From solution to solid state: energy- and electron-transfer in complex materials

d'Aléo, A.

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Chapter 1

Introduction

Abstract

This Chapter starts with a short overview of the processes that can take place within a molecule when it is excited by light. The focus is on the general photophysical properties and on the different photoinduced processes that occur. Especially, electronic energy and electron transfer are introduced and the mechanism and the kinetic treatments of these transfer processes are described.

Since pyrene is a central chromophore in this Thesis, examples of pyrene derivatives covalently bound to other groups are given and the phenomena occurring in these systems are described, focusing on the factors that determine whether an electron or an energy transfer occurs. At the end of the Chapter, the scope of this Thesis is given. The systems and the processes investigated as well as, when possible, future perspectives and applications are illustrated.
Chapter 1

The interaction of molecules with light is of great fundamental and practical importance and, especially, the way molecules absorb light, emit light and lose energy has been studied for a long time. Upon excitation of the ground state, molecules reach an electronically excited state, which is higher in energy and differs from the initial state by its energy content, structure and electron distribution. As the energy is quantized, the excitation energy must match the energy gap between the ground state and the considered excited state.

Once the molecule is excited by absorption of a photon, it can decay to the ground state by the emission of a photon (fluorescence), which generally occurs from the first excited singlet state. Many other pathways for de-excitation can occur (Figure 1a): internal conversion followed by vibrational relaxation nonradiative decay (i.e., direct return to the ground state without emission of luminescence), intersystem crossing (possibly followed by emission of triplet state (phosphorescence), intramolecular charge transfer and conformational changes. Within the same molecule, the different de-excitation pathways can be illustrated using the simple Jablonsky diagram (Figure 1b).

\[ \text{hv} \rightarrow \text{MOLECULE IN EXCITED STATE} \]

As can be seen from Figure 1b, the de-excitation pathways may compete with fluorescence emission if they take place on a time scale comparable to the excited state (lifetime \( \tau_0 \)). All nonradiative processes, as illustrated in Figure 1b, decrease the luminescence quantum yield (\( \phi_0 \)) which can be defined as the ratio of the number of photons emitted and the number of photons absorbed by the molecule. These two relevant quantities can be expressed as:

\[ \tau_0 = \frac{1}{(k_f + k_{nr})} = \frac{1}{(k_f + k_{ic} + k_{isc})} \] (Eq1)

Figure 1. a: Possible deactivation pathway of excited molecules. b: Jablonsky diagram showing radiative and non-radiative transitions between singlet (S) and triplet (T) state.
where $k$ is the decay rate constant and $f$, $ic$, $isc$ and $nr$ are stated for fluorescence, internal conversion, intersystem crossing, radiative and nonradiative decay, respectively.

In the presence of a suitable quencher molecule, inter- and intra-molecular quenching processes can occur. For intermolecular processes, fluorescence quenching occurs when the excited state molecule is deactivated by collisional contact with a quencher molecule in solution (*i.e.* the colliding molecules are not altered chemically). For this type of quenching, the decrease in emission intensity is described by the ratio of the fluorescence in absence of quenching to the fluorescence in the presence of quencher by the Stern-Volmer equation:

$$\frac{\phi}{\phi_0} = 1 + K_{SV} [Q] = 1 + k_q \times \tau_0 \times [Q]$$

where $\phi$ is the luminescence quantum yield of the quenched molecule defined below, $K_{SV}$ is the Stern-Volmer quenching constant and $k_q$ is the bimolecular quenching constant.

$$\phi = \frac{k_f}{(k_f + k_{ic} + k_{isc} + k_q)}$$

Quenching data are usually presented as plot of $\phi / \phi_0$ versus $[Q]$, giving a linear dependence. This plot should yield an intercept of unity on the $y$-axis and a slope equal to $K_{SV}$. The quantity $1 / K_{SV}$ is the quencher concentration at which $\phi / \phi_0 = 2$ (*i.e.* 50% of the luminescence intensity is quenched).

In such case, the quenched lifetime can be estimated using Eq 5 where $k_q$ is calculated from Eq 3. As we have shown above, $\tau_0$ can be calculated from the kinetics of all the processes occurring in the molecule after excitation. Analogously, $\tau$ can be estimated applying equation 5. However, in most cases, the easiest way to calculate the quenched lifetime is by time resolved spectroscopy. The combination of Eq 1 and Eq 2 with Eq 4 and Eq 5 gives the expressions (Eq 6 and Eq 7) for the rate constants of the quenching process.

$$\tau = \frac{1}{(k_f + k_{ic} + k_{isc} + k_q)}$$

$$k_q = \frac{\phi_0 / \phi - 1}{\tau_0}$$

$$k_q = \frac{1}{\tau - 1 / \tau_0}$$
These equations are extremely useful to calculate the rate constants for intramolecular processes. Amongst the quenchers, one of the most well known species is dioxygen. Molecular oxygen is normally present in its triplet ground state (which explains its reactive bi-radical like behaviour). Collision of oxygen with a singlet excited state leads to an enhancement of non-radiative singlet to triplet conversion with subsequent quenching of the luminescence.

