Controlling Charge and Energy Transfer Processes in Artificial Photosynthesis

From Picosecond to Millisecond Dynamics

MAGNUS BORGSTRÖM
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Abstract

This thesis describes an interdisciplinary project, where the aim is to mimic the initial reactions in photosynthesis. In photosynthesis, the absorption of light is followed by the formation of charge-separated states. The energy stored in these charge-separated states is further used for the oxidation of water and reduction of carbon dioxide. In this thesis the photo-induced processes in a range of supramolecular complexes have been investigated with time resolved spectroscopic techniques. The complexes studied consist of three types of units; photosensitizers (P) capable of absorbing light, electron acceptors (A) that are easily reduced and electron donors (D) that are easily oxidised. Our results are important for the future design of artificial photosystems, where the goal is to produce hydrogen from light and water.

Two molecular triads with a D-P-A architecture are presented. In the first one, a photo-induced charge-separated state was formed in an unusually high yield (p>90%). In the second triad, photo-irradiation led to the formation of an extremely long-lived charge-separated state (τ = 500 ms at 140K). This is also the first synthetically made triad containing a dinuclear manganese unit as electron donor.

Further, two sets of P-A dyads are presented. In both, the expected photo-induced reduction of the electron acceptor is diminished due to competing energy transfer to the triplet state of the acceptor.

Finally, a P-P-A complex containing two separate photosensitizers is described. The idea is to produce high-energy charge-separated states by using the energy from two photons.

Keywords: Artificial photosynthesis, Electron transfer, Energy transfer, Ruthenium, Manganese, Charge-separated state, Donor-acceptor

Magnus Borgström, Department of Physical Chemistry, Box 579, Uppsala University, SE-75123 Uppsala, Sweden

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List of Publications

This thesis is based on the following papers.

I  Distance-independent Photoinduced Energy Transfer Over 1.1 to 2.3 nm in Ruthenium-tris(bipyridine)-Fullerene Assemblies
F. Chaignon, J. Torroba, E. Blart, M. Borgström, L. Hammarström, F. Odobel

II  Electron Donor-Acceptor Dyads and Triads Based on Tris(bipyridine) Ruthenium(II) and Benzoquinone: Synthesis, Characterization, and Photoinduced Electron Transfer Reactions
M. Borgström, O. Johansson, R. Lomoth, H. Berglund-Baudin, S. Wallin, L. Sun, B. Åkermark, L. Hammarström

III Electron Donor-Acceptor Dyads Based on Ruthenium(II) Bipyridine and Terpyridine Complexes Bound to Naphtalenediimide
O Johansson, M. Borgström, R. Lomoth, M. Palmblad, J. Bergquist, L. Hammarström, L. Sun, B. Åkermark

IV Intramolecular Charge Separation in a Hydrogen Bonded Tyrosine-Ruthenium(II)-Naphtalene Diimide Triad
O Johansson, H. Wolpher, M. Borgström, R. Lomoth, L. Hammarström, J. Bergquist, L. Sun, B. Åkermark
*Chemical Communications* **2004**, *194*, 194-195

V Light Induced Manganese Oxidation and Long-lived Charge Separation in a Mn$_2$$^{III}$-Ru$^{II}$-acceptor Triad
M. Borgström, N. Shaikh, O. Johansson, M. Anderlund, S. Styring, A. Magnusson, L. Hammarström
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VI Rapid Energy Transfer in Bichromophoric N$_6$/N$_3$C Ruthenium(II) Complexes
S. Ott, M. Borgström, L. Hammarström, O. Johansson
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Femtosecond Pump-Pump-Probe Investigation of a Ru(II)-Ru(II)-Acceptor Triad: Attempts at Achieving High Energy Charge-Separated States
M. Borgström, S. Ott, R. Lomoth, J. Bergquist, L. Hammarström, O. Johansson
Manuscript in preparation

Apart from the above mentioned papers I have also contributed to the following papers not included in the thesis, but referred to in the text.

Synthesis of a Ru(bpy)₃-type Complex Linked to a Free Terpyridine Ligand and Its Use for Preparation of Polynuclear Bimetallic Complexes
H. Wolpher, P. Huang, M. Borgström, J. Bergquist, S. Styring, L. Sun, B. Åkermark
Catalysis Today 2004, 98, 529-536

Synthesis and Properties of an Iron Hydrogenase Active Site Model Linked to a Ruthenium tris-bipyridine Photosensitizer
H. Wolpher, M. Borgström, L. Hammarström, J. Bergquist, V. Sundström, S. Styring, L. Sun, B. Åkermark
Inorganic Chemistry Communications 2003, 6, 989-991

Model of the Iron Hydrogenase Active Site Covalently Linked to a Ruthenium Photosensitizer: Synthesis and Photophysical Properties
S. Ott, M. Borgström, M. Kritikos, R. Lomoth, J. Bergquist, B. Åkermark, L. Hammarström, L. Sun
Inorganic Chemistry 2004, 43, 4683-4692

Sensitized Hole Injection of Phosphorous Porphyrin Into NiO: Towards New Photovoltaic Devices
M. Borgström, E. Blart, G. Boschloo, E. Mukhtar, A. Hagfeldt, L. Hammarström, F. Odobel
Submitted to Journal of Physical Chemistry B.

Synthesis and Characterization of Dinuclear Ruthenium Complexes Covalently Linked to Ru(II) tris-bipyridine: an Approach to Mimics of the Donor Side of PSII
Accepted in Chemistry - a European Journal

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Comments on my participation

I am responsible for all photophysical and photochemical work in papers I-XI, except for the laser flash/EPR studies of paper V. I contributed to the writing in all papers and carried the main responsibility for the writing in papers II, V and VII. In paper XII I performed parts of the femtosecond transient absorption measurement.
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What is it all about?

The condition of our planet could be better. Accelerating use of fossil fuels has reduced the reserves and drastically increased carbon dioxide levels in the atmosphere. We must do something! Our future energy supply has to be taken from large energy reservoirs and also be ‘clean’. Three possible alternatives are: thermal energy from the earth’s interior, nuclear energy from fusion or light energy from the sun. We go for the sun.

The incoming sunlight that reaches earth has a power of $1.76 \times 10^5 \text{ TW}$ and depending on the latitude the average power during daytime lies in the range 0.3-1.0 kW/m$^2$. In the year 2000 the total global energy consumption corresponded to an average power of 12.8 TW. Thus, in theory utilization of sun energy should be enough to produce all energy we need.$^1$ Our strategy when it comes to harvest sun energy is to mimic the green plants ability to convert light energy into chemical fuels. The plants have had over three billion years to optimize their processes, hopefully pretty close to perfection.

The success of photosynthesis lies in its ability to take electrons from water, for further use in the conversion of carbon dioxide to carbohydrates. The process is not very efficient and only ca. 1-5 % of the incoming light can be stored as biomass.$^2$ In oxygenic photosynthesis the initial photo-driven reactions takes place in two membrane bound protein complexes called photosystem I and II (PS I and PS II). Pigments in PS I and PS II absorb photons and in a first step the energy is converted into high-energy molecules like ATP and NADPH, later used for the reduction of carbon dioxide.$^3$ The stoichiometry of the initial reaction depends on many factors, like light intensity and protein environment. In its most energy efficient form, the balanced formula below should pretty well describe the reaction.

$$2H_2O + 4ADP + 2NADP^+ \rightarrow 4ATP + 2NADPH + h\nu \rightarrow O_2$$

It is interesting to estimate how efficient the formation of ATP and NADPH can be, based on the excited state energy of the pigments initiating the reaction. The unique chemistry in the reaction above is the oxidation of water. To make it possible with a minimum amount of energy consumed, four electrons have to be removed from two water molecules in a single step. Assuming pH 7 the free energy need for the full reaction in equation 1 will
then be 5.83 eV. Eight photons are required to drive the reaction and their energy, initially collected by the 'antenna system', is directed towards a chlorophyll in the reaction center. The total energy stored in 8 excited chlorophylls is 14.36 eV ($E_{00}=\Delta G^\theta$) and thus based on equation 1, ca. 40% of this energy can be converted to ATP and NADPH.

In an artificial photosystem the natural choice for the electron source would, in analogy with nature, be water. The reduced chemical fuel could on the other hand preferable be something else than carbohydrates. Since hydrogen is a possible base for future's energy economy, reduction of protons seems attractive. The free energy necessary to oxidize two water molecules and reduce four protons in a neutral water solution is 4.92 eV.

![Figure 1](image_url)

**Figure 1.** The three necessary building blocks in an artificial photosystem; an electron donor capable of oxidizing water (D), a photosensitizer collecting the light energy (P) and an electron acceptor capable of reducing protons. The vertical dotted line indicates how the reaction in principle can be separated into two parts by the use of two photosensitizers (P1 and P2), either connected by covalent bonds or a long range connection through a wire.

In order to create a functioning artificial photosystem at least three molecular units with different functions are required. First of all sunlight has to be absorbed by a photosensitizer (P) (Figure 1) producing an excited state capable of initiating electron movements in the system. In figure 2 the absorption spectra of the two photosensitizers Zinc(II)-tetraphenylporphyrin (Zn$^{II}$-TPP) and Ruthenium(II) tris-bipyridine ([Ru(bpy)$_3$]$^{2+}$) are shown. These photosensitizers are commonly used in artificial photosystems. The figure also contains the action spectrum correlating to the oxygen evolution from photosynthesis. The wavelength distribution of the sun intensity on earth is also included in the figure and shows that ca 40% of the sun energy lies in the range 300-600 nm where most pigments on earth absorbs. It is worth noting how efficient the photosynthetic proteins absorb light over the full range of the visible spectrum. This is due to the large number of pigments in to the antenna system. The artificial photosensitizers, based on only one chromophore, have more narrow absorption bands.
Figure 2. Comparison between the action spectrum for oxygen evolution of natural photosynthesis (solid line) and the spectra from two common photosensitizers used in artificial photosynthesis systems; Ruthenium *tris*-bipyridine ([Ru(bpy)$_3$]$^{2+}$) (dashed line) and Zinq-tetraphenylporphyrin (Zinc-TPP) (dotted line). The gray line shows the intensity distribution of the sun radiation in the same wavelength region.

Once the photosensitizer has been excited, the extra energy contained in it can be used to move an electron and a 'hole' across the system, creating a potential. The electron ends up on the acceptor side (A), while the hole ends up on the donor side (D). After two subsequent excitations a catalyst attached to A performs the proton reduction ($2\text{H}^+ + 2e^- \rightarrow \text{H}_2$). On the contrary, four excitations are necessary before the donor side catalyst (D) can perform the water oxidation ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^-$).

To succeed with this molecular architecture, a few problems have to be tackled. First of all the excited photosensitizer have to donate electrons to the reductive side of the system and extract electrons from the oxidizing side. These electron transfer events have to be controlled and well understood. A few of the electron transfer events will also be directly coupled to proton transfer (a field where the theories are still rather undeveloped, as are experimental model systems).\cite{5,9} Secondly, since water oxidation and proton reduction involve movement of four and two electrons respectively, accumulative electron transfer to the catalytic sites is necessary. Thirdly, since water oxidation and proton reduction are very slow reactions the transferred charges in the system has to remain separated for a long time for the reactions to occur. A fourth consideration is the use of
more than one photosensitizer. Nature uses two reaction centers (one each in PS I and II) and the 'antenna system' contains over hundred different chromophores for efficient light harvesting. Why should we be satisfied with one? In total, this makes the construction of an artificial photosystem a very delicate and complex matter.

In this thesis I present some of the work I have contributed to during my five years in the group. The systems studied are based on ruthenium-ligand photosensitizers with intense absorption in the visible region. Ruthenium chromophores are usually very robust, contrary to the fragile chlorophylls used in photosynthesis. For example ruthenium-tris-bipyridine can be stored for months in aqueous solution. As potential water oxidation catalyst we mimic nature and use manganese complexes.

