since charge carrier recombination should also be impaired.

For a more profound discussion of the luminescent behavior, theoretical calculations of the emissive states are necessary. Important absorption and emission features of L0–L3 and building blocks 3 and 8 are summarized in Table 2.

Table 2. Absorption and emission data of ligands L0–L3 and intermediates 3 and 8 measured in dichloromethane (absorption maxima $\lambda_{\text{abs}}$; emission maxima $\lambda_{\text{em}}$).

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\lambda_{\text{abs}}$ [nm] $^{[a]}$</th>
<th>$\lambda_{\text{em}}$ [nm]</th>
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<tbody>
<tr>
<td>L0</td>
<td>250 (6), 285 (13)</td>
<td>368</td>
</tr>
<tr>
<td>L1</td>
<td>285 (20)</td>
<td>326, 338, 353</td>
</tr>
<tr>
<td>L2</td>
<td>293 (23)</td>
<td>374, 402, 424, 445</td>
</tr>
<tr>
<td>L3</td>
<td>297 (25)</td>
<td>332, 345, 373, 400, 421</td>
</tr>
<tr>
<td>3</td>
<td>277 (3)</td>
<td>375</td>
</tr>
<tr>
<td>8</td>
<td>277 (6)</td>
<td>372, 422</td>
</tr>
</tbody>
</table>

$^{[a]}$ Extinction coefficient (c/10$^3$ M$^{-1}$ cm$^{-1}$) in brackets.

The absorption and emission data of L1 to L3 indicated that the substitution of the bipyridine frame with aromatic moieties resulted in significant changes in the electronic properties of the ligands.

Conclusions

Herein we presented a rational synthesis concept for increasing the distance between anchoring unit and bipyridine coordination sphere. We employed phenylene and triazole units as rigid and aromatic linkers to prepare elongated ligands L1–L3 compared to the original 4,4’-bis[die-thyl(methylene)phosphonate]-2,2’-bipyridine (L0). For L1 and L2, this elongation was analyzed by X-ray crystallography and led to an increase in linker length from 5.5 Å to 15.8 Å. The vast potential of click chemistry should give versatile opportunities to employ different building blocks for tuning the extent of linkage and thereby the photophysical properties of bipyridines and their metal complexes. The photophysical studies in this contribution support the assumption that the linkers enhance the performance of chromophores or photocatalysts by shifting their absorption bathochromically. The elongated bipyridines might also slow down unfavorable recombination processes between semiconductor surfaces and photoactive units in DSSCs or DSPECs. The application of the ligands L1–L3 in metal complexes and their effects on the performance of corresponding DSSCs and DSPECs, are currently under investigation.

Experimental Section

Methods and Materials: $^1$H (400.13 MHz), $^{13}$C NMR (101 MHz or 126 MHz) and $^{31}$P (161.98 MHz) spectra were measured with a
Brucker DRX 400 or Brucker DRX 500 spectrometer. The NMR spectra were recorded in [D₆]DMSO or CDCl₃ at 298 K. ¹H-NMR and ¹³C-NMR chemical shifts were referenced to the solvent peak for DMSO or chloroform.

MS analysis was performed with a Bruker solariX (2010) Hybrid 7T FT-ICR.

The crystal suitable for X-ray analysis was mounted using a Microlab Cryoserve and equipped with an Atlas detector, from Agilent Technologies. The structures were solved by direct methods (SHELXS) and refined by full-matrix least-squares techniques against F² (SHELXL 2013).[48] If not stated otherwise, the hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.

The UV/Vis-spectra were recorded with a JASCO Spectrometer V-670. Quartz cells with a 10 mm path length were used.

The emission spectra were recorded with a JASCO 25 Spectrofluorometer FP-8500. Quartz cells with a 10 mm path length were used.

If not mentioned otherwise, all experiments were performed under aerobic conditions.

**Starting Materials:** Starting materials were purchased from commercial sources and used without further purification.

**Ligand Synthesis and Characterization**

**L0** was prepared according to literature procedures.[29]

4,4'-Bis(hydroxymethylphenyl)-2,2'-bipyridine (1): This compound was prepared by a modified literature procedure.[33] The reaction flask was charged with 4-[hydroxymethyl]phenylboronic acid (2 mmol, 304 mg), 4,4'-dibromo-2,2'-bipyridine (1 mmol, 314 mg), toluene (60 mL), and degassed aqueous sodium carbonate solution (2 M, 21 mL) under argon. Then, the first portion of Pd(PPh₃)₄ (3 mol-% based on 4,4'-dibromo-2,2'-bipyridine, 35 mg) was added to the solution. After two days of boiling at reflux, a second portion of Pd(PPh₃)₄ (35 mg) was added, and the solution was heated to reflux for another 24 h. After the mixture cooled to room temperature, the toluene was evaporated. The crude product was washed sequentially with water, EtOH and Et₂O to give 4,4'-bis(hydroxymethylphenyl)-2,2'-bipyridine (1) in 82% yield (302 mg).

Compound 1 shows poor solubility in both organic and aqueous solvents. ¹H NMR (400 MHz, [D₆]DMSO, 25 °C): δ = 8.73 (d, J_HH = 5.2 Hz, 2 H), 8.67 (d, J_HH = 1.3 Hz, 2 H), 7.81 (d, J_HH = 8.2 Hz, 4 H), 7.77 (dd, J_HH = 5.2, J_HP = 1.8 Hz, 2 H), 7.48 (d, J_HH = 8.2 Hz, 4 H), 5.30 (s, 2 H, OH), 4.56 (s, 4 H, CH₂- OH) ppm. HRMS (ESI): m/z calcd. for [M + H]+: 369.15975; found: 369.15979.

4,4'-Bis(bromomethylphenyl)-2,2'-bipyridine (2): This compound was prepared by a modified literature procedure.[33] The bipyridine (500 mg) was added to a mixture of copper sulfate pentahydrate (60 mg, 0.24 mmol) and (+)-sodium ascorbate (NaAsc; 117 mg, 0.59 mmol) in H₂O (25 mL). Upon the addition of the aqueous suspension to the orange organic phase, a black precipitate formed instantly. The mixture was stirred for 12 h and then poured into a saturated aqueous ethylenediaminetetraacetic acid (EDTA) solution (500 mL) and stirred for 14 h to remove Cu²⁺. The resulting blue solution was extracted several times with CHCl₃. The combined organic extracts were dried with anhydrous MgSO₄, and the CHCl₃ was evaporated to afford the crude product. Flash chromatography using a 5:1 CHCl₃/MeOH eluent gave the title compound as a yellowish powder in 53% yield (258 mg).

4,4'-Bis(ethylphenyl)-2,2'-bipyridine (4): This compound was prepared according to literature.[42] Compound 3 (0.63 g, 2.34 mmol) was added to a solution of 4 (134 mg, 0.66 mmol) in CH₂Cl₂ (25 mL), which was followed by the addition of a mixture of copper sulfate pentahydrate (60 mg, 0.24 mmol) and (+)-sodium l-ascorbate (NaAsc; 117 mg, 0.59 mmol) in H₂O (25 mL). Upon the addition of the aqueous suspension to the orange organic phase, a black precipitate formed instantly. The mixture was stirred for 12 h and then poured into a saturated aqueous ethylenediaminetetraacetic acid (EDTA) solution (500 mL) and stirred for 14 h to remove Cu²⁺. The resulting blue solution was extracted several times with CHCl₃. The combined organic extracts were dried with anhydrous MgSO₄, and the CHCl₃ was evaporated to afford the crude product. Flash chromatography using a 5:1 CHCl₃/MeOH eluent gave the title compound as a yellowish powder in 53% yield (258 mg).
Crystal data for L2: C30H46N6O12P2, M_r = 742.70 g/mol, yellow prism, crystal size 0.112 x 0.039 x 0.028 mm, monoclinic, space group P 2_1/n, α = 8.5104(2) Å, β = 14.6092(3) Å, γ = 15.2627(5)°, β = 105.580(2)°, V = 1827.98(7) Å³, T = 150(2) K, Z = 2, ρ_{c fused} = 1.557 Mg/m^3, µ (Cu-Kα) = 1.557 mm, F(000) = 780, altogether 9020 reflexes up to h = 9(10), k = 18(13), l = 19(18), measured in the range of 7.497° ≤ θ ≤ 74.491°, completeness Θ_{max} = 99.7%, 3742 independent reflections, R(f) = 0.0190, 3217 reflections with F_o > 4σ(F_o), 235 parameters, 0 restraints, R_{int} = 0.0536, wR_{2o} = 0.1557, R_{all} = 0.0612, wR_{2o} = 0.1650, GOOF = 1.055, largest difference peak and hole: 0.790 - 0.527 e Å^(-3), CCDC-1400582 contains the supplementary crystallographic data for L2. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Diethyl (4-Bromobenzyl)phosphonate (5): This compound was prepared according to literature.[45]

3'-Azido-4-diethyl(methylene)phosphonato-1',1'-biphenyl (8): This compound was prepared by a modified literature procedure.[42] Compound 7 (1.97 mmol, 630 mg) was dissolved in a mixture of water (15 mL) and concentrated hydrochloric acid (7.5 mL). The solution was cooled to 0°C. NaNO_2 (338 mg, 4.90 mmol) in water (2 mL) was added, and the resulting solution was stirred for 45 min. Then NaN_3 (319 mg, 4.91 mmol) in water (2 mL) was added, and the reaction mixture was stirred for 1 h at 0°C and 3.5 h at room temperature. The resulting solution was extracted several times with CHCl_3 and EtOAc. The combined organic extracts were dried with anhydrous MgSO_4, and the EtOAc was evaporated to afford the product 8 (681 mg, quantitative yield). [H] NMR (400 MHz, CDCl_3, 25°C): δ = 7.45 (s, 1 H), 7.43 (s, 1 H), 7.35-7.26 (m, 4 H), 7.13 (t, J_{H,H} = 1.8 Hz, 1 H), 6.93 (d, J_{H,H} = 7.8 Hz, 1 H), 4.04-3.91 (m, 4 H, PO(OC=CH_2)CH_3), 3.15 (d, J = 21.8 Hz, 2 H, CH_2POCH_2)EtO, 1.18 [(1/2)J_{H,H} = 7.1 Hz, 6 H, PO(OC=CH_2)CH_3] ppm. 13C NMR (101 MHz, CDCl_3, 25°C): δ = 142.64, 140.59, 138.87, 131.16, 134.40, 123.27, 123.76, 117.89, 117.67, 62.64, 33.38 (d, J_{C,P} = 138.4 Hz), 16.48 ppm. 31P NMR (162 MHz, CDCl_3, 25°C): δ = 27.95 ppm. HRMS (ESI): m/z calcld. for [M + H]^+ 346.1315; found 346.1319; IR (KB): ν = 2983, 2907, 2104, 1564, 1480, 1401, 1304, 1249, 1096, 1027, 962, 853, 784, 693, 604, 544 cm^(-1).

L3: This compound was prepared by a modified literature procedure.[42] Compound 8 (0.70 g, 2.03 mmol) was added to a solution of 4 (178 mg, 0.87 mmol) in CH_2Cl_2 (30 mL), which was followed by the addition of a mixture of copper sulfate pentahydrate (80 mg, 0.32 mmol) and (+)-sodium (L)-ascorbate (NaAsc; 155 mg, 0.79 mmol) in H_2O (30 mL). Upon the addition of the aqueous suspension to the orange organic phase, a black precipitate formed instantly. The mixture was stirred for 2 h and then poured into a saturated aqueous ethylenediaminetetraacetic acid (EDTA) solution (600 mL) and stirred for 14 h to remove Cu^2+. The resulting blue solution was extracted several times with CHCl_3. The combined organic extracts were dried with anhydrous MgSO_4 and the CHCl_3 was evaporated to afford the crude product. Flash chromatography using 5:1 CHCl_3/MEOH as the eluent gave the product as a brownish oil with some impurities. This oil was diluted with CHCl_3 and the compound was obtained by precipitation with n-pentane as a brownish powder in 30% yield (235 mg). [1H] NMR (400 MHz, CDCl_3, 25°C): δ = 8.81 (m, 4 H), 8.61 (s, 2 H), 8.08 (d, J_{H,H} = 5.0, J_{H,J} = 1.7 Hz, 2 H), 8.04 (t, J_{H,H} = 1.7 Hz, 2 H), 7.76 (d, J_{H,J} = 7.8 Hz, 2 H), 7.68 (d, J_{H,J} = 7.9 Hz, 2 H), 7.63 (m, 6 H), 7.44 (d, J_{H,J} = 8.3, J_{H,J} = 2.4 Hz, 4 H), 4.10-4.02 (m, 8 H, PO(OC=CH_2)CH_3), 3.25 (d, J_{H,J} = 21.8 Hz, 4 H, CH_2POCH_2), 1.28 [(1/2)J_{H,H} = 7.1 Hz, 12 H, PO(OC=CH_2)CH_3] ppm. 13C NMR (101 MHz, CDCl_3, 25°C): δ = 156.47, 150.20, 146.27, 142.94, 138.94, 138.15, 137.36, 132.06, 130.64, 130.46, 127.76, 127.44, 120.44, 119.85, 119.26, 117.65, 62.36, 33.60 (d, J_{C,P} = 138.3 Hz), 16.52 ppm. 31P NMR (162 MHz, CDCl_3, 25°C): δ = 26.09 ppm. HRMS (MALDI-D): m/z calcld. for [M + H]^+ 895.32448; found 895.32441; IR (KB): ν = 3330, 3282, 2923, 2852, 2334, 1868, 1739, 1233, 1022, 789, 717, 666, 545, 442 cm^(-1).

Supporting Information (see footnote on the first page of this article): Experimental and characterization data, as well as additional figures.
Acknowledgments

This research was supported by the Studienstiftung des deutschen Volkes (M. B.), the Carl-Zeiss-Stiftung (D. S.), the CONCERT Japan and the COST Action CM1202, PERSPECT-H2O.

SUPPORTING INFORMATION

**DOI:** 10.1002/ejoc.201500641  
**Title:** Modular Synthesis of Elongated Phosphonate Bipyridines  
**Author(s):** Markus Braumüller, Dieter Sorsche, Markus Wunderlin, Sven Rau*
1.) Solid state structures
Table S1: Crystal data and structure refinement for (7).

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<th>Value</th>
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Figure S1: ORTEP depiction of (7) in the solid state (ellipsoids drawn at 50% probability).

Table S2: Crystal data and structure refinement for L1.

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Refinement method Full-matrix least-squares on F^2
Data / restraints / parameters 12527 / 0 / 757
Goodness-of-fit on F^2 1.145
Final R indices [I>2sigma(I)] R1 = 0.0476, wR2 = 0.1341
R indices (all data) R1 = 0.0613, wR2 = 0.1442
Largest diff. peak and hole 0.783 and -0.489 e\text{Å}^{-3}

**Figure S2:** ORTEP depiction of L1 in the solid state (ellipsoids drawn at 50% probability).

**Table S3:** Crystal data and structure refinement for L2.

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F(000) 780
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Index ranges -9<=h<=10, -18<=k<=13, -19<=l<=18
Reflections collected 9020
Independent reflections 3724 [R(int) = 0.0190]
Completeness to theta = 67.679° 99.7 %
Refinement method Full-matrix least-squares on F$^2$
Data / restraints / parameters 3724 / 0 / 235
Goodness-of-fit on F$^2$ 1.055
Final R indices [I>2sigma(I)] R1 = 0.0536, wR2 = 0.1557
R indices (all data) R1 = 0.0612, wR2 = 0.1650
Largest diff. peak and hole 0.790 and -0.527 e Å$^{-3}$

Figure S3: ORTEP depiction of L2 in the solid state (ellipsoids drawn at 50% probability).
Figure S4: Superposition of the solid-state structures of (7) (red) and L2 (blue) in order to estimate the O₃-N1 distance for L3; the N-substituted (amine/triazole) phenyl rings were overlayed, the distance between the O₃ centroid and the amine nitrogen was measured for (7), the distance between the pyridyl nitrogen atom N1 and the triazole nitrogen bound to the benzylphosphonate was measured for L2, giving a rough estimation for the O₃-N1 distance in L3 of about 15.8 Å.
2.) $^1$H-NMR-spectra

Figure S5: $^1$H-NMR spectrum of bipyridine (1).