The encounter of triplet ground state molecular oxygen with a molecule in its triplet excited state leads to triplet-triplet annihilation which is accompanied by the formation of the very reactive singlet oxygen, which can be used in the photodynamic therapy of cancer cells.

In the two next paragraphs, the theory and the relevant issues of electron- and energy transfer, two common and very important quenching processes, are briefly described.

### 1.1- Photoinduced electron transfer processes

The photoinduced electron transfer process constitutes one of the most basic photochemical reactions but also one of the most attractive ways to convert or store light energy for further application. This process between a donor (D) and an acceptor (A) can be encountered in two different ways: a) as intermolecular photoinduced process or b) as intramolecular photoinduced process (respectively Figure 2a and Figure 2b).

After excitation, the electron transfer process takes place resulting in a charge separated state which relaxes to the ground state via an electron recombination (back electron transfer). In recent years especially, intramolecular electron transfer processes have received a lot of attention. Very often in these systems, a key element is the bridging ligand connecting the donor and the acceptor species. In fact, the electronic nature, geometry and length of the bridge can determine the strength of the coupling between the two species and, in rigid systems, the donor to acceptor distance.
1.1.1 Thermodynamical considerations

From the electrochemical and photophysical data, it is possible to estimate the thermodynamic energy change for the electron transfer (Gibbs free energy change: $\Delta G_{ct}$) in a system using the Rehm-Weller equation\textsuperscript{[1]} (Eq 8):

$$\Delta G_{ct} = e(E_{ox} - E_{red}) - E_{00} - v(r)$$  \hspace{1cm} (Eq 8)

where $E_{ox}$ is the first oxidation potential of the donor, $E_{red}$ is the first reduction potential of the acceptor, $E_{00}$ is the energy of the 0-0 transition determined by the first maximum of the emission at 77 K of the moiety that is excited (acceptor or donor) and $v(r)$ is a work term arising from e.g. the coulombic interactions between charges. This work term can be expressed as following:

$$v(r) = e^2 / 4\pi\varepsilon_0\varepsilon_s R_{DA} + e^2 / 8\pi\varepsilon_0 (1/r^+ + 1/r^-) (1/\varepsilon_{se} - 1/\varepsilon_a)$$  \hspace{1cm} (Eq 9)

where $e$ is the elementary charge, $\varepsilon_0$ is the vacuum permittivity constant, $\varepsilon_s$ is the dielectric constant of the solvent, $\varepsilon_{se}$ is the dielectric constant of the solvent in which the electrochemistry was measured, $R_{DA}$ is the donor-acceptor distance, $r^+$ and $r^-$ are respectively the effective ionic-radii of the donor and acceptor cation and anion.

The second term in Eq 9, the so called solvation term, accounts for the small ability of the low polarity solvents to stabilize charges, as compared to higher polarity solvents in which the electrochemistry is normally performed.

When electron transfer in the solid state is considered, Eq 10 can be written:

$$\Delta G_{ct} = E_{ox} - E_{red} - E_{00} = \Delta G_{redox} - E_{00}$$  \hspace{1cm} (Eq 10)

This simple equation implies that an electron transfer process can take place from the lowest excited state (with an energy $E_{00}$) if there is enough “driving force” (-$\Delta G_{ct}$) to give an exergonic process.

To finish with the thermodynamic considerations, it can be highlighted that electron transfer can occur from the singlet excited state to a singlet state of the radical ion pair or from a level with a higher multiplicity like from a triplet excited state to a triplet state of the radical ion pair. There are no electron spin restrictions. The process can occur as long as $E_{00} > \Delta G_{redox}$.
1.1.2 Kinetic considerations

The rate of most electron transfer processes can be described with the Arrhenius equation (Eq 11), just like many other chemical reactions:

$$k = A \times \exp\left(-\frac{E_a}{k_B T}\right) \quad \text{(Eq 11)}$$

where $A$ is the pre-exponential factor, $E_a$ is the activation energy, $k_B$ is the Boltzmann constant and $T$ is the temperature.

Equation 11 implies that, if a barrier is present ($E_a \neq 0$), the rate of the process will decrease strongly with temperature (when $T$ goes to 0, $k$ goes to 0). When the barrier is zero, the rate equals the pre-exponential factor and it will be temperature independent.