In Chapter 2 of the thesis the main focus of my work is discussed together with some history of the field in general. Chapter 3 describes the different units of an artificial photosystem in detail. Chapter 4 contains a deeper introduction to the physical background of electron and energy transfer. In Chapter 5 some technical aspects of the measurements are covered and finally in Chapter 6 I go through the results of the molecular systems studied.
What we try to do and what’s already been done in the field of artificial photosynthesis

2.1 The main focus of this thesis

During my five years of research on photo-induced energy/electron transfer in donor-acceptor assemblies I have covered many of the areas relevant to artificial photosynthesis. In this thesis, however, I focus on two parts of the field where there is still much need for improvements. The first is the necessity to produce long-lived charge-separated states. In natural photosynthesis, four electrons have to be extracted from a manganese cluster before the water oxidation can take place. Each oxidation step is preceded by the absorption of a photon to the photosensitizer. Since the absorption rate is modest, the intermediate states where the manganese is partly oxidised, has to live long enough for the next photon to enter the system. A long lifetime of the charge-separated state is also necessary to allow for the slow water oxidation to occur. In PS II, the initial charge separation between a chlorophyll chromophore and an appended pheophytine is very fast (3-20 ps).\textsuperscript{12,13} This is crucial since the electron transfer rate has to compete with the short lifetime of the chlorophyll excited state (\(\tau \sim 5\) ns).\textsuperscript{14} Due to strong communication between the chlorophyll and the pheophytine the charge recombination rate is inevitably fast. Competing electron transfer to a secondary electron acceptor, however, extends the electron-hole distance and decreases the communication (see Figure 3a for details). This means that when the hole finally ends up on the manganese cluster, the electron already resides on a plastoquinone 35 Å away\textsuperscript{15,16} and the charge recombination reaction has slowed down to ca. 1 s.\textsuperscript{17} These are the charge-separated state lifetimes an artificial system has to compete with. For the complex discussed in paper V, comparable recombination rates was observed (see Figure 3b).

The second area covered in this thesis is the use of two photosensitizers instead of one. Nature uses two chromophores (P680 and P700) to drive the reaction and, as was discussed in chapter 1, ca. 40 % of the chlorophyll excited state energy is stored in chemical forms (ATP,
NADPH). Most artificial systems are based on one photosensitizer. If for example \([\text{Ru(bpy)}_3]^{2+}\) is used, more than 60% of the excited state energy (2.1 eV) has to be used for the oxidation of water and reduction of protons. It is clear that \([\text{Ru(bpy)}_3]^{2+}\) has a tough job to do. If two photosensitizers were used instead, a lower efficiency would be necessary. In paper VII a bichromophoric donor-acceptor assembly with a potential total available excited state energy of 3.7 eV is discussed (see Figure 3c). Another advantage with bichromophoric systems is that the two chromophores could be optimized individually either as reductant or as oxidant. This is often a problem when a single photosensitizer is acting as both reductant and oxidant.

**Figure 3.** The analogies with natural photosynthesis and the systems studied in this thesis is schematically illustrated. In (a) the main units of photosynthesis are drawn and the electron flow from \(\text{H}_2\text{O}\) via the membrane bound protein complexes; PSII (and the photosensitizer P680), Cytochrome bf and PSI (photosensitizer P700) finally reducing \(\text{NADP}^+\) by the protein Ferredoxin \(\text{NADP}^+\) oxidoreductase. The proton gradient that builds up over the membrane during the reaction is used to produce ATP in the enzyme ATP synthase. For a more detailed description of photosynthesis go to any basic biochemistry textbook. In (b) the architecture of the donor-chromophore-acceptor system studied in paper V is sketched and in (c) a simplified picture of the bichromophoric system studied in paper VII is shown.
When designing molecular systems with goals like these in mind one undoubtedly comes across unexpected behaviors of the investigated complexes. For example in both papers I and III undesirable energy transfer competed with the desirable electron transfer. Interestingly, the energy transfer rates discussed in paper I were almost distance independent, while in paper III the energy transfer product was only an intermediate state on the way to the desired charge separation. Further, in paper II a small energy difference between donor and acceptor states resulted in a non-obvious quasi equilibrium and in paper III the electron transfer rate increased with increasing donor-acceptor distance in contradiction with theory. One important conclusion from all these observations is that, despite well-developed basic electron transfer theories, it is very difficult to predict how a novel pre-designed donor-acceptor system will behave under experimental conditions. In the same way it is hard to determine expected electron transfer rates from theory. This is a very important statement since it justifies the time consuming experimental works laying the foundation for this thesis.

2.2 Artificial photosynthesis in a historical perspective

In the early 60's the importance of electron tunneling\(^1\) for the mechanism of photosynthesis was realised.\(^18\) The development of a general electron transfer theory had already started to evolve during the 50's, based on experiments on the electron exchange rate between metal ion pairs.\(^19\) Soon the experiments diverged and it was shown in the 70's that the photo-induced excited state of certain chromophores, with ruthenium tris-bipyridine as the leading example, could reduce a range of organic molecules through electron transfer.\(^20\) These discoveries led to the ideas of converting light energy into chemical energy and the field of artificial photosynthesis was born. Actually, the idea to mimic photosynthesis in the hunt for renewable energy sources had been suggested already in 1912, long before the underlying mechanisms were understood.\(^21\)

The construction of a functioning artificial system able to perform water oxidation and proton reduction requires control of the electron transfer reactions. To succeed with this the different components of an artificial photosystem should preferably have a fixed geometry. The general way to achieve this is to use covalently bound systems, and a range of donor-acceptor complexes have been published in the literature to date.\(^22-32\) Some of the early successful reports with covalently bound donor-acceptor systems include a porphyrin-quinone-quinone system published by Mataga and co-

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\(^1\) I use the term electron tunneling synonymously with electron transfer. In electron tunneling/transfer the electron tunnels through the potential barriers in contrast to the electron movement in a conducting wire.
workers in 1983, a carothene-porphyrin-quinone complex published by Gust, Moore and Moore in 1983, an amine-porphyrin-quinone system published by Wasielowski and co-workers in 1985 and a phenothiazine-ruthenium-paraquat complex published by Meyer, Elliot and co-workers in 1987. Later the Gust and Moores group developed their triad system and incorporated it into a liposome vesicle where it could shuffle protons across the membrane producing a proton gradient. By adding the enzyme ATP synthase to the membrane they could also control the production of ATP. This is still one of few examples where molecular based artificial photosystems has been used to produce chemical energy in a stable form.

To mimic the water oxidation in photosynthesis, the construction of donor-acceptor systems capable of shuffling around a single electron is not enough. Accumulative electron transfer is crucial to build up the necessary charge on the catalysts. Apart from our groups’ efforts with sequential manganese oxidation (see below), few reports with photosensitizers inducing accumulative-electron transfer exists. Another area of artificial photosynthesis, not yet coupled to photochemistry, is the research on the molecular catalysts capable of performing water oxidation (briefly discussed in chapter 3) and proton reduction. Intense research to increase the photon-capturing yield of the photosensitizer is also undertaken. This is necessary to be able to excite the same photosensitizer more than once in the short time window available, and thus allow for accumulative electron transfer. Many successful mimics of energy collecting antenna systems have been constructed. Finally, much work is focused on the task of optimizing the photophysical properties of the photosensitizer, for example increasing the excited state lifetime, tuning the reduction potentials and controlling the links to other units in donor-acceptor systems.

In our groups the main area of research so far has been to develop mimics of the donor side of PS II by linking ruthenium chromophores to various manganese complexes. Our result was the first evidence that photo-induced ruthenium(III) could oxidize manganese(II) in a covalently linked synthetic complex. However, energy transfer quenching by the manganese(II) unit became a problem when the distance to the ruthenium was small. The problem was partly solved by tuning the position of the excited state to the bipyridine most distal to the manganese. Nature seems to tackle this problem by adding an intermediate tyrosine, which allows for a long chlorophyll-manganese distance and yet a rapid electron transfer sequence. In later work on a ruthenium(II)-bis-manganese(II,II) complex we could show accumulative electron transfer from the manganese unit to photo-induced Ru III, generated with the sacrificial electron donor cobalt(III)pentaminechloride. The manganese unit could in these experiments be sequentially oxidised from Mn II,II to Mn III,IV.

Recently we have started to explore how to develop the hydrogen evolving side of artificial photosynthesis. The strategy is biomimetic and the models are the catalytic site of the iron only hydrogenases. The
hydrogenases are proteins performing reversible proton reduction in many micro-organisms including photosynthetic cyanobacteria. We have so far been able to show electrochemical evolution of hydrogen in a catalytic way. However our initial attempts to drive the reaction with photons (paper IX and X) did not succeed.
Which units are required for a functioning artificial photosystem

As mentioned in previous chapters at least three units are required for a functioning mimic of photosynthesis. These are the photosensitizer for photon capture and two catalytic sites where the actual redox chemistry can take place. In reality these three units are not enough and intermediate electron acceptors and donors are necessary to control the reaction. Also the properties of the connecting bridges are important for the electronic communication between the different units. In this chapter the individual building blocks of an artificial photosystem are described.

3.1 Photosensitizers

Some desirable properties of a well operating photosensitizer are: stability, high absorption in the visible region, suitable reduction potentials, sufficiently long lifetime of the excited state and a low inner reorganization energy to allow for fast electron transfer. Nature’s use of chlorophylls is not optimal in artificial systems due to its low stability. Three alternative types of photosensitizers are generally considered. Aromatic organic molecules could in principle be used, but the short lifetime of the excited state together with unfavorable redox properties and, typical, a high-energy absorption makes them unattractive in general. One exception is the very popular chlorophyll like porphyrins. Porphyrins are organic molecules with an 18-electron aromatic ring system, where a metal is often coordinated inside the ring to alter molecular properties, such as the reduction potential. For example, zinc(II)-tetraphenylporphyrin (see Figure 1) is easy to oxidize and the singlet excited state lifetimes has a lifetime of ca. 4 ns. An interesting property of the porphyrins is the possibility to drive reactions from a higher lying singlet state that lives for ca. 1 picosecond. A potential problem with singlet excited states is the possibility of fast de-excitation through Förster energy transfer (see Chapter 4).

The third type of commonly used photosensitizer, is transition metal complexes with six electrons in the d-orbitals forming a low spin configuration. When π-accepting ligands coordinate to the metal, these
complexes may give rise to intense metal-to-ligand charge transfer (MLCT) transitions with large absorption bands in the visible region. Depending on their coordinated ligands metals such as Ru$^{II}$, Os$^{II}$ and Re$^{I}$ all possess these MLCT bands.$^{53}$ In this thesis Ru$^{II}$ chromophores are used and a simplified view of the possible transitions in [Ru(bpy)$_3$]$^{2+}$ is sketched in Figure 4.

![Figure 4. The absorption spectrum of [Ru(bpy)$_3$]$^{2+}$ with some of the dominant transitions marked. The orbital energy diagram shows how ruthenium’s d-orbitals are split due to interactions with the ligands. In Ru$^{II}$ electrons are filled up to the t$_{2g}$ orbitals. The state energy diagram show how the initially excited $^1$MLCT state decays to the $^3$MLCT state. The $^3$MLCT state can decay through $^3$MC states reached thermally.](image)

Ligand field theory predicts that in metal(ligand)$_6$ complexes the five degenerated d-orbitals split due to coulombic interactions.$^{55}$ Thus, as seen in Figure 4, the energy levels of the three orbitals with low electron density along the ligand axis will decrease in energy, while the two orbitals with high density along the ligand axis will increase in energy. For [Ru(bpy)$_3$]$^{2+}$ the above mentioned MLCT transition centered around 452 nm has a rather high extinction coefficient around 15 000 cm$^{-1}$M$^{-1}$. Due to the heavy ruthenium ion the initial excited $^1$MLCT state quickly ($\tau < 100$ fs) spin flips into the triplet state,$^{56,57}$ which has a lifetime around 1 µs (298K) and an excited state energy of 2.12 eV.$^{11}$ This triplet excited state is actually split ($\Delta E \sim 100$ cm$^{-1}$) into three close lying states due to low symmetry. The
decay from these $^3$MLCT states, in the absence of an external quencher, occurs via phosphorescence ($\phi=0.06$), non-radiative transitions or via thermal population of higher lying metal centered ($^3$MC) states.$^{58}$

Depending on the relative position of the $^3$MLCT and the $^3$MC states the deactivation through the $^3$MC state can be very fast. For example in $[\text{Ru(tpy)}_2]^2+$ the distorted octahedral symmetry of the molecule decreases the ligand field strength and thereby the energy of the $^3$MC state. Thus the lifetime of the excited state is reduced to ca. 250 ps (298 K).$^{59}$ Population of the short lived $^3$MC states is also seen in $[\text{Fe(bpy)}_3]^2+$ where the ligand field strength is lower due to the lower mass of iron. The opposite effect is observed for $[\text{Os(bpy)}_3]^2+$ where the energy of the $^3$MC states increases due to the heavier nucleus.$^{60}$ The excited state lifetime is however shorter than in $[\text{Ru(bpy)}_3]^2+$ due to faster non-radiative transition, as predicted by the energy gap law.$^{61}$

The magnitude of the electronic coupling between adjacent bipyridine units in $[\text{Ru(bpy)}_3]^2+$ determines if the $^3$MLCT is localized on one of the bipyridines or delocalized over all three of them. Resonance Raman studies have shown that the initial excitation is localized on a single ligand.$^{62}$ There is however an ongoing debate concerning the rate of electron hopping between the different ligands. Some studies indicate that this happens on a timescale of tens of picoseconds,$^{63}$ while other studies show that the initial high anisotropy expected from a localized state is lost within a few hundreds of femtoseconds,$^{64}$ which would then set the limit for the electron hopping rate. This is an important issue since a slow electron transfer rate between the bipyridine ligands might limit the electron transfer to an attached acceptor.