Figure S6: $^1$H-NMR spectrum of bipyridine (2).
Figure S7: $^1$H-NMR spectrum of bipyridine L1

Figure S8: $^1$H-NMR spectrum of bipyridine L2
Figure S9: $^1$H-NMR spectrum of intermediate (7).

Figure S10: $^1$H-NMR spectrum of intermediate (8).
3.) $^{13}$C-NMR-spectra

Figure S11: $^1$H-NMR spectrum of bipyridine L3.

Figure S12: $^{13}$C-NMR spectrum of bipyridine (2).
Figure S13: $^{13}$C-NMR spectrum of bipyridine L1.

Figure S14: $^{13}$C-NMR spectrum of bipyridine L2
Figure S15: $^{13}$C-NMR spectrum of intermediate (7).

Figure S16: $^{13}$C-NMR spectrum of intermediate (8).
Figure S17: $^{13}$C-NMR spectrum of bipyridine L3.

4.) IR Spectra

Figure S18: IR spectrum of bipyridine (1).
Figure S19: IR spectrum of bipyridine (2).

Figure S20: IR spectrum of bipyridine L1.
Figure S21: IR spectrum of bipyridine L2.

Figure S22: IR spectrum of intermediate (7).
Figure S23: IR spectrum of intermediate (8).

Figure S24: IR spectrum of bipyridine L3.
5.) Mass Spectrometry spectra

**Figure S25:** HRMS spectrum of bipyridine (1) (at the top). Calculated Spectrum for \([\text{M}+\text{H}^+])^+\) (at the bottom).

**Figure S26:** HRMS spectrum of bipyridine (2) (at the top). Calculated Spectrum for \([\text{M}+\text{H}^+])^+\) (at the bottom).
Figure S27: HRMS spectrum of bipyridine L1 (at the top). Calculated Spectrum for [M+1H•]+ (at the bottom).

Figure S28: HRMS spectrum of bipyridine L2 (at the top). Calculated Spectrum for [M+1H•]+ (at the bottom).
Figure S29: HRMS spectrum of intermediate (7) (at the top). Calculated Spectrum for [M+1H+]¹⁺ (at the bottom).

Figure S30: HRMS spectrum of intermediate (8) (at the top). Calculated Spectrum for [M+1H+]¹⁺ (at the bottom).
6.) UV/Vis and emission spectra

Figure S32: UV/Vis spectra of intermediates (3) and (8) measured in CH$_2$Cl$_2$ at a concentration of 7x10$^{-5}$ M.
Figure S33: Emission spectra of intermediates (3) and (8) measured in CH₂Cl₂ at a concentration of 7x10⁻⁵ M.
Synthesis and characterization of ruthenium and rhenium dyes with phosphonate anchoring groups†

Markus Braumüller, a Martin Schulz, b,c Magdalena Staniszewska, d Dieter Sorsche, a Markus Wunderlin, e Jürgen Popp, c Julien Guthmuller, d Benjamin Dietzek* b,c,f and Sven Rau* a

Re(L1)–Re(L3), a series of rhenium(1) tricarbonyl chloride complexes with bpy-R2 derivatives L1–L3 (bpy = 2,2’-bipyridine, R represents the substitution at the 4- and 4’-positions), and their corresponding trihomoleptic Ru(L1)2–Ru(L3)2 as well as heteroleptic ruthenium(1) complexes Ru(bbbpy)2(L1) and Ru(tbbpy)2(L2) have been synthesized and characterized. Their applicability as immobilizable metal–organic chromophores in solar and photosynthesis cells is enabled by R, since it includes phosphonic ester groups as precursors for potent phosphonate anchoring groups. Conjugated linkers (phenylene and triazole moieties) serve as distance control between bpy and the anchor. Photophysical and electrochemical studies reveal pronounced effects of the aryl substitution. These effects were further investigated using resonance Raman experiments and supported by theoretical calculations. After hydrolysis the triazole containing Re(L2) was successfully immobilized on NiO, suggesting that its application in photovoltaic cells is feasible. The solid state structures of Re(L0), Re(L0hdrolyzed), Re(L1) and Re(L2) are reported in this paper, enabling the determination of the distances and intermolecular interactions.

Introduction

The utilization of polypyridyl metal-complexes as photosensitizers or photocatalysts is well known. 1–7 Most desirable is their immobilization on metal–oxide semiconductor surfaces (SC) in dye sensitized solar cells (DSSCs) or photoelectrosynthesis cells (DSPECs) since energy conversion on a heterogeneous carrier is beneficial for practical applications. For n-type DSSCs, Ru-polypyridyl complexes have shown the best photovoltaic properties among the metals, whereas their use is limited for p-type DSSCs. 2 However, the utilization of e.g. Ru- or Re-polypyridyl complexes for hydrogen evolution or photocatalytic CO2 reduction on p-type SCs like NiO or TaON seems highly feasible. 3,4,8,9 One important goal is to tune the properties of the dye towards a high light-harvesting ability with respect to the solar irradiation spectrum, since especially the excitation of Re–bipyridyl complexes is typically only achieved under UV-light irradiation with low molar absorptivities. For achieving this aim, modification of the linkage between the semiconductor and the chromophore by the introduction of π-conjugated spacers seems a promising approach. 10–13

Within this context, Meyer and Galoppini have shown that the presence of π-extended rods increases the extinction coefficient of an attached pyrene and shifts the absorbance to the red. 14 Besides, linker elongation controls the efficiency determining factors of a cell, since charge carrier recombination processes and aggregation of the chromophores on the SC surface can be inhibited. 11,15 Hence, for Re- and Ru-complexes, peripheral substitution of the most commonly used original 2,2’-bipyridine (bpy) ligand with aromatic linkers and capable anchoring groups might be a concept with good prospects. 16

For instance, Wu et al. performed structure–property relationship studies for Ru-[(bpy)2(C=N)]2-derivatives, where C=N represents bidentate phenylpyridine derivatives with carboxylate anchoring groups, for their application on NiO in p-type DSSCs. They differ in the number of phenylene spacer units between the Ru-[(bpy)2(C=N)]2 core and the anchoring...
group. With increasing the number of phenylene units in the linker, the interfacial charge recombination rate decreased, and the efficiency of the solar cells was enhanced. Similarly, Housecroft et al. increased the performance of copper(i) dyes with phosphonic acid group functionalized 6,6′-dimethyl-2,2′-bipyridine in n-type DSSCs. The presence of a phenylene spacer resulted in improved efficiencies compared to dyes without this spacer between the bpy core and the phosphonic acid group.

This trend has also been observed for photocatalytically active electrode materials in DSPECs, highlighting the importance of distance control between the semiconductor and the sensitizer or the molecular photocatalyst, respectively, for example, to boost the activity of an immobilized photocatalyst based on a H2: producing photochemical molecular device.

On both n-type SCs like TiO2 and p-type materials like NiO, phosphonic acid derivatives have been shown to be more chemically stable than other anchoring groups. In particular, methyl phosphonic acids show high affinities to these SCs. Additionally, the methyl spacer might prevent charge carrier annihilation in p-type SCs, since the electronic interaction between the bipyridine and anchoring groups is significantly reduced by the CH2 group between them. It was suggested that the π1 effect of carboxylic anchoring groups (without spacers between the ruthenium polypyridyl sensitizer and NiO) hinders hole injection. Whereas there is a high number of Ru-dyes equipped with phosphonate anchoring groups there are few examples for Re-complexes. Itoh et al. described the synthesis of Re(μ) complexes bearing PO(OH)2 groups on terpyridine ligands for immobilization on ITO (indium-doped tin oxide) electrodes and their catalytic activity in O2 reduction. Additionally, Hupp and coworkers investigated electron transfer from Re(L0) and its carboxylate anchor analogue to TiO2 or SnO2 respectively. The injection rate was found to be faster with the phosphonate group than the carboxylate group on both semiconductors.

Generally, for a more chemically stable linkage between the dye and the semiconductor, both positions 4 and 4′ of the bpy should be equipped with anchoring groups.

In our previous study we have designed three new bpy derivatives (L1–L3), which meet the requirements to improve the photovoltaic performance of polypyrrolid metal-complexes. As π-conjugated linkers we inserted first a phenylene group and then a triazole ring with phenylene groups since it is easy to generate them via “click”-chemistry. Their methyl phosphonic ester groups can be easily deprotected to generate the free acid functions, for their utilization as anchoring groups.

In this paper we present the synthesis and characterization of immobilizable monosubstituted Re- and trishomoleptic Ru-bipyridyl-complexes with π-extended ligands based on L1–L3 (Re(L1)–Re(L3) and Ru(L1)–Ru(L3), cf. Fig. 1). Their properties are compared to Re and Ru-complexes Re(L0) and Ru(L0), utilizing ligand L0 without any spacers between the bpy core and the anchoring group. The exemplary hydrolysis and immobilization of one complex (Re(L2)) is presented at the stage of preliminary tests.

Results and discussion

Synthesis

The synthesis of the bpy derivatives L0, L1, L2 and L3 was performed as previously reported. The corresponding Re-complexes were obtained by equimolar reaction of a Re(CO)5Cl-precursor with the bpy derivatives in toluene or methanol respectively. The structures of Re(L0), Re(L0hydrolyzed), Re(L1) and Re(L2) were confirmed by X-ray crystallography. The synthesis of the trishomoleptic Ru-complex analogues was achieved in two steps according to the literature. Initially two equivalents of the bpy derivative are coordinated to the Ru(DMSO)5Cl2-precursor by refluxing in methanol. Then the third equivalent is introduced to the crude product of the first reaction by refluxing in an ethanol/water mixture (3:1). To investigate the localization of the initially excited state and its dependence on phenylene and triazole moieties as spacers between the bpy-core and the anchoring group, three additional Ru complexes Ru(tbbpy)3, Ru(tbbpy)2(L1) and Ru(tbbpy)2(L2) were synthesized and compared to Ru(L1)3 and Ru(L0)3.
**Ru(L2)₃** in resonance-Raman experiments. Ru(tbbpy)₃ and the precursor complex Ru(tbbpy)₂Cl₂ were synthesized according to the literature.³²,³³ Ru(tbbpy)₂(L1) and Ru(tbbpy)₂(L2) were prepared by refluxing equimolar amounts of Ru(tbbpy)Cl₂ and ligand (L1) or (L2) in an ethanol/water mixture (3:1). For photophysical investigations Re(bpy) and Ru(bpy)₃ were synthesized according to the literature.© After purification all new Re- and Ru-complexes were characterized by ¹H- and ³¹P-NMR. Because of solubility limitations in deuterated solvents, no ¹³C-NMR spectra could be obtained for the triazoles containing Re- or Ru-complexes, respectively. For all other complexes these spectra are shown. HRMS (ESI) data are consistent with the desired product for each new Re- and Ru-complex. ¹H-NMR, ¹³C-NMR, IR and HRMS spectra are shown in the ESI (Fig. S1–S32†).

### Crystal structures

Single crystals suitable for X-ray diffractometry were obtained from the rhenium complexes Re(L0), Re(L1), Re(L2), and the free phosphonate complex Re(L0hydrolyzed) (cf. Fig. 2 and 3). Characteristic values of bond lengths and angles are provided in Table 1. Due to the ester hydrolysis with excess triisopropylsilyl bromide, the latter was obtained as a bromido complex after ligand exchange of the axial chloride ligand. According to the CCDC database only one other metal complex with free phosphonic acid substituents at a pyridyl ligand is known in the literature.³⁶ All bond lengths and angles of the rhenium coordination polyhedron are in agreement with structures reported in the literature.³⁷ The geometry of the bipyridine-CH₃-P phosphonic ester/acid moieties agrees well with the data obtained from the respective ligand structures. All ester structures show almost identical bond lengths for the P–O bonds, i.e. 1.57(1) Å for the P–OEt bonds and 1.66(1) Å for the P–O double bonds. The phosphonic acid complex Re(L0hydrolyzed), in contrast to its ester analogues, exhibits an extended hydrogen bond framework in the crystal packing, where two one-dimensional columns along the a-axis of the crystal (Fig. 3) are oriented back-to-back (cf. Fig. S52†). According to the observed distances of 1.524(3) Å for the P–OH bonds and 1.497(4) Å for the P–O bonds, the respective positions of these groups are clearly indicated. The H-bond framework is capped by bridging methanol molecules. It should be noted that the difference between single and double bond is significantly shorter in the phosphonic acid complex (0.027 Å) as compared to the phosphonic ester complexes (0.09 Å), which indicates enhanced delocalization in the acid complex, as would be expected.

The presented complex structures emphasize the recently postulated elongation of metal phosphonate distances within

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**Table 1** Characteristic lengths and angles

<table>
<thead>
<tr>
<th>Substance</th>
<th>N/Re P=O</th>
<th>O/RH bounds</th>
<th>PCH₂</th>
<th>CH₂Ar</th>
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<tbody>
<tr>
<td>L0</td>
<td>5.562</td>
<td>1.791</td>
<td>1.507</td>
<td>115.7°</td>
</tr>
<tr>
<td>Re(L0)</td>
<td>7.505</td>
<td>1.797</td>
<td>1.499</td>
<td>113.9°</td>
</tr>
<tr>
<td>L1</td>
<td>9.807</td>
<td>1.794</td>
<td>1.507(8)</td>
<td>112.0°</td>
</tr>
<tr>
<td>Re(L1)</td>
<td>11.481</td>
<td>1.807</td>
<td>1.512</td>
<td>111.3°</td>
</tr>
<tr>
<td>L2</td>
<td>12.935</td>
<td>1.793</td>
<td>1.510</td>
<td>114.1°</td>
</tr>
<tr>
<td>Re(L2)</td>
<td>14.839</td>
<td>1.793</td>
<td>1.517</td>
<td>112.6°</td>
</tr>
<tr>
<td>Re(L0hydrolyzed)</td>
<td>7.688</td>
<td>1.796</td>
<td>1.504</td>
<td>113.5°</td>
</tr>
</tbody>
</table>

a Distance between the pyridine nitrogen atom (ligands) or the Re center (complexes) and the calculated centroid centered between the phosphonate oxygen atoms. ³ Median values (for details see Fig. S9 in the ESI). ⁴ At refers to aryl, i.e. either pyridyl or phenyl. ⁵ From ref. 16. ⁶ Median values from two molecules in the asymmetric unit.

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![Fig. 2](image-url) **Fig. 2** Solid state structures of Re(L0), Re(L1), and Re(L2) (ball and stick depiction, hydrogen atoms are omitted for clarity).
the ligand series L0, L1, and L2. By the introduction of a phenyl spacer the distance between the rhenium center and the phosphonate anchor (characterized by the average position of the three oxygen atoms) is increased by about 4 Å and by an additional 3.4 Å by the introduction of the triazole spacer. Further information about the polarity of the spacers introduced can be concluded from secondary intermolecular interactions in the crystal lattice. As mentioned above, the predominant effect observed in the phosphonic acid complex is a linear network of hydrogen bonds between the acid groups and two molecules of methanol per complex. The bipyridine scaffold is further slightly twisted as characterized by a torsion angle between the two pyridyl rings of about 13.57°, which seems to be attributed to the overall packing. There are, however, additional short contacts between protons of the bipyridine as well as the methylene group, indicating that both are positively polarized as would be expected. The same is observed in the phosphonic ester complex Re(0), where the methylene group is oriented towards the P-O oxygen atom of a neighboring complex on one side or towards the chloride ligand of another neighboring complex on the other side. In this complex as well, a twist of the bipyridine characterized by a smaller angle of 12.35° with respect to the phosphonic acid complex is apparent. Complexes Re(L1) and Re(L2) both form dimers in the crystal with the chloride ligands oriented in between the spacer groups of the opposite complex (cf. Fig. S53-S56†). That is, in Re(L1), two protons of the phenyl spacer in ortho position with respect to the bipyridine backbone are pointing towards the chloride with an average short contact distance of 3.36(1) Å. Further short contacts between the P-O oxygen atom and the opposite bipyridine support the dimeric structure. In Re(L2), the protons oriented towards the opposite chloride ligand stem from the azide spacer with an average distance of 3.71(1) Å. The triazole nitrogen atoms on the outer rim of the scaffold, in contrast, establish short contacts with protons of an adjacent phenyl spacer. This amphoteric tendency of the triazole ring is well known in the literature and has been suggested as a potential versatile sensing tool.37-39 Finally, it should be noted that the bipyridine scaffolds of neither Re(L1) nor Re(L2) are twisted as has been observed for Re(L0) and Re(L0hydrolyzed). Furthermore, the first spacer unit that is phenyl or triazole, respectively, is coplanar with the bipyridine, whereas in Re(L2), the terminal phenyl unit is slightly twisted with respect to the triazole unit by 11.72° and 23.92°, the rather large deviation of which indicates that this is due to packing effects.

