Ultrafast excited-state dynamics of new chromophoric systems
developed for specific applications

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Abstract
During this thesis multichromophoric systems in solution and assembled on solid surfaces, as well as chromophores bound to DNA have been investigated by a great variety of optical spectroscopic methods, steady-state and time-resolved from the femtosecond to the nanosecond time regimes. While some of the investigated systems are of interest for solar cells, others are interesting as NIR emitters in biological systems with the peculiarity to show chiral selectivity owing to their chemical structure. The close proximity of the chromophores substantially influences the behavior of these compounds after light excitation - on the one hand it enables electron and energy transfer between the molecules designed for solar cell application, on the other hand it alters the photophysics of the NIR emitters after aggregation or DNA binding.
Ultrafast excited-state dynamics of new chromophoric systems developed for specific applications

THÈSE

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While going ahead you should often look backwards, otherwise you forget where you started and where you wanted to go

L. Andreyev
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Only 30 years ago, the term “ultrafast” still meant picosecond time-domain. Nowadays, with the development of femtosecond lasers and the field of nonlinear spectroscopy, we can monitor changes in a system already after the first femtoseconds ($10^{-15}$ s). Only optical spectroscopy provides such a good time-resolution and due to their unique capabilities, femtosecond transient absorption and fluorescence up-conversion have become techniques common to most chemists although the experimental set-ups remain rather difficult to maintain. Moreover, the development towards a broader application field (limited by excitation and detection wavelength), faster data
acquisition and better signal to noise ratio is still ongoing in many laboratories, including ours.

During this thesis multichromophoric systems in solution and assembled on solid surfaces, as well as chromophores bound to DNA have been investigated by a great variety of optical spectroscopic methods, steady-state and time-resolved from the femtosecond to the nanosecond time regimes.

While some of the investigated systems are of interest for solar cells, others are interesting as NIR emitters in biological systems with the peculiarity to show chiral selectivity owing to their chemical structure.

As will be shown, the close proximity of the chromophores substantially influences the behavior of these compounds after light excitation — on the one hand, it enables electron and energy transfer between the molecules designed for solar cell application, on the other hand, it alters the photophysics of the NIR emitters after aggregation or DNA binding.

The thesis is organized in the following way. In the beginning, a brief introduction to the field of photophysics is given and special attention is paid to the processes which dominate the photophysics of the investigated systems. After that, a description of the experimental techniques used is presented together with details on the data analysis performed. Chapters 4 and 5 are devoted to the photophysical properties of the multichromophoric naphthalene diimides (NDIs) compounds in solution and polymerized on a transparent electrode. In the subsequent chapter, the new promising near infrared fluorophores [4]helicene cation derivatives are introduced. In the end, the work will be overviewed with some concluding remarks.
Chapter 2

Theory of light-matter interaction and molecular photophysics

The aim of this chapter is to introduce the concepts and terms used throughout the following chapters. No derivation of the basics is attempted, they can be taken from any textbook, but some are sketched in order to show the applicability of the equations derived. For example, Förster's treatment of dipolar interaction is based on weakly interacting point dipoles, hence it cannot be expected to give accurate results for close lying chromophores.

The chapter will begin by a description of light. This will be followed by the interaction of light with matter and the processes that follow light absorption by molecules, such as energy or electron transfer.
Chapter 2

Finally, the influence of the environment on these processes will be briefly discussed.

Only electronic spectroscopy is at the scope of this chapter, other spectroscopic methods, hence region of the electromagnetic spectrum, would not be presented here.
2.1 Electromagnetic radiation (light)

Light has a pronounced particle-wave dualism. In wave formulation light is a transversal wave with the electric and magnetic field vectors oscillating in mutually perpendicular planes and can be described by the Maxwell equations.\(^1\)\(^,\)\(^2\) The solution depends on the boundary conditions and for an harmonic, monochromatic wave propagating in \(x\)-direction it reads

\[
\tilde{E}(\tilde{x},t) = \tilde{E}_0 \sin(\bar{k}\tilde{x} - \omega t) = \tilde{E}_0 \sin\left[2\pi(-\bar{x}/\lambda + vt)\right] = \\
= \tilde{E}_0 \left\{ \exp\left[2\pi i(\bar{k}\tilde{x} - \omega t)\right] + \exp\left[-2\pi i(\bar{k}\tilde{x} - \omega t)\right] \right\} \quad (\text{eq. 2.1})
\]

where \(\tilde{E}_0\) is the amplitude of the electric field, \(\bar{k}\) the wave vector, \(\omega = 2\pi v\) the angular frequency of the light and \(t\) the time. In vacuum, the wave vector is related to the angular frequency or the wavelength of the light by

\[
\bar{k} = 2\pi/\lambda = \omega/c 
\]

(eq. 2.2)

The speed of light \(c\), which is equal to the phase velocity in vacuum, depends on the medium through which the light propagates, and can be determined in the following way where \(n\) is the refractive index of the medium

\[
c = c_{\text{vacuum}}/n
\]

(eq. 2.3)

It follows that when light passes from one medium into another, the frequency remains constant while the wavelength changes according to \(c = \lambda v\).

The expression for the magnetic field \(B(\tilde{x},t)\) is analog to that given for the electric field in eq. 2.1. Both, electric and magnetic fields of
light are vectors. The electric and magnetic transition moments responsible for light-matter interaction, which will be introduced in the following sections, are also vectors. The directional selectivity that arises from this is of paramount importance for spectroscopic methods such as linear dichroism, circular dichroism or fluorescence polarization anisotropy.

The light is considered linearly polarized in the case when the polarization direction of the light is constant while its amplitude oscillates periodically. If, on the other hand, the amplitude is constant but the direction changes continuously, it is circularly polarized light. Looking at a given time as a function of distance along the

---

**Figure 2.1** Right-handed (A) and left-handed (B) circularly polarized light. The thick line indicates the path of the endpoint of the electric field vector of the circularly polarized light, the thin line that of the linearly polarized light waves.
propagation direction, circularly polarized light forms a helix of constant pitch (Figure 2.1).\(^3\)

Linear polarization can be obtained by superposition of a right-handed and left-handed circularly polarized light. Inversely, circularly polarized light can be derived from superposition of two orthogonal linearly polarized waves with a phase shift of \(\pi/2\) between them (Figure 2.1).\(^3\)

In the corpuscular description, light is envisaged as composed of photons and its quantization can be more easily understood. This quantization is at the heart of Planck's explanation of the black body radiation and of Einstein's description of the photoelectric effect.

Photons are stable, chargeless, massless (at zero speed) elementary particles of spin 1 (bosons) that exist only at the speed of light.\(^2\) Their momentum \(p\) and energy \(E\) are determined by their frequency with Planck's constant \(h\) and the speed of light \(c\) as proportionality factors

\[
p = \frac{h \nu}{c} \quad \text{(eq. 2.4)}
\]

\[
E = h \nu = \frac{hc}{\lambda} = hc\tilde{\nu} \quad \text{(eq. 2.5)}
\]

The quantity \(\tilde{\nu} = 1/\lambda\) introduced in eq. 2.5, is called the wavenumber and commonly used in spectroscopy since, contrary to the wavelength, it is directly proportional to the energy.

**Ultrashort laser pulses**

An optical pulse can be thought of as the result of the interference of many waves of different frequencies. Their interference is destructive almost everywhere in space. Thus, an ultrashort laser pulse cannot be
monochromatic. In analogy with eq. 2.1, the electric field associated with an optical pulse at center frequency $\omega_0$ is defined by

$$E(t) = \tilde{E}_0(t) \cdot \exp(i \omega_0 t)$$

(eq. 2.6)

$$\tilde{E}_0(t) = E_0 \cdot \exp(-t^2 / \tau_G^2)$$

(eq. 2.7)

where $\omega_0$ is the carrier frequency and $\tilde{E}_0(t)$ the pulse envelope, which is described by eq. 2.7 for a pulse with Gaussian shape that has a halfwidth $\tau_G$. Its time evolution is presented in Figure 2.2.

The spectral content and the time evolution are connected to each other by a Fourier transform operation. For a Gaussian envelope function it reads

$$E^*(\omega) = \int_{-\infty}^{\infty} E(t) \exp(i \omega t) dt = \exp \left( - \frac{(\omega - \omega_0)^2}{(2/\tau_G)^2} \right)$$

(eq. 2.8)

where $\omega_0$ is the carrier frequency. In order to produce a short light pulse it is necessary to use a broad enough spectrum. It can be shown that the spectral and temporal width $\tau_p = \sqrt{2 \ln 2} \cdot \tau_G$ (the full width at half maximum of the pulse determined from the intensity profile).
and the spectral bandwidth $\Delta \nu_p = \sqrt{2 \ln 2 / \pi \tau_p}$ are related by an inequality of the type

$$\tau_p \cdot \Delta \nu_p \geq K$$  \hspace{1cm} \text{(eq. 2.9)}$$

where $K$ is a constant which depends on the pulse shape ($K = 0.441$ for a Gaussian pulse). A pulse with minimal time bandwidth product, eq 2.9, is called Fourier transform limited.\(^5\)

The shortest laser pulses that have been realized experimentally have a duration of 80 as (1 as = $10^{-18}$ s).\(^6\) Attosecond pulses, however, can only be obtained with UV light. The shortest laser pulse achieved for visible light has a duration of 2.6 fs and covered a spectral range going from 450 to 975 nm.\(^7\),\(^8\) This corresponds to only 1.3 optical periods.
2.2 Light induced unimolecular processes

The unimolecular (or rather mono-chromophoric) processes of light-matter interaction are sketched in the Jablonski diagram shown in Figure 2.3: absorption, emission (fluorescence and phosphorescence), and non-radiative processes (vibrational relaxation, internal conversion and inter system crossing).

The time-scale at which these processes occur covers the range from femtoseconds to several seconds. Absorption can be regarded as instantaneous, whereas emission of light happens typically on the nanosecond time-scale \((10^{-9}\) s\) if two states of equal multiplicity are involved (fluorescence). It can be even slowed down to seconds in the

![Jablonski Diagram](image)

**Figure 2.3** Jablonski diagram showing the primary photophysical processes: absorption, fluorescence, phosphorescence, vibrational relaxation (VR), internal conversion (IC) and intersystem crossing (ISC) involving the lowest electronic excited \((S_1, S_2, T_1, T_2)\) and ground state \((S_0)\).
case of unequal multiplicity between initial and final state (phosphorescence). As will be discussed in more detail later, the rate constants for non-radiative processes can vary by several orders of magnitude. However, as rough estimates, it is generally assumed that vibrational relaxation in liquid solutions happens within a few picoseconds, internal conversion from $S_1$ with $k_{IC} = 10^7$ to $10^{11}$ s$^{-1}$ and intersystem crossing with $k_{ISC} = 10^7$ to $10^{10}$ s$^{-1}$.9

### Absorption of UV/visible light

Absorption of light by molecules is most frequently discussed in terms of a semi-classical model where light is treated as a (classical) electromagnetic wave and the molecule as a two states quantum system. Using perturbation theory and for the moment neglecting the magnetic field, the time-dependent perturbation Hamiltonian, $\hat{H}'(t)$, can be approximated as the dot product of the electric light field $E(t)$ oscillating with frequency $\nu$ (eq. 2.1) and the dipole operator $\tilde{\mu}$.

$$\hat{H}'(t) = -\tilde{E}(t) \cdot \tilde{\mu} \quad \text{(eq. 2.10)}$$

The dipole operator $\tilde{\mu}$ is simply given by the electronic charge multiplied by the position operator, summed over all electrons.

$$\tilde{\mu} = \sum_i e \cdot \tilde{r}_j \quad \text{(eq. 2.11)}$$

We can assume that $\tilde{E}_0$ is independent of the position of the electron, since the size of a chromophore is much smaller than the wavelength of visible light, which is the range of interest here.
The wavefunction of the perturbed two-level system is a linear combination of the eigenfunctions of the unperturbed system, \( \Psi_i \) and \( \Psi_f \) with energies \( E_i \) and \( E_f \), respectively

\[
\Psi = c_i(t) \cdot \Psi_i + c_f(t) \cdot \Psi_f
\]  
(eq. 2.12)

The time-dependent coefficients \( c_k(t) \) \((k = i \text{ or } f)\) of this superposition state represent the extent to which the system's wavefunction resembles that of a basis state \( \Psi_k \). From this and the time-dependent Schrödinger equation \((i \ \text{is the imaginary number, } h = h/2\pi \text{ with Planck's constant } h, \text{ and } t \text{ represents the time})

\[
\left[ \hat{H} + \hat{H}'(t) \right] \Psi = i\hbar \frac{\partial \Psi}{\partial t}
\]  
(eq. 2.13)

the rate of the transition \( i \to f \), i.e. the rate of increase of \( c_f(t) \), is given as

\[
\frac{\partial c_f}{\partial t} = i \frac{\hbar}{\mu} \left\{ \exp \left[ i \frac{(E_f - E_i + h\nu)}{\hbar} t \right] + \exp \left[ i \frac{(E_f - E_i - h\nu)}{\hbar} t \right] \right\} \bar{E}_0 \cdot \langle \Psi_f | \hat{\mu} | \Psi_i \rangle
\]  
(eq. 2.14)

and the transition probability at a time \( \tau \) after "switching on" the perturbation is the integral over eq. 2.14 from \( t = 0 \) to \( t = \tau \).

\[
c_f(\tau) = \left\{ \frac{\exp \left[ i \frac{(E_f - E_i - h\nu)}{\hbar} \tau \right] - 1}{E_f - E_i - h\nu} + \frac{\exp \left[ i \frac{(E_f - E_i + h\nu)}{\hbar} \tau \right] - 1}{E_f - E_i + h\nu} \right\} \times \bar{E}_0 \cdot \langle \Psi_f | \hat{\mu} | \Psi_i \rangle
\]  
(eq. 2.15)

The first term in brackets describes absorption of light, the second one, that differs only by the sign of the term \( h\nu \), describes stimulated
emission (if assuming that $E_f > E_i$). Transitions can only occur if the energy of the light equals the energy gap between the states, i.e. if the relation

$$h\nu = E_f - E_i$$  \hspace{1cm} (eq. 2.16)

is fulfilled. Otherwise both terms in parentheses in eq. 2.15 are vanishingly small. The quantization of the levels in the molecule leads to a discrete absorption spectrum, thus it is not necessary to treat the light quantum mechanically to obtain this fundamental result.

In reality, light is never strictly monochromatic. Additionally, and in contrast to what has been assumed in the derivation of eq. 2.15, a distribution of the states’ energies is present in liquid samples at room temperatures. When applying these two extensions, the individual transition rates are additive, i.e. the transition probability can be expressed as the integral over all the light frequencies and the distribution of molecular transition frequencies. The result is a golden rule type expression in which the rate of absorption depends on the density of states $\rho_v$

$$\int_0^\infty c_f^*(\tau, \nu)c_f(\tau, \nu)\rho_v d\nu = \left(\bar{E}_0, \left|\Psi_f \right|\Psi_i\right)^2 \rho_v \left(\frac{E_f - E_i}{h}\right) \frac{\tau}{\hbar^2}$$  \hspace{1cm} (eq. 2.17)

In the expression for the absorption, the integral

$$\left\langle \Psi_f \left| \hat{\mu} \right| \Psi_i \right\rangle = \mu_f$$  \hspace{1cm} (eq. 2.18)

is called the transition dipole moment (the vector notation is omitted). It has the unit of charge times distance, and is related to the
oscillatory component of the dipole in a superposition of the ground and excited states.\(^1\) It is a purely quantum mechanical feature that cannot be inferred from classical physics.\(^1\)

The oscillating electric light field interacts with the transition dipole moment of the molecule and induces either absorption or stimulated emission, depending on whether the initial state is higher or lower in energy than the final state. Einstein noted that apart from these two processes, spontaneous emission (fluorescence) needs to be considered to fully describe a two-level system. In his treatment, the probability of each of these transitions is represented by the respective Einstein coefficient and it can be shown that it is directly proportional to the square of the transition dipole moment.

\[
B_{\beta\gamma} = B_{\beta\gamma} = \frac{2\pi}{3h} |\mu_{\beta\gamma}|^2
\]  
(eq. 2.19)

Another way to express the "strength" of a transition is via the so-called oscillator strength \(f\) which can be related to the integral over the absorption spectrum and the Einstein \(B\) coefficient

\[
f = \frac{8\pi^2 m_e \nu_{\beta\gamma}}{3\hbar e^2 n} |\mu_{\beta\gamma}|^2
\]

\[
= \frac{3m_e c \varepsilon_0}{N_A e^2 n} \cdot \ln(10) \cdot \int \varepsilon(\nu) d\nu = \frac{4.3 \cdot 10^{-9}}{n} \cdot \int \varepsilon(\tilde{\nu}) d\tilde{\nu}
\]  
(eq. 2.20)

\[
B_{\beta\gamma} = \frac{3ce_0}{4\pi N_A n} \cdot \ln(10) \cdot \int \frac{\varepsilon(\tilde{\nu})}{\tilde{\nu}} d\tilde{\nu}
\]  
(eq. 2.21)

where \(m_e\) and \(e\) are the electron mass and charge, respectively, \(\varepsilon_0\) the vacuum permittivity and \(N_A\) Avogadro’s constant. The absorption spectrum is not unitless but rather expressed in terms of the decadic
molar extinction coefficient \( \varepsilon \) (hence the numeric factors in eq. 2.20 and 2.21).

**Selection rules**

The oscillator strength can take any value between 0 and 1 (and in presence of excitonic coupling even >1). Low values indicate that a transition is forbidden by one of the selection rules. The oscillator strength associated with a n\( \pi^* \) transition, for example, amounts only to \( f \approx 10^{-3} \) (corresponding to extinction coefficients of a few hundreds of L\( \cdot \)mol\(^{-1}\)\( \cdot \)cm\(^{-1}\)). The transition is said to be symmetry forbidden since the low extinction coefficient can be traced back to the poor overlap of the oxygen lone pair with the \( \pi^- \) system. Vibrations lowering the symmetry (thereby rendering the terms \( \sigma^- \) and \( \pi^- \) orbital approximate) efficiently increase the overlap integral and increase the oscillator strength. It is important to mention that in liquid solution at room temperature this selection rule is only moderately strict.

Another important selection rule is connected with the electron spin. Transitions between two states of different multiplicity are spin-forbidden. Yet, owing to spin-orbit coupling, any state posses a mixed spin character. Although the oscillator strength for \( T_n \leftarrow S_0 \) absorptions is usually very small, they can be observed experimentally under favorable conditions.\(^9\)

**Lambert-Beer law**

Light which passes through a sample can be absorbed by the chromophores presented in the sample if the requirements outlined in the beginning of this chapter are fulfilled. The fraction of light passing through the sample of thickness \( l \) is a function of the
concentration of chromophores $c$ and a proportionality factor that depends on the chromophore and the wavelength

$$A(\lambda) = -\log_{10}\left(\frac{I(\lambda)}{I_0(\lambda)}\right) = \varepsilon(\lambda) \cdot c \cdot l$$

(eq. 2.22)

The dimensionless quantity $A$ is the sample absorbance (also called optical density) and eq. 2.22 is known as the Lambert-Beer law. From its definition and the traditional units of the contained quantities, the decadic molar extinction coefficient (also called molar absorptivity), $\varepsilon$, has the unit $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. It is related to the transition dipole moment or the oscillator strength (eq. 2.20).

