Bridge Mediated Electron Transfer in Conjugated and Cross-Conjugated Donor-Acceptor Compounds

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Abstract

Detailed understanding of electron transfer reactions is important in many aspects of chemistry, biology and solar energy conversion.

The main aim of this thesis is to provide further insight into electron transfer through highly conjugated bridge structures. Towards this end, three series of donor-acceptor dyads have been studied, all using an oligo(1,4-phenylene-ethynylene) moiety as the bridge. A common theme in these series is that they explore the effects of having either an ethynylene or phenylene as the attachment group between the bridge and the donor or acceptor. Photophysical characterization of these dyads was carried out by means of time resolved laser spectroscopy. The results show that having an ethynylene as attachment group results in higher rates for bridge mediated electron and energy transfer compared to similar systems, where a phenylene was used.

It was also found that most of the investigated systems show a fast back electron transfer. A notable exception is a zinc(II) phthalocyanine- gold(III) porphyrin dyad, where very fast photoinduced electron transfer \( k_{PET} = 1.0 \times 10^{12} \text{ s}^{-1} \) was followed by relatively slow back electron transfer \( k_{BET} = 1.0 \times 10^{9} \text{ s}^{-1} \). A complementary DFT investigation indicated that the charge shifted state involves a reduction of the gold ion, rather than the porphyrin ring. This results in lower electronic coupling between the reduced gold porphyrin and the bridge and thus slower back electron transfer.

A series of zinc porphyrin platinum acetylide dyads was used to explore the effects on electronic coupling of different attachment points on the porphyrin ring. For the investigated system it was found that linking at the meso-position results in an eight-fold increase in electron transfer rate compared to the \( \beta \)-position.

In addition, a series of mixed valence compounds was used to investigate electronic coupling mediated by cross-hyperconjugated or cross-\( \pi \)-conjugated bridges. The results indicate coupling elements of 100-400 cm\(^{-1} \), with the cross-\( \pi \)-conjugated bridge having the largest coupling. A complementary TD-DFT study indicates that both through bond and through space coupling can be active in these systems. The relative contribution of these two mechanisms to the electronic coupling is highly conformer dependent.

Keywords: Electron transfer, Ultrafast, Long-range, Intervalance charge transfer, cross conjugation, hyperconjugation

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Till min älskade familj
List of papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


Paper not included in this thesis


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Contribution Report

I  I am responsible for the photophysical characterization and analysis and I significantly contributed to the writing of the manuscript.

II I did all of the photophysical and electrochemical characterization and data analysis and I am the main author of the manuscript text.

III I did most of the photophysical characterization and analysis and I am the main author of the manuscript text. I also took part in the planning and analysis of the quantum mechanical calculations, but I did not perform the calculations.

IV I was part of the planning of the studied dyads and I did all of the photophysical characterization and data analysis. I contributed significantly to the discussion and writing of the manuscript text.

V I was part of the planning of the project and I am responsible for the spectroscopic and computational characterization of the mixed valence compounds. I am also the main author of the manuscript text.
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<tbody>
<tr>
<td><strong>ET</strong></td>
<td>Electron transfer</td>
</tr>
<tr>
<td><strong>PET</strong></td>
<td>Photoinduced electron transfer</td>
</tr>
<tr>
<td><strong>PHT</strong></td>
<td>Photoinduced hole transfer</td>
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<tr>
<td><strong>DFT, (TD-)</strong></td>
<td>Sensity functional theory</td>
</tr>
<tr>
<td><strong>AuP⁺</strong></td>
<td>Gold(III) porphyrin</td>
</tr>
<tr>
<td><strong>c</strong></td>
<td>Speed of light in vacuum</td>
</tr>
<tr>
<td><strong>C₆₀</strong></td>
<td>Fullerene</td>
</tr>
<tr>
<td><strong>FNR</strong></td>
<td>Ferredoxin-NADP(+) reductase</td>
</tr>
<tr>
<td><strong>h</strong></td>
<td>Planks constant</td>
</tr>
<tr>
<td><strong>HOMO</strong></td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td><strong>IC</strong></td>
<td>Intersystem crossing</td>
</tr>
<tr>
<td><strong>ISCS</strong></td>
<td>Inter-system crossing</td>
</tr>
<tr>
<td><strong>IVCT</strong></td>
<td>Intervalance charge transfer</td>
</tr>
<tr>
<td><strong>k_B</strong></td>
<td>Boltzmann constant</td>
</tr>
</tbody>
</table>
| **k_{index}** | Rate constant  
  (The index, denotes which process. 0 as an index denotes a rate in the absence of a quencher) |
| **k_{index}** | Force constant for the i:th vibrational mode |
| **LUMO**     | Lowest unoccupied molecular orbital |
| **NIR**      | Near infrared light |
| **OEC**      | Oxygen evolving complex |
| **OPE**      | oligo(1,4-phenylene-ethynylene) |
| **P₆₈₀**     | The chromophore in the raction center of PS II |
| **P₇₀₀**     | The chromophore in the raction center of PS I |
| **PS**       | Photosystem |
Pt Platinum, but in the context of paper II it also refers to the two types of platinum(II) acetylide polypyridyl complexes that function as electron acceptors.

$r_i$ Radius or distance
SnP Tin(IV) Porphyrin
SOMO Singly occupied molecular orbital
$T$ Temperature
UV Ultra-violet light
$V_{ij}$ Electronic coupling between state $i$ and $j$
ZnP Zinc(II) porphyrin
ZnPc Zinc(II) porphyrin
$\Delta G^\circ$ Free energy driving force
$\varepsilon$ Dielectric constant
  (in the context of electron transfer)
$\varepsilon$ Extinction coefficient
  (in the context of spectroscopy)
$\varepsilon_0$ Permittivity constant in vacuum
$\lambda$ Reorganization energy
  (in the context of electron transfer)
$\lambda$ Wavelength, usually in nm
  (in the context of spectroscopy)
$\nu$ Frequency
$\tau_i$ Lifetime
  (The index, $i$, denotes which process. 0 as an index denotes a rate in the absence of a quencher)
$\phi$ Quantum yield
$\nu$ Wavenumber
DMF N,N-dimethylformamide
PhCN Benzonitrile
DCM Dichloromethane
MeCN Acetonitrile
2-MTHF 2-Methyl tetrahydrofuran
EnT Energy transfer
1. Introduction

I remember the first time I was really captured by electron transfer as a scientific problem. It was in the beginning of my fourth year as an undergraduate and I snuck in to listen to the end dissertation of Magnus Falkenström.\textsuperscript{i} He and his opponent, prof. Sebastiano Campagna, discussed a system with two ruthenium chromophores designed to mimic the Z-scheme of photosynthetic organisms.\textsuperscript{1,2} Although, much of the discussion was beyond my grasp, the idea that one could control photoinduced electron transfer in several steps, struck me as very interesting scientific question. Furthermore, if solved, it could be of great use in artificial photosystems, providing a potent light-powered machinery to drive catalysis.

A year later I started my PhD-studies and I have since then learned that highly controlled electron transfer reactions are the fundamental processes behind many enzymatic processes, not only those in photosynthesis and I have also come to appreciate the importance of being able to control electron transfer in the emerging field of molecular electronics. However, the work presented in this thesis is mainly dealing with how to control photoinduced charge transfer, with the hope to yield valuable information for the design of photoactive systems.

1.1 Photoinduced charge separation, the motor of photosynthesis

The light dependent reactions of photosynthesis constitute an intricate machinery involving two separate Photosystems (PS I and PS II) as well several other large and small proteins and enzymes.\textsuperscript{3} Photosynthesis can in principle be seen divided into two half-cell reactions. At the PS II side a sequential oxidation (removal of electrons) of water occurs and the products are molecular oxygen and free protons, At the PS I side there is a sequential reduction (addition of electrons) of NADP\textsuperscript{+} and a proton to form NADPH (Figure 1). The electron transport chain between PS II and PS I converts the potential energy created by the photoinduced charge separation to a proton gradient. The proton gradient created by the electron transport chain and the ox-

\textsuperscript{i} Formerly known as Magnus Borgström
Reduction processes is subsequently used to convert ADP to ATP, which is the energy currency of the cell. The motor behind all of these oxidation and reduction events is the photo-excitation and subsequent charge-separation of the two photosynthetic reaction centers central, light-absorbing pigments P_{700} and P_{680} of PS I and PS II, respectively. The charge separation processes in PS I and PS II creates electron holes that drive the oxidation processes and activated electrons that drives the reduction.

![Diagram of photosynthesis](image)

**Figure 1.** To the left is a schematic description of the Z-scheme in photosynthesis. The oxygen evolving complex (OEC) and the chromophore P_{680} are two of the components in Photosystem II (PS II, oxidative side). Ferredoxin-NADP(+) reductase (FNR) and P_{700} are parts of Photosystem I (PS I, reductive side). To the right is a schematic example of a potential artificial system. In this scheme a single chromophore absorbs the light and drives the charge separation in the system. Arrows pointing to the right are indicating desired electron transfer processes reactions, while crossed arrows are indicating destructive back electron transfer reactions.

The creation of reactive electrons and electron holes is also the first step in all artificial systems that use light to generate electricity or to drive a chemical reaction. Figure 1 show a simplistic example of an artificial photosynthetic system that uses light to split water to oxygen and hydrogen. The single chromophore absorbs the light and transfers electrons to the proton reducing catalyst and takes electrons from the water oxidation catalyst.

### 1.2 The aim of my research

There are several reasons why the very simple example shown in Figure 1 probably will not work. The ones most relevant for my research are two: first, the difficulty in finding a chromophore that provides enough energy to efficiently drive both the oxidative and the reductive reactions, and second counter-productive back electron transfer.
The first problem might be solved if one could device a two-chromophore system that uses two photons to generate a strongly reductive and strongly oxidative charge separated state, just like PS I and PS II. Moreover, if these two chromophores would absorb light in different parts of the solar spectrum one could also use a larger part of the incoming solar energy, which would be an improvement compared to natural photosynthesis.

The second problem is instead what I have spent most of my research on. We have been trying to find properties in the structures bridging the chromophores that would allow for fast electron transfer in the desired direction, while providing a relatively slow back electron transfer. In general, we have explored conjugated bridges that couple strongly to the chromophores, but that are long and may therefore lead to efficient long-range charge separation.

1.3 Outline of this thesis

I will begin this thesis with a chapter introducing the relevant theoretical concepts. This will be followed by a short description of the methods I used. In chapter 4 I will give an overview of the aim and results of papers I-IV, which all are studies of electron transfer mediated by highly conjugated bridges. Chapter 5 and 6 discusses different aspects of photoinduced electron transfer that are relevant for papers I-IV. Chapter 7 summarizes a study of electronic coupling through cross-hyperconjugated and cross-conjugated bridges.
2. Theory

This chapter will give an orientation of the theoretical concepts that will be used in later chapters. For more extensive description the topics below see for example Parson (spectroscopy), Gilbert and Baggot (photochemistry), Marcus, Bolton and Newton (electron transfer).

2.1 Fundamental concepts

2.1.1 Orbitals, electron distribution,
Quantum mechanics predicts that to fully describe a quantum mechanical system one has to solve the Schrödinger equation. For chemistry the system of interest is typically a molecule or an atom and how the electrons move therein. The Schrödinger equation solutions are called “orbitals” and they are the basis for understanding much of modern chemistry. Each orbital can describe the behavior of up to two electrons, one with spin $\frac{1}{2}$ (“spin up”) and one with spin $-\frac{1}{2}$ (spin down). There are in principle an infinite number of orbitals for any given molecule, each with a specific energy and a unique geometry over the molecule, but only the orbitals with lower energy are of practical interest.

The electrons in a molecule or atom will occupy orbitals according to Hund’s rules and the resulting electron configuration will correspond to the lowest possible energy. This corresponds to the electronic ground state of the molecule. Higher lying electronic states (excited states) can in principle be described by the same set of orbitals as the ground state, and in the simplest cases the excited state can be described by just one change in the electronic configuration. However, in many cases it is necessary to consider a combination of several electronic configurations and their orbital momentum to properly describe an electronically excited state.

For a molecule there are two orbitals of special interest; the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). These two can be used to describe much of the chemical behavior and reactivity of a molecule. Furthermore, in many molecules the lowest excited state corresponds to an electron configuration where an electron transferred from HOMO to LUMO. Orbitals that only are half filled are de-
noted single occupied molecular orbital (SOMO) and occur in molecules that are radicals or that has a ground state with higher multiplicity (see below).