Photophysics

The photophysical properties of the Re- and Ru-complexes were studied in DMF and MeCN, respectively. The absorption spectra of these complexes are typical of rhenium bipyridyl and ruthenium poly(pyridyl) complexes with intense UV bands, assigned to ligand-centered π–π* transitions, and broad bands at the edge of the visible region for Re- and in the visible region for Ru-complexes due to metal-to-ligand charge-transfer (MLCT) transitions (Fig. 4 and 5). Excitation of the MLCT maximum of the presented Re and Ru-dyes leads to phosphorescence around 600 nm. The data are summarized in Table 2.

As a general and important trend a shift of the MLCT absorbance to lower energies and an increase in molar absorptivities can be observed for the complexes bearing elongated bpy derivatives compared to the complexes without π-extended ligands. From Re(L0) to Ru(L0)3 to Re(L3) or Ru(L3), the extinction coefficients are approximately doubled (3.4 × 10² M⁻¹ cm⁻¹ vs. 7.1 × 10² M⁻¹ cm⁻¹ for Re(L0) and Re(L3) and 17.6 × 10² M⁻¹ cm⁻¹ to 29.5 × 10² M⁻¹ cm⁻¹ for Ru(L0) and Ru(L3)), and the MLCT maxima are red-shifted by 15 nm (i.e. 1041.9 cm⁻¹) or 20 nm (i.e., 902 cm⁻¹), respectively, most probably due to the extensive electron delocalization over the whole L3 ligand. Galoppini and coworkers presented structurally related Ru complexes bearing bpy ligands elongated with one triazole and one phenyl group which exhibit extinction
coefficients very close to that observed for Ru(L2)$_3$ ($2.3 \times 10^4 \text{M}^{-1} \text{cm}^{-1}$). The shape of the long wavelength maxima of the new complexes shows the influence of the peripheral substitution pattern since bathochromically shifted shoulders of these MLCT bands appear with regard to that of the related L0 containing compounds. Hupp et al. reported on a similar trend for phenyl- and ethynyl-substituted Re bipyridine complexes. They witnessed an energy decrease (wavelength increase) due to increased intraligand electron delocalization in the MLCT excited state. It is also known that Ru complexes with phenyl-substituted byps have much stronger visible light absorption than the parent bpy complexes. These results are in agreement with time-dependent density functional theory calculations performed on the Ru(L1)$_3$ and Ru(L2)$_3$ complexes revealing the presence of two main MLCT bands with calculated absorption wavelengths of 475 and 454 nm for Ru(L1)$_3$ and 477 and 456 nm for Ru(L2)$_3$. Inspection of the orbital character (see ESI†) shows that these MLCT states display also a non-negligible mixing with π-π* contributions localized on the extended ligands. Moreover, a weaker MLCT state is predicted by the calculations at 505 and 508 nm for Ru(L1)$_3$ and Ru(L2)$_3$, respectively. The presence of this state also contributed to the increased absorption in the red part of the MLCT band. Enhancing the molar extinction coefficient and shifting the MLCT absorption bathochromically is a good strategy to improve the photovoltaic performance of Ru dyes since sunlight harvesting will be more effective. Based on this conclusion, Ru complexes based on L1–L3 are very promising candidates for sensitizers in photovoltaic cells. The introduction of aromatic substituents leads to a new π-π* transition, visible by a shoulder around 335 nm for Re(L1)$_3$–Re(L3) and 358 nm for Ru(L1)$_3$–Ru(L3)$_3$ which is the highest in intensity for Re(L3) or Ru(L3)$_3$, respectively. This observation is supported by one of our previous studies dealing with tetra-phenyl-substituted 1,10-phenanthrolines and their ruthenium complexes. It is also worth noting that while the absorbance maxima of the free ligands are red-shifted from L0 to L3, this trend is not confirmed by the π-π transitions of all metal complexes (e.g. Re(L3)). Additionally, we can see a splitting of the π-π transitions of Ru(L1)$_3$–Ru(L3) in two distinct maxima, one of which is bathochromically (about 20 nm, i.e. 2225 cm$^{-1}$) and one is hypsochromically (about 25 nm, 3250 cm$^{-1}$) shifted with respect to the maxima of complexes without aromatic substituents at the bpy. This phenomenon cannot be observed for the corresponding Re-complexes. Currently it is not possible to give a detailed explanation for these minor effects related to the π-π transitions. The impact of the substitution at the bpy core is also observed for the emission maxima that shifts from the L0 containing complexes to lower energies for the L1–L3 containing ones (e.g. from 599 nm for Re(L0) to 610 nm for Re(L3)). The triazole or phenyl substituents at the bpy should have a more electron donating character compared to directly bound methyl phosphonic ester groups. This electron-push induces a higher electron density at the metal centre of L1–L3 bearing complexes in comparison to the metal centre of Re(L0) and Ru(L0)$_3$. This might be an explanation for the bathochromic shift in emission.

### Electrochemical properties

The electrochemical behaviour of the complexes Ru(L0)$_3$ and Ru(L1)$_3$ was studied in acetonitrile (cf. Fig. 6). Square wave voltammograms are provided in Fig. S33† and the data are given in Table 3. No interpretable voltammogram could be obtained for Ru(L2)$_3$, Ru(L3)$_3$, possibly due to dye aggregation or due to the adsorption of the reduced species onto the surface of the electrode.

The redox potential for the Ru$^{III/II}$ couple in Ru(L0)$_3$ occurs at more positive potential than that of Ru(L1)$_3$. As mentioned before, the phenyl-groups are more electron-donating compared to methyl phosphonic ester substituents, resulting in an eased oxidation of Ru$^{III}$ in Ru(L1)$_3$. At negative potentials three reversible one-electron reductions are observable. The cyclo-

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**Table 2** Absorption and emission data of bpy derivatives, Re and Ru complexes (ligand absorption maxima $\lambda_{\text{abs}}$, MLCT absorption maxima $\lambda_{\text{MLCT}}$, emission maxima $\lambda_{\text{em}}$)

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\lambda_{\text{abs}}$ $[^a] [\text{nm}]$</th>
<th>$\lambda_{\text{MLCT}}$ $[^b] [\text{nm}]$</th>
<th>$\lambda_{\text{em}}$ $[^d] [\text{nm}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>bpy $[^b]$</td>
<td>285 (13)</td>
<td></td>
<td>374</td>
</tr>
<tr>
<td>L0 $[^c]$</td>
<td>250 (6), 285 (13)</td>
<td>368</td>
<td></td>
</tr>
<tr>
<td>L1 $[^c]$</td>
<td>285 (20)</td>
<td>326, 338, 353</td>
<td></td>
</tr>
<tr>
<td>L2 $[^c]$</td>
<td>293 (23)</td>
<td>374, 402, 424, 445</td>
<td></td>
</tr>
<tr>
<td>L3 $[^c]$</td>
<td>297 (25)</td>
<td>332, 345, 373, 400, 421</td>
<td></td>
</tr>
<tr>
<td>Re(bpy) $[^e]$</td>
<td>294</td>
<td>371 (3.4)</td>
<td>598</td>
</tr>
<tr>
<td>Re(L0) $[^e]$</td>
<td>286</td>
<td>372 (3.4)</td>
<td>599</td>
</tr>
<tr>
<td>Re(L1) $[^e]$</td>
<td>301, 335 (18)</td>
<td>381 (7.5)</td>
<td>605</td>
</tr>
<tr>
<td>Re(L2) $[^e]$</td>
<td>298, 335 (17)</td>
<td>386 (6.3)</td>
<td>610</td>
</tr>
<tr>
<td>Re(L3) $[^e]$</td>
<td>283, 335 (19)</td>
<td>387 (7.1)</td>
<td>610</td>
</tr>
<tr>
<td>Ru(bpy)$_3$ $[^d]$</td>
<td>287</td>
<td>451 (14.6), 460 (13.4)</td>
<td>606</td>
</tr>
<tr>
<td>Ru(L0)$_3$ $[^d]$</td>
<td>291</td>
<td>461 (17.6)</td>
<td>614</td>
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<tr>
<td>Ru(L1)$_3$ $[^d]$</td>
<td>265, 309, 358 (28)</td>
<td>477 (28.9)</td>
<td>625</td>
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<tr>
<td>Ru(L2)$_3$ $[^d]$</td>
<td>264, 312, 358 (27)</td>
<td>479 (23.1)</td>
<td>630</td>
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<tr>
<td>Ru(L3)$_3$ $[^d]$</td>
<td>264, 310, 358 (36)</td>
<td>481 (29.5)</td>
<td>626</td>
</tr>
</tbody>
</table>

$[^a]$ Extinction coefficient at the maximum MLCT absorption ($\epsilon$/10$^3$ M$^{-1}$ cm$^{-1}$) in brackets. $[^b]$ Measured in DCM. $[^c]$ Measured in DMF. $[^d]$ Measured in MeCN. $[^e]$ From ref. 16.
voltagograms of the Re complexes Re(L0)–Re(L3) were measured in DMF (Fig. S34–S37†). For Re(bpy) it is known from the literature that the one-electron oxidation is followed by rapid loss of a formal chlorine radical. The reduction of Re(bpy) also leads to chloro ligand loss, which is followed by either solvation or fast dimerization. But at fast scan rates the electrochemical one-electron reduction of the Re complex is reversible, suggesting that the loss of the chloride ligand from the reduced Re complex occurs very slowly. Accordingly, reversible oxidation of Re(L0)–Re(L3) could not be achieved in DMF, but they exhibited one reversible reduction wave followed by an irreversible one. The first one was assigned to the reduction of the bpy ligand and the second irreversible one is accompanied by chlorine ion formation. The values obtained for the first reduction of the investigated metal complexes show rather small shifts of the bpyR → bpyR potentials (E1/2), indicating a similar nature of the π-accepting orbitals. Nevertheless L1–L3 are slightly easier to reduce than L0. This could suggest increased π-conjugation, as derived from the trends in the absorption spectra.

Resonance-Raman experiments

Resonance-Raman spectroscopy was conducted to study the localization of the Franck–Condon point upon absorption of visible light of all ruthenium complexes. In order to do so, resonance Raman spectra of the complexes Ru(L1)3, Ru(L2)3, as well as Ru(tbbpy)2(L1) and Ru(tbbpy)2(L2) were recorded upon excitation at 457 and 488 nm, i.e. at the high and low energy flank of the MLCT absorption band (cf. Fig. 7). Quantum chemical calculations aided the assignment of the Raman bands. The calculated structures correlate well with the ligand structures obtained by the XRD studies performed with the respective rhenium complexes (cf. Theoretical section). The experimental spectra given in Fig. 5 are normalized to the solvent signal at 918 cm⁻¹. The asterisk marks a spectral artifact and the band at 1372 cm⁻¹ is a solvent band.

Fig. 6 Cyclic voltammograms of Ru(L0)3 and Ru(L1)3 measured in MeCN with 0.1 M Bu4NPF6 and a scan rate of 100 mV s⁻¹.

Table 3 Half wave potentials (vs. Fc/Fc⁺) of Ru(L0)3–Ru(L1)3 and Re(L0)–Re(L3)

<table>
<thead>
<tr>
<th>Complex</th>
<th>E½ox [V]</th>
<th>E½red1 [V]</th>
<th>E½red2 [V]</th>
<th>E½red3 [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(L0)3</td>
<td>0.88</td>
<td>1.71</td>
<td>1.88</td>
<td>2.13</td>
</tr>
<tr>
<td>Ru(L1)3</td>
<td>0.83</td>
<td>1.68</td>
<td>1.82</td>
<td>2.06</td>
</tr>
<tr>
<td>Re(L0)6</td>
<td>0.88</td>
<td>1.73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Re(L1)6</td>
<td>1.68</td>
<td>1.65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Re(L2)6</td>
<td>1.65</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Re(L3)6</td>
<td>1.62</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The electrochemical measurements were carried out in anhydrous and argon purged MeCN/0.1 M Bu4NPF6 as the supporting electrolyte.

† Anhydrous and argon purged DMF/0.1 M Bu4NPF6 as the supporting electrolyte.

Fig. 7 The resonance Raman spectra in acetonitrile of Ru(L1)3, Ru(L2)3 as well as Ru(tbbpy)2(L1) and Ru(tbbpy)2(L2), upon excitation at 457 nm and 488 nm. The spectra are normalized to the solvent band at 918 cm⁻¹. The asterisk marks a spectral artifact and the band at 1372 cm⁻¹ is a solvent band.
some bands are observed for Ru(tbbpy)_3 and Ru(tbbpy)_2(L1)
but not for Ru(L1)_3, namely 1318, 1210 (very weak), and 1132,
and are hence assigned to the tbbpy ligand. On the other hand
a band appears at 1329 cm\(^{-1}\) in Ru(tbbpy)_2(L1) and Ru(L1)_3
but not in Ru(tbbpy)_3. In agreement with the calculations the
band at 1329 cm\(^{-1}\) is assigned to the L1 ligand. In the normal-
ized spectra the intensity of the 1329 cm\(^{-1}\) band in
Ru(tbbpy)_2(L1) experiences a less strong enhancement than in
Ru(L1)_3, which supports the assignment. The enhancement of
the tbbpy band at 1318 cm\(^{-1}\) with respect to the L1 band
at 1329 cm\(^{-1}\) is stronger at 457 nm than at 488 nm, indicating
a stronger population of the tbbpy ligand upon excitation at
457 nm. This is in agreement with the decreased intensity
of the bands at 1610, 1534 and 1479 cm\(^{-1}\), which according to
the calculations have contributions from both tbbpy and L1.

The resonance-Raman spectra of the triazole-containing compounds Ru(L2)_3 and Ru(tbbpy)_2(L2) differ markedly from those of Ru(tbbpy)_3 as well as Ru(L1)_3 and Ru(tbbpy)_2(L1), particularly in the region between 1700 and 1400 cm\(^{-1}\) (Fig. S47†). For Ru(L2)_3 bands in this region are observed at 1622, 1566,
1541, 1532, 1519 (shoulder) and 1479 cm\(^{-1}\). For Ru(tbbpy)_3(L2)
the band at 1541 cm\(^{-1}\) is missing and two close peaks appear
at 1534 and 1528 cm\(^{-1}\) (cf. 1532 cm\(^{-1}\) for Ru(L2)_3). The bands
at 1479 and 1280 cm\(^{-1}\) appear for all the investigated Ru com-
ounds Ru(L1)_3, Ru(L2)_3, Ru(tbbpy)_2(L1), Ru(tbbpy)_2(L2) and
Ru(tbbpy)_3 and are assigned to the bipyridine moiety. Based
on the comparison with Ru(tbbpy)_3 and the calculations the band
at 1566 cm\(^{-1}\) is assigned mainly to the triazole while the bands
at 1622, 1541, and 1532 cm\(^{-1}\) have contributions from the
bipyridine and the triazole. In the heteroleptic Ru(tbbpy)_2(L2), contributions from tbbpy are found with bands at 1610 (weak shoulder), 1479, 1323 and 1280 cm\(^{-1}\). The bands with triazole contributions, namely 1622, 1566, 1541, and 1532 cm\(^{-1}\), are more strongly enhanced upon excitation
at 457 nm than at 488 nm. Upon excitation at 488 nm
the band at 1280 cm\(^{-1}\), which is assigned to the bipyridine moiety, experiences a strong enhancement for both Ru(L2)_3
and Ru(tbbpy)_2(L2). Therefore we conclude that the more
energy-rich state is populated with contributions of the triazole
while the low-energy state is dominated by the bpy portion
of L2.