There are many strategies to alter the excited state properties of transition metal complexes. The $^3$MLCT state could be raised or lowered by attaching electron accepting (amides, halogens, etc.) or donating substituents (-CH$_3$, etc.) to the pyridines.$^{65-67}$ An alternative strategy to lower the $^3$MLCT state is to use ligands with more conjugated and lower lying $\pi^*$-orbitals.$^{68-70}$ This strategy has been shown to be more pronounced when the conjugated unit is attached to the 4´ position than to the 5´ position.$^{68}$ By the use of different ligands, in a heteroleptic complex, the excited state can in these ways be localized to a specific ligand.

A potential problem when synthesizing a new donor-acceptor system is the formation of geometrical isomers. Isomers will reduce the spatial control of the different units in the system. Building a donor-chromophore-acceptor assembly from $[\text{Ru(bpy)}_3]^2+$ give, for example, rise to four different geometrical isomers (see Figure 5). To get rid of the isomers it is possible to exchange the bipyridines for terpyridines, giving instead a $C_2$ symmetry.$^{71}$ As mentioned on the previous page the excited state lifetime of $[\text{Ru(tpy)}_2]^2+$ is however very short ($\tau\sim250$ ps). An interesting strategy to solve this problem is to increase the octahedral symmetry of the photosensitizer by adding an extra methylene group between two of the pyridines. In this way
the lifetime of the excited state increased to ca. 15 ns. Another strategy to design long-lived chromophores with C<sub>2</sub> symmetry (used in paper VI and VII) is to use carbanion ligands. With the negative charge on the ligand the chromophore will become a much better reductant (E<sub>1/2</sub> = 0.10 V vs. Fc<sup>+/0</sup>) as compared to [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (E<sub>1/2</sub> = 0.88 V vs. Fc<sup>+/0</sup>).

![Schematic picture showing the possibility for geometrical isomers in a donor-acceptor substituted [Ru(bpy)<sub>3</sub>]<sup>2+</sup>. With a single A-substituent four isomers are possible (A<sub>1</sub>-A<sub>4</sub>). The isomer problem disappears in [Ru(tpy)<sub>2</sub>]<sup>2+</sup> with a C<sub>2</sub> symmetry.](image)

### 3.2 Primary electron acceptors and donors

Small organic molecules and metal complexes are commonly used as redox intermediates in donor-acceptor complexes. Since their role is to shuffle electrons and holes through the system the reduction potential and the electron coupling to adjacent units are the main properties governing their function. Factors like pH and charge, which alters the solvent dependence of electron transfer, can also be important. The driving force for an electron transfer reaction can be calculated with the Rehm-Weller equation:

\[
\Delta G^0 = e \left( E_{1/2} (D_{ox/reduced}) - E_{1/2} (A_{ox/reduced}) \right) + w_p - w_r
\]

In the equation \( E_{1/2} (D_{ox/reduced}) \) and \( E_{1/2} (A_{ox/reduced}) \) are the reduction potentials for the donor and acceptor, \( w_p \) and \( w_r \) are the work terms arising from coulombic interaction and \( e \) is the elementary charge.

\[
w_{r,p} = \frac{e^2 Z_D Z_A}{4\pi\varepsilon_0\varepsilon_{solv}r}
\]
In equation 3 $\varepsilon_{solv}$ is the solvent dielectric constant, and the Z's are the charge on the donor and acceptor.

In this thesis the following electron acceptors has been used in various systems; fulleropyrrolidine ($E_{1/2} = -0.92$ V vs. Fe$^{+0}$ in DMF), benzoquinone ($E_{1/2} = -0.93$ V vs. Fe$^{+0}$ CH$_3$CN), naphtalenediimide ($E_{1/2} = -0.96$ V vs. Fe$^{+0}$ in CH$_3$CN) and pyromellitimide ($E_{1/2} = -1.21$ V vs. Fe$^{+0}$ in CH$_3$CN).

3.3 Water oxidizing site

Once the photo-induced charge separation processes work properly they have to be coupled to water oxidation. Water oxidation is the mystery of PS II and scientists still do not understand the mechanism behind it. A few things are worth mentioning regarding the progress in the field. The water-oxidizing complex in PS II contains four manganese ions together with one calcium ion. For the catalytic cycle to function a chloride ion is also necessary. There is an ongoing debate on what oxidation number the manganese ions reach during the cycle and how many of the manganese’s are actually involved in the direct bond making chemistry. Both questions are of prime interest for the constructions of functioning mimics. Another problem worth considering when thinking in terms of designing mimics is the structural changes which probably accompany the catalytic cycle. These bond changes will probably make the synthetic complexes highly fragile. For example the PS II proteins themselves are very sensitive to light and are frequently replaced. Albeit these replacements are due to damages on the protein structure itself it is still worth mentioning since it reflects the very different conditions between natural and artificial systems.

In the literature a few examples of dinuclear manganese and ruthenium complexes are reported to perform catalytic water oxidation by the use of external oxidants. However, the actual mechanism is debated. The complexes supposed to perform water oxidation all contain two metal ions connected by $\mu$-oxo bridges. In one of the complexes (Figure 6) the proposed mechanism involves formation of a manganese(V)-oxo species, which is believed to undergo nucleophilic attack by a hydroxide ion. This reaction only function with a sacrificial oxygen atom donor. When the complex in Figure 6 was incorporated into a clay catalytic oxygen evolution was possible with a cerium(IV) salt, although very slowly (4 turnovers in 6 hours). Quantum mechanical calculations have suggested that a similar mechanism involving a manganese(VI)oxo species could explain water oxidation within reasonable potentials. In paper VIII we tried to link the same manganese complex directly to [Ru(bpy)$_3$]$^2+$ to see if it was possible to drive the catalytic reaction with light. However, these experiments were not successful. In other manganese and ruthenium complexes capable of
performing water oxidation a bimolecular mechanism is suggested where two manganoses are co-coordinated to water forming a $\mu$-oxo bridge. In one manganese complex with a Mn$_4$O$_4$ cubane structure it was shown that two of the $\mu$-oxo bridges could be converted into water with the hydrogen source phenothiazine.$^8$ This complex however, did not show any catalytic effect. The water oxidation catalysts so far reported all suffer from low stability and breaks down after a few turnovers. If they are to be used in reality they will likely need to be stabilized in some kind of solid frame. In paper V we discuss a triad containing a dinuclear manganese(II,II) unit.

Figure 6. One of few synthetic manganese complexes supposed to undergo catalytic water oxidation.

3.4 Bridges linking the units

The term bridge is somewhat vague but my definition here is a connecting unit, which itself is not reduced or oxidized during the electron transfer process. Even though electrons do not transiently populate the bridge it can alter the communication between the units. The theory of bridge mediated electron/energy transfer will be briefly summarized in chapter 4. In this thesis methylene, amide, phenylene and acetylene bridges have been used. With a flexible bridge based on methylenes it is hard to control the intra-unit separation and thus stiff bridges like phenylenes and acetylenes are often preferred. In paper I we use oligo phenyl acetylene units of varying lengths to bridge the donor-acceptor couple. These units are rigid and have high conjugation and are therefore commonly used. Phenyl acetylenes are also easy to alter chemically by substitutions on the phenyl units. A consideration when using phenyls in the bridge is that the rotational angle between adjacent units could change for different electronic states and this would alter the grade of electronic conjugation.$^{70,85}$ This effect is most likely seen in paper III.
How the units communicate

4.1 Golden rule

The communication between different units in a supramolecular complex depends on the overlap of the wave functions of the initial and final state. Fermi and Dirac have derived a simple expression, valid in the weak coupling limit, predicting the probability per unit time that population of one electronic state dissipates into a different one.\(^8\)

\[
k = \frac{2\pi}{\hbar} |V_{DA}|^2 \delta(E_D - E_A)
\]  

(4)

This often called Fermi golden rule is a cornerstone in quantum chemistry when dealing with intramolecular dynamics. In equation 4 the dirac function \(\delta\) guarantees that energy is conserved and \(V_{DA}\) is the interstate coupling between the initial donor state (D) and the final acceptor state (A). For many applications a valid approximation is to split \(V_{DA}\), which is dependent on both electronic and nuclear interactions, into the electronic coupling \(H_{DA}\) and the vibrational overlap \(\langle \chi_D | \chi_A \rangle\). If transitions between a manifold of vibrational excited states are allowed, with vibrational quantum numbers \(M\) and \(N\), the golden rule expression can then be written as.

\[
k = \frac{2\pi}{\hbar} H_{DA}^2 \left( \sum_{M,N} f(E_{DM}) |\chi_{DM} \rangle |\chi_{AN} \rangle|^2 \delta(E_{D0} - E_{A0} + h\nu(M - N)) \right)
\]  

(5)

In equation 5 \(f(E_{DM})\) is the Boltzmann populated distribution of donor states and \(\nu\) is the fundamental frequency for the vibration in question. The factor in parenthesis is usually referred to as the Franck-Condon weighted density of states. In many systems the Condon approximation is also valid meaning that the electronic coupling \(H_{AD}\) is assumed to be independent on nuclear coordinates. Based on the golden rule it is possible to derive more detailed expressions where electron transfer and energy transfer rates can be predicted from experimental observation.
4.2 Electron Transfer

In donor-acceptor systems designed for artificial photosynthesis it is important that the units of the systems can act independently, since electrons and holes will be shuffled stepwise through the molecular assembly finally ending up on the catalytic sites for water oxidation and proton reduction.ii This condition is achieved if the electronic communication between the units is modest. It is, of course, somewhat diffuse to define what is meant with a modest coupling. Anyway, the condition referred to as non-adiabatic electron transfer occurs when the time scale for nuclear motions is much faster than the time it takes for the electron to tunnel from the donor to the acceptor state. In energetic terms this happens when $H_{DA} < k_b T (0.025 \text{ eV})$.87

In the 50’s R. A. Marcus investigated the behavior of electron transfer based on the golden rule formalism. He concluded that for many common reactions only three experimentally measurable quantities, namely the reaction free energy ($\Delta G^0$) the reorganization energy ($\lambda$) and the electronic coupling ($H_{DA}$) are necessary to determine the electron transfer rate experimentally.88 In Figure 7 the parabolic free energy surfaces (PES’s) for the electronic states of the triad covered in paper V are sketched together with the definitions of $\Delta G^0$, $\lambda$ and $H_{AD}$. In his early work Marcus did not account for the possibility of nuclear tunneling but instead assumed that electron transfer could only occur over the barrier $\Delta G^*$ where the PES’s for the reactant and product state intersects. The assumption that nuclear tunneling is negligible is valid if the intersection point can be reached thermally and the vibrational spacings are small ($k_b T > \hbar \nu$).87 Under these conditions the density weighted Frank-Condon factor in equation 5 can be rewritten according to the general Marcus equation.

$$k_{ET} = \frac{2\pi}{\hbar} \left| H_{DA} \right|^2 \frac{1}{\sqrt{4\pi\lambda k_b T}} \exp\left( -\frac{(\Delta G^0 - \lambda)^2}{4\lambda k_b T} \right) \quad (6)$$

In equation 6 the Frank-Condon factor is split into the pre-exponential factor $\left(1/(4\pi\lambda k_b T)^{1/2}\right)$ arising from the thermal distribution of the donor state, and an exponential factor containing the activation energy $(\Delta G^* = (\Delta G^0 - \lambda)/4\lambda)$ necessary to reach the crossing point.

If nuclear tunneling has to be accounted for, either due to low temperature or if $\hbar \nu > k_b T$ (or if the reaction occurs in the inverted region, iii

---

ii In principle a large electronic coupling could be used in an artificial photosystem to induce a direct charge transfer excitation between two units.
Figure 7. Potential energy surfaces for the different states involved in the photochemistry of the Mn-Ru-NDI triad (D-P-A) discussed in paper V. The dashed line shows the photo-induced charge-separation following the classical Marcus theory where the transition is allowed only at the surface crossing points. The driving force ($\Delta G^0$), the reorganization energy ($\lambda$), the activation energy ($\Delta G^*$) are marked. In the inset, the electronic coupling ($H_{DA}$) is shown as half the energy split between the two adiabatic potential energy surfaces involved in the recombination reaction. The reaction coordinate is arbitrary and not the same for all states.