The Lambert-Beer law is the asymptotic behavior and strictly valid only for infinitely small concentrations. Another necessity is that the absorption band has to be broader than the bandwidth of the light. Then, and if the chromophores are not interacting with each other, absorption is additive meaning that the total absorbance of a sample is the sum of the individual components. This is no longer true if electronic coupling takes place.$^{10}$

**The shape of electronic spectra: the Franck-Condon principle**

While absorption spectra of atoms consist of sharp lines, those of molecules show broad bands and often exhibit some vibrational structure. Polyatomic molecules possess a large number of vibrational levels with a spacing typically 10 times smaller than that between $S_0$ and the closer lying electronic excited states (see Figure 2.3). To describe molecular transitions, it is therefore necessary, to include the vibrational wavefunction in the total wavefunction of the treatment represented above. If the Born-Oppenheimer approximation is valid,
The total wavefunction, $\Psi$, can be factorized into an electronic, $\varphi$, and a nuclear, $\chi$, wavefunction

$$\Psi = \varphi \cdot \chi$$

(eq. 2.23)

The Franck-Condon principle states that the most probable vibronic (= electronic and vibrational) transition is "vertical", as depicted in Figure 2.4, because electronic motion with typical frequencies of $10^{15}$ s$^{-1}$ is much faster than nuclear vibration and as a result the wavefunction of nuclear motion is nearly the same before and after the excitation.

Inserting eq. 2.23 into eq. 2.18 and noting that the electronic dipole moment operator does not act on the nuclear wavefunction yields for a transition between an initial state $\Psi_{in}$ and a final state $\Psi_{fn}$ ($n$ and $m$ denote vibrational quantum numbers)
Chapter 2

\[ \mu_{in \rightarrow fn} = \langle \Psi_{fn} | \tilde{\mu} | \Psi_{in} \rangle = \langle \phi_f | \tilde{\mu} | \phi_i \rangle \cdot \langle \chi_m \chi_n \rangle \]  
(eq. 2.24)

The last term in eq. 2.24 is the nuclear overlap integral and its square is called the Franck-Condon factor. It determines the shape of the absorption spectrum (but not the intensity since \( \sum |\langle \chi_m \chi_n \rangle|^2 = 1 \)).

In most cases, the vibrational wavefunctions differ slightly in the ground and excited electronic states. This occurs due to different electron distributions in the molecule which result in a change of equilibrium geometry (the displaced Morse potentials in Figure 2.4) and the vibrational frequencies. The most intense absorption is then not the zero-zero transition (Figure 2.4B).

The coordinate Q in Figure 2.4 does not necessarily include all normal modes of the molecule; some might not be affected by the electronic transition. Only the Franck-Condon active vibrations contribute to the vibrational structure of the absorption spectrum and change quantum number.

**Exciton splitting**

In molecular spectroscopy, the concept of exciton is used for aggregates of chromophores, for instance the light-harvesting complexes, porphyrin arrays, or simple H- and J-aggregates. Two different types of interactions between the chromophores, Frenkel (strong coulombic interaction) and Wannier-Mott excitons (strong exchange interaction) can be distinguished. In the former one the electron-hole pair remains localized on each chromophore, in the latter they do not. These two limiting cases correspond to Förster and Dexter energy transfer in case of weak interaction between the chromophores (see Chapter 2.3).
The Frenkel excitons will be described in some detail here. Let us consider two chromophores A and B coupled by Coulombic forces. Then, the Schrödinger equation of the excited dimer system

$$\hat{H}_D \Psi_D = E_D \Psi_D \quad \text{(eq. 2.25)}$$

is described by the dimer wavefunction and Hamiltonian

$$\Psi_D = c_A \Phi_A^* + c_B \Phi_{AB}^* \quad \text{(eq. 2.26)}$$

$$\hat{H}_D = \hat{H}_A + \hat{H}_B + V_{AB} \quad \text{(eq. 2.27)}$$

the latter of which differs from the Hamiltonians of the independent chromophores by the interaction energy

$$V_{AB} = \frac{5.04 \cdot f_L^2 \cdot |\vec{\mu}_A||\vec{\mu}_B|\kappa}{n^2 \cdot R^3} \quad \text{(eq. 2.28)}$$

The interaction energy (in cm$^{-1}$) is thus proportional to the transition dipole moments $\vec{\mu}$ (in D) which are located at distance $R$ (in nm) from each other in a geometry that determines the orientational parameter $\kappa$ (see Figure 2.5 and eq. 2.29). The screening by the environment is responsible for the appearance of the Lorentz factor $f_L$ (eq. 2.30).

$$\kappa = \cos \gamma - 3 \cdot \cos \alpha \cdot \cos \beta \quad \text{(eq. 2.29)}$$

$$f_L = \left( \frac{n^2 + 2}{3} \right)^2 n \quad \text{(eq. 2.30)}$$

The limiting cases are parallel, antiparallel and perpendicular orientation. For perpendicular orientation, the interaction vanishes.
\( \kappa = 0 \), whereas for parallel or antiparallel orientation \( \kappa \) can be either \( \pm 1 \) or \( \pm 2 \) depending on relative orientation of the transition dipole moments (Figure 2.5).

In the case of identical chromophores A and B with excited state energies \( E_{A^*} = E_{B^*} = E^* \) there are two solutions to eq. 2.25

\[
\begin{align*}
E_D^+ & = E^* + V_{AB} \\
E_D^- & = E^* - V_{AB}
\end{align*}
\quad \text{(eq. 2.31)}
\]

This means that, in the homodimer system, two transitions (\( D^* \leftarrow D \) and \( D \leftarrow D^* \)) separated by twice the interaction energy (Davydov splitting, Figure 2.6) replace the transition in the non-interacting system which are of equal energy and located on a single chromophore.

The wavefunctions of the homodimer excited states are
The transition dipole moments of the dimer transitions, \( D^+ \leftarrow D \) and \( D^- \leftarrow D \), are the vector sum and difference of the transition dipole moments of the two monomeric chromophores, respectively. The total

\[
\Psi_{D^+} = \frac{\sqrt{2}}{2} \left( \Psi_{A^+ B} + \Psi_{A B} \right) \\
\Psi_{D^-} = \frac{\sqrt{2}}{2} \left( \Psi_{A^+ B} - \Psi_{A B} \right) 
\]

Figure 2.6 Energy scheme for exciton splitting upon interaction of two chromophores A and B in a dimer D

Figure 2.7 Schematical representation of the different ways of aggregation and exciton energy diagram (the ovals correspond to the molecule and the double arrow indicates the polarization axis for the molecular electronic transition)
oscillator strength of the uncoupled system is conserved but redistributed among the two dimer transitions.

In a sandwich like aggregate of two chromophores, the D$^\rightarrow$D transition, which is higher in energy, carries all the oscillator strength while the D$\leftarrow$D transition is dark in absorption and emission (Figure 2.7). As a result, such aggregates, known as H-aggregates, are non-fluorescent\textsuperscript{11} and their absorption spectra are blue-shifted relatively to non-aggregated molecule.\textsuperscript{12}

By contrast, in an in-line association of the transition dipole moments, the lower energy state is bright while the upper one is dark (Figure 2.7). Such aggregates are called J-aggregates and the resulting strengthening of the fluorescence due to coherently coupled chromophores is called superradiance. An absorption band of J-aggregates is red-shifted in comparison with the monomeric chromophore.

Finally, a skew arrangement of the transition dipole moments (Figure 2.7) results in the appearance of two electronic transitions from the ground state. In this case the exciton splitting energy depends by the angle between the chromophores.\textsuperscript{12}

**Circular dichroism**

The peculiarity of chiral chromophores is that they distinguish between right-handed and left-handed circularly polarized light and show distinct refractive indices $n^R$ and $n^L$ and extinction coefficients $\varepsilon_R(\lambda)$ and $\varepsilon_L(\lambda)$ for the two polarizations.

A molecule is chiral if it cannot be superimposed with its mirror image and an isotropic sample is chiral only if the individual
molecules are chiral. In reality, molecules are often not rigid and can interconvert into each other chiral form. Thus, whether a molecule is chiral or not may depend on the height of the inversion barrier and the temperature. Chirality can also be induced, e.g. when an achiral chromophore binds to chiral molecule such as DNA or when it chirally arranges in a dimer. This phenomenon is known as induced circular dichroism.

The optical activity of enantiomers at the Na D line (589 nm) is often used to characterize them as the (-) isomer (laevororotatory) and the (+) isomer (dextrorotatory), respectively. Enantiomers show the same degree of optical activity but with opposite sign. Thus, an equimolar mixture of two enantiomers (a racemate) does not show a circular dichroism signal $\Delta \varepsilon = (\varepsilon_L - \varepsilon_R)$.

In a pictorial description of the origin of the preferred absorbance for one type of circularly polarized light, the electrons may be thought to move in some kind of helix. Circular dichroism involves both electric and magnetic field interactions. The rotational strength (also called rotatory strength), which can be determined from the experimental CD spectrum by integration over the corresponding band is related to the molecular transition moments via the Rosenfeld equation

$$\mathcal{R}_{i \rightarrow f} = 0.248 \cdot \int \frac{\varepsilon(\tilde{\nu})}{\tilde{\nu}} d\tilde{\nu} = \text{Im} \left\{ \langle \Psi_i | \tilde{\mu} | \Psi_f \rangle \cdot \langle \Psi_i | \tilde{\mu}_M | \Psi_f \rangle \right\}$$ (eq. 2.33)

Here $\tilde{\mu}$ is the electric dipole operator defined in eq. 2.18, and $\tilde{\mu}_M$ is the magnetic dipole operator defined as (neglecting higher order multipoles)
with the position operator $\vec{r}_j$ and the linear momentum operator $\vec{p}_j = -i\hbar \vec{\nabla}_j$. For real wavefunctions the Rosenfeld formula may be written as

$$\mathcal{R}_{i \rightarrow f} = \langle \Psi_i | \mu_{ij} | \Psi_f \rangle \langle \Psi_i | \mu_{ij}^M / i | \Psi_f \rangle = \mu_{ij} \mu_{ij}^M \cos(\mu_{ij}, \mu_{ij}^M)$$

(eq. 2.35)
The difference between the absorbances measured with left and right circularly polarized light rarely exceed 0.1% of the total absorbance since it is related only to the helical or asymmetric part of the change that occurs when radiation is absorbed.\(^\text{13}\) On the other hand, a transition that is weak in the non-polarized absorption spectrum, can have a sizable CD signal (and \textit{vice versa}).\(^\text{14}\) For instance, the dipole forbidden transition at 220 nm in \textbf{Figure 2.7} is only observed in the CD spectrum.\(^\text{15}\)

\textbf{Vibrational Relaxation}

According to the Franck-Condon principle, light absorption is "vertical" and does not imply geometrical changes of the molecule. After excitation, the motions of the nuclei are governed by the excited state potential energy surface whose equilibrium geometry does not need to coincide with that of the ground state and subsequently the
geometry of the system changes in time. The vibrational energy that stems from this relaxation and from the excitation itself (unless the photoexcitation was strictly to the electronic excited state's vibrational ground state) will quickly equilibrate among all vibrational modes (intramolecular vibrational energy relaxation, IVR) and dissipate to the solvent (vibrational cooling, VC). Big amounts of vibrational energy are present in a molecule after non-radiative processes such as internal conversion from a higher excited state or electron transfer.\[16\]

IVR is a result of anharmonic coupling between the vibrational normal modes. For medium and large size organic molecules in condensed medium it is an ultrafast process and usually complete in a few hundred femtoseconds although recent results showed that it can be strongly mixed with vibrational cooling.\[17-20\] In general, however, IVR is faster than the time resolution of the set-ups employed during this thesis and was not observed.

The time range of vibrational cooling, on the other hand, is much broader and extends up to several picoseconds in common organic solvents.\[16, 17, 21\] Emission spectra narrow as vibrational cooling takes place.\[22, 23\] Despite intensive study, vibrational cooling is still poorly understood. It is easy enough to describe vibrational cooling in phenomenological terms, but microscopic models have remained scarce. Knowledge about vibrational cooling has come primarily from time-resolved spectroscopy, namely transient absorption in the visible and infrared spectral region, fluorescence up-conversion and anti-Stokes Raman scattering.

Molecules that undergo ultrafast internal conversion have been used to investigate vibrational cooling. In the course of the internal conversion, several eV of electronic energy are converted into
vibrational energy and this energy is then dissipated to the solvent. The most commonly studied molecules include perylene, azulene, $p$-nitroaniline, polyenes such as cis-hexatriene, or β-carotene, and DNA and RNA bases.

The rates for vibrational cooling range from a few to typically 50 ps and depend not only on the nature of the solvent but also on properties of the solute.

**Fluorescence**

Fluorescence spectroscopy is one of the most sensitive detection methods available nowadays. Additionally, it is a selective method since has wavelength dependent character. It can be performed in a time-resolved and time-integrated (steady-state) fashion. The fluorescent properties of a molecule is characterized by the fluorescence quantum yield, $\Phi_{fl}$, defined as the ratio of absorbed to emitted photons and directly proportional to the rate constants of the processes that depopulate the state under consideration. In absence of quenching these are fluorescence (with the rate constant $k_r$), internal conversion ($k_{IC}$) and intersystem crossing ($k_{ISC}$) (see the Jablonski diagram, Figure 2.3).

$$\Phi_{fl} = \frac{k_r}{k_r + k_{nr}} = \frac{k_r}{k_r + k_{IC} + k_{ISC}} = k_r \cdot \tau_{fl} \quad (eq. \ 2.36)$$

For a triplet state decaying to the singlet ground state, the radiative deactivation is called phosphorescence.

In practice, fluorescence quantum yields are measured relative to a reference standard of known emission efficiency since an absolute determination is not so easy.
Here the subscript $S$ indicates the reference standard, $A$ the sample (or reference) absorbance at the excitation wavelength and $n$ the refractive index of the solution. The first term in eq. 2.37 accounts for differences in sample and reference absorbance, i.e. number of excited chromophores. The second term is a correction for the solution optical geometry leading to a dependence of the light intensity captured by the detector on the refractive index.$^{31, 32}$ Finally, the third term represents the ratio of emission intensity of sample and reference compound (integrated over the whole fluorescence spectrum).

The lifetime of an excited state, $\tau_{fl}$, is determined by the sum of all processes that depopulate that state as indicated in eq. 2.38. It means that the value of a rate constant can only be extracted from a lifetime measurement if additionally the quantum yield of the corresponding process is known.

$$\tau_{fl} = 1 / (k_r + k_{IC} + k_{ISC})$$  \hspace{1cm} (eq. 2.38)

$$k_r = \frac{\Phi_{fl}}{\tau_{fl}}$$  \hspace{1cm} (eq. 2.39)

$$k_{nr} = \frac{1 - \Phi_{fl}}{\tau_{fl}}$$

Einstein related the rate of absorption to those of spontaneous and stimulated emission of atoms and Strickler and Berg extended his treatment to molecules. They derived the so called Strickler-Berg
equation through which the radiative rate constant of a state can be deduced from its absorption and emission spectrum.\textsuperscript{34}

\[
k_r = \frac{8000\pi \cdot \ln(10) \cdot c \cdot n_D^2}{N_A} \cdot \int \frac{I(\tilde{\nu}) d\tilde{\nu}}{\tilde{\nu}^3} \cdot \int \tilde{\nu}^{-1} \varepsilon(\tilde{\nu}) d\tilde{\nu} \quad (eq. 2.40)
\]

The numerical factors account for the units of \(\tilde{\nu}\) and \(\varepsilon(\tilde{\nu})\), the second term is the reciprocal of the mean value of \(\tilde{\nu}^{-3}\) over the fluorescence spectrum.\textsuperscript{1, 31} In Einstein's two-level system, absorption and emission are connected via

\[
A_{fi} = k_r = \frac{8\pi hf_L \nu_f^3}{c^3} \cdot B_{if} \quad (eq. 2.41)
\]

In order for the Strickler-Berg relation to be valid, mirror-symmetry must exist between the absorption and fluorescence emission spectrum. In general it is observed that absorption and fluorescence emission spectrum can be superimposed on another when one is mirrored at the 0-0 frequency (see also Figure 2.3). This implies that the frequencies of the vibrational modes do not differ much in the ground and excited state and that a Boltzman distribution (which will under such conditions be identical in the two states) is reached before emission takes place.

Obviously, a mirror image can only be observed on a linear energy scale (e.g. wavenumbers) and when represented as the transition dipole moment or the Einstein coefficient (eqs. 2.19 - 2.21 and 2.40 - 2.41).\textsuperscript{35}

There are several reasons for which the mirror-image law might break down. It might be strong molecular relaxation in the excited state, important distortion by the solvent or heterogeneity in the
absorbing or emitting species. In practice, sample impurities can be another reason but will also lead to a discrepancy between absorption and fluorescence excitation spectra.

**Stokes Shift**

As just mentioned, it is often observed that the fluorescence spectrum is a mirror image of the absorption spectrum. This can be inferred from the Jablonski diagram (Figure 2.3) (which also shows that an absorption spectrum gives information about the vibrational progression in the excited state, whereas the fluorescence spectrum reflects that of the ground state).

Due to geometrical relaxation of the molecule after photoexcitation mentioned before and solvent stabilization of the excited state (see below), the fluorescence spectrum is displaced to lower energies (longer wavelengths) in comparison with the absorption spectrum. The energy difference between the maxima of absorption and emission is called the Stokes shift and is a measure of these two stabilization energies. A large Stokes shift indicates a large displacement of the parabolas in Figure 2.4 and/or important stabilization of the excited state.

**Kasha's and Vavilov's rule**

Until the advent of ultrafast spectroscopy, fluorescence properties were considered as excitation wavelength independent. This is because internal conversion from a higher excited state $S_{n>1}$ to $S_1$ and vibrational and solvent relaxation in $S_1$ are much faster than $k_r$ and at the origin of Kasha's rule (which states that emission always occurs from $S_1$) and Vavilov's rule (the fluorescence quantum yield is not a function of the excitation wavelength). Well known deviations are
benzene (violating Vavilov's rule owing to the "third channel"), porphyrine and azulene (violating Kasha's rule since they show emission from $S_2$).

Nowadays, emission from higher excited states and the effect of internal conversion, vibrational or solvent relaxation on the fluorescence spectrum can be readily observed by time-resolved fluorescence measurements in the femtosecond range. The results confirm that these processes are in general ultrafast and that the rules are valid, but have to be understood as the "long time behavior".

*Fluorescence polarization anisotropy*

The transition dipole moment, $\mu$, introduced earlier is a vector quantity and the interaction strength between an incoming linearly polarized light and $\mu$ is governed by the square cosine of the angle between them. Hence, an isotropic sample becomes anisotropic by excitation with linearly polarized light. This is known as photoselection. Directly after excitation with polarized light or if rotational diffusion is prevented, the emitted light will have a preferred polarization axis, determined by the transition dipole moment of emission. Rotation of the fluorophore during the excited state lifetime randomizes the orientation of the transition dipole moment with respect to the laboratory axis and the anisotropy goes to zero.