According to the classical model developed by Marcus and Hush,[2-4] the first excited state $D^*-A$ (or $D^*$ alone in an intermolecular process) must progress in time to reorganize its nuclear geometry and that of the surrounding environment to the point where the energy of the reorganized state is equal to that of the charge separated state ($D^*-A^-$). Thus, after Frank-Condon excitation, nuclear and solvent reorganization is needed for the charge separation to occur. Sometimes direct excitation into the charge transfer (CT) absorption band can however populate the CT state directly.

In the Marcus model, the rate constant for electron transfer ($k_{\text{CT}}$) can be expressed as follows:

$$k_{\text{CT}} = k_{\text{el}} \times v_n \times \exp\left(-\frac{\Delta G^{\ddagger}}{k_B T}\right) \quad \text{(Eq 12)}$$

where $k_{\text{el}}$ is the electronic transmission coefficient (i.e. the probability that the excited state converts to the charge transfer state when they reach the crossing point as illustrated in Figure 3), $v_n$ is the nuclear factor (i.e. the frequency of passage through the transition state) and $\Delta G^{\ddagger}$ is the free energy of activation.

In Eq 12, $\Delta G^{\ddagger}$ can be expressed as a function of the overall Gibbs free energy change ($\Delta G_o$) and of the total reorganization energy ($\lambda$)\textsuperscript{[5]} as in equation 13:

$$\Delta G^{\ddagger} = \left(\Delta G_o + \lambda\right)^2 / 4\lambda \quad \text{(Eq13)}$$
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Figure 3. Energy profile and kinetic parameters for a unimolecular electron transfer reaction. $\Delta G^\ddagger$ is the free activation energy and $\lambda$ the reorganization energy.

Figure 3 gives a schematic representation of the different parameters considered in the Marcus theory using the two potential energy curves for the excited D-A pair and the charge separated state respectively.

The total reorganization energy ($\lambda$) can also be described as the potential energy change during the nuclear reorganization in response to the electronic changes going from the excited state to the charge separated state. The reorganizational energy consists of two contributions because reorganization will occur through internal reorganization ($\lambda_i$) (within the molecule) and solvent reorganization ($\lambda_s$) since, as previously explained, the reorientation of the polar molecules plays a major role in electron transfer.

$$\lambda = \lambda_i + \lambda_s$$  \hspace{1cm} (Eq 14)

In equation 14, $\lambda_i$ can be calculated using the CT absorption maximum and the CT emission maximum of the electron donor-acceptor system studied in a non-polar solvent (where $\lambda_s \approx 0$). The energy difference between these two states gives $2\lambda_i$. The solvent reorganization ($\lambda_s$) can finally be estimated with equation 15:

$$\lambda_s = \frac{e^2}{4\pi\varepsilon_0(1/n - 1/\varepsilon_s)(1/2r^+ + 1/2r^- - 1/R_{DA})}$$  \hspace{1cm} (Eq 15)

where $n$ is the optical dielectric constant of the solvent, $e$ is the elementary charge, $\varepsilon_0$ is the vacuum permittivity constant, $\varepsilon_s$ is the dielectric constant of the solvent, $\varepsilon_{sc}$ is the dielectric constant of the solvent in which the electrochemistry was measured, $R_{DA}$ is the donor-
acceptor distance, $r^+$ and $r^-$ are respectively the effective ionic-radii of the donor and acceptor cation and anion.

As is clear from equation 13 and as can be seen in Figure 4, the Marcus theory implies that, in the optimal region, barrierless electron transfer can occur. If $-\Delta G < \lambda$, the electron transfer rate increases with larger driving forces. However, in the so-called inverted region, when $-\Delta G > \lambda$, the rate decreases with larger driving forces. The barrier is very thin in the inverted region facilitating nuclear tunneling. In particular, in the inverted region, process rates are higher than expected from the classical Marcus theory.

![Potential energy curves for reactants and products in the three regimes predicted by the Marcus equation](image)

**Figure 4.** Potential energy curves for reactants and products in the three regimes predicted by the Marcus equation

Depending on the coupling between the donor and acceptor, the classical Marcus theory predicts two different cases:

a) adiabatic case (strong electronic coupling, $\kappa_{el} \approx 1$) can be described as following:

$$k_{el} = \kappa_{el} \times v_n \times \exp[-(\Delta G + \lambda)^2 / 4\lambda k_B T]$$  \hspace{1cm} (Eq 16)

b) non-adiabatic case (weak coupling, $\kappa_{el} << 1$)

$$k_{el} = \left(\frac{2\pi^{3/2}}{h}\lambda^{1/2}\right)\left(V_{DA}\right)^2 \times \exp[-(\Delta G + \lambda)^2 / 4\lambda k_B T]$$  \hspace{1cm} (Eq 17)

where $V_{DA}$ is the electronic coupling matrix element. Reactions are non-adiabatic if the electronic coupling matrix element is less than $k_B T$. 