Hydrolysis and immobilization

In order to examine whether the presented compounds are
principally suitable for applications in dye sensitized cells, pre-
liminary investigations into deprotection and immobilization
were performed. Because the presented Re-complexes with its
Cl\(^{-}\) have a labile co-ligand and triazole might be prone to the
harsh hydrolysis conditions we have chosen Re(L2) as a very
challenging reference probe for these experiments. The methyl
phosphonic ester ester groups of Re(L2), which according
hydrolyzed Re(L2) were deprotected by reaction
with Me_3SiBr as reported for similar Re and Ru complexes.\(^{28,31}\) The loss of the ethyl groups of Re(L2) can be traced
by \(^{1}\)H-NMR spectroscopy (Fig. S11†). Neither for Re(L2) nor for
Re(L2 hydrolyzed) a \(^{31}\)P-NMR signal could be obtained in deute-
rated methanol. Addition of tetrabutylammonium hydroxide
(TBAOH) rendered the deprotected species Re(L2 hydrolyzed)
soluble in water and methanol. In the absorption spectra a
bathochromic shift of MLCT maxima could be monitored when
comparing Ru(L2) to its hydrolyzed analogue Re(L2 hydrolyzed)
in 0.01 M TBAOH in MeOH solution (\(\lambda_{\text{MLCT}} = 370 \text{ nm vs.} \\lambda_{\text{MLCT}} = 383 \text{ nm, cf. Fig. 9}\). This shift suggests that ligand sub-
stitution of Cl\(^{-}\) by Br\(^{-}\) or OH\(^{-}\) took place, as similarly wit-
nessed for [ReCl(CO)(bpy)].\(^{17}\) Since the crystal structure of
Re(L2 hydrolyzed) was obtained as a bromide complex, this should
also be the case for Re(L2 hydrolyzed). Additionally, peak clusters
appearing in the high-resolution ESI-mass spectrum of
Re(L2 hydrolyzed) were consistent with the formula of two-fold
deprotonated \([\text{Re(OH)}(L2\text{ hydrolyzed})]^{-} \text{Cl}^{-} \cdots 2\text{H}^{+}\) (m/z = 458.02911) and \([\text{Re(Br)}(L2\text{ hydrolyzed})]^{-} \text{Cl}^{-} \cdots 2\text{H}^{+}\) (m/z = 488.98729), further supporting the mentioned chloride substitu-
tion by hydroxide and bromide. The triazole unit stays intact
during hydrolysis, proving its chemical stability towards
Me_3SiBr. Re(L2 hydrolyzed) was immobilized on a NiO surface on
a FTO glass carrier by dipping the NiO into a 0.5 mM solution
of Re(L2 hydrolyzed) in 0.1 M TBAOH solution in MeOH

\[\text{Ru(tbbpy)}_2(L1) \rightarrow 457 \text{ nm. The calculated spectra are normalized to the most intense band.}\]

**Fig. 8** The experimental resonance Raman spectra in acetonitrile and calculated spectra of Ru(L1)_3 and Ru(L2)_3 are reported for excitation at 457 nm. The calculated spectra are normalized to the most intense band.
upon immobilization of Rubpy they were not discussed in detail, similar bathochromic shifts employed as a substrate in this study (might be the case for p-type semiconductors NiO, which was observed). The sensitized NiO film Re(L2)@NiO was washed several times with MeOH and then analyzed by UV/Vis spectroscopy in the MLCT region. For Re(L2)@NiO the MLCT absorption band of Re(L2) can be observed. The lowest-energy absorption band of Re(L2) around 380 nm shifts to lower energies in the following solvent order: DCM > DMF > MeOH, i.e. absorption bands shift to higher energy with increasing solvent polarity. The maximum MLCT absorbance of Re(L2)@NiO is red-shifted by 17 nm (i.e., 1229.2 cm⁻¹) compared to Re(L2) in DCM (λ<sub>MLCT</sub> = 415 nm vs. λ<sub>MLCT</sub> = 398 nm). From our point of view there are three possible reasons for this red-shift: (1) as described above, the suggested chloride substitution by hydroxide and bromide. (2) Another explanation is the surrounding of the immobilized Re(L2)@NiO, which seems to be nonpolar, according to the aforementioned trend for Re(L2) in different solvents. (3) As is known for Rubpy derivatives immobilized on the n-type semiconductor TiO₂, λ<sub>MLCT</sub> values are lower than those observed in solution as a consequence of the electron accepting character of the semiconductor, which weakens the electronic charge on the dye. The opposite might be the case for p-type semiconductors NiO, which was employed as a substrate in this study (Re(L2)@NiO). Although they were not discussed in detail, similar bathochromic shifts upon immobilization of Rubpy derivatives on NiO can be found in the literature.

### Experimental section

#### Methods and materials

¹H (400 MHz or 500 MHz), ¹³C NMR (126 MHz) and ³¹P (162 MHz) spectra were recorded with a Bruker DRX 400 or Bruker DRX 500 spectrometer. The NMR spectra were recorded in [D₃]MeCN, CDCl₃, CD₂Cl₂ or MeOD at 298 K. ¹H-NMR and ¹³C-NMR chemical shifts were referenced to the solvent peak.

MS analysis was performed with a Bruker solariX (2010) Hybrid 7T FT-ICR.

Electrochemical data were obtained by cyclic voltammetry or square wave voltammetry using a conventional single-compartment three-electrode cell arrangement in combination with a “Parstat 2273 Princeton Applied Research” potentiostat. The measurements were carried out in 0.1 M solutions of Bu₄NPF₆ in dry and argon purged MeCN or DMF. All values were determined with a glassy carbon working electrode and platinum counter and reference electrodes. The measured values were referenced verses the redox couple Fc/Fc⁻ set at E₁/₂ = 0 V.

The crystal suitable for X-ray analysis was mounted using a Micro-Loop and Fomblin oil. X-ray diffraction intensity data were measured at 180 K with a SuperNova (Dual Source) diffractometer, equipped with an ATLAS detector, from Agilent Technologies. The structures were solved by direct methods (SHELXS) and refined by full-matrix least-squares techniques against F<sup>2</sup> (SHELXL 2013). Unless stated otherwise, the hydrogen atoms were included at calculated positions with fixed thermal parameters. All nonhydrogen atoms were refined anisotropically.

The UV/Vis-spectra were recorded with a JASCO Spectrometer V-670. Quartz cells with 10 mm path length were used. The emission spectra were recorded with a JASCO 25 Spectrofluorometer FP-8500. Quartz cells with 10 mm path length were used. Unless mentioned otherwise, all experiments were performed under aerobic conditions.

Resonance-Raman (RR) spectra were obtained by continuous wave excitation at 457 nm (200 mW) and 488 nm (500 mW) with an argon laser (Coherent Innowa 300 MotoFred) and dispersion of the scatter with an Acton SpectraPro 2758i spectrometer (grating 1800 lines per mm) onto a cooled CCD detector (Princeton Instruments). The scatter was collected in 90° geometry using rotating cuvettes in order to minimize photodecomposition. The samples were dissolved in acetonitrile and the concentration was adjusted to an absorbance of about 0.4 at 450 nm. The photostability of the samples under the experimental conditions was verified by comparison of the UV-Vis absorption prior to and after the RR experiment. The obtained spectra were background corrected using the software “R” with the “baselinewavelet” package and are normalized to the acetonitrile signal at 918 cm⁻¹.

#### Starting materials

Starting materials were purchased from commercial sources and used without further purification.

#### Preparation of a porous NiO film

A NiO film was prepared by a modified literature-reported procedure. Standard precursor solution of NiO was prepared by dissolving anhydrous NiCl₂ (1 g) and the triblock co-polymer F108 (1 g) into a mixture of water (3 g) and ethanol (6 g). The solution was stirred for 3 days at 25 °C. The obtained solution was deposited on an FTO glass substrate by the doctor blade method using mending tape (Scotch®) as a spacer. The tape
was removed and the film was then calcined in air at 420 °C for 30 min.

**General procedure for Re-complex formation**

The Re-complexes were prepared by a modified literature-reported procedure.\(^{44}\)

Re(CO)\(_3\)Cl (0.041 mmol) and the bipyridine ligand were equimolarly dissolved in 20 mL toluene (L0, L1) or 15 mL methanol (L2, L3) respectively and heated to reflux, and the mixture was stirred for 3 h. The solvent was then concentrated under reduced pressure and the crude product was precipitated upon the addition of Et\(_2\)O. The product was obtained as a light yellow solid by filtration of the precipitate.

**Re(bpy). Re(bpy)** was synthesized according to the literature.\(^{44}\)

**Re(L0). Re(L0)** was synthesized according to the general procedure for Re-complex formation. Yield: 27.2 mg (0.036 mmol, 87%).

\(^1\)H NMR (400 MHz, CDCl\(_3\), 25 °C): \(\delta = 8.87 \text{ (d, } J_{HH} = 5.8 \text{ Hz, 2H)}, 8.43 \text{ (s, 2H)}, 7.69 \text{ (d, } J_{HH} = 7.9 \text{ Hz, 4H)}, 7.51 \text{ (d, } J_{HH} = 6.0 \text{ Hz, 4H)}, 7.46 \text{ (d, } J_{HH} = 5.8 \text{ Hz, 2H)}, 4.11 \text{ (m, 8H)}, 3.26 \text{ (d, } J_{HP} = 2.20 \text{ Hz, 4H)}, 1.32 \text{ (m, 12H)}.\)

\(^{13}\)C NMR (126 MHz, CDCl\(_3\), 25 °C): \(\delta = 197.22, 153.69, 152.84, 145.87, 128.32, 124.74, 63.09, 34.62, 33.53, 16.52.\)

**HRMS (m/z (ESI, MeCN)):** m/z calcd for [M + Na\(^+\)]\(^{+}\) = 25.32.

**General hydrolysis procedure**

In order to hydrolyze the ester groups, the rhenium complex (0.011 mmol) was dissolved in anhydrous CCl\(_4\) (10 mL) under an argon atmosphere. Anhydrous CH\(_2\)Cl\(_2\) (10 mL) was added for better solubility. Bromotrimethylsilane was added (15 equiv.). The reaction was stirred at 80 °C for 18 h, after which water (10 mL) was added and the reaction was stirred for 30 min. The resulting suspension was extracted several times with CH\(_2\)Cl\(_2\). The combined organic extracts were dried with anhydrous MgSO\(_4\) and the solvent was then removed under reduced pressure. The yellow solid was collected and used without further purification.

**Re(L0)\(_{\text{hydrolyzed}}\). Re(L0)\(_{\text{hydrolyzed}}\)** was synthesized according to the general procedure for hydrolysis. Yield: 9.3 μmol, 85%.

\(^1\)H NMR (400 MHz, MeOD, 25 °C): \(\delta = 8.87 \text{ (d, } J_{HH} = 5.6 \text{ Hz, 2H)}, 8.47 \text{ (s, 2H)}, 7.57 \text{ (d, } J_{HH} = 5.3 \text{ Hz, 2H)}, 3.37 \text{ (d, } J_{HP} = 22.6 \text{ Hz, 4H)}.\)

Crystals suitable for X-ray analysis were obtained by slow evaporation of chloroform. For details see crystal data section in the ESI.\(^{\dagger}\)

**Re(L1). Re(L1)** was synthesized according to the general procedure for Re-complex formation. Yield: 31.9 mg (0.035 mmol, 83%).

\(^1\)H NMR (400 MHz, CDCl\(_3\), 25 °C): \(\delta = 8.87 \text{ (d, } J_{HH} = 5.8 \text{ Hz, 2H}), 8.43 \text{ (s, 2H)}, 7.69 \text{ (d, } J_{HH} = 7.9 \text{ Hz, 4H)}, 7.51 \text{ (d, } J_{HH} = 6.0 \text{ Hz, 4H)}, 7.46 \text{ (d, } J_{HH} = 5.8 \text{ Hz, 2H)}, 4.11 \text{ (m, 8H)}, 3.26 \text{ (d, } J_{HP} = 2.20 \text{ Hz, 4H)}, 1.32 \text{ (m, 12H)}.\)

\(^{13}\)C NMR (126 MHz, CDCl\(_3\), 25 °C): \(\delta = 197.52, 189.87, 156.31, 153.19, 150.80, 135.34, 133.83, 131.02, 127.81, 124.09, 120.89, 62.54, 34.37, 33.27, 16.62.\)

**HRMS (m/z (ESI, MeCN)):** m/z calcd for [M + Na\(^+\)]\(^{+}\) = 22.6 Hz, 4H), 8.47 (s, 2H), 7.57 (d, \(J_{HH} = 5.3 \text{ Hz, 2H}, 3.37 \text{ (d, } J_{HP} = 22.6 \text{ Hz, 4H)}.\)

Crystals suitable for X-ray analysis were obtained by slow evaporation of methanol. For details see crystal data section in the ESI.\(^{\dagger}\)

**Re(L2). Re(L2)** was synthesized according to the general procedure for Re-complex formation. Yield: 35.2 mg (0.034 mmol, 82%).

\(^1\)H NMR (400 MHz, CDCl\(_3\), 25 °C): \(\delta = 9.37 \text{ (s, 2H)}, 8.56 \text{ (m, 4H)}, 8.04 \text{ (d, } J_{HH} = 8.0 \text{ Hz, 4H}), 7.85 \text{ (s, 2H)}, 7.65 \text{ (d, } J_{HH} = 6.6 \text{ Hz, 4H)}, 4.14 \text{ (m, 8H)}, 3.32 \text{ (d, } J_{HP} = 28.6 \text{ Hz, 4H}), 1.34 \text{ (m, 12H)}.\)

**HRMS (m/z (ESI, MeCN/DCM (1:1) + TFA)):** m/z calcd for [M + 1H\(^+\)]\(^{+}\) = 1049.17142; found = 1049.17069; \(M = C_{39}H_{41}ClN_2O_4P_2Re.\)

**IR (KBr):** \(\nu = 2024, 1928, 1894, 1623, 1243, 1025, 959 \text{ cm}^{-1}\).

**General procedure for Ru-complex formation**

The Ru-complexes were prepared by a modified literature-reported procedure.\(^{18}\)

A solution of Ru[DMSO\(_2\)Cl\(_2\) (0.025 mmol) and two equivalents of bipyridine derivative (0.05 mmol) are refluxed in
15 mL methanol for 24 h. During this time the color changed from yellow to dark brown. After removal of methanol at the rotary evaporator the residue was dissolved in a little ethanol. An excess of Et₂O was added to the solution. The resulting brown precipitate was collected and dissolved in an ethanol/water mixture (15 mL/5 mL). The third equivalent of bipyridine derivative (0.025 mmol) was added and the mixture was refluxed for 20 h. During this time the color changed from deep brown to dark red. After removal of most of the ethanol at the rotary evaporator an excess of aqueous NH₄PF₆ solution was added. The resulting red precipitate was collected, washed with water and diethyl ether and dried. The crude product was purified by size exclusion column chromatography with an acetone/methanol/chloroform (3 : 2 : 5) mixture as the eluent.

Ru(bpy)₃, Ru(bpy)₄ was synthesized according to the literature.²³,²⁴

Ru(tbbpy)₂, Ru(tbbpy)₃ was synthesized according to the literature.²³,²⁴

Ru(L₀), Ru(L₁), was synthesized according to the general procedure for Ru-complex formation (36.5 mg, 0.021 mmol, 83% yield starting with Ru[DMSO]Cl₂).

³¹H NMR (500 MHz, [D₃]MeCN, 25 °C): δ = 8.46 (s, 6H), 7.62 (d, J_HH = 5.8 Hz, 6H), 7.35 (d, J_HH = 5.8 Hz, 6H), 4.02 (m, 24H), 3.40 (d, J_HP = 22.5 Hz, 12H), 1.17 (m, 36H).

¹³C-NMR (126 MHz, [D₃]MeCN, 25 °C): δ = 137.53, 152.05, 145.94, 129.56, 126.27, 63.38, 33.99, 32.92, 16.62.


HRMS (m/z (ESI, MeCN)): m/z calcd for [(M − 2PF₆ + 2Na⁺)/4]⁺: 797.95967; found = 797.96090; M = C₁₆₄H₆₅N₅₂O₁₄P₂Ru.

