Photoinduced processes in functionalized and organized dye systems
Nguyen, V.A.

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: http://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
Chapter 1

Highly Organized and Functionalized Dye Systems

Abstract

This chapter contains a brief description of design principles to organize photo- and electro-active chromophores, in which the organization method controls the mediation pathways for e.g. energy or electron transfer. The main discussion is about molecular methods using covalent and non-covalent links, and about the deposition of molecules into thin solid films. The goal is to attain (supra)molecular systems possessing well defined, highly-ordered and functional structures, in which photoinduced processes occur efficiently. In addition, molecular control of the active units with respect to energetics, kinetics, distance, orientation and their interaction (in solution) is essential for a profound comprehension. Controlling and understanding these aspects in thin solid films is a required way to have a rational design of solid state properties and concomitant applications.
Chapter 1

Interaction between light and matter

The interaction of light and matter is an essential phenomenon both in daily life and in science. The process of vision, which governs the appearance of things we see everyday is the most apparent example of such interaction. Another illustration of the importance of the light-matter interaction is the act of chlorophyll in green leaves to harvest and convert sunlight into energy for plants and indirectly (virtually all) energy for humans. Light-matter interaction is a fundamental subject of physics and it has huge applications in other fields, for instance, chemistry, biology, pharmacy, or material sciences. Based on the light-matter interaction, various powerful spectroscopic methods have been developed, which assist scientists in exploring properties of matter and light-induced processes occurring in natural and artificial systems. Recent methods can be applied on very short timescales since fast spectroscopy such as nanosecond (10⁻⁹ s), picosecond (10⁻¹² s) and femtosecond (10⁻¹⁵ s) transient absorption measurements are available. More recently, attosecond spectroscopy (1 attosecond = 1 × 10⁻¹⁸ second), has been developed. The first 80-attosecond pulses of light were created in 2008. The dramatic achievements of such fast spectroscopic methods enable scientists to get thorough insights in transient processes occurring in natural and artificial systems such as light-induced reactions. In this thesis, the term “light” is limited to the range of UV-Vis and infrared wavelengths.

1.1 Photoinduced processes in functionalized and organized systems

Light-induced processes, such as energy and/or electron transfer (EnT and/or ET), and proton-coupled electron transfer (PCET) are crucial and fundamental phenomena in nature as well as in artificial systems. The control of the efficiency, rate and directionality of these types of (photo)induced processes in organized functional systems is of utmost importance for the development of organic opto-electronic devices, like solar cells, LEDs, nonlinear optical (NLO) materials and Field Effect Transistors. Here we give a short theoretical description of these processes.
1.1.1 Energy transfer

Photoinduced energy transfer processes (EnT) are of increasing importance for the development of artificial photosynthetic systems to harvest and then convert sunlight into chemical or electrical energy.\(^5\), \(^8c\), \(^11\) In bridged donor-acceptor systems (D-B-A), the energy transfer can be described as

\[
\text{D}^* - \text{B} - \text{A} \xrightarrow{k_{\text{EnT}}} \text{D} - \text{B} - \text{A}^*
\]

In such a process, energy is transferred from an excited donor species to a ground state acceptor, resulting in the quenching of the D\(^*\) emission. These processes can be described in terms of either electron exchange (Dexter)\(^12\) or dipole-dipole (Förster)\(^13\) interactions (Figure 1.1).

![Figure 1.1 Schematic description of dipole-dipole (Förster) and electron exchange (Dexter) interactions between an excited molecule and a ground-state molecule.](image)

There is a basic difference between the two mechanisms. In the Dexter pathway, the energy transfer occurs through the common frontier orbital interaction (i.e. orbital overlap) whereas the Förster energy transfer results from the Coulombic interaction between the transition dipole moments of the excited state donor and the acceptor. (Figure. 1.1).\(^14\) Therefore, the former occurs e.g. through bond and it is a short range interaction. The distance between donor and acceptor is generally less than 10Å. The latter is a through-space interaction, so the range of dipole-dipole EnT can extend up to 100 Å.\(^15\)
The rate constant for the Förster mechanism can be expressed with the following equation:

$$k_{\text{EnT}}(\text{dipole-dipole}) = \frac{1}{\tau_D} \left( \frac{R_o}{R_{DA}} \right)^6 \quad \text{Eq. 1.1}$$