(see below), equation 6 has to be modified and include terms for electron transfer from vibrational donor states other than those close to the PES crossing point. Some simplifications of the golden rule are however possible also here. Usually only one or a few donor states are populated and if the vibrational frequencies are the same in the donor and the acceptor states the vibrational overlap functions can be condensed to:

$$\left| \left( \chi_{DA} | \chi_{AN} \right) \right|^2 = \left( S_{MA}^N / N! \right) \times \exp(-S_M)$$

(7)
by the use of the Huang-Rhys factor, $S_{\text{H-R}} = \frac{\lambda}{h \gamma_d}$, relating the nuclear displacement between the donor and acceptor states.\(^8\)

Maybe the most important result from the Marcus equation is the introduction of the reorganization energy ($\lambda$). Together with the driving force ($\Delta G^\#$) it condenses the difficult calculation of a range of different vibrational couplings into two measurable quantities. The driving force can be obtained from electrochemical data and the reorganization energy from the temperature dependence of the electron transfer rate. The reorganization energy can be understood as the energy necessary to bring the nuclei of the donor state into the nuclear configuration of the acceptor state, still remaining on the diabatic PES of the donor state. A common convention is to separate nuclei belonging to the molecular system where electron transfer takes place, which contribute to the inner reorganization energy ($\lambda_{\text{in}}$), from nuclei contained in the surrounding medium contributing to the outer reorganization energy ($\lambda_{\text{out}}$). The reorganization energy ($\lambda = \lambda_{\text{in}} + \lambda_{\text{out}}$) can be calculated according to equations 8 and 9.\(^8\)

$$\lambda_{\text{in}} = \frac{1}{2} \sum k_i \Delta q_i^2$$  \hspace{1cm} (8)

$$\lambda_{\text{out}} = \frac{\Delta e^2}{4\pi\varepsilon_0} \left( \frac{1}{\varepsilon_s} - \frac{1}{\varepsilon} - \frac{1}{2a_d} + \frac{1}{2a_A} - \frac{1}{r} \right)$$ \hspace{1cm} (9)

In equation 8 $k_i$ are the normal mode vibrational force constants and $\Delta q_i$ the nuclear displacements for the vibrations. The expression for $\lambda_{\text{out}}$ is based on a model where the solvent is treated as a dielectric medium where the donor and acceptor have spherical form. In the equation $a_1$ and $a_2$ are the radii of the donor and acceptor, $\varepsilon_s$ and $\varepsilon$ are the optical and static dielectric constants of the solvent and $\Delta e$ is the transferred charge. The nuclei of the solvent will only respond to a change in the polarization of the donor-acceptor complex (an effect of the induced electron transfer) if the solvent is polar. For unpolar solvent the contribution to $\lambda_{\text{out}}$ is therefore very small. For donor-acceptor systems in polar solvents $\lambda_{\text{out}}$ is usually in the range 0.5-1 eV.\(^8\) The contribution from $\lambda_{\text{in}}$ to $\lambda_{\text{out}}$ is often small. An exception is found for the triad discussed in paper V where $\lambda_{\text{in}}$ is close to 1 eV.

Another important prediction from the Marcus theory is the so called inverted region. When the driving force is increased the reaction will eventually reach an activation-less region ($\Delta G^\# = \lambda$), when the electron transfer rate will be at its maximum. A further increase of the driving force will slow down the electron transfer rate since the energy at the point where the donor and acceptor PES’s crosses will again increase. An important study in the field of electron transfer was published by Closs and Miller in
where they showed the predicted effect of the inverted region. In that study they determined the electron transfer rate in a range of similar donor-acceptor complexes where they changed the driving force ($-\Delta G^0$) by shifting the reduction potential of the electron acceptor. The inverted region has later been used in many donor-acceptor systems to increase the lifetime of charge-separated states (for example in the triad discussed in paper II). In the inverted region the nuclear overlap increases and quantum effects may have to be included. Thus, the actual decrease in electron transfer rate, with increased driving force, will not be as drastic as predicted from the classical Marcus equation.92

4.3 Energy Transfer

In photosynthesis energy transfer can both be desirable and a problem. Fast energy transfer to the reaction center chlorophylls is important but once the energy is located at the reaction center further energy transfer quenching will just decrease the yield of electron transfer products. Thus, control of the energy transfer pathways is crucial. When the interstate coupling, $H_{\text{DA}}$, is expressed for energy transfer it results in two separate terms depending on if the electrons will interchange between the donor and acceptor units or not.iii If the electrons involved in the transition do not exchange the coupling between the donor and acceptor will be a pure coulombic dipole-dipole interaction and the energy transfer rate will decrease as $1/r^6$ where $r$ is the inter unit distance. This regime of energy transfer is named after Förster who first derived a correct expression for it.93

\begin{equation}
    k_{\text{Förster}} = \frac{9000(\ln 10)\kappa^2 \phi_d}{128\pi^2 n^5 N_A r_0^6 \tau_d} \int_0^\infty F_d(\tilde{\nu}) e_a(\tilde{\nu}) \frac{1}{\tilde{\nu}} d\tilde{\nu}
\end{equation}

In the expression $\kappa$ accounts for the different direction of the transition dipole moments in the donor and acceptor. $\phi_d$ is the fluorescence quantum yield from the donor, $n$ is the refractive index of the solvent and $\tau_d$ is the intrinsic lifetime of the donor excited state. The integral contains the integrated absorption spectrum from the acceptor, $e_a(\tilde{\nu})$ together with the normalized emission spectrum from the donor, $F_d(\tilde{\nu})$. Due to the weak distance dependence of dipole interactions the Förster transfer can take place over very long distances (~100Å).94 Since the Förster mechanism is a dipole interaction the transfer rate depends on the transition dipole moments. Hence

iii Note the similarities with the column matrix $J$ and the exchange matrix $K$ when the Hamiltonian for the many electron Shrödinger equation is solved.
the energy transfer can be very fast for singlet to singlet excited states, for example from the porphyrins $S_1$ states.

The other type of energy transfer occurs if the electrons are exchanged during the reaction. The exchange energy transfer is based on the same physical laws that governs electron transfer. It is thus possible to derive a similar expression for the rate based on $\Delta G^*$, $\lambda$ and $H_{DA}$. This region of energy transfer was first treated by Dexter and the rate decreases exponentially with distance like the orbital overlaps.\(^95\) For singlet to singlet energy transfer the exchange rate is usually small compared to the Förster rate. However for triplet to triplet transitions, due to the low transition dipole moments, the mechanism may dominate and can be observed over distances up to $\sim$10 Å or even longer if the bridging medium mediates the transfer.\(^96\)

### 4.4 Bridge mediated electron and exchange energy transfer

When the intervening region between donor and acceptor is a vacuum the interstate coupling, $H_{DA}$, decreases exponentially with distance in parallel with the decreasing orbital overlap.

$$H_{DA} = H_{DA}^0 \times \exp(-\beta(r_{DA} - r_{DA}^0))$$  \hspace{1cm} (11)

Here $H_{DA}^0$ is the coupling when the donor and acceptor are separated by the distance $r_{DA}^0$, $\beta$ is a constant characteristic for every medium and $r_{DA}$ is the donor acceptor distance. In vacuum a common value of $\beta$ for many molecules is $\sim$3 Å\(^{-1}\), meaning that the decay rate decreases with a factor 20 per Ångström.\(^{31}\) If a medium instead fills up the space in between donor and acceptor, the quantum states of the medium may be involved and significantly increase the interstate coupling, thereby increasing the electron transfer or exchange energy transfer rate.\(^{97}\)

The bridge-mediated transfer can be divided into two separate regions. If the energies of the bridge states are very close or even below the donor state energy, and the vibrational relaxation time is faster than the timescale for electronic tunneling, a ‘hopping mechanism’ is possible where the bridge levels are transiently populated.\(^{87}\) The distance dependence for the ‘hopping mechanism’ is weak and depends only on the coupling between neighboring bridging units multiplied by the number of such units. Electron transfer in this regime can therefore take place over very long distances.

When the energy levels of the bridging units are high or the vibrational relaxation time is too slow to allow for a discrete population of the bridge, the bridge can still mediate an increased transfer rate. The interstate coupling ($H_{DA}$) using a first order perturbation theory, will then depend on the donor-
bridge coupling, $H_{DB}$, the bridge-acceptor coupling, $H_{BA}$, and the energy difference between the donor state and the bridge state. $^{37,28}$

$$H_{DA} = \frac{H_{DB}H_{BA}}{E_B - E_D}$$

Electron transfer in this regime is said to occur through a ‘super exchange mechanism’, and there is an exponential decrease of the interstate coupling with donor acceptor distance, like in equation 11. However, with a significantly lower value for $\beta$ compared to when the intervening space is a vacuum.

Gray and co-workers have studied the distance dependence of electron transfer in proteins and found exponential decays of electron transfer with distance. The observed $\beta$-values lies between 1-1.5 Å$^{-1}$. $^{97,99}$ These $\beta$-values are much lower than in vacuum even though the electron transfer occurs through a mainly saturated bond network of amino acids. When the donor and acceptor are covalently linked by a straight, all-trans, saturated bridge the $\beta$-value is 0.8-1 Å$^{-1}$ and with a conjugated bridge the $\beta$-value can be even lower. $^{31}$ Another interesting study on bridge mediated electron transfer was done by Wasielewski and co-workers. They showed how the transfer mechanism changes from a ‘super exchange mechanism’ to a ‘hopping mechanism’ when the number of units in the conjugated oligophenylene bridge between a phenothiazine and a perylenediimide increased. $^{100}$ We observe a similar tendency for the energy transfer discussed in paper I.
Which laboratory techniques were used

Excited state dynamics can be measured through different kinds of time resolved spectroscopic techniques. In this thesis the main technique used is transient absorption, which measures the changes in absorption of a sample before and after some perturbation of the system. The perturbation in our measurements is a photon transferring the sample molecules into new exciting electronic states. The transient absorption signal can be expressed as:

\[
\Delta \text{abs} = -\log(I_{\text{PIS}}/I_{\text{ref}}) - (-\log(I_{\text{GS}}/I_{\text{ref}})) = \log(I_{\text{GS}}/I_{\text{PIS}})
\]  

(13)

where \(I_{\text{ref}}, I_{\text{PIS}}\) and \(I_{\text{GS}}\) are the intensities of a light beam after it has passed the sample in its ground state \((I_{\text{GS}})\) in its photo-induced state \((I_{\text{PIS}})\) and after having passed a reference medium not containing the sample \((I_{\text{ref}})\). In my work two alternative transient absorption techniques are used covering different time regions. With pump-probe the dynamics from ca. 100 fs up to 10 ns is possible to follow and with flash photolysis we can probe dynamics slower than 20 ns. This leaves a region around ten nanoseconds where no information is obtained. Unfortunately some of the initial processes in both natural and artificial photosystems happen on these time scales. The tens of nanosecond region is not totally invisible however, and it is possible to follow emission dynamics by single photon counting. The photon counting technique allows dynamics slower than \(~10\) ps to be probed.

5.1 Pump-Probe

In the pump-probe technique a pump pulse excites the sample molecules, while a probe pulse is used to measure the absorption. The idea is to use the same light source for both the pump and the probe and in this way let the speed of light determine the instrumental time resolution instead of electronic constraints. In Figure 8 our pump-probe set-up is pictured and shows how the source pulse, with 800 nm wavelength, is split into two parts by a beam splitter. The pump pulse is converted to a suitable pump.
wavelength by non-linear optical effects in an optical parametric amplifier (OPA), before it hits the sample. The probe light passes through a movable delay line before reaching the sample and by changing the path length the sample can be probed at suitable times relative to the time when the pump pulse hits the sample (light travels 1 cm in 33 ps). To probe other wavelengths than 800 nm the probe pulse is focused into an optical medium (sapphire or CaF₂ crystal) where it produces a continuous white light.

The parameters setting the limit for the pump-probe experiment is the precision with which the delay line can be moved and the width of the light pulses. The delay line used in our system can be moved in accurate steps of 10 μm (30 fs) and the pump and probe pulses have a temporal width of ca. 200 fs. Thus the lower detection limit of our system is ca. 100 fs.