Ru(tbbpy)₂(L₁). Ru(tbbpy)₃Cl₂ was synthesized according to the literature.²²

(L₁) (20.8 mg, 0.034 mmol) and Ru(tbbpy)₃Cl₂ (24.2 mg, 0.034 mmol) were dissolved in an ethanol/water mixture (15 mL/5 mL) and refluxed for 20 h. During this time the color changed from deep purple to dark red. After removal of most of the ethanol at the rotary evaporator an excess of aqueous NH₄PF₆ solution was added. The resulting red precipitate was collected, washed with water and diethyl ether and dried. The crude product was purified by size exclusion column chromatography with an acetone/methanol/chloroform (3 : 2 : 5) mixture as the eluent. Ru(tbbpy)₂(L₁) was obtained in 80% yield (42 mg, 0.027 mmol) starting from Ru(tbbpy)₃Cl₂.

¹¹B NMR (400 MHz, [D₃]MeCN + [D]TFA, 25 °C): δ: 9.12 (br, s, 6H), 8.14 (s, 6H), 8.08 (d, J_HH = 5.4 Hz, 6H), 7.97 (d, J_HH = 4.8, 6H), 7.93 (d, J_HH = 7.7 Hz, 6H), 7.83 (d, J_HH = 7.6 Hz, 6H), 7.73-7.65 (m, 24H), 7.44 (m, 12H), 4.10 (m, 24H), 3.37 (d, J_HH = 22.0 Hz, 12H), 1.26 (m, 36H).


HRMS (m/z (ESI, MeCN)): m/z calcd for [(M − 2PF₆ + 2Na⁺)/4]⁺: 797.95967; found = 797.96090; M = C₁₆₄H₆₅N₅₂O₁₄P₂Ru.

Ru(tbbpy)₂(L₂). Ru(tbbpy)₃Cl₂ was synthesized according to the literature.²²

(L₂) (19.3 mg, 0.023 mmol) and Ru(tbbpy)₃Cl₂ (16 mg, 0.023 mmol) were dissolved in an ethanol/water mixture (15 mL/5 mL) and refluxed for 20 h. During this time the color changed from deep purple to dark red. After removal of most of the ethanol at the rotary evaporator an excess of aqueous NH₄PF₆ solution was added. The resulting red precipitate was collected, washed with water and diethyl ether and dried. The crude product was purified by size exclusion column chromatography with an acetone/methanol/chloroform (3 : 2 : 5) mixture as the eluent. Ru(tbbpy)₂(L₂) was obtained in 69% yield (26 mg, 0.016 mmol) starting from Ru(tbbpy)₃Cl₂.

¹¹B NMR (400 MHz, CD₂Cl₂, 25 °C): δ: 11.16 (s, 2H), 10.33 (s, 2H), 8.59 (d, J_HH = 7.8 Hz, 4H), 8.18 (d, J_HH = 5.8 Hz, 2H), 8.11 (d, J_HH = 8.1 Hz, 4H), 7.71 (d, J_HH = 6.1 Hz, 2H), 7.67 (d, J_HH = 6.0 Hz, 2H), 7.61 (d, J_HH = 5.9 Hz, 2H), 7.53 (d, J_HH = 8.7 Hz, 4H), 7.49 (d, J_HH = 7.9 Hz, 2H), 7.37 (d, J_HH = 8.0 Hz, 2H), 4.05 (m, 8H), 3.23 (d, J_HP = 21.7 Hz, 4H), 1.45 (d, 36H), 1.28 (t, J_HH = 7.1 Hz, 12H).

³¹P-NMR (162 MHz, CD₂Cl₂, 25 °C): δ: 25.19.

HRMS (m/z (ESI, MeCN)): m/z calcd for [(M − 2PF₆)/2]⁺: 623.25677; found = 623.25645; M = C₁₆₄H₆₅N₅₂O₁₄P₂Ru.
Theoretical section

To reduce the computational cost of the calculations without affecting the spectroscopic properties, the structures of the complexes were simplified by replacing the tert-butyl and PO₃Et₂ groups by methyl groups. The obtained ligand structures correlate well with the structural data obtained from the XRD studies performed with the respective rhenium(i) complexes. The average deviation of bond lengths is 0.010 Å, with a maximum deviation of 0.019 Å. Differences concerning torsion angles and the distribution of the substituents of ligand L₂ in the rhenium(i) complexes are attributed to packing effects. The geometry, vibrational frequencies and normal coordinates of the ground state were calculated by means of density functional theory (DFT) with the functional B3LYP including empirical dispersion corrections. The 28-electron relativistic effective core potential MWB was used with its basis set for the ruthenium atom. The 6-31G(d) basis set was employed for the ligands. To correct for the lack of anharmonicity and the approximate treatment of electron correlation, the harmonic frequencies were scaled by a factor of 0.97. The vertical excitation energies, oscillator strengths and energy derivatives of the excited states were obtained from time-dependent DFT calculations with the same functional, pseudopotential and basis set. The effects of the interaction with a solvent (acetonitrile, ε = 35.688, n = 1.344) on the geometry, frequencies, excitation energies and excited-state gradients were taken into account by the polarizable continuum model. The nonequilibrium procedure of solvation was used for the calculation of the excitation energies and of the excited-state gradients. The calculations were performed with Gaussian 09 and with a local program to compute resonance Raman intensities. The methodology to calculate resonance Raman spectra is described elsewhere and made use of the so-called simplified Φe method.

Conclusions

Herein we presented the synthesis of a series of rhenium (ReL₁–ReL₃) and ruthenium complexes (Ru(L₁)₂–Ru(L₃)₃) with elongated bpy derivatives with potential phosphonate anchoring groups. We employed phenylene and triazole units as rigid and aromatic linkers to connect the bpy core with phosphonic ester groups as precursors for phosphonate anchoring groups. Thereby, distance control between chromophores and electrode surfaces in solar or photosynthesis cells is enabled. This distance modification was analyzed by X-ray crystallography of Re(L₀), Re(L₁) and Re(L₂). Introduction of a phenylene linker (Re(L₀) → Re(L₁)) increased the distance between the rhenium center and the anchoring group by about 4 Å and an ancillary triazole spacer (Re(L₀) → Re(L₂)) by an additional 3.4 Å.

The photophysical and electrochemical studies in this paper support the assumption that the linkers enhance the performance of chromophores by shifting the absorption of the corresponding complexes to lower energies and increasing their molar absorptivities and π-conjugation. To gain more comprehensive insights into these effects, new heteroleptic ruthenium complexes Ru(tbbpy)₂(L₁) and Ru(tbbpy)₂(L₂) were successfully synthesized. Synthetic access to homoletic as well as heteroleptic ruthenium complexes with ligand L₁ or L₂ enabled useful resonance-Raman experiments. Supported by theoretical calculations these experiments revealed that the introduction of a phenylene moiety to bpy (L₁) leads to an energetic stabilization of the metal to ligand excitation compared to tbbpy. However, tuning of excited states by introduction of an additional triazole unit (L₂) is not straightforward. Excitation with higher energy (λex = 457 nm) populates a state with contributions of the triazole while a low-energy state (λex = 488 nm) is dominated by the bpy portion of L₂. Hydrolysis of the rhenium tricarbonyl chloride complexes Re(L₀) and Re(L₂) with Me₂SiBr led to Re(L₀)hydrolyzed and Re(L₂)hydrolyzed with free phosphonate anchoring groups and also caused ligand exchange of chloride by hydroxide or bromide respectively. However we showed that the triazole unit of Re(L₂)hydrolyzed is not decomposed under these harsh hydrolysis conditions. The solid state structure of Re(L₀)hydrolyzed exhibits a dominant hydrogen bond framework in the crystal packing. No effects on the metal to anchoring group distance could be observed. After immobilisation of Re(L₂)hydrolyzed on NiO the sensitized film was analyzed by UV/Vis spectroscopy to demonstrate principal utilisation of the presented compounds in dye sensitized cells. The application of the ligands L₁–L₃ in different metal complexes and their effects on the performance of corresponding DSSCs and DSPECs are currently under investigation.

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Notes and references

Paper

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1.) H-NMR-spectra

Figure S1: $^1$H-NMR spectrum of Re(L0).
Figure S2: $^1$H-NMR spectrum of Re(L1).

Figure S3: $^1$H-NMR spectrum of Re(L2).
**Figure S4:** $^1$H-NMR spectrum of Re(L3).

**Figure S5:** $^1$H-NMR spectrum of Ru(L0)$_3$. 
Figure S6: $^1$H-NMR spectrum of Ru(L1)$_3$.

Figure S7: $^1$H-NMR spectrum of bipyridine Ru(L2)$_3$. 
Figure S8: $^1$H-NMR spectrum of Ru(L3)$_3$ in [D3]MeCN + [D]TFA (at the top). $^1$H-NMR spectrum of Ru(L3)$_3$ in CD$_2$Cl$_2$ (at the bottom).
Figure S9: $^1$H-NMR spectrum of Ru(tbbpy)$_2$(L1).

Figure S10: $^1$H-NMR spectrum of Ru(tbbpy)$_2$(L2).
Figure S11: Comparison of $^1$H-NMR spectra of Re(L2$_{hydrolyzed}$) (at the top) and Re(L2) (at the bottom).

2.) $^{13}$C-NMR-spectra

Figure S12: $^{13}$C-NMR spectrum of Re(L0).
Figure S13: $^{13}$C-NMR spectrum of Re(L1).

Figure S14: $^{13}$C-NMR spectrum of Ru(L0)$_3$. 
Figure S15: $^{13}$C-NMR spectrum of Ru(L1)$_3$.

Figure S16: $^{13}$C-NMR spectrum of Ru(tbbpy)$_2$(L1).
3.) IR Spectra

Figure S17: IR spectrum of Re(L0).

Figure S18: IR spectrum of Re(L1).
Figure S19: IR spectrum of Re(L2).

Figure S20: IR spectrum of Re(L2$_{\text{hydrolyzed}}$).
4.) Mass Spectrometry spectra

Figure S21: IR spectrum of Re(L3).

Figure S22: HRMS spectrum of Re(L0) (at the top). Calculated Spectrum for [M+1Na']^+ (at the bottom).
Figure S23: HRMS spectrum of Re(L1) (at the top). Calculated Spectrum for \([M+1Na^+]^+\) (in the middle). Calculated Spectrum for the dimer \([2M+2Na^+]^{2+}\) (at the bottom).

Figure S24: HRMS spectrum of Re(L2) (at the top). Calculated Spectrum for \([M+1H^+]^+\) (in the middle). Calculated Spectrum for the dimer \([2M+2H^+]^{2+}\) (at the bottom).
Figure S25: HRMS spectrum of Re(L2$_{\text{hydrolyzed}}$) (at the top). Calculated Spectrum for [M]$^+$ (at the bottom).

Figure S26: HRMS spectrum of Re(L3) (at the top). Calculated Spectrum for [M+1H]$^+$ (in the middle). Calculated Spectrum for the dimer [2M+2H]$^{2+}$ (at the bottom).
Figure S27: HRMS spectrum of Ru(L0)₃ (at the top). Calculated Spectrum for [M - 2PF₆]⁺²⁺ (at the bottom).

Figure S28: HRMS spectrum of Ru(L1)₃ (at the top). Calculated Spectrum for [M - 2PF₆]⁺²⁺ (at the bottom).
Figure S29: HRMS spectrum of Ru(L2)₃ (at the top). Calculated Spectrum for [M − 2PF₆]²⁺ (at the bottom).

Figure S30: HRMS spectrum of Ru(L3)₃ (at the top). Calculated Spectrum for [M − 2PF₆ + 2Na⁺]⁴⁺ (at the bottom).
Figure S31: HRMS spectrum of Ru(tbbpy)$_2$(L1) (at the top). Calculated Spectrum for [M – 2PF$_6$]$^{2+}$ (at the bottom).

Figure S32: HRMS spectrum of Ru(tbbpy)$_2$(L2) (at the top). Calculated Spectrum for [M – 2PF$_6$]$^{2+}$ (at the bottom).
5.) Electrochemical voltammograms

**Figure S33:** Square wave voltammograms of Ru(L0)\textsubscript{3} and Ru(L1)\textsubscript{3}. Potential vs. Fc/Fc\textsuperscript{+}.

**Figure S34:** Cyclovoltammogramm of Re(L0). Potential vs. Fc/Fc\textsuperscript{+}.
Figure S35: Cyclovoltammogramm of Re(L1). Potential vs. Fc/Fc⁺.

Figure S36: Cyclovoltammogramm of Re(L2). Potential vs. Fc/Fc⁺.
Figure S37: Cyclovoltammogramm of Re(L3). Potential vs. Fc/Fc⁺.

6.) Theoretical calculations

Table S 1: Ru(tbbpy)₂L1 main excited states

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Figure S38: Ru(tbbpy)$_2$L1 Resonance Raman spectrum
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Table S 3: Ru(tbbpy)$_2$L$_2$ main excited states

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Image S 7: 234 orbital Ru(tbbpy)$_2$L$_2$

Image S 8: 235 orbital Ru(tbbpy)$_2$L$_2$

Image S 9: 236 orbital Ru(tbbpy)$_2$L$_2$

Image S 10: 237 orbital Ru(tbbpy)$_2$L$_2$

Image S 11: 238 orbital Ru(tbbpy)$_2$L$_2$

Image S 12: 239 orbital Ru(tbbpy)$_2$L$_2$
Figure S39: Ru(tbbpy)$_2$L$_2$ Resonance Raman spectrum

Table S 4: Ru(tbbpy)$_2$L$_2$ Resonance Raman results

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Table S 5: Ru(L1)₃ main excited states
Figure S40: Ru(L1)₃ Resonance Raman spectrum
### Table S 6: Ru(L1)$_3$ Resonance Raman results

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### Table S 7: Ru(L2)$_3$ main excited states

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<th>$\lambda$(nm):</th>
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Image S 19: 398 orbital Ru(L2)$_3$

Image S 20: 399 orbital Ru(L2)$_3$

Image S 21: 400 orbital Ru(L2)$_3$

Image S 22: 401 orbital Ru(L2)$_3$

Image S 23: 402 orbital Ru(L2)$_3$

Image S 24: 403 orbital Ru(L2)$_3$
Figure S41: Ru(L2)_2 Resonance Raman spectrum

Table S8: Ru(L2)_2 Resonance Raman results

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<th>Mode</th>
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**Figure S42:** Calculated structure (xyz coordinates) of Ru(tbbpy)$_2$(L1), simplified by replacing the tert-butyl and PO$_3$Et$_2$ groups by methyl groups.
**Figure S43:** Calculated structure of Ru(L1)$_3$, simplified by replacing the PO$_3$Et$_2$ groups by methyl groups.

**Figure S44:** Calculated structure of Ru(tbbpy)$_2$(L2), simplified by replacing the tert-butyl and PO$_3$Et$_2$ groups by methyl groups.

**Figure S45:** Calculated structure of Ru(L2)$_3$, simplified by replacing the PO$_3$Et$_2$ groups by methyl groups.
7. Resonance Raman Spectra

**Figure S46**: Comparison of Resonance Raman spectra of Ru(L1)$_3$, Ru(tbbpy)$_2$(L1) and Ru(tbbpy)$_3$

**Figure S47**: Comparison of Resonance Raman spectra of Ru(L2)$_3$, Ru(tbbpy)$_2$(L2) and Ru(tbbpy)$_3$
## 8.) Crystal Data

**Table S9: Characteristic lengths and angles**

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<th>CH2Car [Å]</th>
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<td>7.500</td>
<td>1.791(3)</td>
<td>1.500(6)</td>
<td>115.8(3)</td>
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[a] Distance between pyridine nitrogen atom (gands) or Re center (complexes) and the calculated centroid centered between the phosphonate oxygen atoms.

[b] Two molecules in the asymmetric unit.

---

Table S10. Crystal data and structure refinement for **Re-L0**.