Quantitatively, the fluorescence polarization anisotropy (FPA), $r(t)$, is defined as the difference between light detected with the analyzer polarizer parallel and perpendicular to the electric field of excitation, normalized to the total intensity of emission:
\[ r(t) = \frac{I_\parallel(t) - I_\perp(t)}{I_\parallel(t) + 2I_\perp(t)} \]  

(eq. 2.42)

The initial anisotropy, \( r_0 \), depends on the angle \( \theta \) between the transition dipole moment of absorption and emission.

\[ r_0 = \frac{3\cos^2 \theta - 1}{5} \]  

(eq. 2.43)

The limiting cases are parallel (\( r_0 = 0.4 \)) and perpendicular orientation (\( r_0 = -0.2 \)). As mentioned before, rotational diffusion will make the FPA decay to zero with time. Time resolved measurements give therefore a handle to rotational diffusion of a fluorophore in a given surrounding. Usually the FPA decay can be represented by an exponential law with the rate constant called the rotational correlation time, \( \tau_{\text{rot}} \).

\[ r(t) = r_0 \cdot \exp\left(-\frac{t}{\tau_{\text{rot}}}\right) \]  

(eq. 2.44)

The rotational correlation time can be related to properties of the chromophore and the environment via the Stokes-Einstein relation.

\[ \tau_{\text{rot}} = \frac{f \cdot C \cdot V \cdot \eta}{k_B T} \]  

(eq. 2.45)

Here, \( f \) is a factor accounting for the molecule's shape which equals 1 for spherical shape, \( V \) is its molecular volume and \( \eta \) the solvent viscosity. The factor \( C \) describes the interaction between the chromophore and the solvent. As limiting cases can be distinguished\(^{14}\)

- the "slip" boundary condition (\( 0 < C < 1 \)) applies when the solvent molecules exhibit only minor displacement upon rotation of the chromophore. For a spherical chromophore, \( C = 0 \) which
means that the rotation is completely independent of the solvent. If the rotator is aspherical, its reorientation implies displacement of solvent molecules and the value of $C$ depends on the deviation of the chromophore's shape from a sphere,

- the "stick" boundary condition ($C = 1$) applies when the first solvation shell accompanies the chromophore's movement owing to important forces between them. It is typical of polar and charged fluorophores in polar solvents. In the case of strong bonds, for instance hydrogen bonds, $C > 1$, they effectively follow the molecule which is known as the "superstick" condition. The volume of the rotator (the "hydrodynamic volume") is bigger than the molecular volume.

As can be inferred from the correction factors $f$ and $C$ and the importance of molecular interactions such as hydrogen bonds, the Stokes-Einstein relation has severe limitations when used on a molecular scale. In particular, it is not valid to assign a numerical value to the viscosity of a microenvironment.9

Not only rotation can lead to a decay of the FPA signal. Energy hopping, i.e. energy transfer between identical chromophores (see Chapter 2.3), which does not alter the fluorescence spectrum or lifetime, can be detected by FPA.

When a sample contains more than one fluorophore, each with its own anisotropy $r_i(t)$, the total emission anisotropy is the weighted sum of the individual anisotropies:

$$r(t) = \sum_i A_i \frac{\exp(-t/\tau_i)}{I(t)} r_i(t)$$  \hspace{1cm} (eq. 2.46)
At first glance, it is surprising to find that the weighting factor for each anisotropy term depends on the total fluorescence intensity at that time. However, it simply results from the definition of the anisotropy. As a consequence, the FPA decay of a mixture of fluorophores may not decay monotonously and \( r(t) \) should be regarded as an apparent anisotropy because it does not reflect the overall orientation relaxation, as in the case of identical fluorophores. Multiexponential FPA decays can also result from pronounced differences in the rotational correlation times of the three molecular axes owing to a prominent non-spherical shape.

In principle, the anisotropy of a transient absorption signal can be defined and measured in a similar way as was done here for fluorescence emission. However, the overlap of different bands of different sign renders this extremely risky.

Finally, in order to avoid contributions to the signal from rotational diffusion, the angle \( \alpha \) between the excitation light and the detected signal has to be such that \( 2I_\parallel = I_\perp \) which is given for \( \alpha = 54.7^\circ \) and called magic angle configuration.

**Internal conversion and conical intersections**

In a radiative transition, two states are mixed \( \text{via} \) the dipole moment operator at fixed geometry — the transition is "vertical" (Franck-Condon principle). On the other hand, in a non-radiative transition, states mix by virtue of the nuclear displacement operator at constant energy — the transition is "horizontal". Internal conversion (IC), for example, is an iso-energetic process but is followed by rapid vibrational relaxation (VR) and often the ensemble of IC and VR is
not completely correctly subsumed as IC. The VR makes IC an irreversible process in condensed phase.

Non-radiative transitions are not possible within the Born-Oppenheimer approximation. This is because electronic wave functions cannot mix to zero order. The states can be mixed, however, and transitions between states induced by coupled vibrations of appropriate symmetry.\(^{36}\)

The state crossing rate is described by Fermi’s golden rule. For IC the involved states are typically the vibrational ground state of an electronic excited state and a vibrationally highly excited state of a lower electronic state. The coupling element depends, as already said, on nuclear displacement operator.\(^{5}\)

\[
k_{IC} = \frac{2\pi}{\hbar} |V_{IC}|^2 \cdot \rho \cdot FC
\]  
(eq. 2.47)

Here the Franck-Condon factor, FC, is noted explicitly and not included in the density of states \(\rho\) or the coupling element \(V_{IC}\). The density of states increases rapidly with the number of atoms in the molecule and with the energy gap between the electronic states involved. This increase, however, is overcompensated by a decrease in the FC factor. This leads to the so-called energy gap law

\[
k_{IC} = k_{00} \cdot \exp(-\alpha \cdot \Delta E_{00})
\]  
(eq. 2.48)

where \(\Delta E_{00}\) is the energy gap between the 0 vibrational levels and \(k_{00}\) and \(\alpha\) are empirical parameters.\(^{5, 37-39}\) As can be deduced from eq. 2.48, IC is the dominant relaxation mode of higher electronic excited states \(S_{n>1}\) (see Kasha’s and Vavilov’s rule above) while the situation can be very different for the \(S_1\) state.
Another corollary of eq. 2.48 is that molecules with an energetically low lying S\textsubscript{1} state are unlikely to be good fluorophores. Additionally, such molecules are expected to have a low radiative rate constant (eq. 2.41). However, as will be discussed in more detail in Chapter 6, good near-infrared emitters are of paramount importance for numerous applications in chemistry, biochemistry and medicine.

The smaller the energetic spacing between two states, the bigger their coupling matrix element $V_{IC}$. In the extreme case, the potential energy surfaces are degenerate and have a common, 3N-8 dimensional subspace (where N is the number of normal modes) which is commonly known as conical intersection. This opens the pathway for extremely efficient state crossing, far beyond what is described by Fermi’s golden rule (that describes weak coupling only). The ultrafast electronic excited state relaxation of DNA bases is ascribed to a conical intersection accessed by deformation of the ring.\textsuperscript{40}

**Intersystem crossing and Phosphorescence**

Among the small terms usually neglected in the Hamiltonian in absence of heavy atoms is spin-orbit coupling, which cause the pure spin multiplet states to mix to a small degree. The hyperfine interaction term, which describes the coupling of electron and nuclear spin, can have the same effect.\textsuperscript{41}

Spin-orbit coupling can be understood in a primitive way by considering the motion of an electron in a Bohr-like orbit. The rotation around the nucleus generates a magnetic moment; moreover, the electron spins about an axis of its own, which generates another magnetic moment. Spin-orbit coupling results from the interaction between these two magnets.\textsuperscript{9}
These effects are able to compensate for the change of electron spin in a singlet → triplet or triplet → singlet transition and thereby reinforce the otherwise small ISC rates of organic molecules. ISC is greatly accelerated in presence of heavy atoms (it scales with the forth power of the atomic number) owing to enhanced relativistic effects. The enhancement can also be observed when the solvent carries the heavy atom (known as external heavy atom effect).

The rate constant for ISC, \( k_{\text{ISC}} \), is given by the Fermi's golden rule where the coupling matrix element is dominated by the spin-orbit coupling term.

\[
k_{\text{ISC}} = \frac{2\pi}{\hbar} |V_{\text{SO}}|^2 \cdot \rho \cdot FC \tag{eq. 2.49}
\]

Through the density of states, \( k_{\text{ISC}} \) is related to the energy gap between the states involved and this explains why \( S_1 \rightarrow T_1 \) ISC is on average \( 10^9 \) times faster than \( T_1 \rightarrow S_0 \) ISC. Like IC, ISC is iso-energetic but followed by rapid vibrational relaxation and IC in the triplet manifold. Yet, if the lowest triplet state, \( T_1 \), is energetically not much lower than the \( S_1 \) state, thermal population of \( S_1 \) via "reverse-ISC" \( S_1 \leftarrow T_1 \) can lead to fluorescence known as E-type delayed fluorescence. The name comes from eosin, the first molecule for which it was observed. The lifetime of E-type delayed fluorescence is that of the triplet state. Unlike P-type delayed fluorescence (the result of triplet-triplet annihilation, the "P" comes from pyrene), E-type delayed fluorescence is temperature, but not concentration dependent.

The radiative transition between an triplet and the ground singlet state is spin-forbidden and the rate constant is therefore usually very
low, but in the absence of other deactivation processes, phosphorescence can nevertheless be observed. In liquid solution, however, even small amounts of oxygen or impurities efficiently quench triplet state population.

Quenching of triplet states is not always unwanted. In fact, their longevity makes it much easier for electron or energy transfer to become competitive to unimolecular deactivation.

Finally, it should be stressed that the terms singlet and triplet are not restricted to a single chromophore. A radical ion pair formed in an electron transfer reaction can have a total spin of 0 or 1, i.e. singlet or triplet multiplicity. In the latter case, charge recombination is spin forbidden and slow. An example for a such a charge separated state will be given in Chapter 4.
2.3 Bimolecular photoinduced processes

In the previous sections, the photophysics of a chromophore in an unreactive medium have been described. With the description of fluorescence quenching via energy or electron transfer and excited state complex formation with suitable reaction partners, we enter the field of photochemistry. Interactions in the electronic ground state that alter the electronic properties have been considered in Chapter 2.2. As discussed there, they also influence the fluorescence properties.

Fluorescence quenching is the deactivation of an excited state by a photochemical reaction with another molecule or an electronically not conjugated part of the same molecule, but does not lead a chemical modification of the molecule. The fluorophore can, for example, donate the excitation energy to an acceptor (excitation energy transfer, EET) or undergo an electron transfer (ET) reaction, exemplified in the following scheme by charge separation.

\[
\begin{align*}
D^* + A &\rightarrow D + A^* \quad \text{EET} \\
D^* + A &\rightarrow D^+ + A^- \quad \text{photoinduced ET} \\
D + A^* &\rightarrow D^+ + A^- \\
D^* + A &\rightarrow (D \cdot A)^* \quad \text{exciplex formation}
\end{align*}
\]

These processes will be described in more detail in this section. There are other quenching mechanisms such as paramagnetic quenching but they are of minor interest to this work. Furthermore, only the aspects of intramolecular quenching are discussed. In bimolecular
quenching, diffusion has to be taken into account which gives rise to time dependent quenching rate constants.

**Excimer and exciplex fluorescence**

As shown in [Figure 2.8](#) for two identical molecules, there is a stabilization of the complex formed between a photoexcited and a ground state molecule. This complex is called excimer (excited dimer) in the case of identical chromophores and exciplex (excited complex) in the case of chromophores that are not alike.

For typical aromatic fluorophores, the minimum in the excited state potential energy surface (PES) is found at an intermolecular distance of ca. 3-4 Å. Since the ground state PES of the system is repulsive at this geometry, the fluorescence of the excimer/exciplex is structureless even if the monomer spectrum shows vibrational progression. Naturally the stabilization energy depends crucially on the nature of the chromophores and the solvent.

![Figure 2.8](#)

**Figure 2.8** Potential energy surface demonstrating the formation of an excimer of two chromophores M as a function of interparticle distance $r_{MM}$. The excimer fluorescence is structureless.
Energy transfer

Excitation energy transfer (EET) is a form of fluorescence quenching in which the electronic energy of one chromophore, the donor, is transferred to another chromophore, the acceptor. Two mechanisms are usually distinguished (Figure 2.9), electron exchange (Dexter type EET) and dipolar resonance energy transfer (Förster type EET, FRET).

Reabsorption is sometimes referred to as a trivial mechanism of EET. It means the absorption of the fluorescence by another chromophore in samples of high concentration and leads to a diminution of the measured fluorescence intensity. However, it does not alter the fluorescence lifetime since no term adds to the sum of rate constants that depopulate S₁ (eq. 2.38). Contrary to EET of Förster and Dexter mechanisms, reabsorption involves a photon as intermediate.

Förster energy transfer

FRET is the resonant relaxation of one chromophore and excitation of another via dipolar interaction between them. FRET is not a

---

**Figure 2.9** Scheme of Dexter (left) and Förster (right) energy transfer. An electron exchange mechanism is operative in Dexter EET, while dipolar interaction between donor (D⁺) and acceptor (A) are at the origin of Förster type EET.
combined emission-(re)absorption process but non-radiative in nature. It requires therefore:

- energy match between the transitions in donor and acceptor. This can be understood in complete analogy to the condition for light absorption (eq. 2.16) and quantified by the overlap integral between the donor emission and the acceptor absorption — the bigger the overlap, the more efficient the energy transfer,

- a high radiative rate constant of the donor and acceptor transition. This impedes triplet energy transfer on the basis of a dipole mechanism,

- an appropriate relative orientation of the transition dipoles. The closer to parallel or antiparallel they are oriented, the better.

The interaction energy due to electrostatic interaction of the two point dipole moments (the transition dipole moments $\mu_{D^*D}$ of the energy donor and $\mu_{A^*A}$ of the acceptor) is given by

$$V_{\text{dip}} = \frac{\mu_{D^*D}^* \mu_{A^*A}^* \kappa}{4\pi \varepsilon_0 R_{DA}^3 n^2}$$

(eq. 2.50)

where $\varepsilon_0$ is the vacuum permittivity and $n$ the refractive index of the medium. The interaction energy depends on the distance $R_{DA}$ and the mutual orientation of the two dipoles, which enters via the factor $\kappa$ (Figure 2.5).

Förster used this interaction energy in a Fermi golden rule expression to calculate the rate constant for the energy transfer. He identified the density of states in the golden rule expression with the overlap integral between the donor emission and the acceptor absorption and derived the famous equation
\[ k_{\text{FRET}} = \frac{9000 \cdot \ln(10) \cdot \kappa^2 \cdot k^D}{128 \cdot \pi^5 \cdot N_A \cdot n^4 \cdot R_{DA}^6} \cdot \frac{\int I_D(\tilde{\nu}) \cdot \varepsilon_A(\tilde{\nu}) \cdot \tilde{\nu}^{-4} d\tilde{\nu}}{\int I_D(\tilde{\nu}) d\tilde{\nu}} \] (eq. 2.51)

Note, the numerical factors in eq. 2.51 that account for the units commonly used to represent the fluorescence spectrum of the fluorophore, \( I_D(\tilde{\nu}) \), and the absorption of the quencher \( \varepsilon_A(\tilde{\nu}) \) (L·mol\(^{-1}\)·cm\(^{-1}\)), and that the distance between the dipoles, \( R_{DA} \), is in cm.

The transition dipoles are included in an implicit way in eq. 2.51: the donor's \( \text{via} \) the radiative rate constant and the acceptor's in form of the absorption spectrum, both of which are proportional to the transition dipole moment as described earlier (eqs. 2.21 and 2.41). It is from these relations that the factor \( \tilde{\nu}^{-4} \) enters the equation.\(^{14}\)

Förster's treatment allows to calculate the transfer rate constant on basis of easily accessible photophysical characteristics of a given fluorophore/quencher pair. Their distance might be known from the molecular structure and/or quantum chemical calculations in the case of intramolecular EET, or estimated from the Perrin equation for intermolecular EET (eq. 2.52, where \([A]\) is the concentration of the quencher in mol/L).\(^{39}\)

\[ d_{DA} = 6.5 \cdot 10^{-9} \cdot [A]^{1/3} \] (eq. 2.52)

Yet, there are several restrictions to Förster's theory:

- the transition dipole moments are modeled by point dipoles which is only appropriate for a sufficiently large distance between the chromophores. The point dipole is reasonable approximation if the intermolecular distance is more than 4 times the length of the
chromophores, although the relative error can still be substantial.\textsuperscript{1, 42}

- the derivation entirely neglects higher order multipoles. They, however, fall off more rapidly with distance and are not expected to play a role in the presence of the much stronger dipole interactions,

- the relative orientation is not always known accurately. Fortunately already rather small rotational motion is sufficient to make $\kappa^2$ approach $2/3$, the value for random orientation,\textsuperscript{1}

- a distribution of distances leads to non-exponential fluorescence decays (which are usually not resolved) and tends to put too much weight on short distances between the chromophores. However, for a Gaussian distribution (even a broad one) the error is usually below 1%,\textsuperscript{1}

- absorption and fluorescence are sensitive to the environment. A shift in the spectra changes the overlap integral. This might be critical in biological applications if the donor and acceptor are embedded in a protein or DNA. Also, the index of refraction of such environments is in general not known,\textsuperscript{43, 44}

- the distance between donor and acceptor must not change on the time scale of the fluorescence lifetime, otherwise corrections of eqs. 2.51 and 2.53 are necessary.\textsuperscript{9}

Owing to its dipolar nature, FRET is efficient even at long ranges, up to 100 Å.\textsuperscript{9, 14} Rearranging eq. 2.51 and choosing $k_{\text{FRET}} = k$, yields

$$R_0 = \frac{9000 \cdot \ln(10) \cdot \kappa^2}{128 \cdot \pi^5 \cdot N_A \cdot n_D^4} \cdot \sqrt[4]{\frac{\int F_D(\tilde{\nu}) \cdot \epsilon_A(\tilde{\nu}) \cdot \tilde{\nu}^{-4} d\tilde{\nu}}{\int F_D(\tilde{\nu}) d\tilde{\nu}}}$$

(eq. 2.53)
a length that is known as the Förster radius (here the unit of $R_0$ is nm), the distance at which 50 % of the excited state population decays due to EET.

The 6th power dependence on the donor-acceptor distance is approximately linear around $R_0$ and this provides a sensitive experimental measure for the relative position of two chromophores. Indeed, unbeatable spatial "resolution" of 3 Å can be achieved by FRET microscopy. Practically, it has been used as spectroscopic ruler to analyze the conformational change of a protein that brings two molecular subunits closer together or farther apart.45, 46

However, from eq. 2.53 it becomes clear that a precise distance can only be calculated when assuming that $\kappa$ is known and that there are no important solvatochromic spectral shifts (that will alter the overlap integral).

**Dexter mechanism**

As shown in Figure 2.9, double electron transfer is another way to transfer excitation energy from one molecule to another.43, 47 Starting from Fermi’s golden rule D. Dexter derived an expression for the rate constant of EET via electron exchange when identifying the density of states with the overlap integral.48

\[
\kappa_{\text{EET}} = \frac{2\pi}{\hbar} |V_x|^2 \rho \frac{2\pi}{\hbar} |V_x|^2 \int \frac{I_D(\vec{v}) \cdot e_A(\vec{v}) d\vec{v}}{\int I_D(\vec{v}) d\vec{v} \cdot \int e_A(\vec{v}) d\vec{v}} \quad (\text{eq. 2.54})
\]

The magnitude of the coupling matrix element $V_x$ depends on the details of the molecular orbitals involved. For Dexter type EET, spatial overlap of the electronic wavefunctions of energy donor and acceptor is required. $V_x$ is generally taken to fall off approximately as
exp(−β ⋅ R_{DA}) with β on the order of 1 to 2 Å⁻¹. This means that Dexter EET is only efficient at \( R_{DA} < 10 \) Å.⁴²

The contribution of an orbital dependent exchange interaction to long-range EET through a π-conjugated bridge was nicely demonstrated by Strachan et al.⁴⁹ By exchange of a remote substituent they could alter the ordering of the MOs in a diphenyleneethynylene linked bisporphyrin and showed that the rate constant of EET is strongly enhanced when the bridge is attached to the donor at a site that has significant electron density.⁴⁵, ⁴⁹

In most of the cases, dipole interactions are the dominant contribution for EET. Dexter EET can overrule in case of favorably small β values,⁵⁰, ⁵¹ or when the dipole mechanism is suppressed. For example, triplet-triplet EET is not possible \( \text{via} \) the Forster mechanism since the transition dipole moments are far too small (eq. 2.50), a restriction that does not hold for the exchange mechanism.