8
1.2 Electronic energy transfer processes

For molecules possessing low lying excited states that are weakly interacting, energy transfer processes are commonly observed in addition to the intrinsic decay. In an energy transfer process, the excitation energy of the donor is transferred to the acceptor, which has an energetically lower excited state. As a result, the donor returns to the ground state while the acceptor reaches its excited state.

For such energy transfer reactions, the Gibbs energy change ($\Delta G_0$) can be expressed by the difference between the 0-0 spectroscopic energies of the lowest excited states of the donor and the acceptor moieties.

For this process, an experimental determination of the energy transfer rate can be obtained from the luminescence lifetime of the quenched donor ($\tau$) and of un-quenched $D^*$ ($\tau_0$) using Eq 6 or by using the following equation:

$$k_{en} = \frac{1}{\tau_0} I_0 I - 1$$

(Eq 18)

where $I$ and $I_0$ are, respectively, the luminescence intensity of the quenched $D^*$ in the system and of $D^*$ without acceptor.

The non-radiative energy transfer processes can occur by two mechanisms: 1) Förster or Coulombic and 2) Dexter or exchange.

1.2.1 Förster-type energy transfer

Förster energy transfer often also called “coulombic”, “dipole-dipole” or “resonance” energy transfer,[6] takes place through the interaction of the oscillating dipole of the excited donor ($D^*$) with that of the acceptor (A) (see figure 5a).[7, 8] The most important condition to be fulfilled in order to have such type of mechanism, besides of course the thermodynamics, is that there is a good spectral overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor. In fact, since the electrons involved in the energy transfer are not exchanged between the two chromophores, this mechanism does not require overlap of the orbitals of the donor and the acceptor. Therefore, this interaction can take place at long distances (100 Å) and decays inversely with the sixth power of the interchromophore separation. The rate of Förster-type energy transfer can be expressed as in equation 19.

$$k_{en} = 8.8 \times 10^{-25} K^2 (\phi / n^4 \tau r^6) J_F$$

with $J_F = \int F(v)e(v)v^4dv$  

(Eq 19)
where \( \phi \) and \( \tau \) are, respectively, the luminescence quantum yield and lifetime of the donor (D*) in absence of the acceptor (A), \( K \) is the orientation factor and \( J_F \) is the spectral overlap integral of the donor emission and the acceptor absorption. As mentioned above, the rate of energy transfer via the coulombic mechanism depends on the radiative decay rate constant (\( \lambda \), \( \phi \) and \( \tau \)) of D* and on the oscillator strength (\( \epsilon \)) of A. For this mechanism thus no change of spin is “allowed” and the most favored process will be singlet-singlet energy transfer. The triplet-triplet energy transfer is not likely to occur by a Förster mechanism because, in such a case, the overlap integral (\( J_F \)) approaches 0.

![Förster and Dexter-type energy transfer mechanisms](image)

**Figure 5.** Förster- and Dexter-type energy transfer mechanisms.

### 1.2.2 Dexter-type energy transfer

This mechanism often called “exchange”\(^{[9]}\) can be visualized as a double electron transfer process where the excited electron in D* is transferred to the lowest unoccupied molecular orbital (LUMO) of A and, simultaneously, an electron from the highest occupied molecular orbital (HOMO) of A fills the hole in the HOMO of D (Figure 5b). This mechanism requires therefore overlap of the orbitals involved and can occur only at short distances (up to 10 Å)\(^{[7,10]}\). The rate constant for Dexter-type energy transfer can be expressed as following:

\[
 k_{en} = \left( 4\pi^2H^2 / h \right) J_D \quad \text{(Eq20)}
\]

where \( H \) is the inter-component electronic interaction energy between D and A and \( J_D \) is the overlap integral, according to Dexter theory. In the exchange mechanism, only the spin of donor and acceptor as a whole should remain the same. Therefore, processes not allowed by Förster mechanism can occur by Dexter mechanism, such as triplet-triplet energy transfer.
A special type of exchange mechanism is the so called superexchange mechanism, often present in the systems described in this thesis as well as in many natural systems.

In a through bond mechanism, two possible situations can be sketched to describe the role of the bridging ligand in the reaction mechanism. For systems with the same D and A, and therefore the same driving force for the reaction, the relative energies of the donor and acceptor levels will be the same. The HOMO and LUMO orbitals of the bridging ligand will be related to the electronic properties of the subunit and the way they are connected. If the empty orbitals of the bridge lie at much higher energy than the levels of the donor and acceptor, the electron is transferred in a single, coherent step. The empty orbitals of the bridge may only be used as “mediator” (or virtual state): to facilitate the transfer process and the electron will not reside on the bridging ligand during the transfer process. This phenomenon is often called superexchange mechanism. However, if there is good energetic match of the level of the donor and of the bridge, or even if the LUMO of the bridge is slightly lower in energy than the excited state of the donor, the electron may first be transferred from the excited donor to the conjugate bridge, leading to the formation of an intermediate D⁻⁻B⁻⁻A species. Electron transfer from the bridge to the acceptor then occurs by electron hopping over the different bridging unit to complete the global charge transfer process.