**Empirical formula**
C23 H30 Cl N2 O9 P2 Re

**Formula weight**
762.08

**Temperature**
150(2) K

**Wavelength**
0.71073 Å

**Crystal system**
Triclinic

**Space group**
P -1

**Unit cell dimensions**
\[ a = 11.5189(8) \text{ Å} \quad \alpha = 60.874(7)^\circ. \]
\[ b = 12.2876(8) \text{ Å} \quad \beta = 71.142(7)^\circ. \]
\[ c = 12.3796(8) \text{ Å} \quad \gamma = 72.476(6)^\circ. \]

**Volume**
1426.4(2) Å³

**Z**
2
Density (calculated) 1.774 Mg/m$^3$
Absorption coefficient 4.517 mm$^{-1}$
F(000) 752
Crystal size 0.1406 x 0.1214 x 0.0799 mm$^3$
Theta range for data collection 3.416 to 26.372°.
Index ranges $-14\leq h \leq 14$, $-15\leq k \leq 15$, $-15\leq l \leq 15$
Reflections collected 14520
Independent reflections 5826 [R(int) = 0.0383]
Completeness to theta = 25.242° 99.7%
Refinement method Full-matrix least-squares on F$^2$
Data / restraints / parameters 5826 / 0 / 343
Goodness-of-fit on F$^2$ 1.038
Final R indices [I>2sigma(I)] $R_1 = 0.0335$, $wR_2 = 0.0654$
R indices (all data) $R_1 = 0.0422$, $wR_2 = 0.0701$
Largest diff. peak and hole 1.052 and -0.752 e.Å$^{-3}$

Figure S48: ORTEP depiction of Re(L0) in the solid state (ellipsoids drawn at 50% probability).

Crystal data for Re-L0: $C_{23}H_{30}ClN_2O_8P_2Re$, $M_r = 762.08$ g mol$^{-1}$, yellow fragment, crystal size 0.1406 x 0.1214 x 0.0799 mm$^3$, triclinic, space group $P$ -1, $a = 11.5189(8)$ Å, $b = 12.2876(8)$ Å, $c =$
12.3796(8) Å, α = 60.874(7)°, γ = 72.476(6)°, V = 1426.4(2) Å³, T = 150(2) K, Z = 2, 
ρcalc. = 1.774 Mg/m³, μ (Mo-Kα) = 4.517 mm⁻¹, F(000) = 752, altogether 14520 reflexes up to h(-14/14), k(-15/15), l(-15/15) measured in the range of 3.416° ≤ Θ ≤ 26.372°, completeness Θmax = 99.7 %, 5826 independent reflections, Rint = 0.0383, 5136 reflections with F0 > 2 σ(F0), 343 parameters, 0 restraints, R1obs = 0.0335, wR2obs = 0.0654, R1all = 0.0422, wR2all = 0.0701, GOOF = 1.038, largest difference peak and hole: 1.052/-0.752 e·Å⁻³. CCDC 1468795 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S11. Crystal data and structure refinement for Re-L0_OH.

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<td>150(2) K</td>
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<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
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<td>Crystal system</td>
<td>Triclinic</td>
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<td>Space group</td>
<td>P -1</td>
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<tr>
<td>Unit cell dimensions</td>
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<tr>
<td></td>
<td>b = 14.0611(7) Å, β = 82.163(3)°.</td>
</tr>
<tr>
<td></td>
<td>c = 15.4117(6) Å, γ = 81.699(4)°.</td>
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<tr>
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<tr>
<td>Density (calculated)</td>
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<tr>
<td>Absorption coefficient</td>
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<tr>
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<tr>
<td>Independent reflections</td>
<td>5093 [R(int) = 0.0382]</td>
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<td>99.8 %</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
</tbody>
</table>
Data / restraints / parameters

Goodness-of-fit on $F^2$

Final $R$ indices $[I>2\sigma(I)]$

$R_1 = 0.0334$, $wR_2 = 0.0851$

$R$ indices (all data)

$R_1 = 0.0395$, $wR_2 = 0.0871$

Largest diff. peak and hole

1.196 and -1.382 e\(\cdot\)Å\(^{-3}\)

**Figure S49:** ORTEP depiction of Re(L0_hydrolyzed) in the solid state (ellipsoids drawn at 50% probability).

Crystal data for **Re-L0_OH**: C\(_{17}\) H\(_{22}\) Br N\(_2\) O\(_{11}\) Re, $M_r = 758.41$ g mol\(^{-1}\), orange fragment, crystal size 0.1982 x 0.0398 x 0.0396 mm\(^3\), triclinic, space group $P\ -I$, $a = 6.2650(2)$ Å, $b = 14.0611(7)$ Å, $c = 15.4117(6)$ Å, $\alpha = 68.954(4)^\circ$, $\beta = 82.163(3)^\circ$, $\gamma = 81.699(4)$ $V = 1248.56(10)$ Å\(^3\), $T = 150(2)$ K, $Z = 2$, $\rho_{\text{calc}} = 2.017$ Mg/m\(^3\), $\mu$ (Cu-K\(_\alpha\)) = 13.134 mm\(^{-1}\), F(000) = 732, altogether 11751 reflexes up to h(-7/7), k(-17/17), l(-17/19) measured in the range of 7.432$^\circ \leq \Theta \leq 74.488^\circ$, completeness $\Theta_{\text{max}} = 99.8\%$, 5093 independent reflections, $R_{\text{int}} = 0.0382$, 4530 reflections with $F_0 > 2 \sigma(F_0)$, 333 parameters, 3 restraints, $R_1 = 0.0334$, $wR_2 = 0.0851$, $R_1 = 0.0395$, $wR_2 = 0.0871$, GOOF = 1.086, largest difference peak and hole: 1.196/-1.382 e\(\cdot\)Å\(^{-3}\). Disorder of the trans Br-CO orientation was calculated with a main site occupation of 92.6%. The Re-CO geometry was fixed with DFIX and DANG restraints for the PART 2 site due to the respectively low electron density. CCDC 1468796 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
Table S12. Crystal data and structure refinement for **Re-L1**.

<table>
<thead>
<tr>
<th>Property</th>
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<td><strong>Empirical formula</strong></td>
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<td><strong>Formula weight</strong></td>
<td>910.23</td>
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<td><strong>Temperature</strong></td>
<td>150(2) K</td>
</tr>
<tr>
<td><strong>Wavelength</strong></td>
<td>0.71073 Å</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Triclinic</td>
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<tr>
<td><strong>Space group</strong></td>
<td>$P\bar{1}$</td>
</tr>
<tr>
<td><strong>Unit cell dimensions</strong></td>
<td>$a = 7.7823(2),\text Å, \quad \alpha = 98.3880(10),^\circ.$</td>
</tr>
<tr>
<td></td>
<td>$b = 17.7372(3),\text Å, \quad \beta = 90.293(2),^\circ.$</td>
</tr>
<tr>
<td></td>
<td>$c = 26.8707(4),\text Å, \quad \gamma = 99.121(2),^\circ.$</td>
</tr>
<tr>
<td><strong>Volume</strong></td>
<td>3621.54(13) Å$^3$</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
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<tr>
<td><strong>Density (calculated)</strong></td>
<td>1.669 Mg/m$^3$</td>
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<tr>
<td><strong>Absorption coefficient</strong></td>
<td>3.573 mm$^{-1}$</td>
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<tr>
<td><strong>F(000)</strong></td>
<td>1808</td>
</tr>
<tr>
<td><strong>Crystal size</strong></td>
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<tr>
<td><strong>Theta range for data collection</strong></td>
<td>3.401 to 26.371$^\circ$.</td>
</tr>
<tr>
<td><strong>Index ranges</strong></td>
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</tr>
<tr>
<td><strong>Reflections collected</strong></td>
<td>38852</td>
</tr>
<tr>
<td><strong>Independent reflections</strong></td>
<td>14784 [R(int) = 0.0325]</td>
</tr>
<tr>
<td><strong>Completeness to theta = 25.242$^\circ$</strong></td>
<td>99.7 %</td>
</tr>
<tr>
<td><strong>Refinement method</strong></td>
<td>Full-matrix least-squares on $F^2$</td>
</tr>
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<td><strong>Data / restraints / parameters</strong></td>
<td>14784 / 0 / 901</td>
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<td><strong>Goodness-of-fit on $F^2$</strong></td>
<td>1.038</td>
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<tr>
<td><strong>Final R indices [I&gt;$2\sigma(I)$]</strong></td>
<td>$R_1 = 0.0357, , \text{wR}_2 = 0.0746$</td>
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<tr>
<td><strong>R indices (all data)</strong></td>
<td>$R_1 = 0.0488, , \text{wR}_2 = 0.0801$</td>
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<td><strong>Largest diff. peak and hole</strong></td>
<td>1.057 and -0.565 e.$\text Å^{-3}$</td>
</tr>
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</table>

* the correct values cannot be provided due to loss of the crystal
Figure S50: ORTEP depiction of Re(L1) in the solid state (ellipsoids drawn at 50% probability).

Crystal data for Re-L1: C_{35} H_{34} Cl N_{2} O_{9} P_{2} Re, M_r = 910.23 g mol^{-1}, yellow fragment, triclinic, space group P -1, a = 7.7823(2) Å, b = 17.7372(3) Å, c = 26.8707(4) Å, α = 98.3880(10)°, β= 90.293(2)°, γ = 99.121(2) V = 3621.54(13) Å³, T = 150(2) K, Z = 4, ρ_{calc} = 1.669 Mg/m³, μ (Mo-Kα) = 3.573 mm⁻¹, F(000) = 1808, altogether 38852 reflexes up to h(-8/9), k(-21/22), l(-33/33) measured in the range of 3.401° ≤ Θ ≤ 26.371°, completeness Θ max = 99.7 %, 14784 independent reflections, R_{int} = 0.0325, 12134 reflections with F_{0} > 2 σ(F_{0}), 901 parameters, 0 restraints, R_{1,obs} = 0.0357, wR_{2,obs} = 0.0746, R_{1,all} = 0.0488, wR_{2,all} = 0.0801, GOOF = 1.038, largest difference peak and hole: 1.057/-0.565 e·Å⁻³.

CCDC 1468798 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Table S12. Crystal data and structure refinement for Re-L2.

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<td>Wavelength</td>
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<td>Crystal system</td>
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<tr>
<td>Space group</td>
<td>P 21/c</td>
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<tr>
<td>Unit cell dimensions</td>
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<tr>
<td>a</td>
<td>10.6361(8) Å</td>
</tr>
<tr>
<td>b</td>
<td>37.8192(14) Å</td>
</tr>
<tr>
<td>c</td>
<td>11.9861(5) Å</td>
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<tr>
<td>Volume</td>
<td>4654.4(4) Å</td>
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<tr>
<td>Density (calculated)</td>
<td>1.622 Mg/m³</td>
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<tr>
<td>Absorption coefficient</td>
<td>2.805 mm⁻¹</td>
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<tr>
<td>F(000)</td>
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<tr>
<td>Crystal size</td>
<td>0.1197 x 0.0614 x 0.0363 mm³</td>
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<td>Theta range for data collection</td>
<td>3.522 to 26.372°</td>
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<td>Index ranges</td>
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</tr>
<tr>
<td>Reflections collected</td>
<td>29297</td>
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<tr>
<td>Independent reflections</td>
<td>9492 [R(int) = 0.0678]</td>
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<td>Completeness to theta = 25.242°</td>
<td>99.7 %</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<td>Data / restraints / parameters</td>
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<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0494, wR2 = 0.0998</td>
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<td>R indices (all data)</td>
<td>R1 = 0.0754, wR2 = 0.1109</td>
</tr>
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<td>Largest diff. peak and hole</td>
<td>1.587 and -1.157 e.Å⁻³</td>
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</tbody>
</table>
**Figure S51**: ORTEP depiction of Re(L2) in the solid state (ellipsoids drawn at 50% probability).

Crystal data for Re-L2: C_{43}H_{48}ClN_{8}O_{11}P_{2}Re, M_r = 1136.48 g mol^{-1}, yellow fragment, crystal size 0.1197 x 0.0614 x 0.0363 mm³, monoclinic, space group P 2_l/c, a = 10.6361(8) Å, b = 37.8192(14) Å, c = 11.9861(5) Å, β= 105.124(5)°, V = 4654.4(4) Å³, T = 150(2) K, Z = 4, ρ_{calc} = 1.622 Mg/m³, μ(Mo-Kα) = 2.805 mm⁻¹, F(000) = 2288, altogether 29297 reflexes up to h(-13/11), k(-47/47), l(-13/14) measured in the range of 3.522° ≤ θ ≤ 26.372°, completeness θ_{max} = 99.7 %, 9492 independent reflections, R_{int} = 0.0678, 7123 reflections with F_0 > 2 σ(F_0), 595 parameters, 0 restraints, R_{1,obs} = 0.0494, wR_{2,obs} = 0.0998, R_{1,all} = 0.0754, wR_{2,all} = 0.1109, GOOF = 1.017, largest difference peak and hole: 1.587/-1.157 e·Å⁻³. CCDC 1468797 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
Figure S52: Depiction of back to back orientation of two Re(L0$_{\text{hydrolyzed}}$) complexes in the solid state.

Figure S53: Depiction of Re(L1) dimer in the solid state (side view).

Figure S54: Depiction of Re(L1) dimer in the solid state (top view).
**Figure S55:** Depiction of Re(L2) dimer in the solid state (side view).

**Figure S56:** Depiction of Re(L2) dimer in the solid state (top view).
Title: CLICK 'n' Sleep: Light-Switch Behavior of Triazole-Containing Tris(bipyridyl)ruthenium Complexes

Author(s): Markus Braumüller, Magdalena Staniszewska, Julien Guthmuller, Sven Rau

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Photosensors

CLICK 'n' Sleep: Light-Switch Behavior of Triazole-Containing Tris(bipyridyl)ruthenium Complexes

Markus Braumüller,[a] Magdalena Staniszewska,[b] Julien Guthmüller,[b] and Sven Rau*[a]

Abstract: A set of Ru complexes incorporating triazole subunits are presented. They show a solvent-dependent light-switch effect. Theoretical calculations revealed the excited states involved in the emission process. The findings are highly important for future design of light-switch sensors and suggest a severe restriction for functional photomolecular devices synthesized by CLICK chemistry.

Introduction

Since the "CLICK chemistry" methodology emerged in 2001 it has received extensive utilization in diverse fields of chemistry.[1-13] In particular the copper(I)-catalyzed alkyne-alkyne cycloaddition (CuAAC) promoted advances in medicinal chemistry, biochemical studies and materials science.[4-9] The resulting 1,2,3-triazoles are often employed as stable linkers between two chemical or biological components to perform important roles in sensing or to contribute to the coordination of target analytes.[5,10,11] Such a triazole-mediated binding may lead to an optical response event. In the case of luminescent sensors an alteration of luminescence intensity or wavelength may be observed.[11,12] Within the context of luminescent sensors ruthenium complexes have found very interesting applications, because of their photostability and tunable absorption and emission properties.[13-15] Here it is noteworthy that the effect of solvent composition and temperature on luminescence properties of ruthenium complexes is very complex. A sufficiently detailed investigation of the dominating effects demands temperature-dependent measurements, determination of viscosity and correlation between luminescence quantum yields and lifetimes of excited states within this series.[16,17] The involvement of ligand-based excited states may further complicate the picture.[18] A famous example for an Ru complex with an environmentally sensitive "light switch" behavior is [Ru(bpy)3(dpz)2](bpy = 2,2'-bipyridine, dpz = dipyrido[3,2-a:2',3'-c]phenazine).[19] Unlike most (polypyridyl)Ru complexes, [Ru(bpy)3(dpz)2] is nonluminescent in aqueous solution but brightly emits in nonpolar aprotic solvents. Three main possibilities were reported to be potential causes of this behavior: (1) The presence of two types of MLCT states on different portions of the dpz ligand. A bright one localized on the bpy moiety and a weakly emissive dark state mainly localized on the phenazine portion. The light-switch effect is a result of competition between energetic factors that favor the population of the dark state and the entropically favored bright state.[13,20] Brennan et al. suggest the dark state is always lower in energy than the bright one, but in some environments the bright state is within thermal energy of the dark state, leading to the environmentally sensitive light switch.[13,14,20] (2) The presence of other triplet states, e.g. intraligand charge transfers (ILCT) near to the lowest/emissive MLCT state, may quench luminescence and lead to other deactivation processes.[21,22] (3) Hydrogen-bonding interactions between the phenazine nitrogen atoms of dpz and solvent lower the energy of the dark state and thereby quench the luminescence.[13,19,23,24]