**Superexchange mechanism for energy transfer**

Deviations from what is expected on the basis of the two idealized EET models have most frequently been ascribed to superexchange, a long-range through-bond Dexter EET. The term superexchange refers to the enhancement of EET through the intervening structure. This structure is usually covalently bond, but superexchange has also been invoked to be active \( \text{via} \) hydrogen bonds and other weak intermolecular interactions.⁴³

McConnell derived an expression for the interaction energy between a donor and an acceptor, \( V_{DA} \), linked by a bridge of \( n \) identical repeating units.


\[ V_{DA} = \frac{V_{DB} V_{BA}}{\Delta E_{DB}} \left( \frac{V_{BB}}{\Delta E_{DB}} \right)^{n-1} \]  

(eq. 2.55)

where \( V_{DB} \) and \( \Delta E_{DB} \) are the coupling and energy gap between donor and bridge, respectively, \( V_{BA} \) the coupling between bridge and acceptor and \( V_{BB} \) that between two bridge units. This leads to an exponential distance dependence where the exponential term is a function of the length of each bridge unit \( R_B \)

\[ V_{DA} = V_0 \cdot \exp\left(-\frac{\beta}{2} R_{DA}\right) \]  

\[ \beta = \frac{2}{R_B} \ln \left| \frac{\Delta E_{DB}}{V_{BB}} \right| \]  

(eq. 2.56)

This corresponds to a hopping involving virtual states of the bridge. However, only for small donor-bridge energy gaps, \( \Delta E_{DB} \approx k_B T \), the bridge shows up as oxidized or reduced intermediate. Recent work by Albinsson and co-workers\(^42, \)\(^43, \)\(^52 \) stressed the importance of i) structural disorder between the bridge units and ii) the coupling of donor and acceptor to the bridge, \( V_{DB} \) and \( V_{BA} \). It is therefore not valid to talk about a "bridge specific \( \beta \) value"\(^43 \).

**Energy hopping in multichromophoric systems**

EET between identical chromophores is usually termed as energy hopping (EEH). It requires small Stokes shift, otherwise the overlap integral is negligible and the process is inefficient. EEH does neither alter the fluorescence spectrum, intensity, nor lifetime and is not easily detectable by "common" analysis. It can be recognized by fluorescence polarization anisotropy measurements or more sophisticated methods such as photon echo.
Investigation of EEH is of major importance for the understanding of light harvesting in natural photosynthesis where the excitation energy migrates among chlorophyll units within the antennae pigments (see Chapter 4). It is also can be observed in polymers. Since excess energy is rapidly dissipated to the surrounding, EEH is directed, which means that in the end the excitation energy is trapped at the chromophore with the lowest transition energy.

**Electron transfer**

Another interaction between two molecules, which can take place upon photoexcitation is electron transfer. It can be considered as simplest photochemical reaction. Photochemistry takes place on a molecule's excited state potential energy surface (PES). Since the excited state energy surface differs from the ground state energy surface, reactions that do not happen at thermal equilibrium, can readily occur after photoexcitation. As Suppan pointed out, the term "photocatalysis" is in most cases inadequate, since a catalyst is by definition recovered after the chemical reaction. Photoinduced electron transfer (PET) is an example for photoinduced reactions some of which have tremendous importance for life (photosynthesis, vision), science and technology (photography, photopolymerization, solar cells, or light emitting diodes).

Depending on the oxidation state of educts and products, ET reactions are classified as charge separation (neutral educts, charged products), charge recombination (charged educts, neutral products), or charge shift (charged educts and products).

The time scale of an ET reaction can be faster than a vibrational period, which means it can be faster than the time required for geometrical changes of the molecule. At the other extreme is leakage
across semiconductor devices which takes months. The rate constant is determined by the extent of electronic coupling and the crossing over a barrier or tunneling through it.

The classical Marcus-Hush theory

The theory for ET was developed in the 1950s and 60s independently by R. Marcus (Nobel prize in 1992), N. Hush, V. G. Levich and R. R. Dogonaze and later extended mainly by these authors as well as by J. Jortner and P. Barbara.

R. Marcus showed that for a non-adiabatic reaction between an electron donor D and an electron acceptor A the free energy surfaces (FES) of the reactants (DA) and products (D\textsuperscript{+} A\textsuperscript{-}) can be modeled as parabolas (Figure 2.10) and that they are uniquely defined for any physical composite of the reaction coordinate. Moreover, the FES reflects thousands of coordinates owing to the involvement of the solvent. Free rather than potential energy surfaces have to be considered since changes of density of states are important for the progress of the reaction. The abscissa in Figure 2.10 (the reaction

\textbf{Figure 2.10} Cuts in the non-adiabatic FES of reactants DA and products D\textsuperscript{+} A\textsuperscript{-} of an ET reaction
coordinate \( Q \) is the polarization and vibrational energy difference between reactant and product states arising in the molecules and in the solvent.

Within linear response theory, the system then reduces to two parabolas as a function of one reaction coordinate, which takes into account all degrees of freedom of the system.\(^{56, 71, 72}\) When the reactant and product FES are represented as parabolas of identical width, simple geometrical considerations allow to determine the activation energy barrier \( \Delta G^* \) from the free energy difference of the reaction \( \Delta G' \) (Figure 2.10).

Using transition state theory, Marcus derived an equation for the rate constant of thermally activated ET.

\[
k_{ET} = \frac{2\pi}{h} \frac{1}{\sqrt{4\pi \lambda k_b T}} \cdot V^2 \cdot \exp \left[ -\frac{(\Delta G' + \lambda)^2}{4\lambda k_b T} \right]
\]  

(eq. 2.57)

Here \( V \) is the electronic coupling constant which is expected to be small (diabatic coupling) and \( \lambda \) is the reorganization energy, i.e. the energy needed for the reactant system to reach the equilibrium configuration of the products. \( \lambda \) is usually split into intra- and intermolecular contributions, called inner and outer reorganization energy, respectively. The inner (or internal) reorganization energy accounts for the change in bond lengths and angles and can, in principle, be calculated if the force constants \( f \) and relative changes upon ET \( \Delta L \) for all of them are known.

\[
\lambda_i = \sum_j \frac{f_j(R) \cdot f_j(P)}{f_j(R) + f_j(P)} \cdot \Delta L_j
\]  

(eq. 2.58)
The outer, or solvent reorganization energy accounts for the reorientation of solvent molecules and is usually estimated from the Born solvation energy within the dielectric continuum model. 

$$\lambda_s = \frac{e^2}{8\pi \varepsilon_0} \left( \frac{1}{r_A} + \frac{1}{r_D} + \frac{1}{R_{AD}} \right) \left( \frac{1}{n_D^2} - \frac{1}{\varepsilon_r} \right)$$  

(eq. 2.59)

Here $e$ is the elementary charge, $r_A$ and $r_D$ are the radius of donor and acceptor, respectively, and $R_{AD}$ is the distance between them. This dielectric estimate of the solvent reorganization energy makes specific assumptions that the shape of the molecules is spherical.

The use of the dielectric continuum for modeling $\lambda_s$ (eq. 2.59) is a very crude approximation and can be problematic. For example, it is not valid for the ion pair in the direct contact and it predicts that the reorganization energy decreases with increasing temperature, contrary to most experimental results. Nevertheless, the dielectric continuum approach is still the most frequently used one since it is the most general one and relies on a few, experimentally easily accessible parameters.

![Figure 2.11](image)

**Figure 2.11** Appearance of Marcus inverted, barrierless and normal region (from left to right) as result of the vertical displacement of the FES at constant reorganization energy
As can be seen from eq. 2.57, the logarithm of the ET rate constant follows a parabolic behavior when plotted as a function of the free energy of the reaction, $\Delta G^\circ$. This can be understood as the decrease (Marcus normal region, $-\Delta G^\circ < \lambda$) and re-appearance (Marcus inverted region, $-\Delta G^\circ > \lambda$) of an activation energy $\Delta G^*$ when the reaction free energy $\Delta G^\circ$ increases at constant $\lambda$ (Figure 2.11). The maximum rate constant is achieved when the free energy of the reaction equals minus the reorganization energy $\Delta G^\circ + \lambda = 0$ and the last term in eq. 2.57 is maximal (barrierless region).

The first observation of the full "Marcus parabola" in 1984 by Miller, Calcaterra and Closs\textsuperscript{74} (Figure 2.12) confirmed the existence of the Marcus inverted region and paved the way for Marcus' Nobel prize.

Subsequently, the Marcus inverted region was proven for intramolecular charge separation,\textsuperscript{75} intra-\textsuperscript{76, 77} and intermolecular\textsuperscript{78-81} charge recombination, intra- and intermolecular charge shift.\textsuperscript{82}
However, until today, there is no convincing report on the observation of the Marcus inverted region for intermolecular charge separation. This and the observed temperature dependence that is not accounted by the classical Marcus-Hush theory lead to the introduction of more complex models for electron transfer reactions.

**Photoinduced electron transfer**

Marcus derived his model for thermally activated ET but it can be applied equally well to photoinduced ET (PET). A pioneer in the field of PET was A. Weller who, by flash photolysis, proved that the direct product in the fluorescence quenching of D* by A (or A* by D) is the radical ion pair D•+ A•. He also derived the famous Weller equation (eq. 2.60) that allows calculating the free energy of a PET reaction from the excited state energy of the fluorophore $E^*$ and the redox potentials of electron donor and acceptor.

$$\Delta G^\circ = -E^* + E_{ox}^\circ (D) - E_{red}^\circ (A) + C + S \quad \text{(eq. 2.60)}$$

The Coulombic term, $C$, accounts for the electrostatic interaction between the two ions. It appears in eq. 2.60 because the redox potentials are measured for ions at infinite distance, whereas in an ET reaction they are formed in the active complex (see Figure 2.13). It is often expressed as

$$C = -\frac{1}{4\pi\varepsilon_0} \frac{\Delta q^2}{\varepsilon_r \cdot R_{AD}} \quad \text{(eq. 2.61)}$$

where $\Delta q$ is the charge transferred (for example, the elementary charge in case of complete charge transfer) and the other terms have the meaning defined before. This is the description of Coulombic attraction of two point charges in a dielectric medium of static
dielectric constant $\varepsilon$ and strictly valid only for non-contact ions. For the case of contact ion pairs, other models have been proposed. In polar liquids, $C$ is small, typically -0.05 and this value will be used throughout this thesis.

The term $S$ corrects for redox potentials that have not been measured in the same solvent (usually acetonitrile) as used for the ET reaction

$$S = -\frac{e^2}{8\pi\varepsilon_0} \left( \frac{1}{r_A} + \frac{1}{r_D} \right) \left( \frac{1}{\varepsilon_r(\text{CH}_3\text{CN})} - \frac{1}{\varepsilon_r(\text{solvent})} \right)$$

(eq. 2.62)

The semi-classical Marcus-Theory

Eq. 2.57 predicts a vanishing ET rate constant at low temperatures which is at discrepancy with experiment. An importance expansion of the classical Marcus-Hush model was therefore to involve tunneling via high frequency vibrational modes of the products.
In the semi-classical Marcus theory, the ET reaction occurs from the vibrational ground state of the reactants to a high frequency mode of the products and the overall rate constant is the sum of all these channels.

\[ k_{ET} = \sum_n \frac{2\pi}{\hbar} \frac{1}{\sqrt{4\pi \lambda k_B T}} \cdot V_{0\rightarrow n}^2 \cdot \exp \left[ \frac{-\left(\Delta G^* + n\hbar \nu + \lambda \right)^2}{4\lambda k_B T} \right] \]  

(eq. 2.63)

\[ V_{0\rightarrow n}^2 = V^2 \sum_n \frac{S^n}{n!} \cdot \exp(-S) \]

where \( S \) is the electron-vibration coupling constant also known as Huang-Rhys factor. The coupling element, \( V_{0\rightarrow n} \) is then no longer purely electronic but also vibrational. Additionally, the free energy of the reaction depends on which vibrational level is populated in the ET.

Using this model, the Marcus inverted region is less pronounced as can be anticipated in Figure 2.12. At low temperatures, nuclear tunneling through the barrier assures a temperature independent ET pathway even when the crossing over the barrier is not active.

**Solvent effect on ET**

It is very well known that the solvent plays a significant role in determining both the rates and energetics of electron transfer events and this role cannot be ignored in even the most sophisticated structures designed to promote long-lived charge separation. The presence of highly charged ions is thermodynamically disfavored in non-polar solvents, and an ET reaction that takes place in a polar environment, might be suppressed in an apolar medium.
In some cases electron transfer dynamics are dictated by the solvent.\textsuperscript{89, 90} Historically, dynamic solvent effects have been discussed in terms of Kramer's theory. For electron transfers with small barriers, the progress of the reaction can be limited by the motion of the solvent as a consequence of strong dielectric coupling that exists between the developing charge separation on the solute and the solvent dipoles.\textsuperscript{90}

A complete quantum mechanical description of electron transfer must include not only the internal vibrations of the nuclei in the reaction partners, but additionally those of the surrounding medium. This makes the complexity of the problem to increase substantially. In order to make the problem tractable the large number of vibrational modes of both the donor-acceptor system and the solvent are often reduced to two principal vibrations, a high-frequency mode involving the donor and/or acceptor and a low-frequency mode which is most often, but not exclusively, associated with the solvent.\textsuperscript{91}

\textit{Models for ultrafast ET}

Experimentally, it was observed that ET can be faster than diffusional solvent dynamics.\textsuperscript{92-94} This is not possible within the framework of the before mentioned theories since, in Marcus' picture, the solvent polarization drives the ET reaction and it is assumed that at any time the system remains in equilibrium with the environment.

Ultrafast ET reactions are an interesting field of study because they are especially sensitive to nonequilibrium dynamical effects involving nuclear motions of the reactants and the solvent. Such effects can represent a breakdown of the quasi-equilibrium picture of diabatic and transition state theories for thermal ET kinetics.\textsuperscript{56}
ET which is faster than solvation can be treated by the two
dimensional Sumi-Marcus model.\textsuperscript{95, 96} It extends the Marcus model
by a intramolecular dimension which drives the ET reaction. This
allows describing ET faster than solvation (\( k_{ET} \ll \frac{1}{\tau_L} \)) for which
the solvent is not needed to be in quasi-equilibrium with the system
during the reaction or fully relaxed. Such ET is possible when the
process is sufficiently exergonic to be operative even in weakly or
non-polar environments.

The Sumi-Marcus model has been further developed to include high
frequency modes which are treated quantum-mechanically.\textsuperscript{69, 70, 97}

\textit{Distance dependence of electron transfer}

Long-range (off contact) ET, especially in proteins, plays a central
role in biochemistry, including photosynthesis and metabolism.\textsuperscript{56}
Many systematic studies on the distance dependence of ET have
appeared in the last decades.\textsuperscript{42, 56, 93, 98}

All of the above cited models predict distance dependent electron
transfer rates. It is included in the coupling element \( V \) and the solvent
reorganization energy \( \lambda_s \). Whereas the former decays exponentially
with increasing donor-acceptor distance, the latter increases as the
interparticle distance increase, at least within the Born solvation
model (eq. 2.59).

For intramolecular ET, an exponential decay is usually observed
experimentally although hopping and superexchange can complicate
the dynamics and lead to non-exponential behavior.\textsuperscript{42}
2.4 Equilibrium and dynamic solvation

The importance of the solvent for chemistry cannot be emphasized enough. It is heat source and sink thereby promoting chemical reactions, able to stabilize conformers/products/states with respect to each other and facilitates the encounter of reaction partners. Solvation has a dynamic and an equilibrium aspect both of which are discussed in this section.

The solvation energy of a molecule (i.e. the change in Gibbs energy when bringing it from vacuum into the solvent) results from non-specific interactions which do imply neither a fixed stoichiometry nor geometry and from specific interactions which imply association of molecules to some kind of complex. The non-specific interactions are electrostatic forces (classic Coulomb forces between permanent dipole moments), Coulomb forces between permanent and induced dipole moments, and London forces (arising from fluctuating dipoles on the molecules). They lower both, ground and excited state energy, but at different magnitudes and thus causes a variation of the transition energy. In principle higher order multipoles are also involved but except for non-dipolar solvents, such as benzene or 1,4-dioxane, they can be neglected.

The most important specific interactions are hydrogen bonds which can be up to 0.3 eV. Specific interactions are hard to treat in a generalized fashion as they depend as much on the solute as on the solvent.

In general the solvent is described as a continuum and characterized by its dielectric constant $\varepsilon_r$ and refractive index $n$. They are related to the molecular dipole moment $\mu$ and polarizability $\alpha$, i.e. to
microscopic properties, via the Clausius-Mosotti and Debye equation, respectively.

\[
\frac{n^2 - 1}{n^2 + 2} \frac{M_m}{\rho} = \frac{N_A}{3\epsilon_0} \alpha
\]

\[
\frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{M_m}{\rho} = \frac{N_A}{3\epsilon_0} \left( \alpha + \frac{\mu^2}{k_B T} \right)
\]

(eq. 2.64)

where \( M_m \) is the molecular mass and \( \rho \) the density. The polarizability and the permanent dipole moment reflect two distinct contributions of the interaction between a molecule and its surrounding electromagnetic field, namely one that is related to its electron distribution and one that is related to its nuclear configuration. Whereas the electrons can react quasi-instantaneously on an external perturbation (even to the high oscillations of an optical field), the time scale for nuclear reorientation ranges from a few tens of femtoseconds to nanoseconds, depending on the viscosity of the material.

Apart from the transition energy, the solvent can also have severe effects on rate constants and hence the overall \( S_1 \) state lifetime and the fluorescence quantum yield. Fluorescence is therefore an optimal tool to monitor the microenvironment of a local probe molecule, since it offers both, spectral and temporal resolution. For this purpose, both intrinsic and extrinsic fluorophores are used.\(^{22,99}\) The same is true for ET and EET which are affected by the solvent via its electrostatic and dynamic properties.

**Solvatochromism**

The term solvatochromism is used to describe the change of a chromophore's color when dissolved in different solvents. The
different stabilization energy of the electronic ground and excited state lies at the origin of this phenomenon. As mentioned earlier, the largest fraction of the stabilization energy stems from dispersion and dipolar interactions between solute and solvent.

In most cases, the excited state dipole moment has a different magnitude and orientation than that in the ground state. For solvents of similar refractive index and in case when the excited state of the molecule is more polar than the ground state, it will be better stabilized by the solvent and hence the transition energy will decrease with increasing solvent polarity (bathochromic shift). The opposite is true when the ground state is more polar (hypsochromic shift).

Various models have been developed to account for the change of absorption and emission spectra due to the solvent. They can be roughly separated into theoretically derived ones, e.g. the Lippert-Mataga model,\textsuperscript{100,101} and empirical models, e.g. the ET(30) scale\textsuperscript{102} or the Kamlet-Taft linear solvation energy response (LSER).\textsuperscript{103} Empirical models categorize the solvents by the electronic transition energy of one or more solvatochromic reference molecules. These methods account for all interactions occurring between the reference and solvent molecules, while the theoretical ones consider only those interactions which are reflected by $\varepsilon_r$ and $n$. For example, while these two parameters are almost the same for 2-methylbutane and benzene and these solvents are therefore virtually identical in a theoretical polarity scale, their ET(30) parameters differ by a factor of 18.