The fact that electrons also have spin adds an additional property to each electronic state. If there are more electrons with spin up than spin down (or *vice versa*) the molecule is magnetic. To describe this property of a molecule we introduce the concept of “multiplicity”. The multiplicity of a molecule is given by the number of unpaired electrons plus one. Thus, if there are equally many electrons with spin up and spin down the multiplicity is 1 and the state is called a “singlet”. A configuration with one unpaired electron spin is called a “doublet”, two unpaired spins is called a “triplet” and so on. Furthermore, one of Hund’s rules states that given a certain electronic configuration the electronic state with the highest multiplicity has the lowest energy. Consequently, a molecule with two SOMO, such as molecular oxygen (O2) will have a triplet ground state.

### 2.1.2 Light-matter interaction

The fundamental concept behind all spectroscopic techniques is that electromagnetic radiation (light) of a certain wavelength will only interact with matter if it matches an energy gap between a populated and an unpopulated state (ΔE) in the illuminated material. This relationship between energy (E) and wavelength (λ) is expressed in Eq. 2.1.

\[
E = \frac{hc}{\lambda} = h\nu = hc'\nu
\]

Eq. 2.1

Where \( c \) is the speed of light and \( h \) is Planck’s constant. Frequency (\( \nu \) in Hz) and wavenumber (\( \bar{\nu} \), in cm\(^{-1}\)) are common alternatives to describe the energy of the light. Transitions between certain types of states are usually associated with certain regions in the electromagnetic spectrum (Figure 2) and this can be used to select which property of the material is to be investigated. Using microwaves, one can study changes of molecular rotations. Infrared light will probe vibrations of the nuclei in a molecule and visible and UV-light will result in rearrangement of how the valance electrons are distributed between molecular orbitals. Light with even shorter wavelength (*i.e.* more energy), such as far UV or X-ray, will interact with electrons in lower lying orbitals and might even result in ionization of the molecule.

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\*ii When using wavenumbers (cm\(^{-1}\)) one needs to express the speed of light in cm/s, hence \( c' \)
In this thesis we are mainly concerned with electronic transitions in the visible region and these will be further described below. It is important to note that an electronic transition in a molecule can be coupled to vibrational and rotational transitions. This means that there exists a manifold of possible transitions for each electronic excitation, which results in rather broad absorption bands instead of narrow discrete peaks. In condensed phases, further broadening will occur due to perturbations from the surrounding molecules.

2.2.1 Electronic absorption and emission

The absorption of light by a material or solution can empirically be described by Beer-Lambert’s law (Eq. 2.2), which relates the ratio of the incoming \(I_0,\lambda\) and the transmitted \(I_\lambda\) light to the concentration of the absorbing molecules \(c_X\) and path length \(l\) that the light travels through material. The proportionality is constant \(\varepsilon_{\lambda}\) is called the extinction coefficient and it is an experimentally determined property which describes how strong a material or molecule absorbs at that wavelength.

\[
Abs_\lambda = \log \left( \frac{I_0,\lambda}{I_\lambda} \right) = \varepsilon_{X,\lambda} c_X l
\]

Eq. 2.2

Scanning the absorption over a range of wavelengths will result in an absorption spectrum and the observed electronic transitions will appear as peaks positioned at the wavelength that matches the energy of the transition. The peaks will, however, not be equally strong and in order to explain this one has to consider which orbitals that change population between the initial and final electronic state. The transition between orbitals can be described by time-dependent perturbation theory, where the perturbation of the orbitals comes from the electric field of the incoming light. The perturbation causes a temporary superposition of occupied and unoccupied orbitals and while this superposition is present the electron in the orbitals in question will begin to oscillate back and forth between the involved orbitals. This movement of charge will result in an oscillating dipole, which is referred to as the transition dipole \(\mu_{ab}\). The magnitude and direction of \(\mu_{ab}\) is determined by the shape of the involved orbitals. One special case occurs when the interacting
orbitals have the same symmetry. In this case a movement of an electron will result in no net movement of charge and thus no dipole. It is thus important to have orbitals of different symmetries to get a strong $\mu_{ab}$. The strength of the transition dipole describes how strongly the molecule interacts with incoming light and thus the intensity of the absorption. Equations 2.3 describe how one can relate the magnitude of the transition dipole ($|\mu_{ab}|$) to the experimentally observed absorption band.

$$|\mu_{ab}|^2 = \frac{3hc\varepsilon_0\ln 10}{2\pi^2 N_A} \int \frac{\varepsilon(\nu)}{\nu} d\nu$$

Eq. 2.3

Here $h$ is Planck’s constant, $c$ the speed of light, $\varepsilon_0$ is the permittivity constant and $N_A$ is Avogadro’s number. The integral over $\varepsilon(\nu)/\nu$ corresponds to the area under the absorption peak. This relationship will be important later in this chapter and in paper V.

The reverse reaction, when an excited molecule sends out light and returns to the ground state, is called spontaneous emission. The rate of emission is proportional to the integrated strength of the corresponding absorption band (i.e. $\mu_{abs} \approx \mu_{emi}$). However, emission is not the only pathway by which an excited molecule can release the excess energy. Other pathways include vibrational relaxation, internal conversion, intersystem-crossing and rearrangement of bonds within the molecule.

2.2.1 Decay of an excited state

As mentioned above there are several processes that can occur from an excited state and in order to keep track of them all it is convenient to use a Jabłoński diagram (Figure 3). The transition that will dominate the decay path is determined by the rates of the different reactions from that state, therefore these rate constants need to be experimentally determined. However there are a couple of guiding principles.

- Relaxation within the vibrational manifold of an electronic state is very rapid and it can often be assumed to outcompete all other reactions.
- Higher excited states will rapidly (~1 ps) decay to the lowest excited state with the same multiplicity. This process occurs through a combination of internal conversions and vibrational relaxation. Only for the lowest excited state can one assume that the internal conversion is slow enough to allow other processes to compete. This also means that one can assume that other photochemical and photophysical reactions occur from the vibrationally relaxed form of the lowest excited state. This principle is known as Kasha’s Rule.
- Intersystem crossing, ISC, is a process between states of different multiplicities. This process is formally forbidden and usually slow, but it can occur via a mechanism where the electron spin couples to other mag-
netic momenta, such as those formed by an electron orbiting a nuclei. The rate for intersystem crossing can be increased dramatically by the presence of heavy elements, such as gold or platinum.

- Emission from a transition between states of the same multiplicity is called fluorescence, while emission between states of different multiplicities is called phosphorescence. As mentioned above the rate for fluorescence is depends on the strength of the corresponding absorption band. Phosphoresce is, just as ISC, a spin forbidden transition and thus usually slow. It can however be observed in molecules with heavy elements or at very low temperatures, where other competing processes has been slowed down.

![Jablon'ski Diagram](image)

*Figure 3. A Jabłoński diagram illustrating the six most common photophysical reactions. Wavy line denotes changes in energy, either as dissipation of heat through vibrational relaxation, VR, (vertical wavy lines) or as an incoming or outgoing photon diagonal wavy lines). Straight lines corresponds the different photophysical processes.*

The overall rate constant for the decay of an excited state is determined by the sum of the rate constants of all decay pathways. For the lowest singlet excited state in Figure 3 the overall rate constant ($k_0$) is given by Equation 2.4. It is common to use the lifetime ($\tau_0$) instead of the rate constant when one discusses excited states. Lifetime is defined as the reciprocal of the overall rate constant (Eq 2.4) and corresponds to the time it takes for the initial population of the excited state to decay down to $1/e$ ($\sim 37\%$).

$$\tau_0^{-1} = k_0 = k_{fl} + k_{IC} + k_{ISC}$$

Eq. 2.4

---

[iii] Almost always a singlet to singlet process.
[iv] Usually an excited triplet to a singlet ground state reaction.
Here, \( k_{fl}, k_{IC} \) and \( k_{ISC} \) are the rates of fluorescence, internal conversion and intersystem-crossing, respectively. The emission quantum yield of a process is another useful observable of an excited state. It corresponds to the fraction of excited molecules that will decay via emission and is defined according to Equation 2.5.

\[
\phi_{fl} = \frac{\text{# emitted photons}}{\text{# absorbed photons}} = \frac{k_{fl}}{k_{fl} + k_{IC} + k_{ISC}}
\]

Eq. 2.5

If a molecule in an excited state has the possibility of undergoing other reactions the excited state will decay even faster and the emission intensity will decrease. The additional reactions are called quenching reactions and the additional molecule that the excited molecule reacts with is denoted a quencher. There are several types of quenching reactions, but the two that are most important in this thesis are photoinduced electron transfer (PET) and excited state energy transfer (EnT) and they will be described in greater detail below. The rate constant of the quenching reaction, \( k_q \) can be determined using Equation 2.6, where \( \tau_0 \) and \( \phi_0 \) are respectively the lifetime and emission quantum yield of the excited state in the absence of the quencher and \( \tau \) and \( \phi \) are the lifetime and quantum yield for the case where the quencher is present.

\[
k_q = \tau^{-1} - \tau_0^{-1} = \tau_0^{-1} (\phi_0 / \phi - 1)
\]

Eq. 2.6

2.2.3 The absorption of porphyrins

Porphyrins are, due to their strong absorption and fairly long excited state lifetime, a popular chromophore both for solar harvesting purposes and, as in papers I-IV, for fundamental research. Porphyrins have characteristic absorption spectra with two major absorption bands in the visible region. The lower energy band is called the Q-band, while the higher energy band is called the Soret or B-band. The magnitude and position of these bands can be explained by Gouterman’s “four-orbital model”.\(^{11,12}\) In this model the B and Q-band are described as a combination of transitions from the two highest occupied orbitals (\( \psi_1 \) and \( \psi_2 \), with \( a_{1u} \) and \( a_{2u} \) symmetry respectively) and the two lowest unoccupied orbitals (\( \psi_3 \) and \( \psi_4 \), both \( e_g \) symmetry), see Figure 4.
One can learn several things from Gouterman’s analysis. Firstly, the B and Q-band actually consists of two degenerate states, which both have their transition dipoles in the plane of the porphyrin, one is directed along the x-axis, while the other is pointing in the y-direction. Secondly, if ψ₁ and ψ₂ are close in energy the transition dipoles for the Q-band become close to zero, while the transition dipole for the B-band becomes very strong. This explains why symmetric porphyrins have very strong B-band and why the Q-band is so weak. For some porphyrin derivates, such as chlorophyll, the symmetry and energy of the four orbitals has changed so much that Q-band no longer is symmetry forbidden and the strength of the Q- and B-bands are of similar strength. A similar analysis for phthalocyanines shows that the HOMO orbitals are much further separated in energy and consequently both the B- and Q-band have strong transition dipoles, which also are reflected in the absorption spectrum. We will return to the “four orbital model” when we discuss some of the results in Chapter 5 and 6.

2.3 Electron transfer

2.3.1 Marcus theory

Marcus theory is the most successful description of electron transfer both for explaining and predicting electron transfer rates. In its simplest form, there are only four parameters that determine the electron transfer rate, the driving force for the reaction \(-\Delta G^0\), the reorganization energy \(\lambda\), the electronic coupling \(V_{DA}\) and the temperature \(T\) (Eq. 2.7). Figure 5 shows a
simple example of an electron transfer reaction between a reduced benzene molecule (i.e. it has an extra electron) and a neutral benzene molecule. For this self-exchange transfer of an electron from one benzene molecule to another \( \Delta G^\circ = 0 \), which will allow for an easier description of the reorganization energy.

\[
k_{ET} = \frac{\pi \hbar^2}{h^2 \lambda k_B T} V_{DA}^2 \exp \left( -\frac{(\Delta G^\circ + \lambda)^2}{4 \lambda k_B T} \right) \quad \text{Eq. 2.7}
\]

Figure 5. A schematic description of the Marcus reorganization energy. Pictures A-E depict examples of the nuclear coordinate at points A-E. The ovals symbolize the solvent molecules and the shaded side of the oval is the positive side of the solvent dipole. For clarity all the solvents molecules have been drawn with their dipole away from the reduced benzene. This is unlikely to happen for a real case. The orientation of the dipoles stabilizes A and E and destabilizes B and D. Reaction pathways between A and E are described to the right. The electron transfer occurs at the crossing point, C. Note also that the reorganization energy, \( \lambda \), is defined as the energy difference between A and D (or E and B).