In 2011 Jiao et al. presented a triazole-containing 8-hydroxyquinoline (8-HQ) ether, which is strongly fluorescent in nonprotic solvents like MeCN and shows weak fluorescence in water, similar to [Ru(bpy)2(dpz)]2.[25] However, this was attributed to a photoinduced proton transfer (PPT) process involving protic water solvent molecules and the 8-HQ moiety. A contribution of the triazole unit was not discussed.[26-27] Herein we present triazole-containing (polypyridyl)Ru complexes in which the triazole heterocycle itself seems to be responsible for a solvent-dependent light-switch effect. We show that the magnitude of luminescence quenching correlates with the quantity of triazole rings per Ru complex and that the light-switch effect is generally independent of the substitution at the triazole rings. These findings are highly relevant for the targeted design of new switchable photosensors based on solvent-environment changes and suggest a severe limitation for CLICK chemistry as universal tool for the construction of functional photomolecular devices. In our previous studies we presented new bpy derivatives (L1, L2) with z-conjugated linkers and their corresponding Ru complexes.[28,29] Compared to our model complex Ru(L0)2 we inserted first a phenylene group [Ru(L1)L2] and then a triazole ring with a phenylene group [Ru(L2)L2] to elongate the distance between the bpy core and a phosphate anchoring...
group precursor (Figure S1). The anchoring group enables utilization of the complexes in dye-sensitized cells. Photophysical and electrochemical studies supported the assumption that the linkers enhance the performance of chromophores by shifting the absorption of the corresponding complexes to lower energies. Resonance Raman spectroscopy of Ru(tbbpy)_3, Ru(tbbpy)_2(L2) and Ru(L2)_2 revealed that tuning excited states by introduction of a triazole unit (L2) is not straightforward and that the excited state encompasses the bpy-triazole scaffold [tbbpy = 4,4′-bis(tert-butyl)-2,2′-bipyridine]. These experiments were supported by theoretical calculations.[29]

Results and Discussion

A more detailed investigation of the luminescence properties of this series of complexes led to a surprising observation. Contrary to analogous tris(bipyridine)/ruthenium(II) complexes, fluorescence spectroscopic studies revealed that the triazole-containing Ru(L2)_2 complex shows luminescence quenching when increasing the water content in MeCN to a certain amount (Figure S2). Whereas Ru(bpy)_3, Ru(L0)_3, and Ru(L1)_3 show an increasing emission intensity by increasing the water content in acetonitrile, the luminescence intensity of Ru(L2)_2 initially also follows this trend but drops drastically in an MeCN/H_2O (1:9) mixture. To investigate whether this effect is correlated to the triazole moieties within Ru(L2)_2, we decided to study more Ru(II) complexes with different numbers of triazole moieties [Ru(tbbpy)_2(L2), Ru(tbbpy)(L2)_2] or a different triazole substituent [Ru(L3)_3], respectively (Figure 1).

The benzyl substituent of Ru(L3)_3 was chosen to disrupt the π-conjugation over the whole complex. The synthesis of Ru(tbbpy)(L2)_2 and Ru(L3)_3 was achieved in two steps according to a literature procedure.[20] Initially, 2 equiv. of the same bpy derivative were coordinated to an Ru(DMSO)_4Cl_2 precursor by refluxing in methanol. Then the third equivalent was introduced to the crude product of the first reaction by refluxing in an ethanol/water (3:1) mixture. HRMS (ESI) data is consistent with the desired product for the new Ru complexes. Because of solubility limitations in deuterated solvents, no ^13C NMR spectra could be obtained for the triazole-containing Ru complexes as observed previously.[29] ^1H NMR, ^31P NMR and HR mass spectra are shown in the Supporting Information (cf. Figures S10–S13). All emission spectra were measured at the same optical density at the corresponding MLCT maxima (cf. Figures S3–S7).

We observed an increasing magnitude of luminescence quenching by increasing the number of triazoles per ruthenium complex from two to six [Ru(tbbpy)_2(L2) < Ru(tbbpy)(L2)_2 < Ru(L2)_2]. Furthermore, the substitution at the triazole (conjugated vs. nonconjugated) seems to have an influence on the magnitude of the light-switch effect (cf. Figure 2). With benzyl
instead of phenyl bound to the triazole nitrogen atom the luminescence quenching is stronger. The emission data are summarized in Table S1. Within the short timeframes of luminescence measurements photostability of the triazole-containing complexes should not be a cause of the witnessed intensity loss. In order to further investigate this hypothesis, more detailed investigations were performed. Starting at the same optical density at the MLCT maxima Ru(hbpy)$_3$ (λ$_{MLCT} = 453$ nm) and Ru(L3)$_3$ (λ$_{MLCT} = 485$ nm) were irradiated with a 50 mW blue LED (λ = 470 nm) in MeCN/H$_2$O (1:9). Ru(hbpy)$_3$ shows an intensity loss in absorption at the MLCT maximum of 79% within 6 h, whereas in the same time Ru(L3)$_3$ exhibits a loss of only 24%, proving increased photostability compared to the parent Ru(hbpy)$_3$ complex (Figure S18 and S19). Additionally, exposure of Ru(L3)$_3$ in MeCN/H$_2$O (1:9) solution to ambient light for 4 d did only lead to minor changes (less than 15% intensity loss) in the absorbance spectra (Figure S20).

Galoppi and co-workers presented structurally related Ru complexes bearing bpy ligands elongated with triazole and capped with methyl p-benzoate and isophthalate.[15] They investigated protonation effects of the triazole ring on the photoluminescence behavior in THF by addition of aliquots of HCl. With increasing proton concentration they witnessed an increase in luminescence intensity. This finding induced us to investigate the emission behavior in different solvents and to reproduce this result in THF (cf. Figures S8 and S9). For this purpose Ru(L3)$_3$ was chosen, because it shows the strongest light-switch behavior. The photoluminescence intensity decreased in the following solvent order DCM > DMF > THF > MeCN and dropped drastically in a protic THF/H$_2$O (1:9) mixture as well as in MeCN/H$_2$O (1:9). This trend suggests that the character of the solvent has a major influence on the emission behavior. Interestingly, addition of HCl to THF (Figure S9) or THF/H$_2$O (1:9) (Figure S8, bottom) did lead to a decrease in luminescence intensity in the case of Ru(L3)$_3$, highlighting the importance of the triazole-based substitution.

A theoretical investigation was performed to identify the excited state(s) playing a role in the emission properties of the complexes. To this aim, the structure of the complex Ru(tbppy)$_2$(L2) was simplified by replacing the tert-butyl and PO$_2$Et$_2$ groups by methyl groups, resulting in the model complex Ru(Me(bpy))(L4) (cf. Figure S14). The vertical excitation energies of the five lowest triplet excited states were calculated with TDDFT at the ground state (S$_0$) and at the lowest triplet state (T$_1$) geometries. The results obtained at the T$_1$ geometry are reported in Table S2, whereas the data at the S$_0$ geometry are given in Table S4. The excited-state energies calculated in acetonitrile reveal that the lowest triplet state (T$_1$) is mainly of MLCT character, with the LUMO localized on the bpy portion of ligand L4 (cf. Table S7 and Figure S15). The second triplet state (T$_2$) is found ca. 0.2 eV higher and corresponds to a mixing of MLCT and IL contributions, with charge transfer occurring on

---

**Figure 2.** Emission spectra of Ru(tbppy)$_2$(L2)$_2$, Ru(tbppy)(L2)$_3$, Ru(L2)$_3$ and Ru(L3)$_3$ in MeCN with differing water content. Identical excitation conditions for measuring the emission spectra at identical optical densities at the corresponding MLCT.
the ligand L4 (MLCT, IL). The higher excited states have MLCT character with charge transfer to the ligand L4 (Td) and to the terminal ligands Mepy (T1 and T3). The results obtained in water using PCM present very small differences in comparison to acetonitrile. For example, the emission wavelength of the T1 state is only increased by ca. 1 nm in water. This value agrees with the small shift of 3.5 nm observed experimentally for Ru(bpy)3L2 (Table S1). Additionally, the calculation with DFT of the adiabatic emission wavelengths including zero-point vibrational corrections give values of 649.3 and 652.7 nm in acetonitrile and water, respectively. These values are in nice agreement with the experimental emission wavelengths. Therefore, we conclude that emission occurs from the lowest MLCT state (T1).

For the archetypical [Ru(II)(bpy)2(dpz)] complex, a proposed model to explain the light-switch effect is to assume that a dark state quenches the luminescence of the lowest MLCT state. If these two states are in close energetic vicinity, this can lead to thermally activated competition between the dark and bright states, which can be tuned by the environment. In the case of the Ru(Mepy)3L4 system, the second triplet state (T2) is only ca. 0.2 eV above T1. Because T2 contains a significant contribution of IL charge transfer, we might assume that it is less emissive than T1 and consequently that it can be responsible for the quenching of the luminescence in water. In earlier theoretical studies on [Ru(II)(bpy)2(dpz)]2, it was suggested that the changes observed in the experiment for the light-switch effect arise from the formation of hydrogen bonds between water molecules and the complex. In particular, changes in the character of the triplet states and modification of their relative energies were obtained. Therefore, we investigated possible effects of hydrogen bonding on the triazole rings by including explicit water molecules in the calculations (cf. Figure S17). The results obtained for the cluster of six water molecules, forming hydrogen bonds with the four nitrogen and two hydrogen atoms of the triazole rings, are presented in Tables S2, S4, and S5. The effects of hydrogen bonds do not modify the orbital character of the five lowest triplet states, and their energies are only slightly modified in comparison to those of acetonitrile. T2 is stabilized by only ca. 0.01 eV, which is slightly surprising since hydrogen bonding was expected to lead to a larger effect for this state due to its IL character. These results indicate that the quenching of the luminescence might originate from subtle couplings between the involved states.

As an extreme scenario, the excited states of a protonated version of Ru(Mepy)3L4 were calculated (cf. Tables S3 and S4). Following the values of the natural charges obtained in water, two protons were bound to the nitrogen atoms N1 and N4 (cf. Figure S14 and Table S6). The properties of the two lowest triplet states at the T1 geometry are reported in Table S3. The lowest triplet state (T1) is noticeably stabilized in comparison to the nonprotonated complex, leading to a predicted wavelength of emission of 811 nm, which is significantly higher than the measured emission wavelength. Therefore, this MLCT state is lower in energy than the emissive state. The character of T1 is also modified due to protonation and presents additional charge transfer to the triazoles (see Figure S16). The second triplet state (T2) has an MLCT/IL character with also more charge transfer to the triazoles and has a predicted wavelength of 713 nm. As an alternative explanation for the light-switch effect, we propose that the 3MLCT state in aqueous solution can be described as a radical-anion localized on the triazole unit, which then represents a relatively strong base, and an RuIII centre (Scheme 1).

![Scheme 1](image)

Scheme 1. Localized charge excitation: (i) electron transfer Ru2+ → MLCT, (ii) proton movement H2O → triazole(π). R2 = CH3, R1 = C6H4-C6H5.

A similar effect was suggested for a tris(heteroleptic) ruthenium complex incorporating dpz and 5,6,6’,7’-tetramethyl-2,2’-bibenzimidazole.[21] Our assumption is supported by the fact that upon addition of HCl to THF or THF/H2O (1:9) the emission intensities of Ru(L3)3 are even further diminished as for the untreated solvents (Figure S8, bottom, and Figure S9). After protonation, the complex should relax to the lowest triplet states. According to the calculations, these states have lower energies than the observed emission energy, and they have a more pronounced charge-transfer character to the triazoles. Therefore, we assume that they are dark and that radiationless relaxation occurs. We propose this to be the origin of the light-switch effect observed here. This interpretation also allows an explanation for the more pronounced emission quenching for Ru(L3)3 compared to Ru(L2)3. If the conjugation over the whole ligand is disrupted by a methylene spacer like in L3, the electron density at the triazole moiety is higher, making it more prone to protonation.

Conclusions

We presented different RuII complexes incorporating triazole subunits introduced to their bipyridine ligands by CLICK chemistry. These complexes show a solvent-dependent light-switch effect, which is clearly correlated to the presence and number of triazole subunits. The theoretical investigation revealed the nature of the emissive MLCT state and indicated the presence of a second triplet state close in energy, which has an MLCT/IL character. Based on our experimental evidence that protonation of the triazole unit leads to a loss of emission intensity, we propose a light-initiated proton transfer from water to triazole. This protonation stabilizes potentially dark excited states. However, further theoretical investigations will be required to unravel the detailed mechanism responsible for the light-switch effect. Furthermore, detailed photophysical characterization
with time-resolved spectroscopic methods has to be performed in order to gain a deeper understanding. However, already the preliminary findings presented here are highly relevant for the design of new switchable photosensors and might imply a major restriction for the utilization of CLICK chemistry. Even though CuAAC is indeed suitable to connect important function-owning molecular building blocks, the resulting triazoles are by no means innocent with respect to the desired overall function of the target functional devices, e.g. dye-sensitized solar or photochemical cells, for which (poly)pyridylRu sensitizers have shown excellent photovoltaic properties.252-271

Experimental Section

Methods and Materials: 1H (400 MHz), 31P (162 MHz) NMR spectra were measured with a Bruker DRX 400 spectrometer. The NMR spectra were recorded in [D2]MeCN at 298 K. 1H NMR chemical shifts were referenced to the solvent peak. MS analysis was performed with a Bruker solariX (2010) Hybrid 7T FT-ICR instrument. UV/Vis spectra were recorded with a JASCO spectrophotometer V-620. Quartz cells with a 10 mm path length were used. The emission spectra were recorded with a JASCO 25 spectrophotometer PF-8500. Quartz cells with a 10 mm path length were used. If not mentioned otherwise, all experiments were performed under aerobic conditions. The examined complexes were completely soluble under all experimental conditions.

Starting Materials: L0, L1, L2, and L3 were prepared according to literature procedures.288-289 Ru(bpy)3 was purchased from commercial sources and used without further purification. Ru(L0)2, Ru(L1)2, Ru(bpy)(bpy)L2 and Ru(L3)2 were prepared as described previously.290

General Procedure for the Ru Complex Formation: A solution of Ru(DMSO)Cl3 (0.02 mmol) and 2 equiv. of bipyrindine derivative (0.04 mmol) were refluxed in methanol (15 mL) for 24 h. During this time the color changed from yellow to dark brown. After removal of the methanol with a rotary evaporator, the residue was dissolved in a small amount of ethanol. Excess Et2O was added to the solution. The resulting brown precipitate was collected and dissolved in an ethanol/water (15 mL/5 mL) mixture. The third equivalent of bipyrindine derivative (0.02 mmol) was added, and the mixture was refluxed for 20 h. After this time, the color changed from deep brown to dark red. After removal of most of the ethanol with a rotary evaporator, excess NH4PF6 was added to the solution. The resulting red precipitate was collected, washed with water and diethyl ether and dried. The crude product was purified by size exclusion column chromatography with an aceton/methanol/chloroform (3:2:5) mixture as eluent.

Ru(bpy)(L2)2; Ru(bpy)(L2)2 was synthesized according to the general procedure for Ru complex formation, yielding the PF6 salt of Ru(bpy)(L2)2 [21 mg, 0.014 mmol, 72% yield starting with Ru(DMSO)Cl3]. 1H NMR (400 MHz, [D2]MeCN, 25 °C): δ = 9.18-9.11 (m, 6 H), 8.55 (s, 2 H), 8.06-7.39 (m, 30 H), 4.01 (m, 16 H), 2.07 (m, 2 H), 1.24 (m, 36 H) ppm. 31P NMR (162 MHz, [D2]MeCN, 25 °C): δ = 25.25 ppm. HRMS (ESI, MeCN): calcld. for [M – 2 PF6]/22 H2O; 927.30445; found 927.30580; M = 639.0H2O·N4P2O12PF6·Ru.

Ru(L3)2; Ru(L3)2 was synthesized according to the general procedure for Ru complex formation, yielding the PF6 salt of Ru(L3)2 [27 mg, 0.015 mmol, 75% yield starting with Ru(DMSO)Cl3]. 1H NMR (400 MHz, [D2]MeCN, 25 °C): δ = 8.96 (s, 6 H), 8.50 (s, 6 H), 7.82-7.76 (m, 12 H), 7.46-7.35 (m, 30 H), 5.64 (s, 12 H) ppm. HRMS (ESI, MeCN): calcld. for [(M – 4 PF6)/2]2+ 756.2784; found 756.2762; M = 469.0H2O·N4P2O13PF6·Ru.