In Eq.1.1, $\tau_D$ is the lifetime of the excited state donor in the absence of an acceptor. $R_o$ is the critical Förster radius for energy transfer, and $R_{DA}$ is the donor-acceptor separation. The Förster radius $R_o$ can be calculated according to Eq. 1.2

$$R_o = 0.2108 \left[ \kappa^2 \phi_D^0 n^{-4} \int_0^\infty \frac{I_D(\nu)\epsilon_A(\nu)}{\nu^4} d\nu \right]^{1/6} \quad \text{Eq. 1.2}$$

where $\kappa$ is the orientation factor, $\phi_D^0$ is the emission quantum yield of the reference donor chromophore. $\nu = \frac{1}{\lambda}$ is the wavenumber. $I_D(\nu)$ is the corrected fluorescence intensity of the donor with the total intensity normalized to unity, $\epsilon_A(\nu)$ is the molar absorption coefficient of the acceptor and $n$ is the refractive index of the solvent. The Förster radius depends on the overlap of the donor emission and the acceptor absorption spectra which are expressed by the spectral overlap integral in Eq.1.2. In the systems in which the transition is forbidden, the Förster mechanism cannot be used to describe the energy transfer because these processes are not allowed in dipole-dipole interaction. In these cases, the kinetic description of the processes in the systems can be approached by applying the Dexter mechanism. The rate constant of the Dexter mechanism is described by Eq. 1.3

$$k_{\text{EnT}}(\text{electron exchange}) = \frac{4\pi}{h} K J_{\text{ex}} \exp\left( -\frac{2R_{DA}}{R_o} \right) \quad \text{Eq. 1.3}$$

The exchange interaction integral, $J_{\text{ex}}$ of the spectral overlap between the normalized donor emission and the normalized acceptor absorption spectra is expressed by

$$J_{\text{ex}} = \int_0^\infty I_D(\nu)\epsilon_A(\nu) d\nu \quad \text{Eq.1.4}$$
The value of $J_{\text{ex}}$ does not depend on the actual magnitude of $\varepsilon_A$. $K$ is related to the specific orbital interactions, $R_{DA}$ is the donor-acceptor separation relative to their Van der Waals radii, $R_o$.

The Dexter model can be used either for allowed transitions or forbidden transitions in donor and acceptor. In the case of an energy transfer process occurring in systems which are at short distance and possess allowed transitions, both mechanisms can be involved.

### 1.1.2 Photoinduced electron transfer

In natural as well as artificial systems, light-induced intermolecular and intramolecular electron transfers are important processes.\textsuperscript{16}

\[
D^-B^-A \xrightarrow{hv} D^*-B^-A \quad (\text{or } D^-B^-A^*)
\]

\[
D^+B^-A \xrightarrow{\text{ET}} D^{++}B^-A^* \quad (\text{or } D^-B^-A^* \xrightarrow{\text{ET}} D^{++}B^-A^*)
\]

Upon excitation, a donor gives an electron to an acceptor. The excited species can be either electron donor or acceptor (Figure 1.2)

---

**Figure 1.2** Representations of electron transfer, in terms of frontier orbitals. Left: the electron donor is excited. The electron is transferred from the LUMO of the donor ($D^*$) to the LUMO of the acceptor ($A$); Right: The electron acceptor is excited, the electron is transferred from the HOMO of ground state $D$ to HOMO of $A^*$. 

The requirement of electronic interaction for electron transfer to happen in a donor-acceptor system is very similar to the case of the energy transfer exchange mechanism, in which the overlap between the orbitals of donor and acceptor is substantial\textsuperscript{16a, 17} (i.e. a strong electronic coupling between the donor and acceptor). Regarding energetic requirements, it is necessary to obtain a net driving force ($\Delta G^o < 0$) for the electron transfer reaction from the donor to the acceptor. It depends on the redox potentials of the donor, acceptor as well as the intermediate charge carriers, the arrangement between donor and acceptor (both distance and orientation), and the environment (e.g. solvent).\textsuperscript{18}

Many studies on photoinduced electron transfer processes have been performed, focusing both on theoretical and experimental aspects in an effort to get insight in the ET reactions, and to achieve a highly efficient ET process and minimize the rate of the reverse ET (charge recombination). The goal is to attain (meta)stable charge separated states which have a high potential application in solar energy conversion.\textsuperscript{7d, e, 11d, 19}

Studies on the theories of photoinduced electron transfer provide methods to predict the dependence of the electron transfer rates ($k_{ET}$) on the distance and driving force between the donor and acceptor, according to the following equations:\textsuperscript{20}

$$k_{ET} = \kappa \nu_N \exp(-\Delta G^\neq/k_B T) \quad \text{Eq. 1.5a}$$

$$\Delta G^\neq = \frac{(\lambda + \Delta G)^2}{4\lambda} \quad \text{Eq. 1.5b}$$

where $\kappa \nu_N$ is related to the electronic interaction between the donor and the acceptor, in which $\nu_N$ is an electronic factor (of order $1 \times 10^{13}$ s$^{-1}$) which is a function of the vibrational frequencies involved in coupling vibration and electronic motion, and $\kappa$ is the electronic transmission coefficient. For “adiabatic” reactions (i.e. the interaction between the D and A is important), the $\kappa$ value is approximately unity.\textsuperscript{20a, 21}

The last term of Eq. 1.5a contains both driving force ($\Delta G$) and the reorganization energy ($\lambda$) for electron transfer (Eq. 1.5b). The latter consists of a solvent
reorganization ($\lambda_s$) and an internal reorganization ($\lambda_i$) energy of the system, $\lambda = \lambda_i + \lambda_s$. The solvent reorganization energy can be estimated by the equation:  

$$\lambda_s = \frac{e^2}{4\pi\varepsilon_0} \left( \frac{1}{r} - \frac{1}{R_c} \right) \left( \frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s} \right)$$ 