To produce the very short light pulses, a mode locked Ti-sapphire laser, pumped by an Argon-ion laser, is used. The output from the Ti-sapphire laser is low intensity 800 nm pulses at 76 MHz with a temporal width of ~80 fs. To increase the pulse energy necessary for the experiments the intensity of the pulses is first decreased by broadening their spectral width. Some of these weaker pulses are further amplified in a second Ti-sapphire medium. After recompressing the pulses the output at 800 nm is ca. 1 mJ, with a frequency of 1 kHZ. These pulses can be used in the experiments.

To be able to measure the ground state spectrum and calculate the Δabs-data a chopper blocks every second pump pulse. The transmitted probe light is then detected on a photoactive diode array and a computer program calculates the Δabs-signal. For a more detailed description of the system see the papers.

Figure 8. The experimental setup used in the pump-probe experiments.
5.2 Flash photolysis

In the flash photolysis technique a Q-switched Nd:YAG laser generates light pulses with a temporal width of ca. 5 ns. After passing an OPO, pulses with ca. 20 mJ energy are obtained, tunable from 410-680 nm. The laser pulse excites the sample while a probe light (150 W Xe-lamp) irradiates the sample. The transmitted probe light enters a monochromator and light with the selected wavelength is collected by a photo multiplier. The current signal generated is then converted to readable data in a digital oscilloscope. Figure 9a shows a simplified view of the setup.

5.3 Time-correlated single photon Counting

Time-correlated single photon counting is a statistical method to measure time-resolved emission. In this method one photon at the time is collected by a photo multiplier. Light pulses, with a frequency of 200 kHz and a wavelength of 400 nm, enter the instrument. The pulses are focused on the sample and perpendicular to the incoming light the emission is detected by a micro channel plate photo multiplier. Since the method is statistical, the intensity of the pump light has to be weak enough so that only one photon reaches the photo multiplier during the experimental time window. The time between the arrival of this photon and the arrival of the light pulse to the system, detected by a photodiode is then stored. By collecting a large number of data points a histogram with hits versus time can then be generated. Figure 9b shows a simplified view of the setup.

![Figure 9. The experimental setup used in, (a) the flash photolysis experiments and (b) the photon counting experiments.](image-url)
About the systems investigated in this thesis

The research on artificial photosynthesis, in our group, has so far mainly focused on the water oxidizing donor side. In those works external electron acceptors, like methylviologen or cobolt(III)pentaminechloride, have been used to remove electrons from the excited chromophore. For the control of the charge separation and the very fast initial electron transfer events necessary for artificial photosystems, intramolecular electron acceptors will be crucial. All papers in this thesis involve intramolecular electron acceptors to achieve better control of the initial electron transfer events in artificial photosystems. In this chapter the interesting observations in a diverse range of systems are summarized.

6.1 Ruthenium(II)-Fullerene

(Paper I)

This study was from the beginning initiated to investigate the use of C60 fullerenes as electron acceptors. The high aromaticity of fullerenes makes them easy to reduce and up to 6 reversible reductions are possible to detect with cyclic voltametry.101 Another favorable property with the fullerenes is the low reorganization energy required for reduction. This is an effect of the large size of the molecule, effectively delocalizing the charge. The low reorganization energy favors fast forward electron transfer in the Marcus normal region and slow recombination in the inverted region. The behavior has been observed in porphyrin-fullerene dyads.102,103 However, only a few examples of electron transfer from RuII to fullerene have been reported.104,105 This is due to the low lying triplet state of fullerenes, which favors energy transfer over electron transfer. In our study three [Ru(bpy)3]2+-C60 dyads linked by phenyl-acetylene spacers of varying length (1.1-2.3 nm) was investigated. Figure 10 shows the three dyads together with their references lacking the fullerene units.

If the ruthenium excited state is quenched by the appended C60 unit, three different mechanisms are possible. The first possibility is electron transfer, *RuII-S-C60 → RuIII-S2-C60+. The driving force in acetonitrile calculated from the Rehm-Weller equation is almost equal for all three
dyads, \( \Delta G^0 = -0.25 \text{ eV} \). The second alternative would be energy transfer, \( *Ru^{II}-S-C_{60} \rightarrow Ru^{II}-S_2-*C_{60} \). The triplet state of the fullerene lies at 1.45 eV giving a driving force, \( \Delta G^0 = -0.56 \text{ eV} \). Finally there is the possibility for initial electron transfer followed by subsequent decay to the fullerene triplet state.

The absorption spectra of all complexes can be understood as a sum of the individual components. However, in Ru \( II-S_2-C_{60} \) and Ru \( II-S_3-C_{60} \) the increasing strength of the \( S_0S \) \( ^* \) transitions of the phenyl-acetylene bridge significantly overlaps with the ruthenium MLCT transition centered around 450 nm. Still, the MLCT band is always the transition with lowest energy. In the photochemical experiments the complexes were excited with 485 nm light where only the ruthenium unit absorbs. The transient absorption spectra (Figure 11) show that the photo-induced process, in all three dyads, is energy transfer since the product formed after ~1 ns has the characteristic absorption peak around 690 nm probing the fullerene triplet state. Further evidence for the energy transfer mechanism come from the lack of absorption around 1000 nm where the reduced C\(_{60}\) radical is expected to absorb,\(^{106}\) and by flash photolysis experiments determining the lifetime of the produced state to ~20 \( \mu \text{s} \), in accordance with data for \( 3C_{60} \).\(^ {107} \)

The quenching rate was similar in all three dyads irrespective of the spacer length (\( \tau = 0.6-0.9 \text{ ns} \)) as indicated by both emission and transient absorption experiments. This is contrary to the expected exponential decay with distance if the quenching process would be a simple exchange energy
Figure 11. Transient absorption spectra of Ru$^{II}$-S$_{1}$-C$_{60}$ (a), Ru$^{II}$-S$_{2}$-C$_{60}$ (b) and Ru$^{II}$-S$_{3}$-C$_{60}$ (c) recorded at different times after excitation with a 485 nm laser pulse; 10 ps (solid line), 200 ps (dashed line), 800 ps (dashed-dotted line) and 5 ns (dotted line). (CH$_{3}$CN, 298 K)

transfer mechanism. These distance independent observations can be explained in two ways, either the ruthenium $^{3}$MLCT state is delocalized out on the spacer, decreasing the actual donor-acceptor distance, or bridging states may be populated, thus controlling the observed quenching rate.

To understand the distance independence of the energy transfer the solvent dependence of the steady state emission was studied. For Ru$^{II}$-S$_{1}$ the emission maxima increased by almost 20 nm when lowering the polarity of
the solvent from acetonitrile, via ethanol to dichloromethane. This is expected if the lowest excited state has charge transfer character as is the case for ruthenium $^3$MLCT states. In Ru$^{II}$-S$_3$ the solvent dependence was not observed at all. Solvent independence could in this case be expected if the nature of the excited state is of $\pi \rightarrow \pi^*$ character. This is possible if the lowest excited state is solely located on the phenyl acetylene spacer. Our interpretation is thus that as the spacer length increases the lowest excited state changes from $^3$MLCT character to $^3$LC (ligand centered) character. Emission spectra of the references recorded at 77 K also supported the idea that the nature of the excited state change when increasing the bridge length. The emission spectra are shown in figure 12. A qualitative difference of the spectra is seen, and from a spectral fit using Gaussian functions, the nuclear displacement measured as the Huang-Rhys factors ($S = \frac{\lambda}{\hbar \nu}$) could be extracted. The Huang-Rhys factor for the dominant vibration (ca. 1500 cm$^{-1}$) of Ru$^{II}$-S$_3$ was very low ($S = 0.66$), as was the bandwidth of the vibronic transitions. These observations are not likely for MLCT transitions where the displacement of the nuclear coordinate is expected to be larger.$^{89}$ A final observation arguing against a $^3$MLCT character of the Ru$^{II}$-S$_3$ excited state is its lifetime in de-aerated solution. In acetonitrile the lifetime is as long as 2.2 $\mu$s probably arising from an organic triplet highly quenched by a strong spin orbit coupling with the heavy ruthenium nucleus.

![Figure 12](image.png)

**Figure 12.** Overlay of the emission spectra of the reference complexes Ru$^{II}$-S$_1$ (solid line), Ru$^{II}$-S$_2$ (dashed line) and Ru$^{II}$-S$_3$ (dotted line). (Butyronitrile, 77K)
Thus, with a change in the nature of the lowest excited state the actual
distance from the excited state to the fullerene could remain more or less
intact explaining the similar quenching rates. This means that the energy
transfer mechanism seem to change from an uphill hopping or a super
exchange mechanism to a general hopping mechanism. This interpretation is
coherent with the reported energy of the spacer triplet states in the range of
1.9-2.1 eV.\textsuperscript{108}

In conclusion paper I describes three Ru-bridge-C\textsubscript{60} dyads where the
distance independent energy transfer observed is explained by a hopping
mechanism where the excited states of the bridge are transiently populated.

\textbf{6.2 Ruthenium(II)-quinone} \hfill (\textit{Paper II})

In this study we focused on systems with benzoquinone as the primary
electron acceptor. Quinones are attractive to use since they are present in
natural photosynthesis where they are reduced in two steps before leaving
the PS II complex in exchange for an unreduced quinone. Quinones were the
first type of electron acceptor to be used in a covalently linked donor-
acceptor system with a porphyrin as photosensitizer.\textsuperscript{33} Since then a range of
quinone systems based on porphyrins, but only a few based on transition
metals like ruthenium and rhenium have been reported.\textsuperscript{109-112} When we
started to work with benzoquinone our intention was to use it as a primary
acceptor before further electron transfer to a secondary Co\textsuperscript{III} acceptor, which
could function as a reductive catalyst in an artificial photosystem. Instead the
experiments led to the construction of a monometallic triad, with a long-
lived charge-separated state formed in high yield, and a dyad system where
the charge-separated state was formed in a quasi equilibrium with the
ruthenium excited state.

In figure 13 the structures of the complexes studied are shown. In the
visible region above 400 nm only the ruthenium chromophore absorbs. The
semiquinone radical has a broad absorption around 450 nm.\textsuperscript{113} Since this is
exactly where the ruthenium MLCT state absorbs it is not ideal for detection
with transient absorption techniques. The oxidized phenotiazine with a peak
around 510 nm is, however, rather easy to detect.\textsuperscript{114}

As implied above, reduction of the Co\textsuperscript{III} unit in the Ru\textsuperscript{II}-BQ-Co\textsuperscript{III} triad
did not occur and the complex behaved exactly like the dyad Ru\textsuperscript{II}-BQ.
Photo-induced electron transfer has earlier been shown to occur from
[Ru(bpy)]\textsuperscript{3+} to [Co(bpy)]\textsuperscript{3+} in covalently linked systems.\textsuperscript{115,116} The electron
transfer from a doublet 2BQ\textsuperscript{*} to the lowest reduced 4Co\textsuperscript{II} quartet is spin
forbidden but there is still enough driving force for an allowed transition
reaching a higher lying 2Co\textsuperscript{II} doublet (\Delta G\textsuperscript{0} = -0.58 ev).
Figure 13. Structures of the compounds studied in paper II.

Time resolved emission and transient absorption measurements on Ru$^{II}$-BQ showed that the forward electron transfer rate from the excited state to the quinone was, $k = 5 \times 10^9$ s$^{-1}$, while the recombination reaction occurred with the rate, $k = 4.5 \times 10^8$ s$^{-1}$.

In the dyad PTZ-Ru$^{II}$ we introduced the very popular electron donor phenothiazine. The reason for this was to prolong the charge separation lifetime giving time for Co$^{III}$ reduction to take place in the PTZ-Ru$^{II}$-BQ-Co$^{III}$ tetrad. However, instability problems already in the triad discouraged us from attempting the synthesis of the tetrad. In PTZ-Ru$^{II}$ photon counting experiments showed single exponential emission decay with a lifetime of 90 ns indicating that reductive quenching takes place with the rate, $k_{ET} = 1.2 \times 10^7$ s$^{-1}$ ($k_{ET} = 1/\tau_{obs} - 1/\tau_{Ru(II)}$). Pump-probe measurements however indicated something else. In Figure 14a the transient absorption spectra recorded at 4 ps and 4 ns after excitation is shown. A new absorption grows in with a time constant of 7 ns around 510 nm where the charge-separated state is expected to absorb. However, the spectrum still retains much of the excited-state character after 4 ns. The inset to the figure shows the spectral shape after 4 ns when the excited state contribution is subtracted, and can be attributed to the charge-separated state. Figure 14b shows the decay of the transient absorption spectra containing attributes from both the excited state and the charge-separated state. Our conclusion is that within 7 ns a quasi equilibrium between PTZ-$^a$Ru$^{III}$ (82%) and PTZ$^a$-Ru$^{III}$-(bpy)$_2$(bpy$^-$) (18%) is established. Assuming a Boltzmann distribution, the values in parenthesis's (population ratios) suggests a reaction free energy ($\Delta G^0$) of 0.044 eV. This is
Figure 14. Transient absorption spectra of Ru$^\text{II}$-PTZ (a and b) and of PTZ-Ru$^\text{II}$-BQ (c and d). The spectra of Ru$^\text{II}$-PTZ was recorded at; (a) 4 ps, 4 ns (b) 40 ns, 120 ns and 360 ns after excitation. The inset in 4c shows the spectra of Ru$^\text{II}$-PTZ after 4ns with the contribution from the excited state subtracted. The spectra of Ru$^\text{II}$-PTZ-BQ was recorded at; (c) 4 ps, 100 ps, 400 ps, 1 ns (d) 22 ns, 50 ns, 150 ns and 250 ns after excitation. In (a) and (c) the excitation wavelength was 480 nm. In (b) and (d) the excitation wavelength was 460 nm (CH$_3$CN, 298 K)

in good agreement with the electrochemical results suggesting $\Delta G^0 = 0.070$ eV.