On the other hand, when using an empirical scale, one compares the solute under investigation with the probe molecule used to set up the polarity scale and has to choose a proper scale, i.e. one with a
chemically related reference molecule. The empirical scales always reflect a combination of nonspecific and specific interactions and it is usually impossible to unravel their relative importance. The Kamlet-Taft LSER scale attempts to isolate the solvent's hydrogen bonding abilities from the non-specific interactions.\textsuperscript{103} Here, the solvent is parameterized by its hydrogen bond donating (\(\alpha\)) and accepting (\(\beta\)) ability and its dipolar "strength" (\(\pi^*\)).\textsuperscript{103, 104} The transition energy in a given solvent is then

\[
\tilde{\nu}_s = \tilde{\nu}_{\text{vac}} + a \cdot \alpha + b \cdot \beta + c \cdot \pi^*
\]

(eq. 2.65)

where \(\tilde{\nu}_{\text{vac}}\) is the transition energy in vacuum, the parameters \(\alpha\), \(\beta\) and \(\pi^*\) are the solvent properties mentioned before and the parameters \(a\), \(b\) and \(c\) describe the solute's susceptibility to the respective type of interaction.\textsuperscript{105}

The most frequently used theoretically founded model for solvation is the one derived independently by Lippert and by Mataga.\textsuperscript{100, 101} It is based on the Onsager cavity field where a point dipole resides in a cavity of radius \(r_A\) inside a dielectric continuum. This dipole polarizes the solvent giving rise to an electric field \(E_r\) with which it can interact.\textsuperscript{14, 32, 100}

\[
E_r = \frac{\mu^2}{8\pi\varepsilon_0 r_A^3} \left[ f(\varepsilon_r) - f(n_D^2) \right]
\]

(eq. 2.66)

\[
E_{\text{int}} = -\mu \cdot E_r = -\frac{\mu^2}{4\pi\varepsilon_0 r_A^3} \left[ f(\varepsilon_r) - f(n_D^2) \right]
\]

(eq. 2.67)

where
The Debye function \( f(n^2) \) and the Onsager function \( f(\varepsilon_r) \) account for the instantaneous and the reorientational part of the solvent response, respectively. For non-dipolar solvents their difference and therefore the solvation energy is expected to vanish. For a more realistic description, dispersion interactions have to be included extending eq. 2.70 to

\[
\Delta \tilde{\nu}_{\text{abs}} = \Gamma \frac{\alpha_e - \alpha_g}{4\pi\varepsilon_0 r_A^3} f(n^2) + \frac{\mu_g (\mu_e - \mu_g)}{4\pi\varepsilon_0 r_A^3} \left[ f(\varepsilon_r) - f(n^2) \right] \quad (\text{eq. 2.71})
\]

where \( \Gamma \) is a fluctuation factor.\(^{14}\)

The main limitations of the Lippert-Mataga model are the assumption of a spherical solute shape and the point dipole approximation which are rather crude approximations for typical organic chromophores.
Solvation dynamics

So far, the equilibrium situation of solvation has been discussed. As mentioned before, the solvent response to an electronic transition is only partially instantaneous, and partially delayed. The non-instantaneous part, which describes re-orientational motion of solvent molecules, is the abscissa in Figure 2.14.

Directly after photoexcitation, the solvent shell around a chromophore corresponds to the ground state equilibrium geometry and charge distribution. Since these two properties of the chromophore are usually distinct in ground and excited state, the surrounding solvent molecules will establish a new equilibrium polarization. Reorientational motion of the solvent molecules following light absorption leads to a decrease of the emission energy. The dynamics of this solvent response can be studied by time-

![Figure 2.14](image)

**Figure 2.14** Effect of dipolar interactions between fluorophore and solvent. The energy surfaces are assumed to be parabolic functions of the solvent coordinate\(^{14}\)
resolved fluorescence. It should be stressed that this process is not vibrational cooling described before.

Maroncelli and co-workers studied intensively solvation dynamics using time-resolved fluorescence. They extracted typical solvation times for a large set of common organic solvents and ionic liquids.\textsuperscript{105-109}

Under proper conditions, the normalized spectral response function (the fraction of the shift in transition energy at time $t$ of the total shift)

$$S_{\nu}(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)}$$

(eq. 2.72)

provides an experimental equivalent of the solvation energy response considered in theory and molecular dynamics simulations. It can be related to the solvent fluctuations within linear response theory\textsuperscript{110}

$$S_{\nu}(t) \approx C_{\Delta E}(t) = \left\langle \frac{\partial \Delta E(0) \partial \Delta E(t)}{\partial \Delta E^2} \right\rangle$$

(eq. 2.73)

The experimentally measured time-dependent Stokes shift was reproduced by multiexponential functions. The authors revealed complex solvent dynamics showing huge inertial sub-100 fs contribution to the overall relaxation. From molecular dynamics simulations these contributions were understood as liberational motion of a few solvent molecules while the slower parts of the solvent dynamics arise from diffusive rotational and translational solvent motion.\textsuperscript{110, 111}

The critical points of the time-dependent Stokes shift method are the time-zero spectrum, the potential contribution of intramolecular
relaxation and of specific interaction and finally the limited time resolution. Nonetheless it was found that the nature of the probe molecule has only a minor influence on the time constants extracted and that they, indeed, reflect the solvent response.\textsuperscript{22}
The aim of this chapter is to introduce the spectroscopic techniques, which have been used during this thesis. Since most of these spectroscopic set-ups are home-built, attention will be paid not only to the data treatment, but also to the principles and technical specifications. At the beginning a short introduction to the field of non-linear optical spectroscopy will be given due to its crucial importance to the methods described thereafter. With this background in mind, additionally to steady-state apparatus, the femtosecond up-conversion and transient absorption set-ups will be introduced. Finally, details about the sample preparation will be presented.
3.1 Non-linear optical effects

All processes discussed in Chapter 2 belong to the field of linear spectroscopy where the response is directly proportional to the light intensity. With the advent of lasers invented 50 years ago, a new field in optics which utilizes the higher order terms of the optical susceptibility has opened. It is crucial to notice (and to assure when performing the measurement) that the sample response in ultrafast fluorescence and transient absorption spectroscopy scales as well linearly with the intensity of the excitation pulse. Non-linear processes are extensively used for the modification of the laser fundamental output (e.g. via second harmonic generation) or as part of the detection (e.g. sum frequency generation in the fluorescence up-conversion set-up). At the same time they give rise to unwanted effects such as cross phase modulation or the coherent signal. These processes and their impacts on ultrafast spectroscopy will be briefly described below.

Second harmonic and sum frequency generation

These two processes are attributed to the second order non-linear effects and extensively exploited in ultrafast laser spectroscopy. In order to obtained second harmonic (SH) and sum frequency generation (SFG) an intensive electric field and a material with no centro-symmetry are required. In this case, the second-order susceptibility, $\chi^{(2)}$, is nonzero and the nonlinear polarization of material, $\vec{P}^{(2)}$, depends on the square of the applied electric field.

$$\vec{P}^{(2)} = \chi^{(2)} \cdot \vec{E}(\vec{x}, t) \cdot \vec{E}(\vec{x}, t)$$  \hspace{1cm} (eq. 3.1)
Assuming two electric fields oscillating at frequency $\omega_1$ and $\omega_2$ and propagating along the $x$-axis, at $x=0$, $\vec{E}^2(x,t)$ can be rewritten as:

$$
\vec{E}^2(t) = \frac{1}{2}(A_1^2 + A_2^2) + \frac{1}{2}A_1^2 \cos(2\omega_1 t) + \frac{1}{2}A_2^2 \cos(2\omega_2 t) + A_1A_2 \left\{\cos[(\omega_1 + \omega_2)t] + \cos[(\omega_1 - \omega_2)t]\right\} 
$$

This can be simplified as:

$$
\vec{E}^2(t) = \frac{1}{2}(A_1^2 + A_2^2) + \frac{1}{2}A_1^2 \cos(2\omega_1 t) + \frac{1}{2}A_2^2 \cos(2\omega_2 t) + A_1A_2 \left\{\cos[(\omega_1 + \omega_2)t] + \cos[(\omega_1 - \omega_2)t]\right\} 
$$

The terms oscillating with frequency $2\omega_1$ and $2\omega_2$ in eq. 3.2 are responsible for SHG. This processes can also be visualized by considering an exchange of photons between the different frequency components of the field (Figure 3.1A) — two photons of frequency $\omega_i$ simultaneously turn into one photon of frequency $2\omega_i$ in a single quantum-mechanical process.

Another term of eq. 3.2 oscillates with frequency $(\omega_1 + \omega_2)$ and is responsible for SFG. In this case, a photon of frequency $\omega_1$ and photon of frequency $\omega_2$ are converted into a photon of frequency $\omega_3 = \omega_1 + \omega_2$ (Figure 3.1B).

Efficient generation of SH or SF signal can be achieved only in special geometrical conditions which also known as phase matching conditions.
\[ \Delta \vec{k} = 0 \quad \text{(eq. 3.3)} \]

It occurs when the momenta are conserved and thus the phases of the incoming and outcoming electric fields are matched. If this is not the case (phase matching condition is not fulfilled), the wave generated at \( x \) interferes destructively with that generated at \( x + \Delta x \) and the overall intensity drops dramatically.

The phase mismatch is defined as \( \Delta \vec{k} = \vec{k}_1 + \vec{k}_2 - \vec{k}_3 \), and equals zero (eq. 3.3) when \( \vec{k}_{2\omega_1} = 2\vec{k}_{\omega_1} \) in the case of SHG and when \( \vec{k}_{\omega_3} = \vec{k}_{\omega_1} + \vec{k}_{\omega_2} \) in the case of SFG. To fulfill the phase matching condition for three collinear waves means to match the refractive indices of the different frequencies.\(^{113, 114}\) This can be achieved in a birefringent crystalline material with more than one optical axis. Usually it is possible to choose the orientation of the crystal such that the phase matching condition can be fulfilled.

During this thesis, SHG has been exploited for generating 400 nm excitation light from the Ti:sapphire output in the transient absorption set-up. Also it was used for doubling of the output of the MaiTai Ti:sapphire oscillator in the up-conversion set-up. SFG was used for converting the spontaneous fluorescence signal by mixing it with the laser beam in up-conversion set-up. More technical details are presented in Chapter 3.2.

**Optical parametric amplification**

The idea of an optical parametric amplifier (OPA) is based on difference frequency generation (DFG) and presented in Figure 3.2. A strong pump pulse leads to a non-linear polarization through the second order polarizability, \( \tilde{P}^{(2)} \) (see above). Just like for SHG and SFG, energy \( (\omega_{\text{pump}} = \omega_{\text{signal}} + \omega_{\text{idler}}) \) and momentum conservation
(\vec{k}_{\text{pump}} = \vec{k}_{\text{signal}} + \vec{k}_{\text{idler}}) lead to phase matching conditions that can be fulfilled on a macroscopic scale in a birefringent crystal, such as for example BBO.\textsuperscript{113, 114}

If the incident angle on the crystal is different for pump and signal beam, the arrangement is called a non-collinear OPA (NOPA). Such an optical amplifier can give 30 fs pulses after recompression.\textsuperscript{115} The NOPA is an extremely useful tool since it allows to obtain femtosecond optical pulses in a broad spectral window.\textsuperscript{116} During this thesis, the home-build NOPA has been used for generating “pump” pulses in region between 490 and 700 nm for the femtosecond transient absorption set-up (see Chapter 3.2).

**White light generation**

Tight focusing of an subnanosecond laser pulse into nearly any dielectric medium results in spectral broadening. If the obtained laser pulse covers all the visible range, it is often called a white light continuum or supercontinuum.\textsuperscript{117} White light generation has been observed in gases, liquids, and solids\textsuperscript{118} but the most commonly used source for spectrally flat white light is nowadays CaF\textsubscript{2}. Numerous non-linear effects are important for the generation and the process is still not fully understood.\textsuperscript{119} Self-focusing of the incident laser beam

![Diagram of OPA process](image)
Chapter 3

has an initiator role but many processes stemming from the third-order nonlinear susceptibility as well from an ionization and plasma generation are involved.

Experimentally, the intensity, stability and spectral width of the white light depends on the position of the focus, the laser pulse width and the polarization of the pulse.\textsuperscript{117, 119} Too high incident light intensities result in spatial chirp, filamentation and strong modulations of the spectrum.\textsuperscript{117} White light generation is crucial for transient absorption technique, since it gives possibility to record spectra over the whole visible region simultaneously.

**Chirp of ultrashort laser pulses**

In eq. 2.2, the wavevector was defined for vacuum. In a medium, it becomes

\[ k = k_{\text{vac}} \cdot n(\omega) \]  \hspace{1cm} (eq. 3.4)

Any medium has dispersion, i.e. the refractive index, \( n \), is a function of the frequency (or the wavelength), as indicated in eq. 3.4, and since ultrashort laser pulses are necessarily spectrally broad, the wavevector varies for the components of the pulse. The derivative of \( k \) with respect to \( \omega \) is the inverse of the group velocity.

\[ k' = \frac{dk}{d\omega} = \frac{1}{\nu_g} \]  \hspace{1cm} (eq. 3.5)

Group velocity is the rate at which the pulse envelope advances and, in a medium, is different from the phase velocity, \( \nu_{ph} \), which is the rate at which the phase front propagates in a medium. In vacuum
\[ \nu_g = \nu_{ph} = c \] since there is no dispersion. For visible light and most materials, the group velocity is slower than the phase velocity.²

The second derivative of the wavevector is the group velocity dispersion, GVD.

\[ k'' = \frac{\partial^2 k}{\partial \omega^2} = \frac{\partial(1/\nu_g)}{\partial \omega} = GVD \quad \text{(eq. 3.6)} \]

GVD causes a laser pulse to broaden temporally when passing through a transparent medium. The laser pulse is said to get "chirped". In a chirped pulse, the frequency is not constant in time. Such a laser pulse can be described by eq. 3.7

\[ E(t) = \tilde{E}_0(t) \cdot \exp(i\omega_0 t + i\beta t^2) \quad \text{(eq. 3.7)} \]

where the pulse envelope is defined by eq. 2.7. For most materials the chirp parameter \( \beta \) is greater than zero (positive chirp) and the instantaneous frequency of the pulse increases with time. In other words, the red part prevails the blue (see Figure 3.3).
Negative chirp can be achieved using a prism or grating compressor.\textsuperscript{120} Such arrangements are used in laser spectroscopic set-ups to shorten laser pulses after passage through optical elements. A very compact version that allows for rapid changes has been proposed by Akturk et al.\textsuperscript{121} recently and is implemented in our TA set-up.

**Cross phase modulation**

Cross phase modulation (CPM) refers to a situation where the strong pump pulse modulates the refractive index of the sample and the cuvette windows. This time-dependent change of refractive index affects the probe pulse if it overlaps temporally with the pump. This is a non-resonant process and occurs even if the sample is completely transparent to the laser wavelengths.

The shape of CPM signal (\textbf{Figure 3.4C}) can be explained by the effect of the strong pump pulse on the phase of the probe pulse. The non-linear refractive index (or susceptibility) is a function of the light intensity, $n_{NL}(I(t))$. When the probe pulse overlaps the leading edge of the pump, it experiences an electric field that increases with time and since $n_{NL} > 0$ the refractive index increases with time. In turn, this leads to an increase of the phase of the electric field as a function of time and since the instantaneous frequency is the negative of the derivative of the phase with respect to time ($\omega = -\frac{\partial \phi}{\partial t}$), the frequency $\omega$ decreases. In other words, the spectrum shifts to the red (right part of \textbf{Figure 3.4B}).\textsuperscript{122} In complete analogy does the falling edge of the pump pulse to a blue shift of the probe pulse. There is no energy exchange between pump and probe, only a shift "within" the probe pulse.
The difference of group velocity between pump and probe complicates the response of a sample cell of non-negligible thickness because the pump field is time-coincident with different parts of the probe field throughout the cuvette.

Several groups\textsuperscript{122-124} have simulated CPM and found reasonable, however not perfect agreement with experimental data.

\textbf{Figure 3.4} Illustration of the origin of CPM. Pump pulse and its effect on the refractive index (A), effect of the time dependent pump laser field on the probe pulse which is centered at frequency $\omega_0$ (B) and resulting TA spectrum (C)

The difference of group velocity between pump and probe complicates the response of a sample cell of non-negligible thickness because the pump field is time-coincident with different parts of the probe field throughout the cuvette.
Coherent signal

Photoexcitation needs two interactions of the incident light field with the molecule. The first induces a coherence between the initial and final state and the second creates the excited state population.\textsuperscript{4} If in transient absorption spectroscopy, the pump and probe pulse overlap in time in the sample, these two interactions might result from different laser pulses. Interactions with such a "mixed" order (pump-probe-pump or probe-pump-pump) lead to the so-called coherent signal (often called coherent artifact) in transient absorption spectroscopy. It is present in the spectra during pulse-probe overlap, i.e. during the approximately first 200 fs and prevents data analysis of the spectra at short pump-probe time delays, unless it is sorted out from the sequential signal.

Ernsting and co-workers could show that the coherent signal carries in principle the same information as the sequential signal (that results from pump-pump-probe interaction).\textsuperscript{125} The authors could assign the vibronic structure in the coherence spectrum to stimulated Raman scattering between vibrational levels in the first excited electronic state.
3.2 Experimental techniques and methods

In the following subchapters, all spectroscopic techniques employed during this thesis to get experimental data will be described. Attention will be devoted to their principles and design. Additionally, the treatment of the experimental data obtained by different techniques will be discussed.

Steady-state apparatus

Absorption and Fluorescence

Steady-state absorption spectra were measured on a Cary 50 (Varian) and fluorescence spectra on a Cary Eclipse (Varian) spectrometer, respectively, in 10 mm cuvettes. Fluorescence emission and excitation spectra were corrected for the wavelength sensitive response of the spectrometer and transformed to an energy scale in order to judge mirror-image symmetry.\(^5\) Due to imperfection of the fluorimeter's calibration function at wavelengths below ca. 300 nm, deviations between absorption and fluorescence excitation spectra are unavoidable in the UV. The sample absorbance was kept below an optical density of ca. 0.3 in the maximum in the visible spectral region for all fluorescence experiments in order to avoid the effect of reabsorption.

Determination of individual absorption spectra of monomeric and aggregated \([4]\)helicene derivatives. As stated in Chapter 2, absorbance is additive. If the concentration of each chromophore is known, the absorption spectra of their mixture can be decomposed into the absorption spectrum of each of them separately. This was utilized to obtain the absorption spectra of monomeric and aggregated \([4]\)helicene derivatives (HelR) (Chapter 6). The relative fraction of each of these
forms was determined from the amplitude of the fluorescence decay (for details see below). The matrix eq. 3.8 has been solved using MatLab (The Mathworks Inc.)

\[
\begin{pmatrix}
    A_1^1 & \cdots & A_1^n \\
    \vdots & \ddots & \vdots \\
    A_m^1 & \cdots & A_m^n
\end{pmatrix} = \begin{pmatrix}
    \varepsilon_1' & \varepsilon_1'' \\
    \vdots & \ddots & \vdots \\
    \varepsilon_m' & \varepsilon_m''
\end{pmatrix} \cdot \begin{pmatrix}
    c_1' & \cdots & c_n' \\
    c_1'' & \cdots & c_n''
\end{pmatrix} \quad \text{(eq. 3.8)}
\]

where \(A_x^\lambda\) is the absorbance of sample \(x\) at wavelength \(\lambda\). Usually 8-10 absorption spectra with different ratios of monomeric (\(c'\)) and aggregated (\(c''\)) form have been recorded for the determination of the matrix with the extinction coefficients, \(\varepsilon\). The smoothness of the resulting spectra was taken as an indication of the appropriateness of this procedure.

**Determination of the binding constant.** In the DNA titration experiments, the absorption spectra of HelR has been corrected for dilution. The concentration of free and bound form has been calculated using eq. 3.8, where \(\varepsilon\) for free HelR has been determined from an absorption spectrum without DNA (assuming that only the monomer is present in solution) and for DNA bound HelR from a spectrum at high DNA concentration (assuming that all dye molecules are bound). It is important to mention, that the total HelR concentration was kept constant.