Eq. 1.6

In Eq. 1.6, $\varepsilon_{op}$ ($= n^2$) and $\varepsilon_s$ are the optical and static dielectric constants of the medium, $n$ is the solvent refractive index. $r = \frac{r^+ + r^-}{2}$ is the average ionic radius; $r^+$ and $r^-$ are the effective radii of donor and acceptor, respectively. They can be estimated using a “spherical” approach. $R_c$ is the center-to-center distance of the considered donor and acceptor. It can be seen that the term $\lambda_s$ also depends on the distance between the two units, so it contributes a secondary distance-dependent effect to the electron transfer rate.

The driving force of the photoinduced electron transfer ($\Delta G$) in a solvent with relative permittivity $\varepsilon_s$ can be estimated by the equation (written here for neutral starting species)$^{22}$

$$\Delta G = e[E_{D^{++}/D} + E_{A^{--}/A}] - \Delta E_{0,0} - \frac{e^2}{4\pi\varepsilon_0 \varepsilon_s R_c} + \frac{e^2}{8\pi\varepsilon_0} \left( \frac{1}{r^+} + \frac{1}{r^-} \right) \left( \frac{1}{\varepsilon_{EC}} - \frac{1}{\varepsilon_s} \right)$$ 

Eq. 1.7

in which $E_{D^{++}/D}$ and $E_{A^{--}/A}$ are the electrode potentials of the donor (D) and the acceptor (A), respectively; $\varepsilon_{EC}$ is a relative permittivity of the reference solvent. The zero – zero transition energy, $E_{0,0}$, of the excited chromophore can be determined from the intersection of the steady-state absorption and emission spectra.

According to Eq. 1.5, the electron transfer rate is governed by the electronic coupling, the reorganization energy and the driving force of the D-B-A system. In long distance systems, the ET is a non-adiabatic reaction because the electronic coupling between D and A is weak. In the non-adiabatic reaction, $\kappa << 1$, the term $\kappa \nu_N$ is given by Eq. 1.8 based on quantum mechanical approaches.$^{20a, 21b}$
\[ \kappa V_N = \frac{4\pi^2}{h} V_{DA}^2 \frac{1}{(4\pi\lambda k_B T)^{1/2}} \]  

Eq. 1.8

with \( V_{DA} \) is the electronic coupling matrix element, of which the distance dependence can be approximated as exponential:

\[ V_{DA} = V_o \exp\left[-\frac{\beta(R_c - R_o)}{2}\right] \]  

Eq. 1.9

where, \( \beta \) is the distance attenuation factor, \( R_c \) is the center-to-center distance of the considered donor and acceptor and \( R_o \) is the separation when the two units are in Van der Waals contact. \( V_o \) is the electronic coupling corresponding to \( R_o \).

Hence, rate constants for long-range electron transfer can be determined by Eq. 1.10.

\[ k_{ET} = \frac{4\pi^2}{h} V_{DA}^2 \frac{1}{(4\pi\lambda k_B T)^{1/2}} \exp\left[-\frac{(\Delta G + \lambda)^2}{4\lambda k_B T}\right] \]  

Eq. 1.10

There are two proposed mechanisms for long-range electron transfer processes, a hopping (multi-step through space) pathway and a superexchange (single step through bond coupling) mechanism. In the former, the electron moves through the bridge and is localized at the bridge in a certain time. It has a rate weakly dependent on bridge length. On the other hand, the latter has a contribution of the bridge orbitals which support the electron transfer between the donor and acceptor.

1.1.3 Proton coupled electron transfer (PCET)

In this section, another fundamental reaction playing an important role both in nature and artificial systems is shortly introduced. In this reaction, both electron and proton transfer processes occur, and it is termed as proton-coupled electron transfer. An example for the PCET in nature is a transmembrane proton-pumping event in bacterial reaction centers (e.g. chromatophores from “Rhodospirillum rubrum”). Such a reaction is also essential for artificial photosynthesis, solar fuel cell technology, and energy conversion devices, such as solar cells. In the photoinduced PCET process, either a donor or an acceptor is excited by light. After that, the electron
transfer and proton transfer can proceed in the system. Depending on the nature of the studied systems, the proton transfer process can be a first step (i.e. the proton transfer followed by electron transfer channel, PT-ET mechanism) or the second step (i.e. the electron transfer followed by proton transfer, ET-PT). Assuming the donor is excited, a general description of PECT can be as follows:

\[
\text{D-H} \xrightarrow{h\nu} \text{D-H}^* \xrightarrow{k_{\text{PCET}}} \text{D-H} - \text{A}^* \\
\]

The recent consideration in PCET theories is based on Marcus theory and theories applying to “vibrationally non-adiabatic proton transfer”. Hammes-Schiffer et al. have developed a theory by generalizing the PCET theory proposed by Cukier and co-workers. They introduced two collective solvent coordinates corresponding to electron and proton transfer. No further discussion on kinetic and mechanistic aspects of PCET will be given in this thesis.