The quasi equilibrium could also explain the observed dynamics in two similar systems where reductive quenching rates were estimated from emission decay data.$^{106,117}$ In the [Ru(bpy)$_2$(dmbPTZ)]$^{2+}$ dyad the driving force for reductive quenching is $\Delta G^0 \sim -0.10$ eV and the reported quenching rate $k \geq 2.8 \times 10^8$ s$^{-1}$. For the [Ru(dmb)$_2$(dmbPTZ)]$^{2+}$ dyad the driving force is $\Delta G^0 \sim 0.10$ eV and the reported quenching rate $k \sim 4 \times 10^7$ s$^{-1}$. Thus a 0.2 eV lowering of the driving force gives an increase in quenching rate with a factor $\geq 700$. If the rate difference is explained by an increase in driving force for the forward electron transfer reaction, a factor 50 increase in rate is expected.$^{iv}$ For the equilibrium model the expected increase in rate is instead

$^{iv}$ This is based on the derivative of the Marcus expression, $d(\ln k_{ET})/d(\Delta G^0) = 1/k_b T (\Delta G^0/\lambda + 1) \sim 1/0.050$ eV when $(\Delta G^0 \sim 0)$. The difference in $\Delta G^0$ of 0.2 eV then gives a factor 50 rate difference $(\ln(50) \sim 0.2/0.050)$.  

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a factor 2000 \((\exp(0.2eV/k_bT))\), in better agreement with the experimental data. An interesting aspect with the quasi equilibrium is that the actual reductive quenching could in principle be much faster than the rate we observed from emission decay data. This possibility has been overlooked in earlier Ru-PTZ dyads and in some cases led to erroneous Marcus type analysis of the electron transfer rates.\textsuperscript{118}

Already the electrochemical investigation of PTZ-Ru\textsuperscript{II}-BQ suggested that we could expect problems with the stability of the complex. The first oxidation of the PTZ unit was irreversible and subsequent scans over the BQ/BQ\textsuperscript{−} and PTZ\textsuperscript{**}/PTZ potentials resulted in the decrease of these peaks together with formation of additional peaks. The interpretation would be that the PTZ\textsuperscript{**} radical reacts with the neutral benzoquinone forming a new species. The photo-induced experiments showed emission quenching with a time constant of 200 ps similar to the observations in Ru\textsuperscript{II}-BQ. However, with increasing light exposure a new long-lived emission with different spectral features and a lifetime of 65 ns grew in. We believe that this is due to a coupling reaction between the BQ\textsuperscript{−} and PTZ\textsuperscript{**} radicals forming a new species with properties similar to the PTZ-Ru\textsuperscript{II} dyad. Apart from the stability problems the triad worked as expected and produced a long-lived excited state, in high yield \((\phi_C>90\%\)) , that lived for 80 ns and stored 1.32 eV of chemical energy, which is 63% of the excitation energy.

![Reaction scheme for PTZ-Ru\textsuperscript{II}-BQ.](image)

**Figure 15.** Reaction scheme for PTZ-Ru\textsuperscript{II}-BQ.
The transient absorption spectra of PTZ-Ru$^{II}$-BQ shows formation (Figure 14c) and decay (Figure 14d) of the PTZ$^{+}$-Ru$^{II}$-BQ$^{+}$ state. The slow recombination (80 ns) is partly an effect of the inverted region ($-\Delta G^{0} > \lambda$). The inverted region has previously been used to achieve long-lived charge separation in systems similar to ours. In our system however, the charge separation is unusually efficient ($\Phi_{CS}>90\%$). This is a combined effect of the slow PTZ-Ru$^{III}$-BQ$^{+}$ → PTZ-Ru$^{II}$-BQ recombination (2 ns) in combination with the fast PTZ-Ru$^{III}$-BQ$^{+}$ → PTZ$^{+}$-Ru$^{III}$-BQ$^{+}$ charge shift reaction (<200 ps).

The reaction scheme in Figure 15 summarizes the photo-induced processes in PTZ-Ru$^{II}$-BQ.

Two main conclusions from paper II can be extracted. First, a quasi equilibrium is established between the excited state and the charge-separated state in $^*\text{Ru-PTZ}^{+}$. This makes the analyses of the actual electron transfer rate more difficult. Second, the triad formed a long-lived (80 ns) charge-separated state, PTZ$^{+}$-Ru$^{II}$-BQ$^{+}$, with a very high quantum yield, $\Phi_{CS}>90\%$.

6.3 Ruthenium(II)-Diimide (Papers III, IV and V)

In this chapter we introduce diimides as electron acceptors. The diimides are expected to be more stable than the quinones and with a higher triplet energy compared to the fullerenes, energy transfer will hopefully not be a severe problem. Most diimides also display sharp and characteristic absorption bands in their reduced form making them easy to detect spectroscopically. In our initial trials with naphthalene diimides (NDI) we also wanted to incorporate chromophores with a C$_2$ symmetry. Previous publications on Ru$^{II}$-NDI systems had shown sub nanosecond quenching of the ruthenium excited state$^{120,121}$. Unfortunately none of our dyads based on ruthenium(II) bis-terpyridine chromophores showed any noticeable quenching. Instead we returned to the workhorse [Ru(bpy)$_3$]$^{2+}$. Our [Ru(bpy)$_3$]$^{2+}$-NDI dyads showed efficient charge separation and encouraged us to incorporate a BPMP-ligand (Figure 16) as electron donor. Previous studies with external acceptors have shown that the BPMP-ligand is able to donate an electron to Ru$^{III}$ from a hydrogen bonded tyrosine and if two manganese ions are ligated forming a Mn$^{II,II}$ complex the manganese can be oxidised all the way up to Mn$^{II,III}$.

The structure of a few of our investigated complexes is shown in Figure 16. I will start to discuss the photophysical behavior of the dyad systems followed by the triads. In the Ru$^{II}$-NDI dyad excitation of the ruthenium unit was followed by rapid electron transfer ($k = 5\times10^9$ s$^{-1}$) to the NDI unit as deduced from emission as well as transient absorption data (Figure 17a). The transient absorption analysis was easy due to the characteristic NDI$^{+}$ absorption at 474 nm ($\varepsilon = 23000$ M$^{-1}$ cm$^{-1}$) and 605 nm ($\varepsilon = 6400$ M$^{-1}$ cm$^{-1}$).
Figure 16. Structures of the compounds studied in paper III-V.

Due to fast recombination \( (k = 7 \times 10^9 \text{ s}^{-1}) \) this dyad was not suitable to use for triad design. To slow down the recombination reaction we increased the donor-acceptor distance by adding a phenylene unit or a phenylmethylene unit in the bridge. The emission from the Ru\( ^{\text{II}} \)-\( \Phi \)-NDI and Ru\( ^{\text{II}} \)-\( \Phi \)-CH\(_2\)-NDI dyads was quenched with single exponential lifetimes of 6.4 ns and 7.9 ns respectively. However, the quenching mechanism was not as easy to understand as in the Ru\( ^{\text{II}} \)-NDI dyad. Figure 17b shows the transient absorption spectrum of Ru\( ^{\text{II}} \)-\( \Phi \)-NDI recorded after 50 ns. This spectral shape decayed back to zero with a rate of \( 2.6 \times 10^7 \text{ s}^{-1} \). The same trend was seen for Ru\( ^{\text{II}} \)-\( \Phi \)-CH\(_2\)-NDI but here the transient spectrum decayed with a rate of \( 5.9 \times 10^7 \text{ s}^{-1} \). The spectrum in Figure 17b seem to contain the NDI\( ^{\ast} \) radical with a pronounced peak around 474 nm. However, the expected absorption around 605 nm is absent. Also the magnitude of the 474 nm signal is smaller than expected based on the kinetic data. Our interpretation of the data is that the recorded spectra actually probes the NDI triplet excited state. Since the
Figure 17. Transient absorption spectra of Ru$^{II}$-NDI (a) and Ru$^{II}$-Ph-NDI (b). The spectrum of Ru$^{II}$-NDI was recorded at 10 ps (solid line), 100 ps (dashed line) and 400 ps (dotted line) after excitation with 400 nm light. The spectrum of Ru$^{II}$-Ph-NDI was recorded 50 ns after excitation with 460 nm light. (Acetonitrile, 298K)

$^3$NDI* state has an intrinsic lifetime of 62 μs,$^{123}$ the nanoseconds decay of the transient spectra must probe the electron transfer reaction Ru$^{II}$-$\cdot$$\cdot$$\cdot$-NDI$^*$ → Ru$^{III}$-$\cdot$$\cdot$$\cdot$-NDI$^*$. The explanation agrees with the reported $^3$NDI* spectra, which exhibit the 474 nm absorption but lacks the absorption above 520 nm.$^{123,124}$ The proposed mechanism in Ru$^{II}$-$\cdot$$\cdot$$\cdot$-NDI is shown in the reaction scheme in Figure 18a.

Figure 18. Reaction scheme for Ru$^{II}$-$\cdot$$\cdot$$\cdot$-NDI (a) and Mn$_2$$^{II,II}$-Ru$^{II}$-(NDI)$_2$ (b).
An interesting observation is that the electron transfer rate in Ru\textsuperscript{II}-\(\varphi\)-CH\(_2\)-NDI (\(k = 5.9 \times 10^7\) s\(^{-1}\)) is even faster than in Ru\textsuperscript{II}-\(\varphi\)-NDI (\(k = 2.6 \times 10^7\) s\(^{-1}\)) despite the longer donor-acceptor distance. We believe that this is an effect of the rotational angle of the bridging phenyl unit. In Ru\textsuperscript{II}-\(\varphi\)-NDI the proximity to the NDI unit forces the phenyl unit to lie out of plane due to steric effects. This effect is less pronounced in Ru\textsuperscript{II}-\(\varphi\)-CH\(_2\)-NDI.

Another aspect to consider when using diimides as electron acceptors is that the LUMO’s of the diimides often have nodes and very low electron density on the nitrogens where the donor is usually attached.\textsuperscript{85} This will decrease the orbital overlap and thus the electronic coupling. In still unpublished work we tried to solve this problem by attaching a ruthenium chromophore to a naphtalene diimide via the carbon skeleton (Figure 19). In the Ru-yn-\(\varphi\)-NDI-\(\varphi\)-yn-Ru complex the excited state was quenched very fast. The kinetic analysis required a biexponential function to fit the data with lifetimes of ~5 and ~50 ps (298K). In the reference Ru-yn-\(\varphi\)-NDI complex with the same bridge but connected via the diimide through the nitrogen the quenching rate was much slower and had a single exponential lifetime of 63 ns (298K). Unfortunately the recombination in Ru-yn-\(\varphi\)-NDI-\(\varphi\)-yn-Ru was too fast for the charge-separated state to be detected, even when a relatively non-polar solvent like dichloromethane was used.