1.3 Pyrene as electron- or energy Donor or Acceptor

Polycyclic aromatic hydrocarbons are well known for decades and they often are fluorescent compounds that emit with a good efficiency. These molecules, such as naphthalene, anthracene or pyrene and their derivatives, have been used because of their high quantum yield of emission, because of \( \pi-\pi \) interactions which can occur in the excited states to form an excimer (excited state dimer) or exciplexes (excited state complexes) and also because of their low lying triplet excited states.

Pyrene, in particular, has attracted a lot of attention because of its high stability in the solid state, its efficient excimer formation and as it can be easily functionalized.\cite{12-15} In addition to the interesting fluorescent properties mentioned before, the presence of a low lying triplet excited state in pyrene and its derivatives (\( ^3\text{Py}^* \)) can be detected, with a phosphorescence in the range 600 to 650 nm.\cite{16} A special way to populate this triplet state is the use of “sensitizers” which possess a triplet excited state slightly higher in energy than that of pyrene. Especially ruthenium polypyridyl complexes in which the lowest excited state is a triplet metal to ligand charge transfer (\( ^3\text{MLCT} \)) state, close in energy to the triplet of pyrene,
are interesting candidates for this purpose. In this case, pyrene is likely to act as triplet energy acceptor that also behaves as a long-lived energy reservoir that repopulates the excited state of the metal complex.

In many systems, the redox potentials of pyrene derivatives remain unchanged as compared to pyrene itself. Both processes are usually irreversible yielding an oxidation potential around +1.35 V and a reduction potential around -1.90 V vs SCE in acetonitrile.

1.3.1 Pyrene as electron donor or acceptor

1.3.1.a. Pyrene as electron donor

As explained previously, the Rehm-Weller equation gives information on the thermodynamic factors of electron transfer processes (Eq 9). This equation compares the electrochemical gap to the photophysical gap and results in a negative value when electron transfer is favorable as in equation 22:

\[ 0 > E_{ox} - E_{red} - E_{00} \]  

(Eq22)

The fact that for pyrene \( E_{00} = 3.28 \) eV (maximum emission at 77K\(^{[16]} \) and \( E_{ox} = +1.35 \) V vs SCE\(^{[17]} \) means that an electron acceptor that is reduced at -1.93 V vs SCE or at a less negative potential can act as electron acceptor. Thus, many organic groups can participate as electron accepting quencher for pyrene.

In such a case, the charge-separated state is composed of the radical cation of the pyrene and of the radical anion of the (covalently bound) acceptor. This excited state can be detected by using transient absorption spectroscopy in which a transition between 470 and 490 nm can be observed, that belongs to the radical cation of the pyrene unit\(^{[18\text{-}20]} \). This transition should be accompanied by transitions belonging to the radical anion.

Systems containing good electron acceptors, such as dicyanovinyl-benzene covalently linked to pyrene, have been reported. Interestingly, this acceptor-structure is derived from tetracyanoquinodimethane, which is part of the donor-acceptor molecule originally proposed by Aviram and Ratner for molecular rectification.\(^{[21]} \) For these systems (1 and 1n, see figure 6), electron transfer has been shown to occur but the process depends on the dynamics of the chain conformations.\(^{[22]} \) Rhodamine derivative (2)\(^{[23]} \) has been prepared and shows that reversible photoinduced electron transfer occurs from the pyrene to the positively charged...
rhodamine. For 2, De Schryver et al. also proved that the population of the CT state results in the formation of the locally excited triplet state of the rhodamine. Also, simple acceptor groups such as benzonitrile (3) or benzaldehyde (4)\(^\text{24}\) have been covalently linked to the pyrene unit. These molecules show the radical cation of the pyrene that forms around 470 nm in the transient absorption spectra. It has been shown that after excitation, the compound 3 relaxes by mutual twisting of the two subunits towards a more planar geometry.\(^\text{24}\) The modified pyrimidine nucleosides 5 populate a CT state in its excited state. Fiebig et al. show that ultra fast proton coupling occurs upon formation of this CT state.\(^\text{25}\)

![Chemical structures](image)