The binding constant \(K\) and the parameter \(n\) have been calculated using the excluded site model of McGhee and von Hippel\(^{126}\)

\[
\frac{r}{[\text{dye}]} = K \cdot (1 - n \cdot r) \cdot \left(\frac{1 - n \cdot r}{1 - (n - 1) \cdot r}\right)^{n-1} \quad \text{(eq. 3.9)}
\]
where \( r = \frac{[\text{dye} \cdot \text{DNA}]}{[\text{dye}]} \) is the ratio of bound to free dye. The parameter \( n \) represents the number of DNA base pairs that are occluded by the bound dye due to occupation and/or structural perturbation. Only the data with 15 to 80% of the bound dye was used in the fit.\(^{22,127}\) Deviations of the data points from linear indicate either more than one binding mode or dye-dye interaction, or both.\(^{126}\)

**Circular Dichroism**

The principle of circular dichroism is described in the Chapter 2. It was measured using a dichrograph, which modulates a monochromatic beam of light between left-handed and right-handed circular polarization.\(^{5}\) The spectra are plotted in mdeg (mdeg = 3298.2 \( \Delta \varepsilon \)).

The set-up used consists in a Jasco J-815 spectropolarimeter. The sample was measured in a 10 mm cuvette which does not change the polarization of light at room temperature. The shown in this work spectra are an average over at least 8 scans.

**Linear Dichroism**

Linear dichroism (LD) spectroscopy is usually used to study the three dimensional structures of molecules in crystals or stretched polymer films. Also it can be used to detect interactions between a small molecule and a biological macromolecule via indirect orientation.\(^{13}\) The advantage of the LD spectroscopy is that it provides structural information which cannot be obtained with other methods. An analysis of sign and relative amplitude of the measured LD can be used to unravel the binding geometry in terms of angles between the absorbing dye transition moments and the macroscopic sample orientation axis.\(^{13}\) It is important to mention
that LD cannot directly tell where the molecule binds to DNA but only at which angle. However, very often this information is sufficient for inferring the binding mode if orientation of the molecular transition dipole moments is known (see Chapter 6).

**Principle.** The electronic transition dipole moment (and the same applies to magnetic transition moments that are important in circular dichroism) for absorption of light introduced in Chapter 2 is a vectorial property of the molecule. Hence, the probability for absorption of linearly polarized light by a chromophore is proportional to $\cos^2 \alpha$, where $\alpha$ is the angle between the transition dipole moment and the electric field vector.\(^{31}\) Obviously, in an isotropic sample with randomly oriented chromophores, no macroscopic preference for light absorption exists. However, if the chromophores are oriented, for example in a crystal, information about the transition dipole moments axis with respect to the orientational axis can be extracted from LD measurements.

The LD is defined as the difference in absorption of light linearly polarized parallel and perpendicular to an orientational axis.\(^{15}\)

$$LD = A_\parallel - A_\perp$$  \hspace{1cm} (eq. 3.17)

For a determination of the orientational geometry, the so-called reduced linear dichroism, $LD'$, which is normalized to the absorption of the isotropic sample, $A_{iso}$, is more useful. It is independent of sample concentration, pathlength and dipole strength and depends only on the molecular orientation of transition dipole moments.

$$LD' = \frac{LD}{A_{iso}} = \frac{A_\parallel - A_\perp}{A_{iso}}$$  \hspace{1cm} (eq. 3.18)
A vast variety of methods to orient molecules exist: crystals are intrinsically organized samples, stretching of polymer films leads to orientation of adsorbed or incorporated molecules, electric and magnetic fields have been employed, as well as evaporation or assembly. Samples can also be oriented by DNA (if it binds to DNA), since DNA is a long rigid polymer and easily aligns in a flow.

Most methods do not lead to a perfectly oriented sample. In practice it is therefore necessary to introduce a parameter to take into account the average over the distribution of the angle $\theta$ between the local orientation and the macroscopic orientation direction.

$$S = \frac{1}{2} \cdot (3\cos^2 \theta - 1)$$ (eq. 3.19)

Under the assumption of uniaxial sample orientation (for which a single parameter, $S$, is sufficient to describe the orientation), the $LD$ and $LD'$ at a selected wavelength are relate to the angle $\alpha$ between the molecular orientation direction and the respective transition dipole moment as (Figure 3.5)

$$LD = \frac{3}{2} \cdot A_{iso} \cdot S \cdot (3\cos^2 \alpha - 1)$$ (eq. 3.20)

$$LD' = \frac{3}{2} \cdot S \cdot (3\cos^2 \alpha - 1)$$

Using eq. 3.20, the angles between each transition dipole moment and the flow orientation can be easily determined when the orientational parameter $S$ is known. Since it is commonly accepted that DNA bases are oriented at 86° to the helix axis (orientational axis), $S$ can be determined from the $LD'$ of the $\pi\pi^*$ transition of DNA bases at
260 nm. However this is valid only if dye binding does not perturb the DNA structure.

**Set-up.** LD spectra were measured using a Jasco J-720 CD spectropolarimeter with an Oxley prism, which converts the incident circularly polarized light to linear. A home-made outer-rotating Couette flow cell with 1 mm path length was used to orient the samples. All spectra were baseline corrected by subtraction of the spectra recorded without rotation.

**Spectroelectrochemical Cell**

In order to identify intermediates from electron transfer reactions in the TA spectra, an optically transparent thin layer electrochemical (OTTLE) cell designed by F. Hartl was used. This cell consists of

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**Figure 3.5** A - Schematic diagram of an LD experiment. $z$ is the macroscopic direction of orientation, B - calculated LD spectra for different angles $\alpha$. 
platinum working and counter-electrodes and a silver pseudo-reference electrode. It has been modified by an additional 0.5 mm spacer to increase the optical pathlength and hence it become no longer an OTTLE cell in a strict sense. Solutions in acetonitrile (Rotidry, < 10 ppm water, used as received) containing 0.1 mol/L tetrabutylammonium hexachloroantimonate (dried in vacuo at 105°C) were oxidized or reduced potentiostatically (BASi 50W potentiostat) and the spectral changes during electrochemical transformation recorded on a Cary 50 absorption spectrometer.

The working and the counter-electrode are meshes and the absorption spectrum of oxidation or reduction products has been measured through the hole in the working electrode. This means that short-lived products cannot be observed because they decompose before they diffuse into the observation window. In order to prevent this, experiments with reduced temperature can be performed. However our set-up did not allow for temperature control and all experiments have been done at room temperature.

Cyclic voltammograms have been measured by Matile and co-worker\textsuperscript{129-131} for all compounds therefore the reversibility and the redox potentials have not been determined using the spectro-electrochemical cell. The potential has been slowly increased or decreased until changes in absorption spectrum were apparent.

**Time-Correlated Single Photon Counting**

To record time-resolved fluorescence decays on a pico- to nanosecond time scale, time-correlated single photon counting (TCSPC) was used. For this technique the time delay between the excitation pulse and the detection of a photon emitted by the sample is determined electronically \textit{via} the charge of a capacitor. Collecting many such
timing events, a histogram of the fluorescence time evolution is reconstructed and it can be shown that this histogram represents the population decay of the emitting state.$^{132}$

The time resolution of TCSPC is not as good as that of the fluorescence up-conversion technique described below but it is advantageous for states that have a low radiative rate constant, $k_{\text{rad}}$, and/or a long lifetime (as it does not suffer from a walk-off between pump and probe beam inherent to ultrafast laser spectroscopy).

**Set-up.** Two different laser diodes (LD-400B for 395 nm excitation and LD-470 for 470 nm excitation, both purchased from Picoquant) were used as excitation light source in the time-correlated single photon counting. Fluorescence was collected at 90° with respect to the pump pulse on a Hamamatsu H5783-P-01 photomultiplier tube (PMT). The emission path contained an analyzer polarizer for polarization dependent measurements (otherwise set to magic angle) and filters in order to suppress the excitation light and to choose a specific emission wavelength. The signal counting rate at the constant fraction discriminator was kept at least 100 times lower than the laser repetition rate (adjusted between 10 and 40 MHz) to avoid the so called pile-up effect.$^{132}$

The sample optical density was below 0.3 in the 10 mm cuvette. The FWHM of the IRF (determined from the signal of a LUDOX scattering sample) was ca. 210 ps. Fluorescence lifetimes were obtained as least square fit of multi-exponential functions convoluted either with the Gaussian function or the experimental IRF. Fitting was performed with Igor Pro (*Wavemetrics*) or MatLab (*The Mathworks Inc.*) using a script written by Arnulf Rosspeintner.
Interference bandpass filters or a variable veril filter (both having a FWHM of 10 nm) were used to select the observation wavelength of emission. Unless explicitly mentioned, the filter was chosen such that the fluorescence at the maximum of the steady-state spectrum was monitored.

**Determination of the ratio of HelR monomer and aggregate.** A set of fluorescence decays with different ratio of monomer and aggregated HelR has been used. First, all kinetics have been analyzed globally by a two-exponential function. One lifetime, $\tau_1$, was attributed to the monomer and the other one, $\tau_2$, to the aggregated HelR. After that, the amplitudes corresponding to $\tau_1$ have been multiplied by $\tau_1$ and the fluorescence quantum yield of HelR monomer. The same has been done with the amplitudes corresponding to $\tau_2$. The obtained values were directly proportional to the concentration of each form. Since the total concentration of HelR in solution was known, the concentration of each form was easily accessed.

**Fluorescence up-conversion**

*Principle.* This technique is based on optical gating of the spontaneous, laser induced fluorescence by means of another laser pulse, the so-called gate. By spatially overlapping this gate pulse with the fluorescence signal in a non-linear crystal, the temporally coincident "slice" of the fluorescence is up-converted via SFG (see Chapter 3.1) and this UV signal is detected on a photomultiplier tube. Since the efficiency of the up-conversion process depends on the fluorescence intensity at the moment of overlap in the crystal (and the phase matching condition), the recorded UV signal is a direct measure of the time-dependent fluorescence. The total of the fluorescence evolution at a selected emission wavelength is then reconstructed by
scanning the pump-gate time delay. The phase matching condition requires a different angle between the crystal optical axis and the laser pulses for each fluorescence wavelength. Therefore time traces are recorded for different emission wavelengths. Naturally, the total intensity at each wavelength must be related to the steady-state (i.e. time-integrated) signal at this wavelength.

**Set-up.** The set-up is based on the commercial FOG100 (CDP Lasers & Scanning Systems) but has been largely modified. Initially a Tsunami Ti:sapphire oscillator (Spectra Physics, 800 nm 120 fs pulses at 82MHz repetition rate) was used but later replaced by a MaiTai (Spectra Physics) which can be tuned between 680 and 1040 nm.

The fundamental of the laser oscillator was split into pump and gate beam, the former of which was frequency doubled in a BBO crystal to give an excitation pulse between 340 and 520 nm. This beam was focused on the sample contained in a 1 mm spinning cell from which the fluorescence was collected, sent through a filter to suppress the excitation light, and focused on the SFG crystal where it overlapped spatially with the gate pulse. The time delay of the gate pulse was controlled by a translation stage.

The up-converted UV signal was sent through a filter to remove the gate pulse, spectrally purified by a monochromator and monitored by a PMT in photon counting mode.

The polarization of the pump pulse was controlled with respect to the SFG crystal axis by means of a $\lambda/2$ waveplate. In this way, pure population decays (at magic angle) or anisotropy decays (from the signal at parallel and perpendicular orientations) were obtained.
The sample absorbance was typically 0.1-0.3 at the excitation wavelength over 1 mm pathlength. Sample stability was checked by comparison of the absorption spectra before and after measurement.

Data treatment. Fits were done with Igor Pro (Wavemetrics) using multi-exponential fit functions convoluted with a Gaussian-shape IRF. This can be done analytically to give, in the case of a bi-exponential decay, the following function.

\[
I(t) = A_0 + \frac{A_1}{2} e^{-k_1(t-t_0)} \left[ \frac{k_1^2 \beta^2}{4} \right] \left[ 1 + \text{erf} \left( \frac{t-t_0 - \frac{k_1 \beta^2}{2}}{\beta} \right) \right] \\
+ \frac{A_2}{2} e^{-k_2(t-t_0)} \left[ \frac{k_2^2 \beta^2}{4} \right] \left[ 1 + \text{erf} \left( \frac{t-t_0 - \frac{k_2 \beta^2}{2}}{\beta} \right) \right]
\]

where \( I(t) \) is the measured fluorescence intensity as a function of time, \( A_i \) the amplitude (\( A_0 \) is the offset accounting for the dark counts from the PMT) and \( k_i = \tau_i^{-1} \) the rate constant of the \( i \)th process, \( t_0 \) time zero and \( \beta \) the width of the excitation pulse. The fit functions were implemented in Igor Pro by Guillaume Duvanel.\(^{51}\)

**Transient absorption**

**Principle.** Transient absorption (TA) is a pump-probe technique where a first, so-called “pump” laser pulse excites the sample, populating the excited state and triggering subsequent photochemical reactions. A second pulse, termed “probe”, measures the sample absorption at a given time delay after photoexcitation. The photoinduced changes are usually represented as absorption difference signal, \( \Delta A \), calculated
from the unperturbed sample absorbance and the aforementioned time dependent transient signal (see Figure 3.6). Femtosecond time resolution can be obtained when the pump-probe time delay is controlled optically, i.e. if it is determined by the relative path length of the two beams. Then, it can be varied easily and in an automated fashion with a retroreflector mounted on a computer controlled translational stage.

Using spectral broadening of ultrashort laser pulses in condensed media known as white light generation (see above), the transient absorption spectrum between ca. 350 and 800 nm (these values may vary a lot from one set-up to another as they depend on the laser

Figure 3.5 Scheme of the transient absorption set-up used in this thesis. NOPA - noncollinear optical parametric amplifier, BS - beamsplitter, HR - hollow retroreflector, L - lens, F - filter (HR800HT400-720 mirror)
central wavelength, the material used to broaden the laser pulse, the optics and detection system) can be collected at once allowing for a detailed measurement of spectral changes occurring with time.

The power of TA is to identify intermediate states that are non- or hardly emissive, thus invisible to time-resolved fluorescence measurements.

As said before, the TA spectrum is a difference signal and it contains several contributions as indicated in Figure 3.6: i) the so-called ground state bleach (GSB), which stems from depletion of the electronic ground state by the pump pulse, ii) stimulated emission (SE) \( S_n \rightarrow S_0 \) and iii) excited state absorption (ESA) stemming from transitions of the \( S_m \leftarrow S_n \ (m > n \neq 0) \) type (absorption of an excited state).

**Figure 3.6** Origin of the contributions to a TA spectrum. After photoexcitation by the pump, a bleach signal, excited state absorption (ESA) and stimulated emission (SE) will add to \( \Delta A \). Subsequent excited state dynamics is illustrated by intersystem crossing (ISC) which will populate the triplet state and hence triplet-triplet absorption (TTA) will be present in the TA spectrum.
state to a higher excited state, e.g. $S_5 \leftarrow S_1$) or from absorption of other transients such as a triplet state, or ions formed in charge separation reactions.

The time evolution of these signals does not need to be identical as the simple example of the population of a triplet state shows. While the SE will vanish with a rate constant $k_{S1} = k_{rad} + k_{IC} + k_{ISC}$, the characteristic time for the GSB decay will be the one of the triplet state lifetime (provided significant population of this state). The time evolution is therefore a function of the observation wavelength unless a global fit procedure with linked lifetimes is used. Such a procedure yields decay associated difference spectra (DADS) or species associated difference spectra (SADS), depending on the fit function.$^{133}$

Set-up. The TA set-up used in this thesis is based on an amplified Ti:sapphire laser system (Millenia, Tsunami, Empower seeding or pumping a Spitfire regenerative amplifier, all by Spectra Physics) whose output consists of 150 fs broad laser pulses centered at 800 nm at 1 kHz repetition frequency (Figure 3.5). Approximately 250 µJ were separated from the Spitfire laser beam for the pump laser pulse. The pump pulse was either frequency doubled in a 1 mm BBO crystal or sent to a home-build non-collinear optical parametric amplifier (NOPA), which provided laser pulses between 490 and 700 nm. The polarization of the pump pulse was controlled with respect to the white light probe pulse by means of a $\lambda/2$ waveplate. The intensity of the pump pulse was adjusted to ca. 1 µJ at the sample and the beam was focused on the sample to diameters of ca. 300 µm.
The two-stage NOPA used is based on the design by Riedle and co-workers. The outcoming lasers pulses are re-compressed in a folded SF10 prism compressor to 60 to 100 fs FWHM.

Ca. 1 μJ were spectrally broadened in a 3 mm CaF$_2$ window to obtain a white light (WL) used as probe pulse. The CaF$_2$ window was constantly moved in a Lissajous-type fashion to avoid damage. The WL was recollimated by a quartz lens and focused on the sample by a CaF$_2$ lens to a diameter of ca. 60 μm, well below the diameter of the pump beam, to avoid walk-off when scanning the pump-probe time delay.

The remaining 800 nm fundamental was almost entirely removed from the WL by an 800 nm mirror with antireflection coating in the 400 to 720 nm spectral range placed after the quartz lens and the spectrum further flattened by an aqueous CuSO$_4$ solution placed after the sample cell. The use of lenses instead of reflective optics leads to chromatic aberration. This, together with fluctuations of the WL lead to spectral distortions above ca. 720 nm.

The 1 nJ WL obtained in the CaF$_2$ window were split into two parts, the signal and the reference beams. The first overlapped with the pump beam in the sample while the other one did not (Figure 3.5). Both beams were spectrally dispersed in ANDOR Technology SR163 spectrographs and imaged onto back-thinned CCD detectors (Hamamatsu S07030-09). The detection system has been assembled by Entwicklungsburo Stresing, Germany.

The pump beam was chopped at half the laser frequency and TA spectra were calculated, in principle, from two consecutive probe pulses only. The reference probe beam served to correct for fluctuations of the WLC on a shot-by-shot basis in order to improve
Chapter 3

the signal to noise ratio. Tests showed that the reference beam does not need to propagate through the sample and therefore it was directly sent to the detector. Typically 1500 difference spectra were averaged to obtain a satisfactory signal to noise ratio.

Liquid samples were contained in a 1 mm quartz cell (having two 1.3 mm windows) and were agitated by nitrogen bubbling or a home-build teflon stirrer (for high viscous samples). In such cases the sample absorbance was adjusted to 0.1-0.3 at the excitation wavelength. Sample stability was verified by the absence of significant changes of the steady-state absorption spectrum during the TA scan.

For solid samples (SOSIPs on ITO surface), a translational stage similar to the one used for the white light generation was constructed which allowed for Lissajous-type movements of the sample during the measurement. Due to the low sample absorptivity, 3000 spectra were collected at each pump-probe time delay in this case.

Data treatment. The chirp of the WL was determined by measuring the optical Kerr effect (OKE) signal in pure solvent and fitting the maxima of the OKE signal with a third-order polynomial. The TA spectra were then corrected by interpolation along the time axis (MatLab, The Mathworks Inc.).

There are several unwanted contributions to the TA signal during temporal overlap of the pump and probe pulse, namely the coherent signal, cross phase modulation and stimulated Raman from the solvent. No attempts were made to subtract them. The imperfection in the positioning of the translational stage (ca. 3 fs) does not allow for such a procedure. Furthermore, singular value decomposition (SVD), used by several groups for data analysis or
smoothing, was not employed. Instead, a tail fit to the dynamics cut at ca. time-zero plus one time the IRF (200 fs determined as the FWHM of the OKE) was performed using the Igor Pro software. At this time delay, their contribution to the TA signal is negligible.

The fit was done globally using multi-exponential functions with linked lifetimes at 5 nm intervals and yielded decay-associated difference spectra (DADS) for each of the lifetimes of the fit function. Their interpretation is not always straightforward owing to overlap of SE, GSB and an unknown number of ESA bands that might arise from different transients. Additional complications stem from spectral shifts due to vibrational and solvent relaxation. In contrast to fluorescence bands, ESA bands can shift not only bathochromically but also hypsochromically.