Reorganization energy (\( \lambda \))

If the two benzene molecules are in a solution the solvent molecules will arrange different around them. The solvent molecules around the reduced benzene will try to stabilize the charge by orienting their positive side toward the negative charge, while the solvent molecules around the neutral benzene will be more randomly oriented. Changing the orientation of the solvent molecules will cost energy and larger changes will result in larger energy costs. Marcus theory assumes that these changes can be described by a parabola of free energy vs. the nuclear reaction coordinate (\( q \)). In the case in Figure 4 there are two relevant parabolas, depending on whether the ex-
cess electron is on the right or left benzene molecule. The two parabolas will have the same shape, and in this case they have their energy minima at the same energy level, but at different positions along the nuclear reaction coordinate \((q)\). Electrons move much faster than nuclei so if an electron transferred between the two benzene molecules the surrounding molecules would have no time to adopt. Thus, if the system is at position A an electron transfer would result in point B rather than point E. This would break the first law of thermodynamics (conservation of energy) and can thus not occur. This indicates that in order to transfer an electron one first need to change the nuclear coordinates such that the donor and the acceptor state have the same energy. The reorganization energy \((\lambda)\) is defined as the free energy cost of moving along the nuclear coordinate of one parabola to the position above the minimum of the other (i.e. from A to D or from E to B). The actual electron transfer reaction will not happen at the nuclear coordinates close to either minima, but will rather happen around the crossing point of the two curves (C). This satisfies the principle of energy conservation.

The reorganization energy is usually divided into an outer term \((\lambda_{\text{out}})\), accounting for the cost of reorganizing the surrounding molecules, and an inner term \((\lambda_{\text{in}})\) describing costs for changing bond lengths and bond angels within the electron donor and acceptor. The later term can be estimated from Equation 2.8.

\[
\lambda_{\text{in}} = \frac{1}{2} \sum_i k_i (\Delta q_i)^2 \tag{2.8}
\]

Where \(k_i\) is the force constant for the \(i\):th vibrational mode and \(\Delta q_i\) is how much the nuclei move along this mode.

The outer reorganization energy can be estimated by modeling the reactants as point charges inside cavities in a dielectric continuum. The cost of changing the charge in these cavities is then given by the change in Born energy. Assuming that the charges changes between 0 ↔ ±1 and that the reactants are spheres with the radii \(r_D\) and \(r_A\), separated by the distance \(R_{DA}\) one get Equation 2.9.

\[
\lambda_{\text{out}} = \frac{e^2}{4\pi \varepsilon_0} \left( \frac{1}{2r_D} + \frac{1}{2r_D} - \frac{1}{r_{DA}} \right) \left( \frac{1}{n^2} - \frac{1}{\varepsilon_{\text{solv}}} \right) \tag{2.9}
\]

From this we can conclude that the solvent reorganization becomes large if the molecule is small, if the electron transfer distance is large and if the surrounding solvent is polar i.e. has a high dielectric constant \((\varepsilon)\).

\(^\dagger\) We will sew in section 2.3.7 that this reaction can occur if it also involves absorption of a photon with the right energy. This typ of process is called optical charge transfer.
Driving force (-\(\Delta G^\circ\))

The driving force is the difference in free energy between the relaxed product state and the relaxed reactant state. In the case with the two benzene molecules the driving force was zero, but if the electron accepting benzene was replaced by a molecule that is easier to reduce, such as naphthalene or anthracene, one would get a larger -\(\Delta G^\circ\) and the reaction would be exothermic. This would correspond to a lowering of the parabola describing the product state (Figure 6). A change in driving force will affect the crossing point between the two curves (i.e. the transitions state). The energy barrier for the transition state (\(\Delta G^\ddagger\)) can be expressed in terms of the driving force and the reorganization energy (Eq. 2.10).

\[
\Delta G^\ddagger = \left(\Delta G^\circ + \lambda\right)^2 / 4\lambda
\]

Eq. 2.10

From this one can conclude that an increase in driving force will result in a smaller reaction barrier for electron transfer, until the point where -\(\Delta G^\circ = \lambda\). A further increase in driving force from this point will result in an increase in reaction barrier and thus slower electron transfer rates. The region where -\(\Delta G^\circ < \lambda\) is called the Marcus normal region, while the region where -\(\Delta G^\circ > \lambda\) is called the Marcus inverted region (Figure 6).15,16

![Figure 6](image)

Figure 6. To the left is the illustration on how the barrier for ET changes with driving force. The reorganization energy is the same in the three cases. Enlargement of the crossing point illustrates the splitting of the two diabatic states in to two adiabatic states. The splitting between the two states corresponds to twice the electronic coupling (\(V\)). To the right is an illustration on how the rate is expected to change with driving force. The dotted line the Marcus inverted region is more similar to observed data.15 This trend can be accounted for by including higher vibrational states of the of the product state.

The free energy changes for electron transfer can be estimated from the reduction potentials of the electron donor (\(E^\circ_{(D_{\text{ox/D})}}\)) and the electron acceptor (\(E^\circ_{(A/A_{\text{red}})}\)). For photoinduced electron transfer one also needs to account for the excited state energy \(E_{00}\). These estimates are all summarized in the Rehm
-Weller equation describing photoinduced electron transfer (Eq. 2.11) and the corresponding back electron transfer (Eq. 2.12).

\[
\Delta G_{\text{PET}} = e \left( E_{D}^{\text{red}} - E_{A}^{\text{red}} \right) - E_{00} + w + C \quad \text{Eq. 2.11}
\]

\[
\Delta G_{\text{BET}} = e \left( E_{A}^{\text{red}} - E_{D}^{\text{red}} \right) - w - C \quad \text{Eq. 2.12}
\]

*C* is a correction factor for cases where the reduction potentials are measured in a different solvent than the electron transfer measurements (Eq. 2.13).

\[
C = \frac{e^2}{4 \pi \varepsilon_0} \left( \frac{(z_{D}^{\text{red}})^2 - (z_{D})^2}{2r_{D}} + \frac{(z_{A}^{\text{red}})^2 - (z_{A})^2}{2r_{A}} \right) \left( \frac{1}{\varepsilon} - \frac{1}{\varepsilon_{\text{ref}}} \right) \quad \text{Eq. 2.13}
\]

\(w\) is a correction term that describes the Coulombic interaction between the charges \((z)\) on the donor and acceptor. This term is mainly important for reactions in non-polar solvent or when the electron transfer distance is short (Eq. 2.14).

\[
w = \frac{e^2}{4 \pi \varepsilon_0 \varepsilon} \left( \frac{z_{D}^{\text{red}} z_{A}^{\text{red}} - z_{D} z_{A}}{R} \right) \quad \text{Eq. 2.14}
\]

**Electronic coupling (V)**

From the discussion around reorganization energy we learned that the electron transfer only occurs close to the crossing point of the two parabolas, *i.e.* with energy conservation in the energy transfer step. The second criterion is that there should be some coupling element between the reactant and product state. *The interaction between the reactant and product states (both diabatic) results in an avoided crossing and the formation of two adiabatic states. The magnitude of the splitting is related to the strength of the interaction and it correspond to twice the coupling element, \(V\), \((V\) is often denoted electronic coupling). The evaluation of the electronic coupling can often be simplified by assuming that the reactant and product state can be described by the frontier orbitals of the electron donor and acceptor.

The value for electronic coupling is the most difficult of the four parameters in Marcus theory to estimate from other types of experiments. As a consequence much research has focused on finding trends in different series of electron donor-acceptor systems which could be used to predict the behavior

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**vi** Eq. 2.13 and 2.14 are formulated for the general case, here no charge has been assumed. The same equations are often reported for the special case where \(z_A\) and \(z_B\) only adopt values between -1 and 1.

---

**vii** *I.e.* the integral \(<R| H |P>\) has off diagonal elements, \(V_{RP}\) and \(V_{PR}\), which are non-zero. Here \(|R>\) and \(|P>\) are the reactant and product state respectively and \(H\) is the electronic Hamiltonian.
in other systems. The value for electronic coupling should in principle be accessible through quantum chemical calculation, but the complexity and size of the donor acceptor systems have generally made this a very difficult task.

2.3.2 Distance dependence in electron transfer

From the criteria that orbital overlap is needed one also obtains the intuitive result that the electron donor and acceptor molecules need to be close in space for the reaction to occur (< 10 Å). Since the amplitude of the orbitals tends to fall off exponentially with distance one can also expect an exponential decay of the electronic coupling as the molecules moves further apart. This distance dependence has been observed in a large body of experiments and is commonly described by equation 2.15.\textsuperscript{15,19-25}

\begin{equation}
V = V_0 \exp\left(-\beta / 2(d - d_0)\right)
\end{equation}

Where $V$ is the expected coupling at the center to center distance $d$. $V_0$ is the coupling at the center to center distance $d_0$ (usually at van der Waals contact) and $\beta$ is an attenuation factor that is specific for the medium between the electron donor and acceptor. The attenuation factor for a saturated carbon chain is typically 1 Å\textsuperscript{-1} and the same is true for electron transfer in proteins. In contrast, if the donor and acceptor are linked via a conjugated bridge the attenuation factor can be much smaller (0.01 - 0.1 Å\textsuperscript{-1}), which allows for rapid electron transfer over longer distances.

2.3.3 Mechanisms for long range electron transfer

There are two main mechanisms that can explain long range electron transfer. The first is electron hopping, in which the electron moves in a series of shorter electron transfer steps, transiently reducing or oxidizing the bridging units along the way. This can be a very efficient way to transport charge, but it requires that the bridging units have reduction potentials that are thermally accessible from the reactant state (Figure 7).
The other mechanism is called McConnell super-exchange and in this mechanism the coupling between the electron donor and acceptor is mediated via coupling to virtual states of the bridging units. The overall donor acceptor coupling can be understood as the product of the coupling elements between neighboring units, i.e. the donor and bridge ($V_{DB}$), the bridge and the acceptor ($V_{BA}$), and between the different units in the bridge ($V_{BB}$). It is important to note that in this mechanism the bridge is never actually reduced or oxidized, so the energy difference between the donor states and the virtual bridging states can be quite large. This energy difference is however still of importance as it modulates how strong the bridge states mix with the donor and accepting states (Eq. 2.16).\[ V_{DA} = \frac{V_{DB}V_{BA}}{\Delta E_{DB}} \left( \frac{V_{BB}}{\Delta E_{DB}} \right)^{N-1} \] Eq. 2.16

Recently it has been suggested that McConnell super-exchange should be complemented by a Gamow type tunneling model for cases where the bridge is highly conjugated. This is because the description of the bridge as a series of electronically coupled subunits starts to break down for highly conjugated bridges, since it is difficult to define the subunit. Furthermore, the distance dependence for the electronic coupling for Dexter type energy transfer starts to deviate from exponential dependence for highly conjugated bridges. This is an observation that can be accounted for by the Gamow model. The Gamow tunneling model treats the bridge as an energetic barrier, which has the width of the bridge length and the height corresponding to energy difference between the bridge state and the reactant state. Both of these properties are in principle experimental observables, however further
corrections are generally needed to account for the non-rectangular shape of the barrier in real systems.

2.3.4 Electron transfer and hole transfer

In the discussion above the electron transfer was either mediated via virtual states where the bridge is reduced or via states where the bridge is oxidized. Transfer via oxidized bridge states is denoted hole transfer and can be described by the same principles and theory as electron transfer (transfer mediated via reduced bridge states). The distinction between hole transfer and electron transfer is useful for identifying which states of the bridge are of most importance for the charge transfer. For electron transfer it is virtual states corresponding to a reduced bridge that is most important, while hole transport is mainly dependent on virtual states corresponding to an oxidized bridge. In general, both electron transfer and hole transfer are active in mediating the charge transfer, but in certain cases one is expected to dominate over the other. Photoinduced charge transfer is one such process, where for cases when the electron donor is the excited chromophore electron transfer tends to dominate, while excitation of the electron acceptor moiety results in hole transfer (see Figure 8).