![Figure 19. Structure of Ru\textsuperscript{II}-yn-\(\varphi\)-NDI-\(\varphi\)-yn -Ru\textsuperscript{II} and Ru\textsuperscript{II}-yn-\(\varphi\)-NDI.](image)

As a continuation of the diimide work the Ru\textsuperscript{II}-\(\varphi\)-NDI unit was linked to a BPMP-donor containing a hydrogen-bonded tyrosine (as indicated by NMR) as well as two tertiary amines. For synthetic reasons two NDI units were attached to [Ru(bpy)\(_3\)]\(^{2+}\) (a possible side effect of this is that the donor might donate two electrons, if both NDI units are reduced). In this study Ala-Ru\textsuperscript{II}-(NDI)\(_2\) was used as a reference compound. The reference showed biexponential excited state quenching with \(\tau_1 = 27\) ns (75 %) and \(\tau_2 = 7\) ns (25 %). The biexponentiality could possibly be explained by different isomers. The excited state is located on the Ala-ligand and different isomers thus give different distances to the NDI units. No transient absorption signal from NDI* or \(^*\text{NDI}\) was observed indicating a fast recombination. The reason why the energy transfer path observed for Ru\textsuperscript{II}-\(\varphi\)-NDI is not seen here is probably an effect of the lower excited state energy (2.05 eV). The
BPMP-Ru\textsuperscript{II}-(NDI)\textsubscript{2} triad showed similar emission quenching but the transient absorption spectrum displayed a long lived species attributed to NDI\textsuperscript{*}. The radical was formed in \textasciitilde10\% yield (upper inset Figure 20). The oxidised donor had a too low extinction coefficient to give detectable absorption\textsuperscript{125} and the observed NDI\textsuperscript{*} signal was used to probe the fully charge-separated state BPMP\textsuperscript{**}-Ru\textsuperscript{II}-(NDI\textsuperscript{*}))(NDI). The decay of the charge-separated state was not single exponential but could be described with two exponents ($k_1 = 3.3 \times 10^6 \text{ s}^{-1}$ and $k_2 = 1.0 \times 10^5 \text{ s}^{-1}$) plus a long-lived residual, finally quenched by oxygen on the minute timescale as detected by steady-state absorption (see Figure 20). Cyclic voltametry on BPMP-Ru\textsuperscript{II}-(NDI)\textsubscript{2} suggested that the hydrogen bonded tyrosine as well as the tertiary amines were able to donate an electron to Ru\textsuperscript{III}. To prove this, we synthesized a triad where the electron donating ability of the tyrosine was blocked by methylation. The BPMP(Met)-Ru\textsuperscript{II}-(NDI)\textsubscript{2} triad generated the oxygen quenched long-lived NDI-radical with a \textasciitilde5\% efficiency, but the phases recombining on a ns-us time scale in the previous complex were not observed (see Figure 20). It thus seems that the amine can function as an irreversible electron donor, while the hydrogen bonded tyrosine is responsible for the reversible charge-separated state.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure20}
\caption{Transient absorption traces for BPMP-Ru\textsuperscript{II}-(NDI)\textsubscript{2} (solid line) and BPMP(Met)-Ru\textsuperscript{II}-(NDI)\textsubscript{2} (dotted line) probed at 474 nm. The upper inset shows the transient absorption spectrum of BPMP-Ru\textsuperscript{II}-(NDI)\textsubscript{2} recorded at 250 ns (solid line) and 10 \textmu s (dotted line) after 455 nm excitation. (CH\textsubscript{3}CN, 298 K)}
\end{figure}
The final part of this work was to coordinate manganese to the BPMP-ligand. This is the same dinuclear Mn$_{II,II}$-unit that in earlier studies has shown a three step oxidation when linked to [Ru(bpy)$_3$]$^{2+}$. EPR-spectroscopy was used to characterize the redox states of the manganesees in the Mn$_2^{II,II}$-Ru$_{II}$-(NDI)$_2$ triad. The first two oxidations of Mn$_2^{II,II}$(BPMP)(OAc)$_2$ from Mn$_{II}$ to Mn$_{III,III}$ were reversible and found at 0.10 V and 0.63 V (vs. Fc$^{+/0}$) in CH$_3$CN. The initial photo-induced processes in Mn$_2^{II,II}$-Ru$_{II}$-(NDI)$_2$ can be understood in the same way as in BPMP-Ru$_{II}$-(NDI)$_2$, with fast formation of NDI$^x$ followed by manganese centered oxidation of the donor unit. In Mn$_2^{II,II}$-Ru$_{II}$-(NDI)$_2$ the charge-separated state, Mn$_{II,III}$-Ru$_{II}$-(NDI)(NDI$^x$) was formed with a 20% yield (298K). The decay of the charge-separated state was very slow and gave with a three exponential fit; $\tau_1 = 15$ $\mu$s (50%), $\tau_2 = 200$ $\mu$s (25%) and $\tau_3 = 2.3$ ms (25%). Compared to earlier published triads based on Ru$_{II}$ our complex has a more than two orders of magnitude longer charge-separated state lifetime. A reaction scheme for the process is shown in Figure 18b.

To understand the unusually long-lived charge-separated state we decreased the temperature to estimates the activation energy for the reaction. To maintain a liquid phase the lowest temperature used was 140 K, somewhat above the glass temperature of butyronitrile. At this temperature both the rate for NDI-reduction and charge recombination was slowed down remarkably as seen in Figure 21. The charge recombination could be well fitted to two exponents with lifetimes $\tau_1 = 100$ ms (45%), $\tau_2 = 500$ ms (55%). These timescales are comparable to the ones observed in natural photosynthesis and slow enough to encourage us to use a laser flash/freeze

![Figure 21](image_url)

**Figure 21.** (a) Transient absorption traces of Mn$_2^{II,II}$-Ru$_{II}$-(NDI)$_2$ (circles) probing the build up the NDI-radical at 474 nm. For the reference Ala-Ru$_{II}$-(NDI)$_2$ (squares) no long-lived NDI-radical was formed. The inset shows the transient absorption spectrum recorded 1 ms after excitation. (b) Transient absorption traces of Mn$_2^{II,II}$-Ru$_{II}$-(NDI)$_2$ (circles) probing the decay of the NDI-radical at 474 nm. (Butyronitrile, 140 K)
Figure 22. EPR-data showing the change in concentration of Mn(II,II) (circles), Mn(II,III) (squares) and NDI-radical (triangles) with increasing number of laser flashes at 140 K. The inset shows how NDI-radical decays in parallel with the regeneration on Mn(II,II) when the photo irradiated sample was incubated in the dark. (Butyronitrile)

quench techniques to capture the redox states of the manganeses. The induced changes could then be measured with EPR.\(^v\) Actually, 500 ms is too fast to be detected with the freeze quench technique, but the EPR data trapped an even slower charge separation product that lived for ~120 s (the millisecond phases could be detected with time resolved EPR, however, since the time resolved EPR spectra were collected at 140 K, this technique only allowed for detection of the NDI\(^*\) radical). In Figure 22 the build up of Mn\(^{II,III}\) and NDI\(^*\) with increasing light exposure at 140K is shown in parallel with the disappearance of the Mn\(^{II,II}\). When the flashed sample is put in the dark the NDI\(^*\) signal decays in parallel with the reappearance of Mn\(^{II,II}\) (Figure 22, inset). The EPR and optical experiments strongly suggest that the photo-induced processes, irrespective of temperature, really involve reversible manganese oxidation.

To determine the activation energies for the reaction, Arrhenius plots for the initial electron transfer and the recombination reaction were drawn (Figure 23). For the forward electron transfer, the analysis using the Marcus equation gave a total reorganization energy of ~0.8 eV, typical for

\(^v\) These experiments were performed by flashing the sample outside the EPR-machine followed by rapid (2-3 s) cooling of the sample to 4 or 11 K, where the manganese spectrum could be taken.
intramolecular electron transfer in polar solvents. For the recombination however, the reorganization energy was as high as ~2.0 eV. If this is correct a large amount of the reorganization has to come from inner reorganization, i.e. changes in bond lengths, of the Mn$_2$(BPMP)(OAc)$_2$ unit. A comparison of the crystal structures of the Mn$^{II,II}$(BPMP)(OAc)$_2$ and Mn$^{II,III}$(BPMP)(OAc)$_2$ states showed that this assumption is reasonable.$^{126,127}$ It thus seems that the intrinsic properties of manganese slow down the electron transfer rate due to large bond reorganizations. It is interesting to see that the recombination in our triad occurs in the ‘Marcus normal region’ and still contain as much as 1.07 eV of chemical energy. Most previous triads have relied on the inverted region to achieve slow recombination.

In the literature there are a few examples of triads and tetrads based on porphyrins, where the charge-separated state lifetimes are comparable to ours.$^{76,128}$ Fukuzumi and co-workers have also recently published results suggesting a very long-lived charge-separated state ($\tau \sim 2$ h) for a 9-mesityl-10-methylacridinium ion in benzonitrile solution.$^{129}$ Their conclusions were based on the detection of the reduced acceptor only. Nitrile solvents contain small amounts of amines, which are potential electron donors. Maybe the amines could react with the oxidised donors in a bimolecular reaction producing long-lived acceptor radicals. This has been the subject of a recent debate.$^{130,131}$ For correct analysis of long-lived charge-separated states it is

Figure 23. Marcus plots showing the temperature dependence of the rate constant ($\ln(kT^{1/2})=f(T^{-1})$). Data for the charge separation (Mn$_2$$^{II,II}$.Ru$^{II}$-(NDI)$_2$$\rightarrow$ Mn$_2$$^{II,II}$-Ru$^{II}$-(NDI)(NDI$^*$) ) is marked with circles and the data for the recombination (Mn$_2$$^{II,III}$.Ru$^{II}$-(NDI)(NDI$^*$) $\rightarrow$ Mn$_2$$^{II,II}$-Ru$^{II}$-(NDI)$_2$ ) is marked with squares.
therefore of prime importance to detect both the oxidised donor and the reduced acceptor. In our triad the EPR experiments clearly showed that both the oxidised manganese unit and the reduced NDI unit live for a long time.

A final remark on the behavior of Mn$^{III,III}$-Ru$^{II,II}$-(NDI)$_2$ is that the electron transfer is suppressed in a solid medium. Instead initial energy transfer to the $^3$NDI* is observed in analogy with the observations in the Ru$^{II}$-$\phi$-NDI and Ru$^{II}$-$\phi$-CH$_2$-NDI dyads.

In summary, we have tried to optimize the use of the electron acceptor NDI and incorporated it into a Mn$^{II,II}$-Ru$^{II}$-(NDI)$_2$ triad so the electron transfer reaction from Mn$^{II,II}$ to Ru$^{III}$ could be studied. The results showed that the Mn$^{II,II}$ unit was rapidly oxidised while the recombination reaction occurring in the Marcus normal region was very slow, probably due to a high inner reorganization energy. In the future we will dissolve the triad in aqueous medium and try to achieve accumulative electron transfer, as has been previously shown in Ru$^{II}$-Mn$^{II,II}$ dyad.

6.4 Bichromophoric systems (Papers VI and VII)

In the final part of this thesis we study donor-acceptor complexes with two chromophores. The aim is to use the energy from two photons in the generation of a high-energy charge-separated state. Another benefit with a bichromophoric system, built on a D-P$_1$-P$_2$-A design is that the two photosensitizers (P$_1$ and P$_2$) can be individually optimized. Thus P$_2$ could be designed as a good reductant of the acceptor unit (A), while P$_1$ could be optimized to oxidize the donor unit (D). When creating donor-acceptor complexes based on a single photosensitizer (D-P-A), the chromophore has to function both as oxidant and reductant, often resulting in a compromise.

In this work we have synthesized the Ru$^{II}$-Ru$_C^{II}$-PI triad with a P$_1$-P$_2$-A architecture. The Ru$^{II}$ unit is based on a [Ru(bpy)$_3$]$^{2+}$ chromophore with a high potential for the Ru$^{3+/2+}$ redox couple ($E_{1/2} = 0.91$ V vs. Fc$^{+/0}$). The Ru$_C^{II}$ unit on the other hand has a carbanion ligand, making it a better excited state reductant ($E_{1/2}(\text{Ru}^{3+}/*/\text{Ru}^{2+}) = -1.53$ V vs. Fc$^{+/0}$) compared to the Ru$^{II}$ unit ($E_{1/2}(\text{Ru}^{3+/2+}) = -1.24$ V vs. Fc$^{+/0}$). Due to the anionic ligand in Ru$_C^{II}$, the ligand field is also increased and raises the energy of deactivating metal centered states. This permits us to use two tridentate ligands and still maintain a long-lived excited state lifetime ($\tau \sim 4$ ns). Chromophores with tridentate ligands will also give a complex with $C_2$-symmetry, where the potential problem with isomers is diminished. As electron acceptor in the investigated triad we chose a pyromelitimide. In Figure 24 the Ru$^{II}$-Ru$_C^{II}$-PI triad together with some reference complexes are shown.
Two types of bimetallic Ru$^{II}$-RuC$^{II}$ dyads with either a phenyl or an acetylene link were used as references to investigate the photo-induced processes between the metal complexes. These bridging units are commonly used and can provide sufficient electronic coupling to allow for fast photo-induced electron/energy transfer, still maintaining the ground state properties of the individual units. The absorption spectra of Ru$^{II}$-φ-RuC$^{II}$ and Ru$^{II}$-yn-RuC$^{II}$ have the same shape as the sum of the two isolated chromophores spectra but with higher total intensity. Thus the dipole moments of the transitions have increased, due to the Ru-Ru interaction, but there is no evidence for new transitions arising from strong electronic coupling. The absorption from the Ru$^{II}$ unit peaks around 450 nm and above 500 nm absorption from the RuC$^{II}$ dominates. By the use of 550 nm light the RuC$^{II}$ unit can thus be excited selectively. The Ru$^{II}$ unit cannot be excited selectively, but with 450 nm light 40% of the absorbed light is captured by the Ru$^{II}$ unit while 60% is captured by the RuC$^{II}$ unit.