The number of exponents needed to satisfactorily describe the temporal evolution of the TA data was determined by visual inspection of the traces and the residuals. Owing to the fact that many ultrafast processes do not follow exponential kinetics and due to sample inhomogeneity, several lifetimes might, in fact, be associated with the same process. In particular ultrafast electron or energy transfer can take place on the same time scale as vibrational relaxation, within a few picoseconds. Thus, it is experimentally very challenging to distinguish them.

In cases where the charge separation (CS) is slow compared with the charge recombination (CR) process, the dynamics of the TA signal associated with CS state population, $A_{\text{CSS}}^{\text{obs}}(t)$, is proportional to the following equation

$$A_{\text{CSS}}^{\text{obs}}(t) = \frac{1}{k_{\text{CS}} + k_{\text{CR}}} \left( e^{-k_{\text{CS}} t} - e^{-k_{\text{CR}} t} \right) + C,$$
\[ A_{\text{CSS}}^{\text{obs}}(t) = c \int_0^t P_{\text{CSS}}^{\text{int}}(t - t') F(t') dt \]  

(eq. 3.21)

where \( c \) is a constant, \( P_{\text{CSS}}^{\text{int}}(t) \) is the time profile of the CSS population that would be observed if it would be populated instantaneously and \( F(t) \) is its time-dependent buildup rate. It can be determined from the decay of the excited state population upon CS, \( P_{\text{CSS}}^{\text{CS}}(t) \), which can be extracted from the fluorescence decay.

\[ F(t) = - \frac{\partial P_{\text{LES}}^{\text{CS}}(t)}{\partial t} \]  

(eq. 3.22)

**Laser flash photolysis**

Laser flash photolysis experiments were performed in a setup with a picosecond Nd:YAG laser at 532 nm excitation. Probing was performed with a continuous Hg lamp through interference filters and additional filters to cut the excitation light. Detection was realized \textit{via} a PMT to a fast digital oscilloscope. The obtained data have been fitted using a mono-exponential function.
3.3 Samples and Solvents

The organic solvents, methanol (MeOH), ethanol (EtOH), pentanol (PeOH), acetonitrile (ACN), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), dichloromethane (DCM), dimethylformamide (DMF) and chloroform (CHCl₃) were of the highest commercially available grade and used as received (from Fluka). Phosphate buffered saline (PBS, pH 7.4) was purchased from Invitrogen. Water was doubly distilled and deionized. Heavy water was ordered from Armar Chemicals. Salmon sperm DNA was purchased at Invitrogen and conditioned by standard recipes. For LD experiments, calf-thymus DNA was ordered from Sigma-Aldrich. The stock solutions of DNA were stored at -20°C. The N,N-dimethylaniline (DMA) solution was freshly distilled before use. Tetranitromethane (TNM) as well as 1-methylnaphthalene were used as received (from Aldrich).

Helicenes were synthesized and isolated in the group of Prof. Jérôme Lacour. The compounds were received as powder and for each experiment, fresh solution have been prepared. It was dissolved in a small amount of DMSO to which non-buffered or buffered aqueous solution was added. The rate of the DMSO in the final solution was less than 1%.

The NDIs were synthesized in the group of Prof. Stefan Matile. The compounds were received in MeOH solution. No special preparation of the compounds for measurements has been done. The SOSIP architectures have been assembled on 0.3 mm ITO plate and experiments were performed without any modification.
Chapter 4

Artificial multichromophoric systems

Technological progress and global improvements in living standards make humans depending on energy sources. In the last ten years the total energy need increased by 20% and it is predicted to be continuously growing.\textsuperscript{141, 142} The main sources of energy nowadays are fossil fuels (coal, petroleum and natural gas), which provide almost 90% of the energy consumed.\textsuperscript{143} However, fossil fuels are not renewable resources and, in the near future, humans will face serious difficulties concerning energy demands.

Solar energy is renewable and sustainable and considered as one of the potential solutions. During one hour, Earth receives $4.3 \times 10^{20}$ J of energy from the sun. This is more than the world’s energy
consumption per year \((4.1 \times 10^{20}\text{ J})\). Yet, at the present moment solar electricity provides less than 1% of world’s electricity. The tremendous gap between our actual use of energy and the undeveloped capacity of solar energy defines the challenge in solar energy research.

Using photosynthesis, plants, algae and some type of bacteria can efficiently convert energy of the sun into chemical energy. For this property, nature uses a highly organized light capturing and electron transporting system, which consists of photosystem I (PI), photosystem II (PII), plastoquinone, plastocyanin, cytochrome and ATP synthase (Figure 4.1).

**Figure 4.1** Schematical representation of the electron and proton transfer in the plants photosynthesis.

PI and PII are composed of the light-harvesting complex I (LHI), the light-harvesting complex II (LHII) and the photosynthetic reaction center (RC). The LHI and LHII are built from a large number of identical, noncovalently self-organized chlorophylls and carotenoids, which absorb light energy and transfer it to the
photosynthetic reaction center (RC), where electron-hole separation occurs. The strong energy hierarchy in the light-harvesting system defines an excitation energy transfer cascade. The LHII can transfer energy to another LHII or to LHI, whereas LHI can transfer excitation energy only to the RC.

The electron transport cycle starts at the RC of PII from where it passes through plastoquinone, cytochrome and plastocyanin to the RC of PI. The electron which is excited in the RC of PI leads to reduction of NADP⁺ to NADPH. The hole, which is produced in the RC of PII is filled by an electron from the water oxidation. The large proton gradient produced by electron transfer across the membrane drives synthesis of ATP from ADP.

Based on the example of natural photosynthesis, several ways to improve the overall power conversion efficiency of existing solar photovoltaics can be proposed. First, implementing multicolor chromophores, which absorb light over entire solar spectrum, will improve the light harvesting of the device. Second, introducing a redox gradient will a meliorate hole and electron splitting in the photo-generated excitons. Also, it is commonly accepted that formation of a sufficiently long-lived charge-separated state results in an improved splitting efficiency. Finally, mobility of electron and hole can be enhanced by aligning their transport channels on a molecular level. All these points should be taken into consideration in the development and modification of photovoltaic devices.

Four $\rho$-octiphenyl (POP) rods each carrying eight blue ($B$) core-substituted naphthalene diimides (NDIs) have been shown to self-organize via $\pi$-stacking to a helical tetrameric assembly ($B$-POP$_4$) in lipid bilayer membranes (Figure 4.2B). Matile and co-workers showed that upon photoexcitation, $B$-POP$_4$ assemblies act as
membrane electron channels and create a transmembrane pH gradient (Figure 4.2C). Femtosecond time-resolved fluorescence and transient absorption spectroscopy provided unambiguous evidence of symmetry-breaking charge separation (CS), which occurs between two B-NDI units. After that, the electron and hole migrate and lead

Figure 4.2 A - Molecular structure of the B-NDI unit, B - self-organized transmembrane supramolecular assembly B-POP₄, C - schematic representation of the lipid bilayer membrane with B-POP₄ assembly (blue lines) and mechanism of its photosynthetic activity.¹⁵⁰

Figure 4.3 Molecular structure and energy levels of the HOMO (solid line) and LUMO (dashed line) in differently substituted NDI molecules, ρ-octiphenyl (POP) and oligophenylethynyl (OPE). Numbers indicate maxima of the absorption and emission spectra in nanometers.¹⁵²
to quinone (Q) reduction and ethylenediaminetetraacetic acid (EDTA) oxidation. Hence, consisting of numerous identical fluorophores, the artificial $B$-$\text{POP}_4$ assembly demonstrates two key properties of the light-harvesting antenna and reaction center — light harvesting and separation of the electron/hole pair.

Minor chemical modification in the NDI core leads to tremendous changes of the molecular photophysical characteristics. Figure 4.3 shows the structure and molecular frontier orbitals of differently substituted NDIs, which were synthesized in the group of Prof. Matile. Table 4.1 presents their redox potentials determined by cyclic voltammetry.

**Table 4.1** First oxidation and reduction potential vs. Fc/Fc$^\circ$ of the core-substituted NDIs obtained from cyclic voltammetry of dichloromethane solution.

<table>
<thead>
<tr>
<th></th>
<th>$Y$</th>
<th>$R_{\text{Cl}}$</th>
<th>$R_{\text{Br}}$</th>
<th>$R_0$</th>
<th>$B$</th>
<th>OPE</th>
<th>POP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{ox}}$/eV</td>
<td>1.36</td>
<td>1.11</td>
<td>1.1</td>
<td>0.95</td>
<td>0.55</td>
<td>0.8</td>
<td>0.95</td>
</tr>
<tr>
<td>$E_{\text{red}}$/eV</td>
<td>-0.98</td>
<td>-1.02</td>
<td>-1.05</td>
<td>-1.05</td>
<td>-1.24</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The photoinduced electron transfer in the multichromophoric systems consisting of $B$- and $R_{\text{Cl}}$-NDIs has been investigated thoroughly previously. Owing to the favorable properties of the NDIs that have been unraveled in these studies and due to their tendency to self-assemble, Matile and co-workers proposed to use different core-substituted NDIs attached to a scaffold to design a highly organized $n/p$-heterojunctions architecture with a redox gradient along the heterojunction. However, in order to construct an artificial supramolecular architecture with predicted and
controlled functionality, the photophysics of each building block has to be understood.

In the following chapters, the ultrafast excited-state dynamics of three multichromophoric photosystems with yellow ($Y$), red-bromo ($R_{Br}$) and pink ($R_O$) NDIs attached to a POP and oligophenylethynyl (OPE) scaffold will be described in detail. Additionally, the photophysics of a multichromophoric system composed of perylene diimide (PDI) and POP scaffold will be presented. The obtained knowledge can guide their future applications in photovoltaics.
4.1 Yellow NDI artificial photosystems

This chapter is devoted to the photophysical processes occurring in 2,6-dialkoxy-naphthalenediimide monomeric (Y-MON) and multichromophoric systems (Figure 4.4). Introduction of electron-donating dialkoxy core substituents decreases the HOMO-LUMO gap compared to the non-substituted NDI and shifts the lowest absorption band to the visible region. The first reduction and oxidation potential of Y-MON have been found at $E_{\text{ox1}} = +1.36$ V and $E_{\text{red1}} = -0.98$ V vs. Fc/Fc$^+$ by the cyclic voltammetry experiments (Table 4.1).$^{130, 154}$ The differences in the molecular orbital energy between Y-MON, $p$-octiphenyl (POP) and other substituted NDIs (Figure 4.3 and Table 4.1) suggest that Y-MON should efficiently accept electrons and, thus, provide access to the multicolor redox gradient in the $n$-channel of the oriented supramolecular $n/p$-heterojunctions.

![Molecular structures of the Y-MON, Y-DIM and Y-POP (R = Y-MON)](image)

**Figure 4.4** Molecular structures of the Y-MON, Y-DIM and Y-POP (R = Y-MON)
Molecular modeling reveals strong (-0.78 eV) face-to-face $\pi-\pi$ interactions between totally planar $Y$-MONs.\textsuperscript{130} For comparison, the interaction energy within guanine-cytosine pair is -0.82 eV. Hence, $Y$-MONs attached to the $p$-octiphenyl scaffold ($Y$-POP) (Figure 4.4) have been used as building blocks for constructing a layer-by-layer zipper architecture on a gold surface.\textsuperscript{130}

The experiments, presented in this chapter have been performed on $Y$-MON, $Y$-DIM and $Y$-POP (see Figure 4.4) in solution in order to fully understand their photophysics. The obtained results can be projected on the artificial zipper assembly for predicting its behavior.

**Results**

**Steady-state measurements.** The absorption spectra of $Y$-MON, $Y$-DIM and $Y$-POP consist of two bands with maxima around 470 nm and 360 nm (Figure 4.5). The 470 nm absorption band originates from the $S_1 \leftarrow S_0$ electronic transition, which has charge-transfer character and strongly depends on the nature of the NDI core substituents. In $Y$-DIM and $Y$-POP this band is substantially broadened and approximately 180 cm$^{-1}$ red-shifted probably due to an excitonic interaction between the chromophoric units. The same effect has been reported for other core substituted multichromophoric NDIs systems.\textsuperscript{139} The absorption band with a maximum around 360 nm is a $\pi-\pi^*$ transition involving the NDI centre and does not depend on the core-substituent. Finally, the band which peaks at 320 nm arises from the POP scaffold and can be clearly seen for the $Y$-POP system.

All three compounds have identical fluorescence spectra with a maximum at 489 nm (Figure 4.5), which do not depend on the wavelength of excitation for $420 \text{ nm} < \lambda_{\text{exc}} < 500 \text{ nm}$. It is worth mentioning that the fluorescence excitation spectra of the investigated
Artificial multichromophoric systems

chromophoric systems, \textit{Y-MON}, \textit{Y-DIM} and \textit{Y-POP}, differ slightly from each other (Figure 4.6). This might be due to the presence of

\textbf{Figure 4.5} Intensity-normalized absorption and fluorescence spectra of \textit{Y-MON}, \textit{Y-DIM} and \textit{Y-POP} in MeOH

\textbf{Figure 4.6} Intensity-normalized fluorescence excitation spectra of \textit{Y-MON}, \textit{Y-DIM} and \textit{Y-POP} in MeOH
two or more distinct emitting species. Indeed, as evidenced in Figure 4.5 and in fluorescence experiments not shown, small contributions of fluorescent impurities become apparent for $\lambda_{\text{exc}} < 420$ nm (for Y-MON) and $\lambda_{\text{exc}} > 500$ nm (for Y-DIM and Y-POP).

The fluorescence quantum yields of Y-MON, Y-DIM and Y-POP are represented in the Table 4.2. Multichromophoric systems have much smaller a fluorescence quantum yield than Y-MON. Moreover, the decrease of the quantum yield goes in parallel with the increase in number of fluorophores in the system. This clearly points to the existence of another, non-fluorescent deactivation pathway in the multichromophoric Y-NDIs systems.

**Spectroelectrochemical experiments.** Oxidation and reduction of Y-MON in dichloromethane (DCM) have been performed in a spectroelectrochemical cell (see chapter Chapter 3.2). During one-electron oxidation, the disappearance of the 360 and 470 nm bands accompanies the increase of the absorbance in the 370 - 440 nm spectral region and above 490 nm (Figure 4.7A). The experiments have been performed until no further change in the absorption spectrum was detected. The presence of the 470 nm peak in the final spectrum indicates that the oxidation was not quantitive, and thus the absorption spectrum of neutral Y-MON overlaps with the absorption spectrum of the radical cation Y-MON$^{+}$.

During one-electron reduction, the shape of the absorption spectra did not change and only a decrease in the band intensity was observed (Figure 4.7B). Two possible hypothesis can be proposed. Either the radical anion Y-MON$^{-}$ absorbs in the same spectral region as neutral Y-MON with a very similar absorption spectrum, or the radical anion is not stable. Usually, radicals have absorption
bands in all the visible spectral range down to the near IR.\textsuperscript{155-157} The most probable explanation for the absence of such bands in Figure 4.7B is the instability of the radical anion on the timescale of the electrochemical experiment.

**Time-resolved fluorescence measurements.** Figure 4.8 shows the nanosecond fluorescence decays of Y-MON, Y-DIM and Y-POP measured by the TCSPC technique. To reproduce the time-profiles, a multiexponential function has been convolved with a Gaussian function. The fluorescence decay of Y-MON can be reproduced by a biexponential function with lifetimes of 2.1 ns and 7.4 ns (Table 4.2).
Chapter 4

It suggests the presence of two emitting populations with distinct excited-state lifetimes. Taking into consideration that at this excitation wavelength the fluorescence spectrum has additional contributions on the blue edge, the nanosecond component with small amplitude might stem from an impurity as mentioned before.

To satisfactorily reproduce the nanosecond fluorescence decays of \textit{Y-DIM} and \textit{Y-POP} three exponential functions were required. However, the relative amplitudes of the two long time constant of 1.5 ns and 5.5 ns to the total decay are rather small.

![Figure 4.8](image)

\textbf{Figure 4.8} Intensity-normalized fluorescence decays of \textit{Y-MON}, \textit{Y-DIM} and \textit{Y-POP} in MeOH at 500 nm after 395 nm excitation and best multiexponential fits

The early fluorescence decays of \textit{Y-MON}, \textit{Y-DIM} and \textit{Y-POP} in MeOH after 400 nm excitation registered at 490 nm are shown in \textbf{Figure 4.9}. The time profile of \textit{Y-MON} can be well reproduced by a fast component of 28 ps and slow component of 2.1 ns (Table 4.2). For an unambiguous assignment of these lifetimes, time resolved emission spectra (TRES) are required. However, according to the TA
data shown below, the fast component of the fluorescence decay most likely originates from vibrational or solvent relaxation. Vibrational relaxation probably contributes more, since the chromophores have been excited to a higher excited state. The slow component, $\tau_{fl2}$, is in

![Fluorescence decay](image)

**Figure 4.9** Intensity-normalized early fluorescence decay at 490 nm of Y-MON, Y-DIM and Y-POP in MeOH after excitation at 400 nm. The black lines represent the best fits to the data

**Table 4.2** Fluorescence quantum yields, time constants with relative amplitudes and average time constant, $\tau_{av}$, obtained from the global analysis of the fluorescence time profiles of Y-MON, Y-DIM and Y-POP in MeOH

<table>
<thead>
<tr>
<th>System</th>
<th>$\Phi_{fl}$</th>
<th>$\tau_{fl1}$</th>
<th>$\tau_{fl2}$</th>
<th>$\tau_{fl5}$</th>
<th>$\tau_{fl4}$</th>
<th>$\tau_{fl5}$</th>
<th>$\tau_{av}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-MON</td>
<td>0.078</td>
<td>28 ps (0.12)</td>
<td>2.1 ns (0.74)</td>
<td>7.4 ns (0.14)</td>
<td></td>
<td></td>
<td>2.6 ns</td>
</tr>
<tr>
<td>Y-DIM</td>
<td>0.019</td>
<td>1.42 ps (0.29)</td>
<td>11.5 ps (0.28)</td>
<td>208 ps (0.28)</td>
<td>1.5 ns (0.12)</td>
<td>5.5 ns (0.05)</td>
<td>410 ps</td>
</tr>
<tr>
<td>Y-POP</td>
<td>0.008</td>
<td>0.54 ps (0.27)</td>
<td>4.1 ps (0.39)</td>
<td>37 ps (0.21)</td>
<td>2.2 ns (0.12)</td>
<td>5.5 ns (0.01)</td>
<td>330 ps</td>
</tr>
</tbody>
</table>
good agreement with the results obtained by TCSPC and reflects the $S_1$ population decay.

For reproducing the early time profiles of Y-DIM and Y-POP at least three exponential functions are necessary (Table 4.2). On average they are much faster than those of Y-MON. Approximately 90% of the Y-DIM and Y-POP fluorescence decay occurs on a time scale shorter than 200 ps. This substantial difference between Y-MON and the multichromophoric systems can be originates from an additional non-radiative deactivation pathway.