![Figure 8](image)

*Figure 8. To the left is a frontier orbital model of the difference between having the donor or acceptor moiety excited. When the donor is excited \((D^\ast)\) electron transfer mechanism (i.e. via LUMO) dominated the charge transfer due to the smaller energy gap between the relevant orbitals. The case is reversed for when the acceptor is excite. To the right is a state diagram description of why electron transfer dominates upon donor excitation.*

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\[\text{Also here one can use a simpler description based on frontier orbitals. This is because the electronic state of the reduced bridge is dominated by properties of the LUMO and similarly is the properties of the oxidized bridge dominated by HOMO.}\]
2.3.6 Mixed valance compounds and the Robin-Day classification

Mixed valance compounds are a group of (usually) inorganic complexes where a metal occurs in more than one formal oxidation state. A classical example is the Creutz–Taube ion, (Figure 9), which has two ruthenium ions with identical ligand surrounding, but with an odd number of electrons to distribute between the two metal centers.31,32

In complexes with weak electronic coupling between the two sites the unpaired electron will be localized on one of the two sites (e.g. Ru$^{2+}$-Ru$^{3+}$), while a strong electronic coupling will cause the electron to be delocalized evenly over the two sites (e.g. Ru$^{2.5+}$-Ru$^{2.5+}$). Robin and Day suggested that a mixed valance compound could be divided into three classes.33

**Class I.** The electron is localized on one site and the coupling between sites is so low that the electron will not exchange on the timescale of interest.

**Class II.** The electron is still localized on one site but the coupling between the two sites as fairly strong and the electron will be able to transfer between the two sites.

**Class III.** In this case the electronic coupling is very strong and the electron is delocalized between the two sites.

Using the principles from Marcus theory one can describe the two sites with parabolas (Figure 10). In class I there is no coupling and the two parabolas
cross. In class II there is some coupling and the two parabolas interacts to form two new states; a lower state with two energy minima and an excited state with one energy minima. As the coupling increases the barrier between the two energy minima decrease till a point is reached where there is no barrier at all. This means that the electron is delocalized and over the two sites and thus falls under class III. The Creutz-Taube ion is believed to be on the border between class II and III.34

2.3.7 Intervalence charge transfer bands

Mixed valance complexes of class II and III often display absorption band that is linked to charge transfer from one site to two the other, often denoted as intervalence charge transfer bands (IVCT bands). In Figure 10 one can see that the energy of the IVCT band is related to Marcus parameters. For class III the energy position of the IVCT band corresponds to the twice the electronic coupling, while the absorption maxima for a class II compound corresponds to the reorganization energy for the charge transfer. The electronic coupling \( V \) in a class II compound can be calculated using generalized Mulliken-Hush (GMH) theory.35,36 For a two state description of the IVCT-band one get Equation 2.17, which relates the electronic coupling to the position \( \nu_{max} \) and the transition dipole \( \mu_{ab} \) of the IVCT band and change in static dipole moment between the final and initial state \( \Delta \mu_{21} \).

\[
V_{12} = \frac{\mu_{ab} \nu_{max}}{\Delta \mu_{21}} \quad \text{Eq 2.17}
\]

The transition dipole can be evaluated with Eq. 2.3, while the change in static dipole moment often can be calculated from the electron transfer distance \( r \) times the elemental charge \( \Delta \mu_{12} = r^* e \).

2.4 Energy transfer

Energy transfer is another class of processes by which electronic excited states can become quenched. There are several types of energy transfer mechanisms, but the two most important for this thesis is Förster resonance energy transfer and Dexter energy transfer.

2.4.1 Förster resonance energy transfer

Energy transfer is another class of processes by which electronic excited states can become quenched. There are several types of energy transfer mechanisms, but the two most important for this thesis is Förster resonance energy transfer and Dexter energy transfer.
2.4.1 Förster resonance energy transfer

When two transition dipole moments are close enough they will start to interact. The strength of this interaction is determined by the strength and orientation of the individual dipole moments, and if the two transitions dipole moments overlap in energy. The interaction between the two dipoles can result in the de-excitation of the energy donor and the simultaneous excitation of the energy acceptor. This process is called Förster resonance energy transfer (Figure 11) and the theory behind it can be summarized in Eq. 2.18 and 2.19.

$$k_{FRET} = \frac{8.78 \times 10^{23} \kappa^2 \phi_0}{n^4 \tau_0} |r_{DA}|^{-6} J$$  \hspace{1cm} \text{Eq 2.18}

$$J = \int I(\lambda) e(\lambda) \lambda^4 d\lambda$$  \hspace{1cm} \text{Eq 2.19}

In this equation the energy overlap is described by an overlap integral of the emission and absorption spectra. To get the correct units, nm should be used for wavelength ($\lambda$), the emission spectra should be normalized to an area of 1 and the absorption spectra should be expressed in extinction coefficient with the units [M$^{-1}$ cm$^{-1}$]. By using the extinction coefficients for the absorption spectrum one describes the strength of the transition dipole moments for absorption, while the strength of the emission transition dipole moment is accounted for by the emission rate ($k_f = \phi_0/\tau_0$). The relative orientation of the two vectors are described by $\kappa^2$, which can range between 0 (perpendicular) and 4 (parallel). The refraction index ($n$) describes how strongly the medium between the energy donor and acceptor screens the dipole-dipole interaction. Förster theory also predicts a strong distance dependence ($|r_{DA}|^{-6}$, $r_{DA}$ expressed in Å). Due to this feature FRET has been used as a “molecular ruler” to determine unknown distances e.g. between two amino acids in a folded protein with an unknown structure.\textsuperscript{38}

![Figure 11. Frontier orbital description of Förster resonance energy transfer (left) and Dexter energy transfer (center and right).](image)

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Under optimal conditions FRET can be very fast, which is something that is utilized by photosynthetic organisms. They use large antenna complexes with hundreds of chromophores to capture the sunlight. By having the chromophores arranged in an optimal fashion they can use FRET to transfer the captured energy from the antenna systems to the photosynthetic reaction center. This way hundreds of chromophores can collaborate to drive a single photosynthetic center.

2.4.2 Dexter energy transfer.
In the Dexter mechanism the energy is transferred via two simultaneous electron transfer events (Figure 11).\textsuperscript{39} Energetic overlap between the donating and accepting states is still necessary, but the strength of the transition dipole moments is not relevant anymore. Instead one uses the overlap integral of the normalized spectra to get the overlap in the density of states (\(\rho_{DA}\), Eq.2.20).\textsuperscript{ix} The relationship between Dexter energy transfer and electron transfer also makes the electronic coupling (\(V_{DA}\)) important for the energy transfer rate (Eq. 2.21).

\[
\rho_{DA} = \int I_{\text{norm}}(\vec{v}) Abs_{\text{norm}}(\vec{v}) d\vec{v} \\
\text{Eq 2.20}
\]

\[
k_{\text{Dexter}} \propto V_{DA}^2 \rho_{DA} \\
\text{Eq 2.21}
\]

Just as electron transfer Dexter energy transfer is usually a short range reaction (<10 Å). Dexter energy transfer can, however, also be mediated via the Super-exchange mechanism, which can allow it to be efficient over longer distances. Note also that, in contrast to Förster energy transfer, Dexter energy transfer allows for change in the multiplicity of the energy donor, as long as the energy acceptor also changes its multiplicity.

\textsuperscript{ix} The overlap in Eq 2.12 is best evaluated on an energy scale
3 Methods

In this chapter I will give a brief introduction to the concept of electron donor-bridge-acceptor systems, which are the basis for papers I-V.

3.1 Donor bridge acceptor dyads

Covalently linked donor-bridge-acceptor dyads have, since the first studies in the mid-eighties, been the main workhorse in electron transfer studies. The great success of these systems stems for a couple of favorable properties. First of all the covalent link between donor and acceptor circumvents the diffusion step, which often is the rate limiting step for bimolecular electron transfer reactions. Secondly, by systematically changing the bridging unit one can get insights in how the bridge affects the electron transfer. Thirdly, dyads can function as model systems and potential building blocks for practical application, most notably solar energy conversion.

The characterization of a dyads system requires suitable reference molecules for the donor and acceptor and the references have two main functions.

a) To help with the assignment of observed signals in the dyad, i.e. whether a signal comes from the donor, the acceptor or the bridge or if the signal is due to a new property, unique to the joint dyad system.

b) To determine properties that is intrinsic to the different moieties, e.g. the lifetimes, quantum yields and reduction potentials. Comparing these values to those associated with the dyad system allow one to draw conclusions about additional reaction that appear in the dyads system (see section 2.2.3).

3.1.1 Photoinduced processes in donor acceptor dyads.

The photophysical characterization of dyad can be separated in two main steps. The first is to determine energy of the relevant excited states and charge separated states. The energy of a charge separated state can be calculated via the Weller equation (Eq 2.6). Furthermore, the singlet excited state energies can be calculated as the average between the absorption and fluorescence maxima. In those cases that triplet state energies are important one
can use the phosphorescence spectrum or if that is not possible use triplet energy sensitization.

From the emission spectra one also note if emission quantum yield is lower than in the references, which can be used to confirm the presence of a quenching process. However, to get reliable information about the nature of the quenching process, one needs to do time resolved measurements. In this thesis I have used both time resolved emission and time resolved absorption techniques.

The two main benefits with time resolved emission is that it usually has a good signal to noise ratio and that it only monitor the emissive states. These properties make it ideal for determining the rate for the quenching mechanism, but it cannot determine what the quenching reaction is.

Time resolved absorption can help to resolve that question. In this technique one follow how the absorption spectrum changes as the reaction proceeds. This makes it possible to monitor formation and decay of states that do not emit, such as a triplet state or a charge separated state. For electron transfer studies it is important to have some absorption feature that can identify the charge separated state, e.g. an absorption peak that is unique for the oxidized donor or the reduced acceptor. To know what spectroscopic features to look for in the time resolved experiments one can measure the absorption spectra of the oxidized donor reference and the reduces acceptor reference.
4 Photoinduced electron transfer: summary of the results in paper I-IV

In this chapter I will briefly present the aim and the results from the photo-physical characterization of papers I-IV, while chapter 5 and 6 will discuss different aspects that spans over more than one paper. For a more thorough description of the results I refer to the respective paper.

4.1 Introduction and aim

**Paper I and III:** In these two papers we wanted to investigate long range electron transfer in zinc phthalocyanine (ZnPc) based donor-bridge acceptor system (Figure 12). Phthalocyanines absorb strongly in the red part of the spectrum, which is attractive for solar light harvesting, but they have been far less investigated in electron donor-acceptor systems than porphyrins. We were especially interested in the aspects of having a strong electronic coupling between the bridge and the donor or acceptor, which we hoped would result in high yield for long-range photoinduced electron transfer.

![Figure 12. The structures of the three ZnPc-dyads that were studied in paper I and III](image)

"Figure 12. The structures of the three ZnPc-dyads that were studied in paper I and III"
**Paper II:** This study was a continuation of an earlier investigation on a series of metalloporphyrin - platinum acetylide donor-acceptor dyads.\textsuperscript{40} In the previous study the rate for photoinduced electron transfer (PET) and the subsequent back electron transfer (BET) had been very high. Moreover, BET was so much faster than PET that no CS state could be detected. The aim of this follow-up study was to investigate if changes to the linking position and linking group of the bridge to the porphyrin could slow down in particular the back electron transfer rate (Figure 13).

![Figure 13. The five zinc porphyrin-platinum acetylide dyads and triads studied in paper II.](image)

**Paper IV:** In previous studies of bis-porphyrins with direct ethynyl linking, the back electron transfer has been very rapid.\textsuperscript{41,42} As excited states and radicals can be very differently delocalized onto the bridge, we wanted to investigate systems where only either the donor or the acceptor is linked via an ethynyl group (Figure 14). The choice of porphyrins as donor and acceptors was motivated by the aim of having as similar interaction as possible between how the donor and acceptor interacts with the bridge. Also, both Zn(II)- and Sn(IV)-porphyrins are fluorescent, which should facilitate the studies. The asymmetry in coupling was achieved by having a oligo(phenylene-ethynylene) bridge, that on one side is attached via a phenyl group, while it on the other side is attached via an ethynyl group. Moreover, in the systems where the ethynyl group is on the ZnP, energetic considerations gave that hole transfer via excitation of the SnP group could possibly proceed rapidly via a hopping mechanism, while the back reaction would be limited by a relatively slow super-exchange.
Figure 14. The two dyads that were studied in paper IV. The lower case e next to “OPE”, denotes which chromophore that is attached via an ethynyl group.