**Figure 6.** Examples of pyrene systems containing good electron acceptor groups.

Also weak electron acceptor groups such as polypyridine units have been used in association with pyrene (Figure 7). Bipyridine directly connected to the pyrene unit (6),\(^\text{26}\) bridged by oligo-phenylene-ethynylene (OPE) (7)\(^\text{27, 28}\) or terpyridine covalently linked by a dietylnylthiophene moiety (8)\(^\text{29}\) can be used as donor-acceptor systems. In all these systems, the CT state is not reached in low polarity solvent (the local excited (LE) state is lower in energy than the charge separated state) but, when increasing the polarity of the solvent, a red-shift of the emission can be observed (solvatochromic shifts are typical for CT states).
Metal complexes in which the ligand is bearing a pyrene unit that show photoinduced electron transfer behaviour have also been reported, as for example, zinc complexes 9 (Figure 8). This complex shows electron transfer from the pyrene moiety to the nitrobenzene guest-ligand that has a reasonable acceptor character. For the molecules 10 and 10b, Fages et al. reported that electron transfer from the pyrene unit to the bipyridine acceptor is assisted by the zinc center. As 10 is the zinc complex of 7, it is interesting to notice that the stronger solvatochromic shift observed for 10 can be explained by the increase of the electron withdrawing behaviour of the bipyridine complexed to zinc ion.
1.3.1.b. Pyrene as electron acceptor

With the reduction potential of pyrene being equal to $-1.9$ V, equation 21 gives $E_{\text{ox}} < +1.18$ V vs SCE using the 0-0 transition at 3.28 eV. Thus, a large range of electron donors is suitable to participate in electron transfer interactions with pyrene.

In this case, the radical anion of the pyrene is formed in association with the radical cation of the donor. The photoinduced electron transfer can be observed with transient absorption spectroscopy resulting in the formation of a band at 490 nm that can be attributed to the radical anion of the pyrene.\textsuperscript{[31]}

Indeed, with good donors such as dialkylaniline (11)\textsuperscript{[32-35]} or its derivatives (12) photoinduced electron transfer processes can be observed. With such molecules, Singer \textit{et al.}\textsuperscript{[32]} and Techert \textit{et al.}\textsuperscript{[35]} have shown the occurrence of twisted intramolecular CT states. Phenothiazine (13) and its derivatives also act as good electron donor and the formation of the radical anion of the pyrene was reported.\textsuperscript{[31]} For these molecules, a correlation between the Rehm-Weller equation (Eq 3) and the electron transfer capacity was found.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure9.png}
\caption{Examples of pyrene systems containing aniline-type electron donors.}
\end{figure}
For molecule 14, a luminescent CT state has been reported, and its formation has to
compete with intermolecular exciplex formation. In such systems, it has been demonstrated
that electron transfer occurs from the methoxy-aniline to the pyrene unit. Furthermore, 14 was
used to show that, at high pressure, three emitting states are observed: the LE state, the intra
and the intermolecular exciplex emission.136, 37

Dendrimers have also been used for the study of these processes. Polyether dendrons
end-capped with pyrene combined with one dendron that is functionalized with a methoxy-
aniline (15) reveal the occurrence of photoinduced electron transfer when the concentration is
low enough too avoid excimer formation.38

1.3.2 Pyrene as energy donor or acceptor

As energy transfer always proceeds to a state of lower energy and the first excited
singlet state of pyrene is relatively high in energy (3.28 eV), this state is mainly used as
energy donor state. The low-lying triplet state of pyrene (1.84 eV) is mostly used as energy
acceptor (and long lived energy reservoir). These special triplet state properties have resulted
in the study of pyrene in combination with appropriate organic dyes or metal complexes in
order to obtain a low lying excited (3MLCT) state of the same multiplicity close to the pyrene
triplet state. The interaction of the two triplet states can be tuned in such a way that the long-
lived triplet state of pyrene repopulates the emissive 3MLCT state, thus extending the lifetime
of this state. Like all triplet states, the triplet state of pyrene is highly sensitive to oxygen and,
due to its very long intrinsic lifetime, small traces of oxygen can still influence its emissive
properties.

Ford et al. reported that the chromium complex 16 presents the particularity to release
NO upon excitation. The authors suggest that a fast energy transfer process from the ligand
centered π-π* state to the Cr(III)-centered ligand field state leads to the subsequent cleavage
of the complex.39

Indeed, using other polycyclic aromatic systems (naphthalene or anthracene), as in 17,
provides a good way to add a low triplet excited state close to that of the pyrene. In these
systems, energy transfer between the two triplet states can be observed. Upon complexation
with zinc, the complex 17Zn shows also efficient energy transfer over distances ca. 1.2-1.5
nm, which is attributed to a Förster-type mechanism.40
The combination of pyrene with ruthenium or osmium polypyridyl complexes has been studied extensively\cite{41,42} in order to create triplet Metal-to-Ligand Charge Transfer (MLCT) transition lying close to the triplet of the pyrene (200 < \Delta E < 900 cm^{-1} for ruthenium).