### 1.2 Organizing mediation in building highly organized and functionalized systems.

The photoinduced processes occurring in D-B-A systems depend not only on the characteristics of each moiety (for example, redox potentials and frontier molecular orbitals) but also on the arrangement between these species. In intermolecular systems (i.e. the donor and acceptor are not connected), the energy and charge transfer processes can be influenced by the involvement of diffusion by which the donor and acceptor come close to a distance which allows an efficient reaction. Therefore, processes occurring in these systems require high concentrations of components.

To solve this (diffusion) problem, enormous efforts have been made during recent decades to (partially) control the distance between a donor and an acceptor as well as their relative orientation. There are two main approaches: (1) linking D-A chromophores by covalent bonds such as flexible or rigidly linear, helical or...
scaffold\textsuperscript{36} bridges, or by non-covalent bonds \textit{i.e.} relative weak interactions between D and A such as coordination bonds,\textsuperscript{8c, 8e, 37} electrostatic interactions (salt bridges),\textsuperscript{38} $\pi$-stacked interaction\textsuperscript{39} or hydrogen bonding;\textsuperscript{11d} (2) organizing the chromophores in the solid state as \textit{e.g.} thin films.\textsuperscript{40}

Linking chromophores together to form desired multicomponent systems, in which donor - bridge - acceptor (D-B-A) (supra)molecules play a key role, are typical designs that are of great interest. In such dyads, the bridge is not only the component which connects the chromophores but also plays a fundamental role in mediating the electron and energy transfer. Therefore, by changing the structural features of the bridge, it is possible to tune the properties of D-B-A systems. The choice of spacers is also very important in designing desired functionalized and organized systems.

There are various classes of spacers, such as conjugated and non conjugated hydrocarbons (flexible, semi-flexible or rigid frameworks),\textsuperscript{11g, 41} macro-cyclic compounds (host units),\textsuperscript{11c, 42} peptide oligomers,\textsuperscript{43} and protein frameworks.\textsuperscript{44} Here we give a brief description of several representative categories.

\textbf{1.2.1 Linear alkanes as bridges}

In this section, we give a short description of two distinct saturated alkanes acting as chromophore connectors. The first one is based on (poly)methylene chains which give a large number of conformations due to the rotational freedom of the alkyl groups. The other is the so-called “norbornylogous” spacer which consist of polynorbornane and bi-cyclo[2.2.0]hexane units and is rigid, giving well-defined, fixed distance and fixed orientation of the donor and acceptor.

In various bridge categories, methylene chains are the simplest structures which have a considerable flexibility.\textsuperscript{41f, 45} The chain length and dynamics which results from conformational changes of a flexible spacer can control the rates and efficiencies of EnT and ET transfer processes.\textsuperscript{46} The longer the length of the chain is, the slower the electron transfer occurs.\textsuperscript{45c, 45e, 47} Conformations of this type of dyads can be classified
into two limiting forms; one is fully extended and in the other, the chain is folded so that the donor and acceptor are in close proximity.\textsuperscript{41f, 48}

**Figure 1.3** *Two limiting configurations of a C60-(CH2)2-PDI dyad. a) folded conformer; b) extended conformer (from reference 48). See also chapter 2.*

Generally, saturated hydrocarbon bridges act as an insulator\textsuperscript{49} in the D-B-A systems; \textit{i.e.} donor and acceptor are isolated by the bridge at a certain distance. In the case of flexible spacers, at large number of methylene groups (\(n > 6\)), the possibility of the folded-conformer formation decreases due to the restriction of the entropic criterion. However, the work of Borkent \textit{et al.}\textsuperscript{45b} in the late 1970s (the structures are shown in Figure 1.4) indicated that even when the number of methylene groups were up to 7, the fast electron transfer was still observed (the rate constant was a factor of \(10^9\ s^{-1}\)). This implied a new mechanism for electron transfer which is known as through-sigma-bond coupling.

**Figure 1.4** *The molecular structures studied in Borkent’s work.\textsuperscript{45b}*

One of scientists’ ambitions is to predict the photophysical behavior of donor-acceptor systems depending on the distance between the two units, in an effort to create new systems with desired properties for various applications. Although polymethylene chains can be readily functionalized with dyes, their flexibility due to rotations around the methylene bonds leaves their structures poorly defined. Therefore, the distances and orientation between donor and acceptor are unpredictable and hard to control.
Chapter 1