The time resolved experiments showed that energy transfer occurred from Ru$^{II}$ to RuC$^{II}$ when the dyads were excited with 450 nm light ($\tau \sim 1.5$ ps in Ru$^{II}$-φ-RuC$^{II}$ and $\tau \sim 0.7$ ps in Ru$^{II}$-yn-RuC$^{II}$). Figure 25 a-b shows pump-probe transient absorption kinetics probed at 500 nm, where the ground state bleach from excited state RuC$^{II}$ is dominant. When the dyads were excited at 450 nm (Figure 25 a and b, circles) the energy transfer...
dynamics is observed, as the RuCII excited state signal grew in. These dynamics were absent when a 550 nm pump was used, selectively exciting the RuII unit (Figure 25 a and b, squares). To exclude that the observed dynamics were due to vibrational relaxation the reference complex RuCII was used. Irrespective of excitation wavelength this chromophore showed the same transient absorption data, without any ~1 ps component (Figure 25 c). At longer times, more dynamics occurred in the dyads on the ca. 100 ps time scale. As with the energy transfer these dynamics were only observed with 450 nm pump light (Figure 25 d and e, circles). We tentatively ascribe these slow dynamics to the rotation of the entire ruthenium units around the bridging axis. The time scale is quite reasonable for rotation, since [Ru(bpy)3]2+ in CH3CN shows rotational diffusion with (τ ~ 50 ps).64

Knowing that the Ru-Ru dyads functioned as predicted we turned to the electron acceptor side of the system. Pyromellitimide (PI) (E1/2 = -1.21 V vs. Fe3+/2) was chosen instead of naphthalenediimde (NDI) (E1/2 = -0.97 V vs. Fe3+/2), since the lower reduction potential in the former molecule allows more energy to be stored in the charge-separated state. The reduced PI has pronounced absorption bands in the red region of the visible spectrum (ε715 = 27800 M⁻¹cm⁻¹). For the RuCII-PI dyad the emission was only slightly

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**Figure 25.** Transient absorption traces of RuII-yn RuCII (a and d), RuII-π RuCII (b and e) and RuCII (c and f). The complexes where excited at either 450 nm (circles) or 550 nm (squares). In a and b the energy transfer dynamics is shown when the complexes are excited with 450 nm. The dynamics is not seen in the reference RuCII. (CH2Cl2, 298K)
Figure 26. Transient absorption data for RuC\textsuperscript{II}-PI showing the excited state recovery around 510 nm and the formation and decay of the PI\textsuperscript{+} radical around 715 nm. The overlaid line is the transient spectra recorded after 125 ps. Excitation at 550 nm. (CH\textsubscript{2}Cl\textsubscript{2}, 298 K)

quenched compared to the reference chromophore and the forward electron transfer rate could be calculated to $k_{\text{FET}} = 7.7 \times 10^7$ s\textsuperscript{-1}. No PI\textsuperscript{+} radical was observed in the pump-probe experiments, indicating a rapid back electron transfer. In analogy with the Ru-NDI dyads described in the previous chapter maybe a methylene link would provide a slower back electron transfer relative to the forward reaction. In RuC\textsuperscript{II}-PI the PI\textsuperscript{+} radical could be detected, giving the forward ($k_{\text{FET}} = 4.5 \times 10^9$ s\textsuperscript{-1}) and back electron transfer rates ($k_{\text{BET}} = 1.6 \times 10^{10}$ s\textsuperscript{-1}) in dichloromethane. The charge separation was also observed in acetonitrile and toluene. Figure 26 shows the transient absorption data for RuC\textsuperscript{II}-PI displayed as a contour plot.

To investigate the photochemical properties of the triad Ru\textsuperscript{II}-RuC\textsuperscript{II}-PI we performed a pump-pump-probe experiment. The aim was to induce the reaction, Ru\textsuperscript{II}+RuC\textsuperscript{II}-PI $\to$ Ru\textsuperscript{III}-RuC\textsuperscript{III}-PI\textsuperscript{+}, with the first pump and the reaction, *Ru\textsuperscript{II}-RuC\textsuperscript{III}-PI$^*$ $\to$ Ru\textsuperscript{III}-RuC\textsuperscript{II}-PI$^*$, with the second pump (Figure 27). In the experiment both pump pulses had the wavelength 450 nm. Since both Ru\textsuperscript{II} and RuC\textsuperscript{II} absorb around 450 nm, the initial pulse can excite any of the two chromophores. When Ru\textsuperscript{II} is excited the energy transfer reaction, *Ru\textsuperscript{II}-RuC\textsuperscript{II}-PI $\to$ Ru\textsuperscript{II}+RuC\textsuperscript{II}-PI, takes place, in analogy to the observations.
in the Ru$^{II}$-Ru$_C^{II}$ dyads discussed above. Thus all the excited state energy quickly end up on the Ru$_C^{II}$ unit, from which further electron transfer to the PI unit occurs. In the same way as discussed above the forward and back electron transfer rates was calculated from a biexponential fit to the data ($k_{FET} = 6.2 \times 10^9$ s$^{-1}$ and $k_{BET} = 1.0 \times 10^{10}$ s$^{-1}$). After 125 ps, when the population of the charge-separated state had highest concentration, the second pump came in and excited the sample once again. In theory the fraction of this pulse exciting the Ru$^{II}$ unit could lead to formation of the, hopefully long-lived, Ru$^{III}$-Ru$_C^{II}$-PI$^{+}$ state. The energy of this charge-separated state would be as high as 2.12 eV.

![Figure 27. Reaction scheme for Ru$^{II}$-Ru$_C^{II}$-PI.](image)

In Figure 28 single pump-probe transient absorption kinetics are shown where the pump wavelength is 450 nm (Figure 28a) and 550 nm (Figure 28b) respectively. The data show how the charge-separated state, probed at 715 nm, is formed irrespective of wavelength (squares). The energy transfer
Figure 28. Transient absorption kinetic traces for Ru$^{II}$-Ru$_C^{II}$-PI pumped at 450 nm (a) or 550 nm (b) and probed at 510 nm (circles), 650 nm (diamonds) and 715 nm (squares). The data shows how the 450 nm excitation initiates energy transfer ($\tau_{\text{ENT}} = 2.1$ ps) between the Ru units. For the electron transfer ($\tau_{\text{FET}} = 160$ ps and $\tau_{\text{BET}} = 100$ ps) reaction the same dynamics is observed irrespective of pump wavelength (CH$_2$Cl$_2$, 298 K).

induced with 450 nm pump is also seen as an increase of the 510 nm bleach (circles). Since the system function as a combined antenna/charge separation device it is interesting to note how much the total absorption cross section (from the MLCT bands) increases in the Ru$^{II}$-Ru$_C^{II}$-PI triad as compared to the Ru$_C^{II}$-PI dyad. The analysis show that the total light absorption, in the triad, increase with a factor 3.

Unfortunately the pump-pump-probe experiments did not result in formation of the doubly excited charge-separated state, at least not with a lifetime longer than the Ru$^{II}$-Ru$_C^{II}$-PI state. However, the quality of the data exclude that this was due to an experimental failure to create a sufficient fraction of the doubly excited species. Instead the explanation why the Ru$^{III}$-Ru$_C^{II}$-PI$^*$ state is not observed could either be fast recombination or competing reactions such as unwanted energy transfer quenching or fast PI$^*$ to Ru$_C^{III}$ recombination.

In conclusion, upon irradiation the Ru$^{II}$-Ru$_C^{II}$-PI triad initiates two very fast consecutive processes. Rapid energy transfer from the Ru$^{II}$ to the Ru$_C^{II}$ unit, $k_{\text{ENT}} = 4.8 \times 10^{11}$ s$^{-1}$, followed by electron transfer from the *Ru$_C^{II}$ to the PI unit, $k_{\text{FET}} = 6.2 \times 10^9$ s$^{-1}$.
6.5 Conclusions

It is very hard to predict the behavior of pre-designed supramolecular systems, and the experiments often leads to unpredicted surprises.

In this thesis I have investigated a number of donor-acceptor complexes. The intention is to mimic the primary charge transfer events occurring in photosynthesis. All the investigated complexes contain electron acceptors covalently linked to a ruthenium based photosensitizer. The optimization of the initial electron transfer process led to failures and successes. In a few systems electron transfer failed due to competing energy transfer or due to fast internal decay of the photosensitizer.

One successful system, however, was a PTZ-Ru\textsuperscript{II}-BQ triad (Figure 13) where the photo-induced charge-separated state, PTZ\textsuperscript{**}-Ru\textsuperscript{II}-BQ\textsuperscript{+}, was formed in a very high yield, $\phi > 90\%$. A high yield is crucial for a proper functioning of a potential artificial photosystem, but few systems have reported a yield as high as our.

Another successful system was a Mn\textsuperscript{II,III}-Ru\textsuperscript{II}-(NDI\textsubscript{2}) triad (Figure 16). In this system the charge-separated state, Mn\textsuperscript{II,III}-Ru\textsuperscript{II}-(NDI\textsuperscript{+})(NDI), was only formed in a 20\% yield (298 K). The outstanding performance of this triad was however the remarkably long lifetime, $\tau \approx 2\text{ ms}$ (298 K) of the charge-separated state. Our explanation to the long lifetime is the high inner reorganization energy of the reaction, increasing the activation energy. The recombination reaction in our triad occurs in the Marcus normal region. This is, according to our knowledge, contrary to all other dyads, triads or tetrads reported in literature where the recombination occurs in the inverted region. Really slow recombination might be hard to achieve in the inverted region due to enhanced nuclear tunneling.

A potential problem when designing artificial photosystems is the high light to chemical energy efficiency necessary to be able to oxidize water. We try to solve this issue by using two chromophores in the triad Ru\textsuperscript{II}-Ru\textsuperscript{II}-PI (Figure 24). Using the energy of two photons would drastically increase the available excited state energy. The results did not show formation of the charge-separated state, Ru\textsuperscript{III,II}-Ru\textsuperscript{II}-PI\textsuperscript{+}. However, the total absorption cross section of the triad increased with a factor 3 compared to the Ru\textsuperscript{II}-PI dyad. This is an effect of the fast energy transfer, $^\ast$Ru\textsuperscript{II}-Ru\textsuperscript{II}-PI $\rightarrow$ Ru\textsuperscript{II}$^\ast$Ru\textsuperscript{II}-PI, allowing for the Ru\textsuperscript{II} unit to function as a small antenna.
I den här avhandlingen förekommer prefixet 'photo' 95 gånger. Uttrycket 'electron transfer' förekommer 77 gånger, ordet 'donor' förekommer 75 gånger, ordet 'acceptor' 69 gånger och uttrycken 'charge-separated state' eller 'charge separation' förekommer tillsammans 47 gånger. Det blir en hel del upprepningar... Samtidigt har dessa ord en väldigt central betydelse i mitt arbete och det flödar inte precis av synonymer.


I Figur 29 visas en schematisk bild av ett 'konstgjort fotosystem'. När det konstgjorda fotosystemet blir belyst fångar ett färgämne ('photosensitizer') i systemet upp energin från en foton (ljuspartikel). Den extra energin tillförs en elektron som rastlöst börjar leta efter något att vidare distribuera energin till. Om inget något finns kommer energin efter en


Hur gör vi då för att se hur elektroner hoppar? Vi använder oss av en teknik som kallas tidsupplöst spektroskopi. Varje experiment startas genom att en kort och kraftig laserpuls belyser våra molekylkomplex. Rastlösa elektroner kommer att börja vandra runt i systemet och beroende på vart elektroner biverken sig kommer färgen på hela komplexet att skifta.

Genom att undersöka hur komplexens förmåga att absorbera ljus, med en viss färg, förändras med tiden kan vi sedan bestämma hur elektronen rör sig.
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