4.2 Results

The results from the photophysical characterization are summarized in Table 1, which shows the relevant rate constants and driving forces for the compounds in paper I-IV. The results indicate that all of the dyads studied do undergo photoinduced electron transfer. However, with the exception of ZnPc-OPE-SnP and ZnPc-OPE-AuP+, the subsequent back electron transfer is faster. The ratio of the forward and back electron transfer are in many cases so unfavorable that direct observation of the charge separated state has not been possible. Electron transfer has instead been supported via indirect arguments, such as solvent dependence and exclusion of other possible quenching mechanisms.

Table 1. Summary of rate constants from papers I-V.

<table>
<thead>
<tr>
<th>Paper</th>
<th>Compound</th>
<th>Solvent</th>
<th>$r_{DA}$</th>
<th>PET $^c$</th>
<th>PHT $^c$</th>
<th>BET $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>($\text{Å}$)</td>
<td>($10^{10}$ s$^{-1}$)</td>
<td>($\Delta \Delta G$) (eV)</td>
<td>($10^{10}$ s$^{-1}$)</td>
</tr>
<tr>
<td>I, III</td>
<td>ZnPc-OPE-SnP</td>
<td>PhCN</td>
<td>34</td>
<td>7.7</td>
<td>0.68</td>
<td>25</td>
</tr>
<tr>
<td>III</td>
<td>ZnPc-OPE-AuP+</td>
<td>PhCN</td>
<td>34</td>
<td>100</td>
<td>0.61</td>
<td>(500)$^{EnT/IC}$</td>
</tr>
<tr>
<td>III</td>
<td>ZnPc-OPE-C$_{60}$</td>
<td>PhCN</td>
<td>31</td>
<td>0.11</td>
<td>0.89</td>
<td>~5</td>
</tr>
<tr>
<td>II</td>
<td>ZnP-m-e-Pt$^+$</td>
<td>DMF</td>
<td>15</td>
<td>16</td>
<td>0.34</td>
<td>-</td>
</tr>
<tr>
<td>II</td>
<td>ZnP-m-φ-Pt$^+$</td>
<td>DMF</td>
<td>15</td>
<td>10</td>
<td>0.41</td>
<td>83</td>
</tr>
<tr>
<td>II</td>
<td>(ZnP-m-φ)$_2$-Pt</td>
<td>DMF</td>
<td>15</td>
<td>7.7</td>
<td>0.37</td>
<td>77</td>
</tr>
<tr>
<td>II</td>
<td>ZnP-β-Pt$^+$</td>
<td>DMF</td>
<td>12</td>
<td>2.2</td>
<td>0.33</td>
<td>-</td>
</tr>
<tr>
<td>II</td>
<td>(ZnP-β)$_2$-Pt</td>
<td>DMF</td>
<td>12</td>
<td>1.6</td>
<td>0.29</td>
<td>-</td>
</tr>
<tr>
<td>IV</td>
<td>ZnP-e-OPE-SnP</td>
<td>DCM</td>
<td>36</td>
<td>0.08</td>
<td>0.43</td>
<td>(2.0)$^{EnT}$</td>
</tr>
<tr>
<td>IV</td>
<td>ZnP-OPE-e-SnP</td>
<td>DCM</td>
<td>36 ($3.1)^{EnT}$</td>
<td>~0.1</td>
<td>0.33</td>
<td>~2</td>
</tr>
</tbody>
</table>

$^a$ PhCN = Benzonitrile, DMF = N,N-Dimethylformamide, DCM = Dichloromethane. $^b$ Metal- to-metal distance. $^c$ Observed rates and driving forces for photoinduced electron transfer (BET), Photinduced hole transfer (PHT) and back electron transfer (BET).
4.2.1 ZnPc-OPE-acceptor (paper I and III)

Coming back to the aim of the different studies we can see that the Zinc phthalocyanine based systems, presented in paper I and III, indeed undergo efficient and rapid long-range electron transfer. The use of an ethynyl group to link bridge to the zinc phthalocyanine results in a strong electronic coupling. This is especially apparent in the case for ZnPc-OPE-AuP⁺, where the strong electronic coupling not only results in a very rapid electron transfer, but also strongly affects the steady state absorption spectrum. The influence of the ethynyl group will be discussed more in chapter 5. Comparing the rates for back electron transfer for ZnPc-OPE-AuP⁺ and ZnPc-OPE-SnP, there is a fairly large difference in rate even though the driving force is similar and the connection to the bridge at a first glance looks the same. We hypothesized that the difference was due to how the excess electron was localized on the reduced acceptors, specifically a metal-based reduction of the Au⁺ unit instead of ring-based reduction for SnP. A DFT study of the reduced acceptors gave very strong support that this indeed is the case. The localization of the excess electron in the acceptor and the electron hole in the donor will be further discussed in Chapter 6.

4.2.1 ZnP-Pt (paper II)

The results for paper II show that changes in the linking group decreased the electronic coupling and therefore slowed down the photoinduced electron transfer. The back electron transfer is still very rapid and no significant build-up of charge-shifted or charge separated state could be observed. However, in two of the dyads, ZnP-m-ϕ-Pt⁺ and (ZnP-m-ϕ)₂-Pt, it was possible to observe signals from the oxidized porphyrin and from these determine the rate for back electron transfer.

It is also noteworthy that a large fraction of the back electron transfer for these systems results in the formation of a porphyrin triplet state. This is especially pronounced in the case of (ZnP-m-β)₂-Pt, where changing the from the polar solvent dimethylformamide (DMF) to the fairly non-polar solvent 2-methyltetrahydrofuran (2-MTHF) results in a large increase in the triplet yield.

The effect of changing from an ethynyl group to a phenyl group as a linking group will be discussed in Chapter 5, while the effects of changing linking position between the meso- and β-postions of the porphyrin, will be discussed in Chapter 6.
4.2.2 ZnP\textit{-asymm}-OPE-SnP (paper IV)

In paper IV we observed photoinduced charge transfer from the lowest excited state, whether it belonged to the acceptor or to the donor. In both ZnP-e-OPE-SnP and ZnP-OPE-e-SnP the chromophore with the lowest excitation energy is the one linking via the ethynyl group. There seems to be no significant difference in rate between the photoinduced electron transfer in ZnP-e-OPE-SnP and the photoinduced hole transfer in ZnP-OPE-e-SnP. The back electron transfer is faster than the forward reaction, once again resulting in a case with fairly small populations of the charge separated state. There is also only small difference in the rates for back electron transfer between the two dyads, showing that the direction of the asymmetric bridge, i.e. whether the ethynyl group points toward the donor or acceptor, has very little influence on the overall coupling between the donor and acceptor.

Furthermore, the excitation of the chromophore linking via the phenyl group resulted in rapid energy transfer to the lower laying chromophore. This fast energy transfer also prevented the detection of any photoinduced hole or electron transfer from the higher lying chromophore. It should be noted that the rate for energy transfer is at least twice as fast as what one would expect for pure FRET. This means that there is a significant amount of long range Dexter energy transfer, as discussed in chapter 5.
5 Influence of linking group for electron transfer mediated via an OPE bridge

5.1 Overview

Papers I-IV investigates the effect of having either ethynylene or phenylene as the linking group between bridge and the electron donor and/or acceptor. These are both natural choices as linking groups for the bridge oligo(1,4-phenylene-ethynylene) (OPE, Figure 15). However, majority of reported studies of electron transfer through OPE bridges has used phenylene as linking group. There are only a few reports in the literature on OPE bridged dyad systems that use direct attachment via ethynlenes, \(^{41-45}\) papers I-IV help to bridge some of that information gap. In this chapter I present examples on how the choice of attachment group affects the rate of electron and energy transfer as well as demonstrate the effect of ethynylene attachment on the absorption spectra. This chapter begins with and introduction to OPE bridges and the consequences of using either an ethynylene or and phenylene as attachment group.

![Figure 15. Structure of an oligo(1,4-phenylene-ethynylene)](image)

5.2 Phenylene vs. ethynylene

Due to their high level of conjugation and their rod-like shape, OPE bridges have been popular in electron transfer\(^{21,28,45,46}\) and electron transport studies.\(^{47-49}\) The conjugation makes OPE a very good mediator for long-range electron transfer, while transport and the linear shape allows for good estimation of the electron transfer distance, which can be difficult to do for more flexible bridges. The alternating topology of the OPE bridge also allows for two different of groups to attach the bridge to the donor/acceptor moiety. In cases where the phenylene is used as the attachment group there is steric interaction between the donor/acceptor moiety and the phenyl group, which
forces the phenyl ring to be twisted out of the conjugated plane of the donor/acceptor. This twist decreases the overlap between the two \( \pi \)-conjugated systems and thus results in weaker electronic coupling.\(^{50} \) This type of steric hindrance can be identified in many different systems where it has been previously demonstrated that the electronic coupling of a system can be affected by the dihedral angle between the two interacting \( \pi \)-systems.\(^{51-53} \) In contrast, when an ethynylene is used as linking motif there is very little steric hindrance and the phenyl group is allowed to rotate freely. Consequently, the phenyl groups in OPE bridge allow the formation of conformers that favor conjugation,\(^{8} \) something which results in a stronger electronic interaction.\(^{42,54-56} \) The use of ethynylene as the attachment groups in donor-OPE-acceptor systems is rare in the literature.\(^{42,57} \) Of the reported systems only one system was suitable for a direct comparison of the effects of ethynylene vs. phenylene attachment; dyads based on OPE-bridged Zn(II)-Au(III) bis-porphyrin.\(^{21,41} \) For this pair of electron donor and acceptor the rates for the photoinduced electron transfer (PET) and the subsequent back electron transfer (BET) were two orders of magnitude faster in the ethynylene attached dyads\(^{41} \) when compared to phenylene attached dyads of comparable length.\(^{21} \) Comparison of the two series of Zn(II)-Au(III) bis-porphyrin dyads illustrates that changing both attachment groups. Continuing on this result we wanted to compare the effect of having an asymmetric OPE-bridge, \textit{i.e.} one ethynylene and one phenylene attachment group, and how the orientation of the OPE bridge makes any difference. The results of this project are presented in paper \textbf{IV} and will be discussed in section 5.4 and 4.6 of this chapter.

5.3 Observations from papers I-IV

5.3.1 Effects on the absorption spectra

The electronic influence effect of having ethynylene as the attachment group is evident in the in the absorption spectra of the respective dyads. Figure 16a and b show two examples of electronic absorption spectra from paper \textbf{IV} (SnP) and \textbf{III} (ZnPc). In the top panel the ethynylene linked SnP shows a distinct redshift of both the B- and Q-band compared to the SnP which has a phenylene as the link between porphyrin and the. Furthermore one can observe that the relative difference in size between the B- and the Q-bands, which are much smaller in the ethynylene linked tin porphyrin compared to the phenylene linked species. Both of these observations can be explained by the effect of orbital mixing between the bridge and the \( a_{2u} \) orbital of the por-

\(^{8} \) The phenyl groups will have a tendency to adopt a coplanar conformer with the donor/acceptor moiety, but the barrier for rotation around an ethynyl group is usually so low that all rotational conformers are populated (see for example Eng \textit{et al.} 2009).
phyrin (see section 2.2.3). Firstly, the orbital interaction causes the HOMO be destabilized which results in smaller HOMO-LUMO gap, thus lowering the excited state energy of both the B- and Q-band. Secondly, the destabilization of the HOMO increases the energy gap between HOMO and HOMO-1, which results in a stronger transition dipole for the Q-band and a weaker transition for the Soret band.\textsuperscript{11,58}

By comparing the two phthalocyanines in Figure 16b it appears that the interaction between bridge and the chromophore mainly affects one of the two Q-band transitions. The result is a distinct split of the Q-band as only one of the two degenerate the transitions is stabilized.

As seen in the examples above it is common that the bridge and the donor or acceptor can have substantial interaction. Less common, however, are situations where the donor and acceptor moieties interact so strongly that it significantly alters the ground state absorption spectrum. ZnPc-OPE-AuP\textsuperscript{+} is a surprising exception and there is a distinct difference between the spectrum of the full system and the spectra of its individual components (ZnPc-OPE and OPE-AuP\textsuperscript{+}) (Figure 16c). The most notable difference is that the fairly sharp B-band of the AuP\textsuperscript{+} (~430 nm) has disappeared and in its place there is new very broad and strong band that covers the spectrum between 300 and 500 nm. When the ZnPc moiety is oxidized the broad band disappears and a sharp AuP\textsuperscript{+} B-band reappears at 430 (see paper III). It appears that the broad band at 300-500 nm is dependent on both AuP and ZnPc which implies that there is a strong charge transfer character to these transitions. TD-DFT calculations\textsuperscript{a} on the full dyads indicate that some of the transitions in the 300-500 nm region that have a charge transfer character to them.