Better candidates for the organization of chromophores in well-defined architectures are rigid hydrocarbon frameworks known as “norbornylous” systems\textsuperscript{21a, 50} (Figure 1.5). This class of spacers is an ideal structure to investigate the effect of distance on photoinduced processes at the long range.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$R_c$(Å)</th>
<th>$R_e$(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Structure 1" /></td>
<td>7.0</td>
<td>4.63</td>
</tr>
<tr>
<td><img src="image2" alt="Structure 2" /></td>
<td>9.0</td>
<td>6.82</td>
</tr>
<tr>
<td><img src="image3" alt="Structure 3" /></td>
<td>11.4</td>
<td>9.40</td>
</tr>
<tr>
<td><img src="image4" alt="Structure 4" /></td>
<td>13.3</td>
<td>11.47</td>
</tr>
<tr>
<td><img src="image5" alt="Structure 5" /></td>
<td>14.9</td>
<td>13.50</td>
</tr>
</tbody>
</table>

**Figure 1.5** Structure of norbornylous donor-bridge-acceptor molecules with different lengths together with center-to-center ($R_c$) and edge-to-edge distance ($R_e$) between donor and acceptor (from reference 21a).

A norbornylous-bridged series with different spacer lengths was studied by Paddon-Row’s and Verhoeven’s groups.\textsuperscript{21a, 41a, b, 50a, 50d, 51} In these D-B-A systems, the electron transfer even occurred efficiently at long distance (~12 Å) where the direct orbital overlap of the donor and acceptor is not possible. In these cases the $\sigma$-bonds of spacers act as “conductors”.\textsuperscript{14}

Singlet-singlet intramolecular energy transfer processes were also detected in bichromophoric molecules containing this type of spacers, connecting the
dimethoxynaphthalene donor to the carbonyl acceptor.\textsuperscript{16d, 21a, 51a, 52} The observed rate constant of the energy transfer process was much larger than the value estimated using the Förster mechanism. It was explained that the energy transfer occurring in such systems was also mediated by the bridge via a through-sigma-bond coupling pathway.

### 1.2.2 Helical architectures\textsuperscript{53} for controlling donor-acceptor separation

It is of utmost importance to get a more thorough understanding of the processes occurring in nature, in order to control them in desirable ways.\textsuperscript{54} The studies on natural systems, for example proteins, are often limited because it is not easy to change their structural features to control the processes occurring in these systems.\textsuperscript{55} Hence, scientists have also paid much attention to designing molecules that contain special features of natural systems as models to test the long-distance electron transfer occurring in nature.\textsuperscript{56} Among the recent designing strategies, the use of helical foldamers\textsuperscript{57} as rigid bridges for organizing chromophores into functional and highly-ordered architectures is of great interest. A foldamer, according to Gellman’s description,\textsuperscript{57-58} is any synthetic oligomer that in solution folds into stable, well-defined conformations. Advantages of this spacer category are their tunability, predictability and ease of their synthesis,\textsuperscript{35b, 59} which enable scientists to prepare and systematically study long range photoinduced processes by changing the number of repeating bridging units. The structural concept of a molecular folding helix is given in Figure 1.6.

![Illustration of a folded molecular helix (from reference 60)](image)

Examples of foldamers are \textit{m}-phenylene ethylene oligomers,\textsuperscript{61} peptides,\textsuperscript{57b, 62} and aromatic oligo-amide foldamers\textsuperscript{63} which can be used as helical bridges. There are
many studies on the long-range photoinduced processes in peptide-bridged donor-acceptor systems, in which the donor and acceptor are either inorganic and/or organic units. Among the bridging peptides, polyprolines have obtained the most interest\textsuperscript{16c,18a,35a,43,55-56,62a,64} due to their secondary structures desirable for studying systematically the dependence of electron transfer rates on donor-acceptor distance.\textsuperscript{55}

Isied\textsuperscript{44,55} and his co-workers reported the intramolecular electron transfer mediated by polyproline oligomer bridges. In their work, the C and N terminals of the polyproline were attached to either metal complexes\textsuperscript{64a,b} or to organic chromophores\textsuperscript{35a} as a donor and an acceptor (D−[Pro]\textsubscript{n}−A, Pro is for proline, n = 1 − 9 in the case of metal complexes, and n = 0 − 3 in the case of organic chromophores as the donor and acceptor).

In the case of the bridge linked with two metal complexes,\textsuperscript{64a,b} they found that the kinetics was mono-exponential indicating the existence of only one conformation. A rapid electron transfer process was still detected at a long distance (40 Å). Weak distance dependence of ET rate was observed at long distance (n \geq 4), $\beta \approx 0.2$ Å\textsuperscript{-1}. Their explanations for the surprisingly low value of attenuation factor are: (i) a small change of reorganization energy ($\lambda$) of the systems with distance (ii) the special interaction of the electron donor [(bpy)$_2$RuL$^+$] with the polyproline bridge (iii) the special features of helical polyproline II structures. The small change in the electron transfer rate with distance in the systems suggested a through bond coupling ET mechanism.

![Figure 1.7 An example of a helical oligoproline complex with Ru-Ru donor and acceptor in Isied's work.\textsuperscript{65} The number of proline units is 6.](image)
In other work\textsuperscript{35a} in which the polyproline bridge was attached to two different chromophores (Figure 1.8) Pyr-(Pro)\textsubscript{n}-DMPD (Pyr = Pyrene-1-sulfonyl, DMPD= N,N-dimethyl-1,4-phenylenediamine, n = 0 – 3), different results were observed.