The ruthenium polypyridine complexes covalently linked to a pyrene unit usually show an extension of the $^3$MLCT lifetime and the occurrence of the second decay belonging to the depopulation of the $^3$Py*.$^{[43-45]}$

For 18, Castellano et al.\cite{46} demonstrated that a very long lived $^3$MLCT state was formed. This long emission lifetime is attributed to equilibration (forward and back energy transfer) of the $^3$MLCT with the $^3$Py*. A similar behaviour for the ruthenium bisterpyridine derivative (19) was found. In the same work, Ziessel, Harriman et al. also show that, for ruthenium complexes 20 and 21, an equilibration between the two triplet states occurs resulting in an increased emission lifetime for the $^3$MLCT-state.$^{[43]}$ They also proved that the platinum unit is a less good conductor than the ethynylene groups. But also in this latter case, the triplet state equilibration is shown to occur.

The behaviour of 22 is important in order to understand the role played by the bridge in such processes. For this complex, Ford et al. described also equilibration between the two states resulting in an increase lifetime.$^{[11]}$ Finally, complex 23 also shows extended lifetimes of the MLCT emission, which depend on the solvent used. Gelhen et al. reported that an energy transfer to the $^3$Py* in low polarity solvents can be observed.$^{[47]}$ The authors found a
slow rate of energy transfer suggesting that the coupling through the amido-connection is weak.

![Chemical structures](image)

**Figure 11.** Pyrene systems containing ruthenium or osmium ions.

1.3.3 Pyrene involved in electron and energy transfer

The study of the platinum (24), iridium (25), ruthenium or rhenium (26-27) complexes, resulted in the observation of a different behaviour, as compared to that found for 18-22. For the platinum complex 24, McMillin and co. presented convincing evidence that luminescence arises, at least in part, from a pyrene to terpyridyl intraligand charge transfer state (ILCT). This behaviour is similar to that reported by Williams et al. for 25, where a deactivation through a slightly emissive low-lying ILCT state is suggested. Fages and Schmehl et al. reported that, for the ruthenium and the rhenium complexes 26 and 27, the weak observed emission arises either from a $^3$ILCT state or from the equilibrium of the $^3$ILCT with the $^3$Py. Interestingly, in these systems the usual $^3$MLCT emission was not observed.
Finally, in our group, the organic compound 28 composed of a perylene core with four appended pyrene units was studied recently and it was proven that both photoinduced electron transfer and energy transfer occur in this system, as well as in molecular squares composed of 28. For these molecules, the fast photoinduced energy transfer is followed by the even faster electron transfer.\textsuperscript{[51]}

1.3.4 Conclusion

Indeed, as can be seen from the large range of molecules presented, the structure of the covalently bound pyrene containing molecules is important in order to predict if any transfer will occur and if so, to identify this process.

In a first approximation, two different cases can be distinguished: 1- organic partners or 2- inorganic partners.

For pyrene systems combined with organic molecules, in the case of a thermodynamically allowed electron transfer process and in absence of low lying triplet
excited state, photoinduced electron transfer occurs either from the pyrene unit or to the pyrene.

In the case where an accessible triplet state is lying close to the $^3\text{Py}^*$, fast energy transfer can be expected. However, if $\Delta G < 0$ (as for 28), it is possible to observe a competing electron transfer process, where the ratio of the rates of the two processes will determine the final outcome.

The combination of pyrene with metal complexes gives the opportunity to study the intricate interplay between a pure organic triplet state and $^3\text{MLCT}$ state. The distance between the two chromophores will govern this interaction, but also the kind of bridge linking the two chromophores and their relative orientation will be of great importance. Furthermore, this combination of chromophores with extended excited state lifetimes can result in systems that are suitable for medical diagnostic applications.

It is interesting to note that, for e.g. complexes 26-27, the $^3\text{MLCT}$ belonging to the metal or the level of the $^3\text{Py}^*$ do not shift much in energy. The energy levels of the two triplet states are neither influenced strongly by substituents nor by their chemical environment.

With regard to charge transfer processes, especially the energetics and the coupling between the polypyridine metal complex and the pyrene is relevant in order to predict if the emission from an MLCT or an ILCT state will be observed. In fact, the occurrence of charge separation in the complex can be anticipated on grounds of the photophysical behaviour of the free ligand, for which low lying CT states must already be observable. The occurrence of electron transfer will then depend on the energy levels of the excited states (the $^3\text{MLCT}$ or the $^3\text{Py}^*$ and the ILCT must be, at least, isoenergetic). As the radical anion of the terpyridine in the complex is stabilized by the direct interaction with the divalent ruthenium ion (lowering the ILCT state) a good estimate can be obtained by studying the protonated ligand or e.g. its zinc complex (see also Chapter 4).