\textsuperscript{a} CAM-B3LYP with 6-31G(d) for light elements and LanL2DZ for Au and Zn. See paper III for details.
5.3.2 Effect on electron transfer rates

In paper II the objective was to reduce the electronic coupling and thus slow down the very rapid electron transfer rates (both PET and BET) that was observed for the ethynylene linked ZnP-Pt dyad \((\text{ZnP-}m\text{-e-Pt}^+)\). In the context of the results that were discussed in section 5.2, we decided to try to reduce the ET rates by shortening the OPE bridge by one ethynyl group and instead have a phenylene as the linking group. Comparing the measured ET rates for \(\text{ZnP-}m\text{-e-Pt}^+\), with those of \(\text{ZnP-}m\text{-}\phi\text{-Pt}^+\) and \((\text{ZnP-}m\text{-}\phi)_2\text{-Pt}\), one can indeed see that the rates of PET decreases by a factor of two. The effect of the linking group is thus much smaller than what was observed for the \(\text{ZnP-OPE-AuP}^+\) systems discussed above. One possible explanation for this is the much shorter ET distances the ZnP-Pt systems and that a change in length of an ethynyl group thus corresponds to a large relative change in ET distance.

In paper I and III the effects of strong electronic coupling between the bridge and the donor and acceptor is apparent. The observed rates of photoinduced electron transfer in \(\text{ZnPc-OPE-SnP} (k_{\text{PET}} = 7.7 \times 10^{10} \text{ s}^{-1})\) and
ZnPc-OPE-AuP\(^+\)\((k_{\text{PET}} = 1.0 \times 10^{10}\ \text{s}^{-1})\) are one-two orders of magnitude faster compared to the PET rate in donor-acceptor dyads with similar \(\Delta G^\circ\) and \(\lambda\) and bridge lengths, but have phenylene linkage between the bridge and the donor and acceptors.\(^{21,59,60}\) The difference in PET rate between ZnPc-OPE-AuP\(^+\) and ZnPc-OPE-SnP was also be attributed to a steric effects, since the vinylene attachment group (ZnPc-OPE-SnP) is slightly twisted out of the porphyrin plane (dihedral angle of 40°).\(^{xi,61-63}\) In contrast to ZnPc-OPE-SnP and ZnPc-OPE-AuP\(^+\), ZnPc-OPE-C\(_60\) has a rather low rate for PET (\(k_{\text{PET}} = 1.1 \times 10^9\ \text{s}^{-1}\)), which most likely is due to the break in conjugation between the OPE bridge and the fullerene, resulting in weak electronic coupling. However it should be noted that this ZnPc-C\(_60\) dyad display slower PET rates than other reported systems.\(^{64}\)

It is noteworthy that the back electron transfer rates for this series have the opposite trend compared to PET, with ZnPc-OPE-C\(_60\) being the fastest and ZnPc-OPE-AuP\(^+\) the slowest. This trend will be discussed further in Chapter 6.

As mentioned above the aim of paper IV was to test if it made any difference whether it was the donor or acceptor that had good electronic coupling to the bridge. This is still work in progress but the results indicate that there is no significant difference in back electron transfer rates. For the photoinduced

\(\text{\footnotesize xi} \) Comparisons between ET rates from two different series of dyads should be done with caution. In this case the \(\Delta G^\circ\) and \(\lambda\) are similar enough between ZnPc-OPE-SnP (paper I), ZnPc-OPE-AuP\(^+\) (paper III) and ZnP-OPE-AuP\(^+\) (Albinsson and coworkers) and the rate difference large enough that the difference in rate has to be due to differences in electronic coupling.

\(\text{\footnotesize xii} \) Oligo(Phenylene-vinylnene) (OPV) is often reported to be an excellent bridges for charge transfer, often with less distance dependence (lower \(\beta\)) than OPE. However in OPV the steric interaction between the phenyl and vinylene is rather small and thus is the dihedral angle between the different small is rather small. In contrast, the steric interaction between the porphyrin and vinylene results in a rather large dihedral angle and thus lower coupling.
processes plan was to compare how the PET (electron transfer driven by the excited state of ZnP) and PHT (hole transfer driven by the excited state of SnP) were influenced by the asymmetric bridge. This comparison could, however, not be made, since a fast energy transfer process outcompeted PET and PHT for the situations where the excited state is on a chromophore with phenylene attachment (see Figure 17 for a schematic state diagram). Photoinduced charge separation (PET or PHT) could be observed from the excited state of the porphyrin moiety with ethynylene linkage. The observed rates ($k_{\text{PET}} = 0.8 \times 10^9 \text{ s}^{-1}$, $k_{\text{PHT}} = 1 \times 10^9 \text{ s}^{-1}$) are quite low both compared to the systems in paper III and to the ZnP-OPE-AuP⁺, systems discussed above. However, this is most probably an effect of the much lower driving force ($\Delta G_{\text{PET}}^\circ = -0.43$, $\Delta G_{\text{PHT}}^\circ = -0.33$) in ZnP-SnP system compared to the others (see Table 1).

5.2.3 Effect on energy transfer rates.

**ZnP-asymm-OPE-ZnP**

The energy transfer processes that were observed in paper IV are surprisingly fast ($k_{\text{EnT}} \approx 2 \times 10^{10} \text{ s}^{-1}$), considering that the center-to-center distance is 36Å. This fast energy transfer can partly be explained by a large spectral overlap between donor emission and acceptor absorption ($J \approx 2 \times 10^{-13} \text{ M}^{-1} \text{ cm}^3$), but the estimated Förster rate ($k_{\text{FRET}} \approx 0.5 \times 10^{10} \text{ s}^{-1}$) is still only a forth of the observed rate. Consequently, there is a significant contribution of bridge mediates Dexter energy transfer in these systems ($k_{\text{Dexter}} \approx 1.5 \times 10^{10} \text{ s}^{-1}$). Similar Dexter rates has been observed for other ethynylene attached bis-porphyrin systems, but it is significantly faster compared to bis-porphyrin systems with phenylene attachment. This once again shows that ethynylene linkages result in a significant increase in electronic coupling compared to phenylene linkages.

5.3 Summary

In this chapter I have discussed and illustrated the strong electronic interaction effect that occurs when the donor and acceptor are linked via an ethynylene instead of a phenylene. This effect manifests itself in both strong perturbation of the electronic absorption spectra and fast rates for both electron transfer rate and bridge mediated energy transfer.
6 Probing differences in electronic coupling using time-resolved laser spectroscopy and DFT calculations

6.1 Outline
In this chapter I will present two examples where the interpretation of the experimental data greatly benefited from qualitative support for the theoretical calculations can be used in the context of photoinduced electron transfer to give qualitative support and explanation to observed experimental trends. The calculations presented herein are based on fairly simple computational protocols and rely on methods that are implemented in quantum chemistry programs, such as Gaussian 09, thus being readily available for other experimentalist.

The first example is from paper II, where we investigated the difference in activity for electron transfer between the meso- and β-position of a porphyrin. The discussion in this chapter will be based on results from paper II as well as examples from the literature and some previously unpublished TD-DFT calculations.

In the second example I will discuss the trend for back electron transfer in the ZnPc-acceptor systems in paper III. Two hypotheses for the observed trend will be discussed: The Marcus inverted region (Ch. 2.3.1) and effects on the electronic coupling due to localization/delocalization of the radical anion. The latter hypothesis will be tested and illustrated with DFT calculations.

6.2 Effect of the attachment position in porphyrins
6.2.1 Experimental trends
Table 2 summarizes the results from paper II and work by Hayes at al. and Song et al. The results show a clear trend in that the meso-position on the porphyrin is more reactive than the β-position both for photoinduced electron transfer and for the subsequent back electron transfer.
Table 2. A compilation of reported systems that compare the electron transfer reactivity of the meso- and \(\beta\)-positions on a porphyrin.

<table>
<thead>
<tr>
<th>System</th>
<th>Solvent (^b)</th>
<th>Position (^c)</th>
<th>(k_{\text{ET}}) (^{d,e}) (ps)</th>
<th>(k_{\text{BET}}) (^{d,e}) (ps)</th>
<th>(k_{\text{PET,meso}}) (^c) (/k_{\text{PET,}\beta})</th>
<th>(k_{\text{BET,meso}}) (^c) (/k_{\text{BET,}\beta})</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnP-e(\phi)-Pt (^{d,e})</td>
<td>DMF</td>
<td>meso</td>
<td>6 (^d)</td>
<td>17 (^e)</td>
<td>7.5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\beta)</td>
<td>45 (^e)</td>
<td>130</td>
<td>7.5</td>
<td>5.0</td>
</tr>
<tr>
<td>ZnP-(\phi)Pl (^g)</td>
<td>2-MTHF</td>
<td>meso</td>
<td>17 (^e)</td>
<td>710</td>
<td>7.5</td>
<td>5.0</td>
</tr>
<tr>
<td>H(2)P-(\phi)-ZnP (^h)</td>
<td>PhCN</td>
<td>meso</td>
<td>6 (^e)</td>
<td>20</td>
<td>3.2</td>
<td>3.3</td>
</tr>
</tbody>
</table>

\(^a\) The abbreviation of the system is based on structural features. “e” denotes ethynylene and “\(\phi\)” is 1,4-phenylene. ZnP and H\(2\)P is zinc and freebase porphyrins respectively. Pt \(^c\) is platinum acetylide and Pl is a pyromellitimide. See respective reference for structures. \(^b\) DMF = N,N-dimethylformamide; 2-MTHF = 2-methyl-tetrahydrofuran; PhCN = Benzonitrile. \(^c\) Ratio of the PET rates respective the BET rates of the meso- and \(\beta\)-linked systems. \(^d\) Monneraeu \(et al.\).40 \(^e\) Paper \(II.\) \(^f\) The back electron transfer was too fast to be determined. \(^g\) From Hayes \(et al.\).68 \(^h\) From Song \(et al.\).69

6.2.2 Frontier orbital analysis

To understand why the different attachment positions on a porphyrin give different reactivity one has to examine the shape and extension of the frontier orbitals and how these orbitals are involved in the electron transfer. Figure 18 shows the frontier orbitals for the three derivatives of zinc porphyrins that were studied in paper \(II\) (ZnP-meso-\(\phi\), ZnP-meso-e and ZnP-\(\beta\)-e). The general shape of the orbitals remain very similar to those of an unsubstituted porphyrin\(^{11}\) (Figure 4 in section 2.2.4) and the most noticeable difference between the three zinc porphyrins is which of the orbitals are delocalized out on the OPE moiety.\(^{xiv}\) For the two porphyrins that have the OPE functionality on the meso-position it is the HOMO, \(\psi_1\) (“pseudo a\(_{2u}\)” symmetry), that is delocalized out on the bridge, while HOMO-1, \(\psi_2\) (“pseudo a\(_{1u}\)” symmetry), has negligible density there. In contrast, for the \(\beta\)-substituted porphyrin the OPE moiety mainly interacts with \(\psi_2\), while the \(\psi_1\) has very little density out on the bridge. The OPE moiety interacts with the two unoccupied orbitals (\(\psi_3\) and \(\psi_4\)) differently and only the LUMO, \(\psi_3\), will have any significant density on the bridging unit.