Photoinduced intramolecular electron transfer from the excited state of DMPD to the pyrene acceptor was detected using time-dependent emission and photon counting experiments. The results showed that the efficiency of the ET process decreased with the increase of the number of proline units. However, monoexponential emission decay was only observed for n = 0, 1 whereas in the case of n = 2, 3, the kinetics were multiexponential, indicating the existence of several conformations of the Pyr-(Pro)\textsubscript{n}-DMPD molecules. Each conformer has its own intrinsic ET rate. This phenomenon was in contrast to the systems in which donor and acceptor were metal complexes.\textsuperscript{64a, b, 65} An explanation was that the nature of the chromophores (Pyr and DMPD) influenced the number of conformations of the system in solution.

![Schematic representations of helical polyproline attached to an acceptor (Pyr) and a donor (DMPD); (Pyr = Pyrene-1-sulfonyl, DMPD= N,N-dimethyl-1,4-phenylenediamine).\textsuperscript{35a}](image)

Tamiaki et al.\textsuperscript{66} synthesized a series of oligoproline-bridged bis(porphyrin) compounds. An intramolecular singlet energy transfer occurred in ethanol from a photoexcited zinc porphyrin moiety to a metal-free porphyrin moiety. Studies of photoinduced processes in a series of compounds, in which one porphyrin moiety contains a zinc (II) ion and the other is iron(III) porphyrin showed an electron transfer reaction in the systems. Based on a weak dependence of the electron transfer rate on spacer distance, they proposed that the ET pathway is through the amide bond in the oligomer linkage.

Another class which can be used as a well-defined structured bridge is aromatic oligoamide foldamers.\textsuperscript{63c} Hydrogen bonds between two non-adjacent quinoline-units
result in the folded conformation. Compared to peptide foldamers\(^{41e}\) this backbone has an extraordinary stability due to the aromatic stacking interaction\(^{67}\) which give potential applications of these structures in material sciences.

Series of helical oligoamide foldamers based on quinoline and its derivatives have been intensively investigated by Huc and his co-workers.\(^{59a, 63b, 67-68}\) Figure 1.9 shows an example.\(^{59a}\)

![Figure 1.9](image)

**Figure 1.9 Structure of quinoline-derived oligoamide foldamers (from reference 59a)**

In their work,\(^{63b}\) they showed very simple principles that can be used to design and synthesize helically folded oligoamides from quinoline amino acid units. These monomers are easy to be accessed, functionalized and assembled into oligomers. The helical structures were proven by single crystal X-ray diffraction. Studies on the effects of temperature and solvent polarity on the systems indicate a remarkable stability of folded conformations. This is due to the \(\pi\)-stacking interactions between quinoline units in addition to the action of hydrogen bonds between amide hydrogens and adjacent quinoline nitrogens. These structures can be predicted by molecular modeling, giving the possibility to design such frameworks. These backbones are good building-block candidates to prepare highly ordered architectures. Surprisingly, quinoline oligomers are rarely functionalized as bridges. The use of a quinoline-based foldamer as a spacer was first studied by Schenning et al.\(^{35b}\) This approach has a great potential application for developing new materials for solar energy conversion (see also chapter 6).
1.2.3 Supramolecular host units as organizing media

Besides linear and foldamer linkages, other interesting candidates which can be used as organizing mediators are host units such as crown ethers, cyclodextrins and calixarenes. There have been intensive investigations on the synthesis, properties and applications of these three macromolecules with respect to host-guest interactions. Within the limitations of this thesis, we only focus on the calixarene family, which is also used as a linkage in the construction of supramolecular structures.

Calixarenes are a class of cyclic oligomers which contain a ring of para-substituted phenols linked by methylene bridges (Figure 1.10). This arrangement forms a hydrophobic cavity which allows calixarenes to bind neutral organic molecules via π-π interaction. An example is the formation of the complexes between various calix[8]arenes and C_{60}, which was the basis of the selective purification of C_{60} and C_{70} on large scale.

The variety of the reactive positions both at the wide rim and the narrow rim results in the fact that calixarenes are excellent scaffolds for designing multichromophic systems. For examples, the wide rim can be functionalized with chromophores such as pyrene, naphthalene, anthracence or perylene; the narrow rim can be functionalized with ion binding ligands. These systems are used as ion sensors based on the quenching or enhancement of fluorescence intensity of the chromophores with and without binding to the ion based on the fact that photoinduced processes are influenced by the ion complexation.
Calixarenes are also used as spacers in building multichromophoric systems due to their well-defined structure. The unlimited modifications of the calixarenes by changing the functional groups at both the lower and upper rim give calixarenes an important role in the bottom up approach of nanotechnology. For instance, the linking of five perylene bisimide (PDI) chromophoric units using calix[4]arenes forms an organized array. This system was used as a light harvesting array for efficient FRET energy transfer processes (Figure 1.11).