1.4 Scope of the Thesis

The research described in this Thesis ranges from the study in solution of electron and energy transfer properties of functionalized metal complexes (Chapter 2, 3 and 4) and the investigation of their non-linear optical (NLO) properties (Chapter 5) to the interaction of metal complexes with noble metal surfaces through sulphur-metal interaction (Chapter 6). This sulphur-metal interaction was further used to create small metal clusters, by using oligothia dendrimers (Chapter 7).
The chromophores that constitute the main systems studied in this thesis are ruthenium polypyridyl complexes and pyrene derivatives. Thus a combination of a prototype of inorganic photochemistry with a classic organic photochemistry textbook molecule is made.

Insight into the interaction of the different excited states of these functionalized complexes and to the role of the bridge-unit is pursued. Surface functionalization, nanoparticle generation and NLO properties are steps toward functional nanomaterials.

In Chapter 2, the equilibration between the $^3$MLCT and the $^3$Py is studied within a system containing a ruthenium trisbpyridine linked to a pyrene unit through an OPE bridge (Figure 13a).

For this molecule, next to the observation of the $^3$MLCT emission, the lowest energy level which can be observed is the $^3$Py* state. The equilibration rate is described and the possible deactivation pathways are proposed (Figure 13b). The complex shows pyrene phosphorescence at room temperature under strict de-aeration conditions.

In Chapter 3, an energy transfer system is presented which incorporates a meta conjugated bridge. For the study of the differences induced by changing the connection point within a bridge, two ruthenium-osmium dinuclear complexes connected by polyphenylene units, where one unit is connected in meta position, were used (Figure 14). The energy transfer from the excited ruthenium-based component to the lowest excited state localized on the osmium unit was established and compared to the analogue molecules connected in para position. The energy transfer was attributed to a Dexter-type (in particular to a superexchange) mechanism.
In Chapter 4, pyrene chromophores covalently linked to a terpyridine unit and its zinc complex (Figure 15a) are studied and compared to the free components and to the bis-protonated form in order to attribute all transitions (absorption, emission and transient absorption).

In this system, it was found that photoinduced electron transfer occurs as presented in Figure 15b. The charge separated state, which contains the radical cation of the pyrene and the radical anion of the terpyridine was observed in polar solvents for the ligand, and also in nonpolar solvents for the zinc complex. In this Chapter, the 'strength' of the electron accepting groups (free terpyridine (Tpy), ZnTpy or H₂Tpy) is discussed and the difference in
the solvatochromic emission shift is explained in terms of the properties of the acceptor moiety.

In Chapter 5, the non-linear optical (NLO) properties of different functionalized electron donor-acceptor metal complexes are studied. The combination of the ILCT state with the usual $^3$MLCT belonging to a ruthenium unit is used in order to enhance the NLO response, which is found to depend on the conjugation length and on the presence of low lying CT transitions. Also, better electron donor groups than pyrene (i.e. dimethylaniline) and reference complexes (acceptor-acceptor complexes) were synthesized and studied (Figure 16).

Figure 17. Structure of the complexes synthesized and studied in Chapter 5
For such systems, a correlation between the emission lifetimes and the electronic distribution on the ligand following the substituting groups was found. Furthermore, the use of ligands that induce the formation of ILCT-states enhances the hyperpolarizability ($\beta$-value) in comparison to acceptor-acceptor complexes (or to acceptor-weak donor group). In this Chapter, the increase of the $\beta$ value with the increase of the conjugation length has been illustrated by adding phenylene units between the electron donor and the metal complex.

In Chapter 6, the study of ruthenium derivatives (free or anchored to a metal surface) is presented. For this work, four ruthenium trisbipyridine complexes containing (protected) alkylthiol chain(s) were synthesized (Figure 17).

![Figure 18: Ruthenium trisbipyridine complexes containing thioacetate groups attached to surfaces in Chapter 6](image)

The metal complexes were studied in solution as well as anchored to noble metal surfaces (Au, Pt). The quality of the layers formed was studied with wettability, electrochemistry and confocal microscopy. The emission quenching by the surface was found to be rather slow and incomplete yielding a quenching rate of $1.7 \times 10^8$ to $2.8 \times 10^8$ s$^{-1}$.

![Figure 19: Dendritic structures and model compounds used for gold nanoparticles formation and stabilization in Chapter 7](image)
Finally, in Chapter 7, the preparation, stabilization and stability of nanoparticles covered by thioether containing dendrimers and other thiol derivatives are described (Figure 18). An effect of the generation of the dendrimer on the size of the nanoparticles is observed as well as on the stability of those nano-assemblies. Changing the structure of the dendrimer results in different stabilizer-nanoparticles assemblies as demonstrated by $^1$H-NMR, HR-TEM and Soxhlet extraction. The reference molecules do not lead to nanoparticle formation, indicating that the structure and generation of the dendrimer is of essential importance in the formation of the dendrimer stabilized gold nanoparticles.

The Chapters in this thesis can be read independently, as they have been written in a form suited for publication in international scientific journals. This has resulted in some unavoidable overlap for some introductory parts.

1.5 References

Introduction