\(^{xiv}\) In the context of the discussion in Chapter 5 it is instructive to compare ZnP-meso-e and ZnP-meso-\(\phi\). Note how having ethynylene as the attachment group (ZnP-meso-e) allows the phenyl group of the OPE bridge to adopt a planar conformer (see Figure 15) and thus allowing the \(\psi_1\) and \(\psi_3\) orbitals to strongly interact with the bridge. In contrast, the porphyrin with phenylene attachment (ZnP-meso-\(\phi\)) has the phenyl group twisted out of the porphyrin plane, resulting in less interaction between the \(\psi_1\) and \(\psi_3\) orbitals and the bridge.
The reactant state for the photoinduced charge transfer in these complexes is the lowest excited state (Q-band) and it is thus necessary to evaluate how the different orbitals are involved in this state. TD-DFT indicate that for the three zinc porphyrins in question, the Franck-Condon state of the lowest excited state is dominated by a \( \psi_1 \rightarrow \psi_3 \) transition, with some additional contribution of \( \psi_2 \rightarrow \psi_4 \). Assuming that this description is valid also for the relaxed excited state, one can conclude that \( \psi_1 \) and \( \psi_3 \) are the orbitals of most interest for describing the reactivity of the excited state of these porphyrins. The LUMO, \( \psi_3 \), has significant density on the bridge in all three porphyrins so this does not seem to be the origin of the differences in ET activity be-

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**Figure 18.** Frontier orbital (Kohn-Sham) of the three derivatives of zinc porphyrins presented in paper II. The orbitals are named according to which orbital they resemble in an unsubstituted porphyrin (Figure 4. Note that the orbitals are ordered according to their energy, thus \( \psi_2 \) is below \( \psi_1 \) for these substitution patterns. The arrows and percentage numbers represent the orbital transitions and their contribution to the lowest excited state calculated by TD-DFT. Several other orbital transitions are also involved in the excited state, but each one contributes to less than 2% to the overall electronic transition.

---

\( \text{ZnP-meso-} \phi \) \( \text{ZnP-meso-} e \) \( \text{ZnP-} \beta -e \)

---

\( \psi_4 \) "pseudo e_g" 
\( \psi_3 \) "pseudo e_g" 
\( \psi_1 \) "pseudo a_2u" 
\( \psi_2 \) "pseudo a_1u"

---

\( ^{\text{xv}} \) Geometry optimization and TD-DFT performed in Gaussian 09 with PBE0/6-31G(d) and PCM = acetonitrile.
tween the meso- and β- linking position. In contrast, \( \psi_1 \) is only delocalized onto the OPE-bridge when it is attached \textit{via} the meso-position, while this orbital has very little density on the bridge when it is attached \textit{via} the β-position. It thus appears that it is the HOMO orbitals that are the key to explaining the differences in meso- and β- position activity.

**6.2.3 Examples from the literature**

A study by Yang \textit{et al.} on Dexter energy transfer in bis-porphyrin dyads gives further insight into this topic.\textsuperscript{44} By using perfluorinated phenyl groups instead of regular phenyl groups as substituents on the three meso-position that are not involved in the bridge, they managed to stabilize \( \psi_1 \), thus making \( \psi_2 \) the HOMO.\textsuperscript{70-72} Energy transfer in these bis-porphyrin systems were faster via the β-position than through the meso-position giving further support to the conclusion that the shape of the HOMO is the key to the electron transfer activity of the lowest excited state (Q-band).

Hayes \textit{et al.}\textsuperscript{68} showed that for regular zinc tetraarylporphyrins it is the β-position that has the highest electron transfer activity for reactions from the second singlet excited state of the porphyrin (B-band). They explain this with the fact that the B-band is dominated by a HOMO-1 to LUMO+1 transition and it is thus the shape of HOMO-1 (in this case \( \psi_2 \)) that determines the activity for electron transfer from the second excited state.

Similar dependencies on electron transfer reactivity on linking position can be found in many other chromophores, for example monoimide- and diimide-derivatives of naphthalenes and perylenes.\textsuperscript{73-76}

**6.2.4 Summary, meso vs. β**

The experimental results described in this part indicate that the meso-positions on regular tetraarylporphyrins are more active for electron transfer than the β-position. This can be explained by that the fact that the lowest exited state is dominated by an orbital transition involving the \( \psi_1 \)-orbital (“pseudo a\textsubscript{2u}“- symmetry). This orbital has a high density on the meso-position, while it is very weak at the β-position and therefore the electronic coupling is higher at the meso-position. Furthermore if the porphyrin has a substitution pattern such that the \( \psi_2 \)-orbital is the HOMO the roles will be reversed and the β-position will be the most active for electron transfer. These results illustrate how the choice of attachment position and substitution pattern can be used to tune the electron transfer activity of porphyrins.
6.3 Back electron transfer in ZnPc-OPE-acceptor dyads

6.3.1 Electron transfer rates and the Marcus inverted region

In paper III we found that the back electron transfer rates for ZnP-OPE-AuP⁺ and ZnP-OPE-SnP (1.0×10⁹ s⁻¹ and 1.2×10¹⁰ s⁻¹ respectively, see Table 1. Ch 4.2) had the opposite trend compared to the rates for photoinduced electron transfer (1.0×10¹² s⁻¹ and 7.7×10¹⁰ s⁻¹ respectively). That ZnP-OPE-AuP⁺ has both the fastest PET and the slowest BET is rather surprising considering that the driving forces and reorganization energies are very similar for the two dyads. xvi One explanation is that BET is in the Marcus inverted region. However, since the difference in driving force is so small one would need to assume a quite small reorganization energy (\(\lambda < 0.5\) eV) to get an effect this large on the ET rates and our estimates of the reorganization indicate that it is at least 0.8 eV. xiv,xvii A reorganization energy of this magnitude suggest the BET reactions are indeed in the Marcus inverted region, but not deep enough to fully explain the rate difference.

6.3.2 Localization and delocalization of the anion radical

As a complementary explanation we proposed that the difference in k_BET between ZnP-OPE-AuP⁺ and ZnP-OPE-SnP is due to differences in where the excess electron is localized in the reduced acceptors. This idea is based on studies by Kadish and coworker, who discovered that a Gold(III) porphyrin can have its first reduction to occur at either at the metal center or at the porphyrin ring, depending on the substitution pattern. 77,78 In contrast, other regular porphyrins, such as Sn(IV) porphyrins, have their first reduction on the porphyrin ring.79 We thus hypothesized that for there is a significant difference in electronic coupling for back electron transfer when the reduction is localized on the metal compared to when it is localized on the porphyrin ring.

xvi Estimates of driving forces indicate that BET is slightly more exothermic in ZnP-OPE-AuP⁺ (\(\Delta G^\circ = -1.16\) eV) compared to ZnP-OPE-SnP (\(\Delta G^\circ = -1.09\) eV). The outer reorganization energies are expected to be the same for the two dyads and was estimated to \(-0.8\) eV in benzonitrile using the dielectric continuum model. See supporting information in paper III for details.

xvii Kadish and coworkers reported reorganization energy of 1.2 eV for reductive quenching of \(^3\)AuP⁺ in benzonitrile. This indicates that our estimate for \(\lambda\) in ZnP-OPE-AuP⁺ is on the low side rather than on the high side. A reorganization this large for ZnP-OPE-AuP⁺ would however mean that the BET would be almost barrier less making the fairly slow back electron transfer even more puzzling.
To test the idea we performed DFT calculations on the reduced form of bridge-porphyrin units and examined where the spin density of the radical anion is localized (Figure 19). For each bridge acceptor system we studied two geometries. The first is the equilibrium geometry of the acceptor before reduction and the second is the equilibrium geometry of the reduced acceptor. The former geometry, denoted “unrelaxed”, should be a fair estimation of the geometry directly after reduction and thus report on which part of the porphyrin is initially reduced. The latter geometry, denoted “relaxed”, should correspond to the geometry that is the reactant state of the back electron transfer. The results indicate that at the unrelaxed geometry both porphyrins have the spin delocalized over the porphyrin ring and even spreading out on the OPE-bridge, thus indicating a large electronic coupling between the bridge and the acceptor. Allowing the nuclear coordinates to relax to their optimal geometry results in almost no change at all for the tin porphyrin, as the reduced acceptor and the bridge are still strongly coupled. In contrast, the relaxed form of the reduced gold porphyrin has almost all of the radical character on the gold ion and very little that is delocalized onto the bridge.\footnote{A similar type analysis for the \textit{ZnPc-OPE-C}_{60} dyad could unfortunately not explain why this dyad had a slow photoinduced electron transfer, while the back electron transfer was very fast. Furthermore, a comparison with other reported systems Bottari \textit{et al.} revealed that \textit{ZnPc-OPE-C}_{60} in paper \textit{III} is a surprising exception to a trend that otherwise show that \textit{ZnPc-C}_{60} systems have a faster rate for PET than BET.} Thus, the lower BET rate in \textit{ZnPc-OPE-AuP}^{+}, compared to the
ZnPc-OPE-SnP, appears to be due to a metal centered reduction of the gold porphyrin. The lower spin density on the bridge indicate that the SOMO orbital which holds excess electron is less coupled to the bridge states compared to the SOMO in the reduced tin porphyrin. This difference in electronic coupling is probably the main reason why back electron transfer is faster in ZnPc-OPE-SnP compared to ZnPc-OPE-AuP⁺.

6.3.3 Summary, AuP⁺ vs SnP
Back electron transfer in ZnPc-OPE-AuP⁺ and ZnPc-OPE-SnP occurs in the Marcus inverted region, but the difference in rate is to large to be explained exclusively by the inverted region effect. DFT indicate that the reduced gold porphyrin, relaxes to geometry where it is the metal center, rather than the porphyrin ring, which is reduced. This stabilizes the reduced acceptor and reduces the electronic coupling to the bridge. SnP and, other regular, porphyrins can not undergo a similar metal based reduction and the result is a reduced species that still is strongly coupled to the bridge. The trapping mechanism that occurs in the gold porphyrin might explain why so many gold porphyrin based dyads have relatively long charge separated lifetime. Furthermore, it would be valuable if this kind of electron trapping mechanism in could be incorporated in a reduction catalyst, thus reducing the rate of counter productive back electron transfer.
7 Charge transfer mediated by cross-\(\pi\)-conjugated and cross-hyperconjugated bridges

7.1 Outline

In Chapter 5 and 6 I discussed different aspects of electron transfer mediated by highly conjugated OPE bridges. In this chapter, concerning paper V, I will instead discuss electronic coupling in systems where the conjugation of the bridge has been interrupted, either by a saturated group (C(Me)\(_2\), Si(Me)\(_2\) or Si(TMS)\(_2\)) or a cross-conjugated functionality (CC(Me)\(_2\)). The electron transfer through these bridging groups was studied by incorporating them in a series of symmetric bis-triarylamines dyads (Figure 20). A one electron oxidation transforms these dyads into mixed-valence compounds, which allowed us to study intervalence charge transfer (IVCT) bands to measure how the electronic coupling varied due to different bridging groups. We also performed quantum mechanical calculation to support and explain the experimentally observed trend.

Figure 20. Structures and abbreviations of the four dyads studied in paper V.
7.2 Conjugation, cross-conjugation and hyperconjugation

Conjugation is a central concept within chemistry and at its core it can be described as the stabilization effects that occur when local orbital fragments are allowed to interact. The most well known type of conjugation occurs in structures with alternation single and multiple bonds. Conjugation also results in strong electronic communication between the different parts of the conjugated system. An additional effect of conjugation is that π-electrons can be delocalized throughout the conjugated system. As previously discussed in Chapter 5, the strong electronic communication in conjugated system can be an efficient mediator for electron and charge transport. However, not all conjugation patterns results in equally strong electronic coupling (Figure 21).

Conjugation stabilization can also occur between two sigma orbitals (σ-conjugation) or between a π- and σ-orbitals (hyperconjugation) and while the effects of these types of conjugation are not as strong as those of π-conjugation, they have been shown to be of importance for several phenomena in organic chemistry.

Recently Emanuelsson et al. reported a study on how cross-hyperconjugation (i.e. the combination of two hyperconjugated system) affects the interaction between two linear π-conjugated systems. Their results indicated that the strength of interaction between the two π-systems can be tuned by varying the substituents on the saturated central atom. The strongest effect from cross conjugation can be seen when electron releasing groups, such as trimethylsilyl (TMS) were used as substituents, which in turn...
can be rationalized by better energetic matching between the $\pi$- and $\sigma$-orbital fragments.

7.3 Electron transfer through cross-$\pi$-conjugated and cross-hyperconjugated bridges

7.3.1 Intervalance charge transfer bands

In paper V we wanted to compare how well the cross-hyperconjugation and cross-$\pi$-conjugation mediates electronic coupling and also if it is possible to tune the electronic coupling in cross-hyperconjugated bridges. We decided that studies of IVCT bands in mixed-valence compounds would be a good method for these specific questions. Building on the work of Lambert and co-workers we designed a series of new bis-triarylamine dyads, which were linked via either a cross-conjugated or a cross-hyperconjugated bridge (Figure 20). These dyads were dissolved in acetonitrile and transformed into mixed-valence compounds via a one electron oxidation using Cu$^{2+}$ as the chemical oxidant. The resulting IVCT bands are all fairly weak (Figure 22), but the spectrum of the mixed-valence form is distinctly different from those of the neutral and twice oxidized forms so the assignment is unambiguous.