![Figure 1.11](image_url)

**Figure 1.11.** An example of light-harvesting array for energy transfer. The calix[4]arenes are used as scaffolds for linking PDI chromophoric units.

1.2.4 Hydrogen bonds in the construction of supramolecules

Using non-covalent interactions such as hydrogen bonding is one important strategy to construct highly ordered structures for supramolecular systems. Hydrogen bonds are very important in biological systems (e.g. DNA). The simplest model is the use of hydrogen bonds in the connection between donor and acceptor molecules. An advantage of hydrogen bonding is that it (partly) holds the donor and acceptor at a certain distance to avoid the effect of diffusion. Therefore, the photoinduced processes can occur efficiently.

Sessler et al. studied a series of hydrogen-bond bridged donor-acceptor systems. Figure 1.12 shows an example, in which a dimethyl-aniline-derivative donor was connected to an anthracene type acceptor via three hydrogen bonds. A significant electron transfer in the system was observed with a charge separation rate constant of
3.5 × 10^{10} \text{ s}^{-1}. It is comparable to the efficiency of the photoinduced electron transfer occurring in covalently linked systems.\textsuperscript{81}

**Figure 1.12** An example of a hydrogen-bond bridged donor-acceptor system.\textsuperscript{79}

Hydrogen bonds do not only play the role of linkage but also influence the photoinduced electron/energy transfer between donor and acceptor in many systems.\textsuperscript{81a, 82} By using mid-IR excitation in 3-pulse laser spectroscopy, Rubtsov et al. disturbed the bridging hydrogen bond. As a consequence, involvement of the hydrogen-bond bridge in the photoinduced electron process from the donor 1 to the acceptor 2 was observed by a slowing down of the rate (Figure 1.12, above).\textsuperscript{83}

In addition to the role of a bridge which may intervene in photoinduced processes in supramolecular systems, hydrogen bonds are also used as assistant-tools to organize flexibly-bridged molecules into desirable structures.

Examples are hemiquinones\textsuperscript{84} (Figure 1.13, see also chapter 5), in which two hydrogen bonds hold the donor (catechol) and acceptor (o-quinone) units in close proximity, which enable the photoinduced processes to occur effectively or aromatic oligomers\textsuperscript{85} (Figure 1.14), aromatic oligoamide foldamers as referred to in the previous part.\textsuperscript{14,63c, 85}

**Figure 1.13** A simple donor-H-bridge-acceptor system, in which two hydrogen bonds hold the covalently linked donor (catechol) and acceptor (o-quinone) units together (see also chapter 5).
In the system shown in Figure 1.14, the hydrogen bonds played a very important role in mediating the intramolecular energy and electron transfer between the two chromophores. When one hydrogen bond was removed, the efficiency of the processes decreased remarkably. And no important interaction between two chromophores was observed when another hydrogen bond was removed.85

![Figure 1.14](image)

**Figure 1.14** *Porphyrin and C60 units covalently linked by hydrogen bonded arylamide-derived foldamer bridge from reference 85.*

1.2.5. Organization in the solid state

The best-known method to organize molecules in the solid state is crystallization. The well defined ordered crystal packing ensures extremely well defined properties. With regard to the application of crystals we can think of NLO (Non-Linear-Optical) crystals (used for e.g. second harmonic generation) which are mostly composed of inorganic materials. Crystals can be grown and deposited from solution, but can also be deposited in a controlled way by using sublimation or Chemical Vapor-phase Deposition (CVD). Making good crystals requires high purity materials and is sometimes very difficult. Whereas there are examples of co-crystals (like the quinhydrone system, see chapter 5), creating useable large crystals of mixed components, is not always attainable.

Next to crystals, also liquid crystalline materials are well known as they are the main components of LCD screens. However, the induction of liquid crystalline behavior requires structural elements (like long hydrocarbon tails) that are not always compatible with the molecular components and the desired function.
Some examples are given here, focusing on perylene derivatives which have a high potential for application in e.g. organic solar cells.\textsuperscript{86}

Zuilhof and Sudhölter, and their co-workers reported the crystallization and phase transitions of three N-alkyl substituted perylene bisimide derivatives (Figure 1.15).\textsuperscript{87} The thin films were prepared by vacuum evaporation on quartz slides.