Theoretical Section: To reduce the computational cost of the calculations without affecting the spectroscopic properties, the structure of the complex Ru(benpy)(L2)2 was simplified by replacing the tert-butyl and PO3Et groups by methyl groups. This model complex is referred to as Ru(benpy)(L4) in the main text. The geometries of the singlet ground state (S0) and of the lowest triplet state (T1) were calculated by means of density functional theory (DFT) with the functional B3LYP including empirical dispersion corrections. Harmonic vibrational frequencies were computed to confirm that the optimized structures correspond to minima on the potential energy surface and were employed to compute the adiabatic emission wavelength of T1. The 28-electron relativistic effective core potential MWA was used with its basis set for the ruthenium atom. The 6-31G(d) basis set was employed for the ligands. The vertical excitation energies of the five lowest triplet states were obtained from time-dependent (TD) DFT calculations with the same functional, pseudopotential and basis set. These calculations were performed at both the S0 and T1 geometries. The effects of the interaction with a solvent (acetonitrile: ξ = 35.688, n = 1.44; water: ξ = 78.353, n = 1.777849) on the geometries and triplet excitation energies were taken into account by the polarizable continuum model (PCM). The non-equilibrium procedure of solution was used for the calculation of the excitation energies. In addition to the PCM, explicit water molecules were added to the calculations to improve the description of the solvent and to investigate possible effects arising from the formation of hydrogen bonds. Hence, the S0 and T1 geometries and the triplet excited state energies were calculated for clusters with two, four and six water molecules forming hydrogen bonds with the triazole rings. In these calculations, the hydrogen atoms on the water molecules were described with the 6-31G(d) basis set, which contains a p polarization function, and the PCM was employed to represent the continuous effects of water. All the computations were performed with Gaussian 09.405

Acknowledgments

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Keywords: Click chemistry · Triazole · Light switch · Ruthenium · TDDFT calculations

SUPPORTING INFORMATION

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Title: CLICK 'n' Sleep: Light-Switch Behavior of Triazole-Containing Tris(bipyridyl)ruthenium Complexes
Author(s): Markus Braumüller, Magdalena Staniszewska, Julien Guthmuller, Sven Rau*
Figures and Tables

Figure S1: Structures of Ru-complexes Ru(bpy)$_3$, Ru(L0)$_3$, Ru(L1)$_3$ and Ru(L2)$_3$.

Figure S2: Emission spectra of Ru(bpy)$_3$, Ru(L0)$_3$, Ru(L1)$_3$ and Ru(L2)$_3$ in MeCN with differing water content. Identical excitation conditions for measuring the emission spectra at identical optical density at the corresponding MLCT.
**Table S1: Emission data**

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\lambda_{em}^{[a]}$ [nm]</th>
<th>$\lambda_{em}^{[b]}$ [nm]</th>
<th>Quenching $^{[b]}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(bpy)$_3$</td>
<td>607.5</td>
<td>606.5</td>
<td>-</td>
</tr>
<tr>
<td>Ru(L0)$_3$</td>
<td>614.5</td>
<td>611</td>
<td>-</td>
</tr>
<tr>
<td>Ru(L1)$_3$</td>
<td>623</td>
<td>626.5</td>
<td>-</td>
</tr>
<tr>
<td>Ru(tbbpy)$_3$(L2)</td>
<td>648</td>
<td>651.5</td>
<td>9.7</td>
</tr>
<tr>
<td>Ru(tbbpy)$_2$(L2)</td>
<td>635.5</td>
<td>642.5</td>
<td>45.1</td>
</tr>
<tr>
<td>Ru(L2)$_3$</td>
<td>627</td>
<td>636</td>
<td>58.6</td>
</tr>
<tr>
<td>Ru(L3)$_3$</td>
<td>630.5</td>
<td>633.5</td>
<td>79.6</td>
</tr>
</tbody>
</table>

[a] measured in MeCN  
[b] measured in MeCN:H$_2$O (1:9)  
[c] luminescence intensity quenching in MeCN:H$_2$O (1:9) vs. pure MeCN

**Figure S3:** Absorbance spectra of Ru(bpy)$_3$, Ru(L0)$_3$, Ru(L1)$_3$, Ru(L2)$_3$ at identical optical density at the corresponding MLCT maxima in MeCN.
**Figure S4:** Absorbance spectra of Ru(bpy)$_3$, Ru(L0)$_3$, Ru(L1)$_3$, Ru(L2)$_3$ at identical optical density at the corresponding MLCT maxima in MeCN:H$_2$O (1:9).

**Figure S5:** Absorbance spectra of Ru(bpy)$_3$, Ru(L0)$_3$, Ru(L1)$_3$, Ru(L2)$_3$ at identical optical density at the corresponding MLCT maxima in MeCN.
Figure S6: Absorbance spectra of $\text{Ru(bpy)}_3$, $\text{Ru(L0)}_3$, $\text{Ru(L1)}_3$, $\text{Ru(L2)}_3$, $\text{Ru(L3)}_3$ at identical optical density at the corresponding MLCT maxima in MeCN:H$_2$O (1:9).

Figure S7: Absorbance spectra of $\text{Ru(L3)}_3$ at identical optical density at the corresponding MLCT maxima in different solvents.
**Figure S8:** Emission spectra of Ru(L3)$_3$ in different solvents (top) and in THF:H2O (1:9) upon addition with aliquots of conc. HCl (bottom). Identical excitation conditions for measuring the emission spectra at identical optical density at the corresponding MLCT (cf. Figure S7).

**Figure S9:** Emission spectra of Ru(L3)$_3$ in THF upon addition with aliquots of conc. HCl. Identical excitation conditions ($\lambda_{ex} = 480$ nm) for measuring the emission spectra at identical optical density at the corresponding MLCT.
NMR-spectra

Figure S10: $^1$H-NMR spectrum of Ru(L3)$_3$.

Figure S11: a) $^1$H-NMR spectrum of Ru(L3)$_3$, b) $^{31}$P-NMR spectrum of Ru(L3)$_3$.
Figure S12: HRMS spectrum of Ru(L3)_3 (at the top). Calculated Spectrum for [M – 2PF_6]^{1+} (at the bottom).

Figure S13: HRMS spectrum of Ru(tbbpy)(L2)_2 (at the top). Calculated Spectrum for [M – 2PF_6]^{1+} (at the bottom).
Figure S14: Calculated structure of Ru(Mebpy)$_2$(L4).

Figure S15: Main orbitals for the cluster with six water molecules. Similar orbitals are obtained in other environments (c.f. Table S4).

Figure S16: Orbitals for the protonated complex.
Table S2: TDDFT vertical excitation energies of the five lowest triplet states of Ru(Mebpy)$_2$(L4) in different environments. The calculations are performed at the T$_1$ geometry.

<table>
<thead>
<tr>
<th>State number and main character</th>
<th>Transitions</th>
<th>Weights [%][a]</th>
<th>Energy [eV][b]</th>
<th>Energy [eV][c]</th>
<th>Energy [eV][d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>T$<em>1$ (MLCT$</em>{L4}$)</td>
<td>HOMO $\rightarrow$ LUMO</td>
<td>91</td>
<td>1.80 (689)</td>
<td>1.79 (690)</td>
<td>1.77 (699)</td>
</tr>
<tr>
<td>T$<em>2$ (MLCT$</em>{L4}$ + IL$_{L4}$)</td>
<td>HOMO-1 $\rightarrow$ LUMO</td>
<td>91</td>
<td>2.00 (618)</td>
<td>2.00 (619)</td>
<td>1.99 (622)</td>
</tr>
<tr>
<td>T$<em>3$ (MLCT$</em>{L4}$)</td>
<td>HOMO-2 $\rightarrow$ LUMO</td>
<td>93</td>
<td>2.23 (557)</td>
<td>2.22 (558)</td>
<td>2.19 (556)</td>
</tr>
<tr>
<td>T$<em>4$ (MLCT$</em>{Mebpy}$)</td>
<td>HOMO $\rightarrow$ LUMO +2</td>
<td>89</td>
<td>2.36 (525)</td>
<td>2.36 (525)</td>
<td>2.37 (522)</td>
</tr>
<tr>
<td>T$<em>5$ (MLCT$</em>{Mebpy}$)</td>
<td>HOMO $\rightarrow$ LUMO +1</td>
<td>87</td>
<td>2.39 (518)</td>
<td>2.39 (518)</td>
<td>2.41 (514)</td>
</tr>
</tbody>
</table>

[a] The reported transitions and weights are for the cluster with six water molecules, the weights for the other environments differ by less than 1%. [b] Corresponding wavelengths (in nm) are given in parentheses. [c] Indicates the solvent described with PCM.

Table S3: TDDFT vertical excitation energies of the two lowest triplet states of the protonated Ru(Mebpy)$_2$(L4) complex in water. The calculations are performed at the T$_1$ geometry.

<table>
<thead>
<tr>
<th>State number and main character</th>
<th>Transitions</th>
<th>Weights [%]</th>
<th>Energy [eV][a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>T$<em>1$ (MLCT$</em>{L4}$)</td>
<td>HOMO $\rightarrow$ LUMO</td>
<td>94</td>
<td>1.53 (811)</td>
</tr>
<tr>
<td>T$<em>2$ (MLCT$</em>{L4}$ + IL$_{L4}$)</td>
<td>HOMO-2 $\rightarrow$ LUMO</td>
<td>95</td>
<td>1.74 (713)</td>
</tr>
</tbody>
</table>

[a] Corresponding wavelengths (in nm) are given in parentheses. [b] Indicates the solvent described with PCM.

Table S4: Ru(Mebpy)$_2$(L4) Excited state table. When different, the main character and transition are indicated next to the energy value.

<table>
<thead>
<tr>
<th>State number and main character</th>
<th>Transitions</th>
<th>Enery [eV] (nm)</th>
<th>Enery [eV] (nm)</th>
<th>Enery [eV] (nm)</th>
<th>Enery [eV] (nm)</th>
<th>Enery [eV] (nm)</th>
<th>Enery [eV] (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MeCN</td>
<td>Water + 2H$_2$O</td>
<td>Water +4H$_2$O</td>
<td>Water +6H$_2$O</td>
<td>Water + 2H$^+$</td>
<td>S$_0$ geometry</td>
</tr>
<tr>
<td>T$<em>1$ (MLCT$</em>{L4}$)</td>
<td>HOMO $\rightarrow$ LUMO</td>
<td>2.23 (555)</td>
<td>2.23 (556)</td>
<td>2.22 (556)</td>
<td>2.25 (552)</td>
<td>2.21 (562)</td>
<td>1.86 (667)</td>
</tr>
<tr>
<td>T$<em>2$ (MLCT$</em>{L4}$ + IL$_{L4}$)</td>
<td>HOMO-1 $\rightarrow$ LUMO</td>
<td>2.29 (540)</td>
<td>2.29 (541)</td>
<td>2.28 (542)</td>
<td>2.31 (536)</td>
<td>2.28 (544)</td>
<td>1.97 (641)</td>
</tr>
<tr>
<td>T$<em>3$ (MLCT$</em>{Mebpy}$)</td>
<td>HOMO $\rightarrow$ LUMO +2</td>
<td>2.41 (513)</td>
<td>2.41 (513)</td>
<td>2.43 (551)</td>
<td>2.40 (516)</td>
<td>2.42 (512)</td>
<td>2.19 (595)</td>
</tr>
<tr>
<td>T$<em>4$ (MLCT$</em>{Mebpy}$)</td>
<td>HOMO $\rightarrow$ LUMO +1</td>
<td>2.43 (511)</td>
<td>2.43 (510)</td>
<td>2.44 (507)</td>
<td>2.42 (512)</td>
<td>2.44 (508)</td>
<td>2.19 (595)</td>
</tr>
<tr>
<td>T$<em>5$ (MLCT$</em>{Mebpy}$)</td>
<td>HOMO-2 $\rightarrow$ LUMO +1</td>
<td>2.49 (496)</td>
<td>2.49 (498)</td>
<td>2.47 (501)</td>
<td>2.50 (496)</td>
<td>2.47 (503)</td>
<td>2.54 (474)</td>
</tr>
</tbody>
</table>

S$_0$ geometry

|                                |             | H-2 $\rightarrow$L-2 70% | H-2 $\rightarrow$L-2 70% | H-2 $\rightarrow$L-2 70% | H-2 $\rightarrow$L-2 70% | H-2 $\rightarrow$L-2 70% |
| T$_1$ (MLCT$_{L4}$)            | HOMO $\rightarrow$ LUMO | 1.80 (689) | 1.79 (690) | 1.78 (696) | 1.79 (690) | 1.77 (699) | 1.53 (811) |
| T$_2$ (MLCT$_{L4}$ + IL$_{L4}$)| HOMO-1 $\rightarrow$ LUMO | 2.00 (618) | 2.00 (619) | 2.00 (620) | 2.01 (615) | 1.99 (622) | 1.74 (713) |
| T$_3$ (MLCT$_{L4}$)            | HOMO-2 $\rightarrow$ LUMO | 2.23 (557) | 2.22 (558) | 2.20 (563) | 2.23 (556) | 2.19 (555) | 1.88 (660) |
| T$_4$ (MLCT$_{Mebpy}$)         | HOMO $\rightarrow$ LUMO +2 | 2.36 (525) | 2.36 (525) | 2.37 (522) | 2.35 (526) | 2.37 (522) | 2.39 (519) |
| T$_5$ (MLCT$_{Mebpy}$)         | HOMO $\rightarrow$ LUMO +1 | 2.39 (518) | 2.39 (518) | 2.41 (514) | 2.39 (518) | 2.41 (514) | 2.57 (483) |

H-2 $\rightarrow$L-2 70%
Table S5: Ru(Mebpy)_2(L4) hydrogen bonds lengths for T1 geometry

<table>
<thead>
<tr>
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<th>Water+2H₂O</th>
<th>Water+4H₂O</th>
<th>Water+6H₂O</th>
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</thead>
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<td>Bond lengths [Å]</td>
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<td>N₁-H₉</td>
<td>1.820</td>
<td>1.810</td>
<td>1.765</td>
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<td>N₁-H₁₇</td>
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<td>-</td>
<td>2.772</td>
</tr>
<tr>
<td>N₁-H₁₈</td>
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<td>3.178</td>
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<td>N₂-H₉</td>
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<td>-</td>
<td>3.035</td>
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<tr>
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<td>2.646</td>
<td>2.604</td>
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<tr>
<td>O₁-H₁₁</td>
<td>1.804</td>
<td>1.798</td>
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<td>-</td>
<td>1.949</td>
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<td>N₄-H₁₉</td>
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<td>O₅-H₈</td>
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<td>2.569</td>
<td>2.590</td>
</tr>
</tbody>
</table>

Figure S17: Calculated structure of Ru(Mebpy)₂(L4) with six water molecules.
Figure S18: Absorbance spectra of Ru(bpy)$_3$ (PF$_6$-salt) in MeCN:H$_2$O (1:9) upon illumination with LED lamp (intensity 50mW, $\lambda$=470nm).

Figure S19: Absorbance spectra of Ru(L3)$_3$ (PF$_6$-salt) in MeCN:H$_2$O (1:9) upon illumination with LED lamp (intensity 50mW, $\lambda$=470nm).
Figure S20: Absorbance spectra of Ru(L3)$_3$ (PF$_6$-salt) in MeCN:H$_2$O (1:9) upon exposure to ambient light.
### Table S6: Ru(Me bpy)$_2$(L4) nitrogen natural charge values in water environment

<table>
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<tr>
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<th>N$<em>{1}$, N$</em>{4}$</th>
<th>N$<em>{2}$, N$</em>{3}$</th>
<th>N$<em>{5}$, N$</em>{6}$</th>
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</thead>
<tbody>
<tr>
<td>Natural charge</td>
<td>-0.269</td>
<td>-0.075</td>
<td>-0.164</td>
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</table>

### Table S7: Ru(Me bpy)$_2$(L4) main orbitals character

<table>
<thead>
<tr>
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<th>S0 geometry</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>MeCN</td>
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<tr>
<td></td>
<td>HOMO</td>
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|       | ![Image](image13) | ![Image](image14) | ![
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References


Acknowledgements Text

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**Keywords:** CLICK chemistry • triazole • light switch • ruthenium • TDDFT calculations