The IVCT bands were analyzed with Generalized Mulliken Hush Theory (GMH, see Ch 2.3.7) and the results are summarized in Table 3. The observed coupling elements, $V_{12}$, ranges between $\sim$110 and 390 cm$^{-1}$, which is substantially lower than the coupling that was observed in a similar bis-triarylamine bridged by a para-phenylene group ($V_{12} = 1000$ cm$^{-1}$). Comparing the four dyads it is surprising that D-CC(Me)$_2$-D and D-C(Me)$_2$-D have almost the same electronic coupling, considering that $\pi$-conjugation usually results in a stronger effects than hyperconjugation. Furthermore, comparing the cross hyperconjugated bridges the most important features for the electronic coupling seems to be whether carbon or silicon is used as the bridging element. The influence of substituents (Me or TMS) seems to be fairly small, which is contrary to the trend that we expected based on the result of Emanuelsson et al. To further investigate these trends we decided to do a quantum mechanical investigation of the mixed-valence compounds.
Figure 22. Near infrared absorption spectra of the Mixed-valence compounds (line, D\textsuperscript{+}D). The twice oxidized dyads are also included for comparison (dotted, D\textsuperscript{+}D\textsuperscript{+}). The dashed dotted line corresponds to the Gaussian peak fit to the IVCT band. The neutral form of the dyads has no absorption below 20×10\textsuperscript{3} cm\textsuperscript{-1}. See paper V for complete spectra.

Table 3. Summary of experimental and computational results

<table>
<thead>
<tr>
<th></th>
<th>Experimental</th>
<th>Calculations</th>
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<tbody>
<tr>
<td></td>
<td>$\nu_{\text{max}}$\textsuperscript{a} (cm\textsuperscript{-1})</td>
<td>$\epsilon_{\text{max}}$\textsuperscript{b} (M\textsuperscript{-1} cm\textsuperscript{-1})</td>
</tr>
<tr>
<td>D-Si(TMS)\textsubscript{2}-D</td>
<td>9900</td>
<td>150</td>
</tr>
<tr>
<td>D-Si(Me)\textsubscript{2}-D</td>
<td>1000</td>
<td>170</td>
</tr>
<tr>
<td>D-C(Me)\textsubscript{2}-D</td>
<td>820</td>
<td>1370</td>
</tr>
<tr>
<td>D-CC(Me)\textsubscript{2}-D</td>
<td>9800</td>
<td>1850</td>
</tr>
</tbody>
</table>

\textsuperscript{a} $\nu_{\text{max}}$ denotes the centre position of the Gaussian fit to the IVCT band. \textsuperscript{b} $\epsilon_{\text{max}}$ is the amplitude of the IVCT band. \textsuperscript{c} $V_{12}$ is the electronic coupling constant acquired from DMH analysis of the experimental IVCT band. \textsuperscript{d} $E_{00, BW}$ is the calculated excitation energy for the IVCT transition. The reported value corresponds to a Boltzmann and oscillator strength weighted average of the 16 calculated conformers. \textsuperscript{e} $f$ is the oscillator strength for respectively the [0°,0°] and [90°,90°] conformer. \textsuperscript{f} $f_{BW}$ is the oscillator strength, corresponding to a Boltzmann weighted average of the 16 conformers. \textsuperscript{g} $V_{12, BW}$ is the calculated electronic coupling using $E_{00, BW}$ and $f_{BW}$.
7.3.2 Theoretical investigation of the mixed valence compounds

The computational protocol used in paper \textbf{V} was an adaption of the method used by Renz et al. and the principles behind the protocol is fairly simple. DFT is used to optimize the ground state of the mixed-valence compounds (+1 charge, doublet). At the optimized geometry a TD-DFT calculation yields the vertical transitions and the IVCT transition can be identified by inspection of the orbital contribution to the transition. The oscillator strength for the calculated IVCT transition is directly linked to the magnitude of the experimental IVCT band and it can thus be used to estimate the electronic coupling.

Before we started the investigation we performed a benchmark test on three different functionals in the Gaussian 09 computational package. The best results were achieved by using the hybrid functional PBE0. The benchmarking test also indicated that it was important to include a solvent model and that a fairly small basis-set (6-31G(d)) was sufficient.

The initial round of geometry optimization resulted quite different conformers for the four dyads. In particular, the rotational conformer around the two ethynyl groups varied. To test the dependence of the electronic coupling on these rotational conformers we performed a relaxed conformational scan between 0°–90° (steps of 30°) for the two relevant dihedral angles. The results from the optimization scans do indeed show there is almost free rotation around the ethynyl bonds. Furthermore, TD-DFT calculations at each of the optimized conformers indicate a pronounced conformational dependence for the oscillator strength of the IVCT transition (Table 8.1). Interestingly, the trend for how the oscillator strength varies with conformational change is different between the four dyads. For \textbf{D-CC(Me)$_2$-D} and \textbf{D-Si(TMS)$_2$-D}, the IVCT transition is strongest at the [0°,0°]-conformer, i.e. when two “inner” phenyl groups are rotated so that they are in the same plane of the two ethynyl groups. In contrast the [90°,90°]-conformer (i.e. when the two inner phenyl groups are rotated out of the plane spanned by the two ethynyl groups) is the one that results in the strongest IVCT transitions for \textbf{D-C(Me)$_2$-D} and \textbf{D-Si(Me)$_2$-D}. This trend can be explained by inspecting the spin densities at the different conformers (Figure 23).

At the [0°,0°]-conformer the electronic coupling between the two triarylamines occurs through the bridging element, via either cross-hyperconjugation or cross-conjugation. One can also see that it is the two dyads with the most spin density at the centre (\textbf{D-CC(Me)$_2$-D} and \textbf{D-Si(TMS)$_2$-D}) which have the strongest electronic coupling at this conformer (Figure 23 and Table 3). At the [90°,90°]-conformer the coupling interaction occur through space between the two ethynyl groups (See schematic cartoon in Figure 23). The effect of this interaction can be seen as weak presence of spin density on ethynyl group on the neutral side. That the through space interaction is stronger in the carbon bridges compared to the silicon bridges can be explained by longer Si-C which moves the two ethynyl groups further apart.
Lastly, at the [90°,0°] and the [0°,90°] conformers (not displayed) the IVCT transitions have zero oscillator strength, thus is both the through space pathway and the cross-conjugated/cross-hyperconjugation pathway blocked. This is another example the effect that two orthogonal π-system has zero interaction (see ch 5). An effect of the conformational freedom is thus that these
dyads dynamically transfer back and forth between being a Robin-Day class I and class II mixed valance compound. This is an effect that probably is common in conformationally flexible mixed-valence compounds, but the class I/II border is rarely discussed in the literature.

When taking conformational freedom into account the calculated electronic coupling elements agree surprisingly well the experimental values.

### 7.4 Summary

Electronic coupling in these dyads occurs through two different interactions: Through space and cross-conjugation/cross-hyper conjugation. The through space interaction is strongest at the [90°,90°]-conformer and the strength of this interaction is linked to the distance and angle between the two ethynyl groups. Cross-π-conjugation and cross-hyperconjugation has the strongest effect at the [0°,0°]-conformer. If one only examine the [0°,0°]-conformer one can see that the cross-hyperconjugation pathway can be tuned by varying the substituents on the saturated bridge. More electron withdrawing groups results in stronger conjugation effects.

**Fotosyntesen**

Fotosyntesen hos växter och alger är ett mycket intrikat maskineri, där ljusenergi omvandlas till kemisk energi i form av energirika ämnen, som sedan används för att omvandla koldioxid till bl.a. kolhydrater. Huvudkomponenterna i de ljusdrivna reaktionerna är två stycken fotosystem (Fotosystem I och II) som båda sitter fast i ett membran (Figur 1). De två fotosystemen är ansvariga för varsin kemisk reaktion. Fotosystem II oxiderar (tar bort elektroner) från vatten (H₂O) och bildar då syrgas (O₂) och fria vätejoner (H⁺). Elektronerna som tagits bort från vattnet fraktas via en elektrontransportskedja till Fotosystem I, denna kedja hjälper också till att förflytta vätejoner från en sida av membranet till den andra sidan. Slutligen så används elektronerna hos Fotosystem I för att reducera (lägga till elektroner) en molekyl som heter NADP+ och som då omvandlas till NADPH. Därmed har det skapats en skillnad i hur många vätejoner det finns på vardera sidan om membranet och denna skillnad kan cellen använda för att skapa ATP. NADPH och ATP används sedan för att fixera koldioxid från luften, som sedan används för att tillverka olika biomolekyler, till exempel socker.

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xiix ATP är cellens energivaluta och kan användas för att driva en mängd olika processer.
Figur 1. Till vänster är en schematisk beskrivning av fotosyntesen. PS I och PS II är de två fotosystemen som finns och pilarna visar hur elektronerna flyttar sig inom systemet. Till höger är en beskrivning av ett enkelt artificiellt system. Överkryssade pilar är reaktioner som är oönskade, eftersom de leder elektronerna i fel riktning. Det är bryggan som binder ihop de olika delarna som jag har ägnat större delen av min forskning åt.

Ljusdriven elektronöverföring

Motorn bakom hela den här processen är två pigment, ett för vardera fotosystem. När deras pigment träffas av ljus så kommer de att snabbt ge bort en elektron till en elektronmottagande molekyl ("elektron acceptor"). Det saknas nu en elektron hos pigmentet (dvs. det är positivt laddat) och denna avsaknad brukar benämnas "elektronhål". Elektronhålet vill reagera med något och ta tillbaka en elektron och det är det som sker när PS II tar elektroner från vattnet. En potentiellt dålig reaktion är om elektronhålet istället reagerar med den elektron som just skickats iväg. För att undvika detta så har evolutionen utvecklat fotosystemen så att de kan kontrollera att elektronerna i regel bara går i en riktning.

Artificiell fotosyntes och solceller.

Solceller fungerar enligt samma principer som fotosyntesen. Det infångade ljuset skapar en aktiverad elektron (negativ) och ett elektronhål (positiv). I solceller leds dessa laddningar i motsatta riktningar och tillsammans skapar de då en ström. I artificiell fotosyntes (Figur 1, höger) så är målet att efterhärma de oxidativa och reduktiva reaktionerna hos fotosyntesen för att på så sätt lagra energin hos elektronerna och elektonhålen i form av energirika molekyler, t.ex. vätgas (H₂).
Min forskning

Precis som hos fotosyntesen skulle solceller och artificiell fotosyntes hämmas ifall elektronhålet reagerade med elektronen som just lämnat. För att undvika detta så är det av största vikt att vi också lär oss bemästra i vilken riktning och hur snabbt elektronerna rör sig, precis som fotosyntesen gör. I min forskning har jag i huvudsak arbetat med att undersöka hur olika bryggestrukturer mellan pigmentet och elektronmottagaren påverkar hur snabbt den ljusdrivna elektronöverföring sker, samt hur snabbt den överförda elektronen kommer tillbaka till pigmentet. Jag har i huvudsak arbetat med långa bryggestrukturer\(^{xx}\) med mycket god ledningsförmåga. Dessa har gjort att jag har kunnat observera mycket snabba reaktioner som sker på tidsskalor på ungefär 1 ps -1000 ps (dvs. 0,000 000 000 001 s - 0,000 000 001 s). Den goda ledningsförmågan hos bryggen har dock även resulterat i att den förflyttade elektronen kommit tillbaka väldigt snabbt och därmed har de undersökta systemen inte varit lämpliga att applicera. Ett undantag var då elektronmottagaren var en guldporfyrin. I detta fall så stabiliserades den mottagna elektronen på guldjonen, vilket gjorde att den stannade kvar mycket längre än hos jämförbara molekyler. Denna typ av stabiliserande effekt skulle kunna inkorporeras i ett aktivt fotosystem där en katalysator skulle fylla samma funktion som guldporfyrinen.

\(^{xx}\) Vilket i dessa sammanhang innebär ungefär 3 nm.
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