The architectures of the liquid crystalline phases display two highly ordered structures, smectic and columnar discotic phases. The former phase was substantiated by the interdigitating alkyl chains whereas the latter phase was favored by the $\pi$-stacking interaction between perylene moieties and the elliptic shape of the molecules. There was a co-existence of several crystalline and liquid crystalline (LC) phases. This enables the production of highly ordered PDI crystals via cooling the liquid crystalline phase of the perylene derivatives. The formed crystalline films have high charge carrier mobility ($\sim 0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) that makes them promising candidate materials for e.g. optoelectronic devices.\textsuperscript{87}

Self-assembled monolayers (SAMs) can be considered as two dimensional crystals because they consist of well ordered packed molecules on a surface. Whereas such monolayers can be used as a functional coating (like self cleaning surfaces) their inherent character makes them unsuitable for e.g. light harvesting. However, there are very elegant examples where perylene bisimides (PDIs) are combined with melamine

**Figure 1.15** *Structures of the molecules and their packing in the solid (3 at 220 °C) studied in reference 87.*
to attain organized multi-component surfaces containing visible light absorbing chromophores (Figure 1.16). A self-assembled monolayer network is formed by using a triple hydrogen bonding motif. These two-dimensional porous networks can act as “nanoscale vessels” for trapping molecules or clusters (e.g. C₆₀). The well-defined organized architectures consisting of C₆₀ and perylene bisimide derivatives might have a potential and interesting application in solar energy conversion, if converted to a multilayer structure.

![Figure 1.16 Structures of (a) melamine, (b) PDI, and (c) the bonding motif and (d) schematic diagram of the network with the unit cell indicated by a dotted rhombus.](image)

If solar energy conversion is the aim, we require relatively thick (50-100 nm) layers that are strongly colored, containing at least two components in an ordered conductive structure. Excitation should result in charge generation and positive and negative charges have to be transported by the materials (while avoiding recombination). Since these materials would have to be cheap in order to be competitive to silicon solar cells, they have to be made with simple techniques like spin coating or inkjet printing. These are the requirements for new materials for solar energy conversion. Our task is to use supramolecular control to obtain highly ordered functional multi-component thin films by e.g. spin coating.

In the current organic solar cells that have been brought on the market by Konarka it is the physics of phase separation together with annealing effects for improving crystalline phases of the fullerene adducts (e.g. PCBM) and conducting polymers (e.g.
P3HT), that control the properties of the materials. Incorportating these aspects into a supramolecular design strategy would be a large step forward.

1.3. Scope and outline of the thesis

This thesis describes photoinduced processes such as energy transfer, electron transfer or proton-coupled electron transfer occurring in organized and functionalized systems and in thin films. In these architectures, the conformational dependence and (e.g. electron transport)-mediation by the bridges can be detected by means of photophysical methods such as femtosecond transient absorption with the support of global and target analysis tools. These studies form a contribution to the basic understanding and the theoretical aspects of photoinduced processes and to design principles for applications in the area of opto-electronic devices.

**Chapter 2** is a detailed description of the photophysical properties and photoinduced processes of novel [60]fullerene-perylene bisimide ($C_{60}$-PDI) dyads in which the PDI chromophore plays the role of a visible-light antenna. After excitation of the PDI moiety, the excitation energy is transferred from PDI to the singlet excited state of the fullerene unit, then the backward energy transfer results in a low-energy triplet state localized on the PDI moiety. The influence of the spacer length and bay-substitution of the PDI unit on the kinetics and spectral features are also discussed. The bridges between two moieties are saturated methylene groups with different lengths. Such a linkage results in two major different orientations of the molecules, the folded and extended conformations which have different rate constants.
In Chapter 3, strong charge transfer (CT) interactions were shown to occur in a system consisting of a calixarene scaffold functionalized with an electron donating pyrene (Py) and an electron accepting perylene bisimide (PDI). Excitation of the PDI chromophore resulted in photoinduced electron transfer from Py to PDI. The calix[4]arene scaffold acts as a partially flexible bridge. Hence, there is a coexistence of the \( \pi \)-stacked and extended forms. Each possesses distinct photophysical and kinetic properties. Thus, in certain solvents (i.e. THF and PhCN), not only a \( \pi \)-stacked conformation but also an extended conformer could exist due to specific solute-solvent interactions competing with \( \pi - \pi \) interaction between the two chromophores. Upon Py excitation, the calix[4]arene scaffold is involved in the charge separation process functioning as the electron donor and Py as electron acceptor. The bridge takes part in the electron transfer processes upon pyrene excitation in the case of the extended conformer.

Chapter 4 presents studies on photoinduced charge separation in Perylene Red (PDI) and pyrene (Py) mixtures which are organized in thin films on quartz. Global analysis of the femtosecond transient absorption data indicates a complex photophysical behavior with various (kinetically different) charge separated states and triplet formation.

Chapter 5 describes the generation of a bi-radical state in a covalently linked catechol-quinone system by using a proton coupled electron transfer reaction (PCET), upon photo-excitation. The hydrogen bond between two moieties keeps them within
favorable distance required for the charge transfer processes. The covalent linkage between the o-quinone and catechol units prevents solvent separation of the two semiquinone radicals.

In Chapter 6, molecular orbital calculations were performed on electron donating (OPV) and electron accepting (PDI) chromophores organized by rigid helical scaffolds, using AM1 semi-empirical method. Previous experimental results showed significant effects of the bridging foldamer on photoinduced charge separation between two units. The calculations are used to visualize the very efficient through foldamer coupling by using a Frontier Molecular Orbital description.

1.4. References


Introduction