The decays of the fluorescence polarization anisotropy (FPA) of Y-MON, Y-DIM and Y-POP in MeOH after 400 nm excitation are represented in Figure 4.10. The initial anisotropy, $r_0$, has been found close to 0.4 for all investigated systems (Table 4.3). This indicates that absorption and emission involve the same transition dipole moment.$^{32}$
The FPA of Y-MON can be well reproduced by a monoexponential function with a 190 ps time constant (Table 4.3). This value is in good agreement with reorientational motions typical for molecules of the same size\textsuperscript{158, 159} and very close to the 180 ps anisotropy decay time, which was previously found for RCl-MON in MeOH.\textsuperscript{22} For multichromophoric Y-DIM and Y-POP an additional lifetime is necessary to satisfactorily reproduce the experimental data (Table 4.3). This additional FPA lifetime amounts to 170 fs and 120 fs for Y-DIM and Y-POP, respectively, and is slightly shorter than the IRF of the set-up while the other lifetime remains essentially unaltered compared to Y-MON. The fast component accounts for ca. 30\% of the anisotropy decay. There is no doubt that the ultrafast anisotropy decay component originates from excitation energy hopping between two Y-NDI units, whereas the second time constant represents reorientational motion of the NDI unit.

**Table 4.3** Parameters obtained from analysis of the fluorescence anisotropy decays of Y-NDIs systems in MeOH

<table>
<thead>
<tr>
<th>System</th>
<th>( r_0 )</th>
<th>( \tau_1 )</th>
<th>( \tau_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-MON</td>
<td>0.36</td>
<td>190 ps</td>
<td></td>
</tr>
<tr>
<td>Y-DIM</td>
<td>0.32</td>
<td>0.17 ps (0.28)</td>
<td>190 ps (0.72)</td>
</tr>
<tr>
<td>Y-POP</td>
<td>0.35</td>
<td>0.12 ps (0.26)</td>
<td>190 ps (0.74)</td>
</tr>
</tbody>
</table>

**Transient absorption measurements.** In order to get a complete picture of the ultrafast excited-state dynamics of Y-NDIs systems, transient absorption (TA) experiments have been performed. The TA spectra on Y-MON in MeOH were recorded upon 400 nm excitation and white-light detection (Figure 4.11A). These spectra consist of a
Figure 4.11 Transient absorption spectra at various time delays of $Y$-MON in MeOH (A), $Y$-MON with 3 M DMA in MeOH (B, experiment performed by Natalie Banerji) and $Y$-MON with 0.1 M TNM in ACN (C) after 400 nm excitation
broad positive band with a maximum around 545 nm and of a negative band below 490 nm. The negative TA signal originates from stimulated emission and bleach of the S$_1$←S$_0$ absorption whereas the positive band can be ascribed to excited-state absorption, which strongly overlaps with the stimulated emission.

During the first few picoseconds, a decrease of the amplitude of the negative band as well as a red-shift and narrowing of the positive band can be observed. This effect can be ascribed to the dynamic Stokes shift of the stimulated emission band, induced by solvent relaxation. The timescale of this spectral dynamics are in good agreement with that reported for the relaxation of MeOH.$^{106}$ After that, the TA spectra remain essentially unchanged and their amplitude decays slowly in agreement with the nanosecond lifetime of the excited state observed by fluorescence.

To identify the spectra associated with Y-NDI radical ions, TA measurements with either an electron donor or an electron acceptor have been performed. Figure 4.11B shows TA spectra of Y-MON with 3 M of the electron donor N,N-dimethylaniline (DMA) in MeOH at different time delays. Already after 1 ps the TA spectrum consists of two bands with maxima around 490 nm and 620 nm. The radical cation of DMA absorbs only very weakly around 475 nm.$^{155}$ Thus, all the observed features can be unambiguously attributed to the radical anion Y-MON$^-$, generated upon photoinduced electron transfer (ET) between Y-MON and DMA. The TA bands decays simultaneously to zero within a few tens of picoseconds by charge recombination (CR) of the geminate DMA$^*/$Y-MON$^-$ pair.

The TA spectra of Y-MON in presence of 0.1 M electron acceptor tetranitromethane (TNM) in acetonitrile are illustrated in Figure 4.11C. At the wavelength of excitation, TNM absorbs weakly.
Figure 4.12 Transient absorption spectra at various time delays of $Y$-MON (A), $Y$-DIM (B) and $Y$-POP (C) after 400 nm excitation
Photoexcitation of TNM was shown to lead to formation of TNM•- anion,\textsuperscript{160} which is known to dissociate within a ps into NO\textsubscript{2} and trinitromethane anion (3NM•-).

3NM•- absorbs below 400 nm and, thus, does not contribute to the TA spectra. The gas phase absorption spectrum of NO\textsubscript{2}, however, shows, apart from the strong absorption below 400 nm, also bands above 630 nm.\textsuperscript{161} Hence, the early TA spectra in Figure 4.11C can be assigned to the excited state absorption of Y-MON and NO\textsubscript{2}. The NO\textsubscript{2} bands are bathochromically shifted by ca. 1000 cm\textsuperscript{-1} when compared to gaseous phase and responsible for the peaks at 670 and 700 nm. It stems from decomposition of directly excited TNM which takes place within the IRF. The photoexcited Y-MON undergoes ET to form Y-MON\textsuperscript{••} and TNM\textsuperscript{••} whose subsequent decomposition prevents ultrafast charge recombination.\textsuperscript{162, 163} The NO\textsubscript{2} radical decays rapidly and the TA spectra measured after ~400 ps originate in good approximation from NDI\textsuperscript{••} solely. This excited-state absorption covers essentially all the spectral observation window and is characterized by a scarcity of structural features.

The TA spectra of Y-DIM and Y-OCT in MeOH are clearly distinct from those recorded for Y-MON (Figure 4.12). In the first 10 ps, the appearance of a new positive band peaking around 500 nm is observed for both multichromophoric systems. The shape of this new band is very similar to that found for a solution of Y-MON with DMA (Figure 4.11B). Thus, formation of the Y-MON\textsuperscript{••} upon photoexcitation is evident. The small shoulder at 545 nm, which is present in the TA spectra at all time delays and especially well seen for Y-DIM system, indicates the presence of a NDI local excited state population. This agrees with the time-resolved fluorescence
measurement, which indicates the presence of approximately 12% long lived fluorescent population.

The TA time profiles at different wavelengths obtained for Y-DIM and Y-OCT have been analyzed globally using the sum of four exponential functions (Table 4.4). The fastest time constant, $\tau_1$, can be associated with the early spectral dynamics due to vibrational and solvent relaxation. The positive band mentioned before builds up with $\tau_2$ and after that decays biexponentially with $\tau_3$ and $\tau_4$. Thus, $\tau_2$ can be assigned to the charge separation (CS) processes, while $\tau_3$ and $\tau_4$ can be attributed to the charge recombination (CR), which overlaps with the decay of the locally excited state.

### Discussion

**Excitation energy transfer.** As discussed earlier, organized multichromophoric systems with well-defined assemblies, like for example light-harvesting complexes in the photosynthetic apparatus, demonstrate highly efficient excitation energy transfer. Semi-empirical quantum chemistry calculations predict a center-to-center distance between two $Y$-NDI units in the $\pi,\pi$-stacked dimers of 3.36 Å and a twist of 44° of the aromatic planes.$^{150}$

<table>
<thead>
<tr>
<th>System</th>
<th>$\tau_1$</th>
<th>$\tau_2$</th>
<th>$\tau_3$</th>
<th>$\tau_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-DIM</td>
<td>0.5 ps</td>
<td>6.5 ps</td>
<td>130 ps</td>
<td>&gt; 2 ns</td>
</tr>
<tr>
<td>Y-POP</td>
<td>0.9 ps</td>
<td>8.7 ps</td>
<td>190 ps</td>
<td>&gt; 3 ns</td>
</tr>
</tbody>
</table>
Excitation energy hopping (EEH) can be detected via time dependent fluorescence polarization anisotropy. The \(Y\)-MON shows an anisotropy decay with a time constant of 190 ps that is consistent with rotational diffusion of the chromophore. It is in agreement with reorientational rates which were found previously for the other monomeric core-substituent NDIs.\(^2\)

\(Y\)-DIM and \(Y\)-POP show anisotropy profiles which are very similar to each other but with an additional, ultrafast decay component of 170 and 120 fs, respectively, which unambiguously reveals intramolecular EEH between NDI units. The second component of 190 ps for \(Y\)-DIM and \(Y\)-POP is the same as the one found for \(Y\)-MON. This indicates that the system of chromophores attached to the scaffold is very flexible and the NDIs move quite freely. In the framework of Förster theory (eq. 2.51 with \(k_{\text{FRET}} = (120 \text{ fs})^{-1}\)), the observed EEH rate constant corresponds to an average distance of ca. 5 Å between two plane-parallel \(Y\)-NDI cores. This is a reasonable result for the flexible POP scaffold although Förster theory is based on the point dipole approximation and is at the limit of applicability for such short distances between the chromophores.

*Photoinduced charge separation.* The 500 nm TA band observed with \(Y\)-DIM and \(Y\)-POP can be safely assigned to a charge-separated state (CSS), with the electron on a \(Y\)-NDI chromophore. Consequently, the strong reduction of the fluorescence quantum yield and fluorescence lifetimes observed by going from monomeric to the multichromophoric \(Y\)-NDI systems originates from photoinduced intramolecular ET. The Weller equation (see Chapter 2.3) allows to estimate the driving force for photoinduced CS to the \(Y\)-NDI\(^{**}/Y\)-NDI\(^*\) CSS and POP\(^{**}/Y\)-NDI\(^*\) CSS and thermal CR back to the ground state. Taking 2.58 eV as the energy of the local excited state
(LES), the redox potentials obtained from cyclic voltammetry (see Table 4.1) and C = -0.05, yields the $\Delta G_{CS}$ and $\Delta G_{CR}$ listed in Table 4.5. They indicate that CS between Y-NDI and the POP scaffold is energetically more favorable than CS between two chromophores.

 POP• is known to absorb only weakly around 500 nm, and thus can not be clearly seen in the TA spectra.\cite{164,165} However, energetic considerations point to a CSS with the hole on the scaffold. Even if the Y-NDI•+/Y-NDI•- CSS is populated, subsequent hole transfer from the Y-NDI•* to the POP should be expected.

The rate constant for CS for Y-DIM and Y-OCT can be deduced from the early fluorescence dynamics. The presence of slow fluorescence decay components indicates that the timescales of CS and CR are partially overlapping. This makes a direct determination of the CR dynamics from the TA data problematical. Hence, in order to determined the intrinsic evolution of the CSS population, the contribution of the LES population was removed by subtracting the fluorescence time profile from the TA profile.

The time trace of the TA signal recorded with Y-POP at 547 nm consists of both LES and CSS population dynamics (Figure 4.13A). The profile of the fluorescence intensity, on the other hand, reflects

<table>
<thead>
<tr>
<th>Donor/Acceptor</th>
<th>$\Delta G_{CS}$/ eV</th>
<th>$\Delta G_{CR}$/ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-NDI / Y-NDI</td>
<td>-0.29</td>
<td>-2.29</td>
</tr>
<tr>
<td>Y-NDI / POP</td>
<td>-0.7</td>
<td>-1.88</td>
</tr>
</tbody>
</table>
only the LES population dynamics. The intrinsic time profile of the CSS population can be obtained by subtracting the fluorescence profile from the 547 nm TA profile and analyze it using eq. 3.21 (Figure 4.13B). Assuming a biexponential CR, time constants of 200 ps and >5 ns with relative amplitudes of 0.73 and 0.27, respectively, were obtained.

In comparison with the B-POP ($\tau_{CR} = 43$ ps) and $R_{CI}$-POP ($\tau_{CR,1} = 98$ ps, $\tau_{CR,1} = 1.1$ ns) multichromophoric systems, the CR dynamics of Y-POP is considerably slower. This difference can be attributed to the nature of the CSS. For energetic reasons, only the NDI$^{+*}$/NDI$^{-*}$ CSS can be populated in B-POP, whereas both NDI$^{+*}$/NDI$^{-*}$ and POP$^{+*}$/NDI$^{-*}$ CSS are accessible with $R_{CI}$-POP and Y-POP. The longer-lived POP$^{+*}$/NDI$^{-*}$ CSS can be explained by a better spatial
confinement of the charges in $Y$-POP. It is also in line with the $\Delta G_{CR}$ values of these two systems, which is substantially bigger for POP•/RCl-NDI•.$^{139}$

**Conclusions**

The obtained results demonstrate that electron transfer is operative in $Y$-NDI multichromophoric systems upon photoexcitation. The introduced dialkoxy core substituents lead to a facilitated charge separation between $Y$-NDI and the POP scaffold. The time constant for CS in the $Y$-POP system ($\tau_{CS} = 8.7$ ps) is faster than that previously observed for the $RCl$-POP system ($\tau_{CS} = 10.6$ ps).$^{139}$ The CR of $Y$-POP, on the other hand, is considerably slower ($\tau_{CR,1} = 200$ ps, $\tau_{CR,2} > 5$ ns) in comparison with the $RCl$-POP multichromophoric system ($\tau_{CR,1} = 98$ ps, $\tau_{CR,2} = 1.1$ ns).$^{139}$

Comparison of $Y$-POP with $B$-POP ($\tau_{CS} = 4$ ps, $\tau_{CR} = 43$ ps)$^{139}$ is not meaningful since the nature of the CSS is different in these two cases, $Y$-NDI•/POP• vs. $B$-NDI•/B-NDI•.

The nature of the CSS in the $Y$-POP system exhibiting a spatial separation of the electron and hole makes it an attractive candidate for $n/p$-heterojunctions architecture, since the NDI units can carry electrons and the POP scaffold holes.
4.2 Red-bromo NDI artificial photosystems

This chapter is devoted to the photophysical behavior of the core-substituted $R_B$-NDI whose structure is shown in Figure 4.14. As has been stated before, the nature of the substituents in the NDI core strongly influences its properties. Compared to $Y$-NDI, introducing a bromo- and a isopropylamino-group in the naphthalene core leads to an increase of the HOMO and LUMO molecular orbital energy levels and a decrease of the gap between them (see Figure 4.3 and Table 4.1). Based on the redox potentials obtained by cyclic voltammetry, $R_B$-NDI can act as electron acceptor against the POP scaffold and can, together with other core-substituent NDIs, be used to construct a redox gradient in the $n$-channel of the supramolecular $n/p$-heterojunctions.\textsuperscript{129}

Special attention will be paid to the $R_B$-NDI multichromophoric system with an oligophenylethynyl (OPE) scaffold. The distance between two NDIs in the OPE system amounts to $\sim 7$ Å and is more

Figure 4.14 Molecular structures of the $R_B$-MON, $R_B$-POP and $R_B$-OPE ($R = R_B$-MON)
appropriate for their π stacking in a zipper assembly. Moreover, the OPE is a better hole conductor and electron donor.\textsuperscript{52, 166} Its absorption band in the visible spectral region makes it easily detectable with our set-up.

All experiments presented in this chapter were carried out in MeOH solution. The aim is to understand the photophysical properties of these constructs and to proof the existence of an additional deactivation pathway via photoinduced electron transfer. Moreover, the influence of the scaffold on the photophysical properties of the total system will be discussed by comparison of NDIs constructs with a POP or an OPE scaffold.

Results

Steady-state measurements. The absorption spectra of R\textsubscript{Br}-MON, R\textsubscript{Br}-POP and R\textsubscript{Br}-OPE in MeOH are represented in Figure 4.15. The lowest energy band with its maximum at 530 nm originates from the S\textsubscript{1} ← S\textsubscript{0} (or LSS ← S\textsubscript{0} (locally-excited singlet state) for R\textsubscript{Br}-POP and R\textsubscript{Br}-OPE) transition. This band is markedly broader and slightly red-shifted (\textasciitilde 250 cm\textsuperscript{-1}) in the multichromophoric R\textsubscript{Br}-POP and R\textsubscript{Br}-OPE systems when compared to monomer R\textsubscript{Br}-MON. This difference is typical of multichromophoric systems and appears to be due to excitonic interaction between the chromophoric units.\textsuperscript{139, 167}

The band with a maximum at 408 nm is present only in R\textsubscript{Br}-OPE and can be assigned to local S\textsubscript{1} ← S\textsubscript{0} absorption of the OPE scaffold.\textsuperscript{168} However, the absorption band around 360 nm with vibrational structure present in all three systems and is due to a π-π* transition of the NDI centre. For the R\textsubscript{Br}-POP this band overlaps with another one centered at shorter wavelength and originating from the local S\textsubscript{1} ← S\textsubscript{0} transition of the POP scaffold.
The fluorescence spectra of all three compounds are almost identical and have the maximum at 586 nm (Figure 4.15). By contrast, the fluorescence quantum yields differ strongly and are almost 30 times lower for the multichromophoric systems (Table 4.6). The presence of a heavy atom strongly influences the photophysical properties of the NDI. Surprisingly $R_{\text{Cl}}$-MON has a lower fluorescence quantum yield ($\Phi_{\text{fl}} = 0.08$)\textsuperscript{139} than the $R_{\text{Br}}$-MON ($\Phi_{\text{fl}} = 0.32$, see Table 4.6) although the only difference on a molecular level consists in the nature of the heavy atom. ISC is of minor importance for $R_{\text{Cl}}$-MON which decays by an intermolecular hydrogen-bonding mechanism,\textsuperscript{98, 139} which, apparently, is less efficient in the bromo analog, which might originate in the halogen’s bulkiness or subtleties of their inductive and mesomeric effects.

**Figure 4.15** Intensity-normalized absorption and fluorescence spectra of $R_{\text{Br}}$-MON, $R_{\text{Br}}$-POP and $R_{\text{Br}}$-OPE in MeOH
Spectroelectrochemical experiments. A solution of $R_{Br}$-MON in dichloromethane (DCM) has been electrochemically oxidized and reduced in a spectro-electrochemical cell (see Chapter 3.2). Absorption spectra have been recorded until no further change in the shape and intensity of the bands occurred. During electrochemical oxidation, only a decrease of the $R_{Br}$-MON bands has been observed, yet, no new features (except a weak absorbance around 400 nm) which would correspond to $R_{Br}$-MON$^{**}$ absorption were detected (Figure 4.16A). Since there was no possibility to make the samples water free, the produced radical cation could simply undergo a fast chemical reaction and form compounds, which absorb just slightly in
the visible spectral region, around 400 nm. Several spectra of NDI radical ions are shown in the appendix (Figures A.1 and A.2). Since the absorption features typical of NDI radical ions\cite{169,170} are absent in Figure 4.16A, these spectra are not assigned to $R_{Br}$-MON$^{+}$.

By contrast, electrochemical one-electron reduction leads to formation of $R_{Br}$-MON$^{-}$ clearly seen by absorption spectroscopy (Figure 4.16B). Similar to the radicals of NDIs, $R_{Br}$-MON$^{-}$ has bands throughout the visible and near infrared (NIR) region. It is important to mention that the efficiency of the reduction is probably lower than 100\% and thus the spectrum of the $R_{Br}$-MON$^{-}$ is contaminated with that of neutral $R_{Br}$-MON in the region between 450 - 570 nm and below 380 nm.

*Time-resolved fluorescence measurements.* The fluorescence decay of $R_{Br}$-MON recorded by TCSPC upon 469 nm excitation can be reproduced by a monoexponential function with a 3.75 ns lifetime.

![Intensity-normalized fluorescence decays of $R_{Br}$-MON, $R_{Br}$-POP and $R_{Br}$-OPE at 580 nm in MeOH after 469 nm excitation recorded by TCSCCP and the best multiexponential fits](image)

**Figure 4.16** Intensity-normalized fluorescence decays of $R_{Br}$-MON, $R_{Br}$-POP and $R_{Br}$-OPE at 580 nm in MeOH after 469 nm excitation recorded by TCSPC and the best multiexponential fits.
This is longer than the 2.3 ns lifetime of $R_{Cl}$-MON$^{139}$ and in agreement with the larger fluorescence quantum yield. The early fluorescence dynamics of $R_{Br}$-MON after 400 nm excitation is represented in Figure 4.17. The convolution of a Gaussian with a biexponential function has been used to reproduce the intensity-normalized fluorescence dynamics at 570 nm after excitation at 400 nm. Solid lines represent the best fits to the data.

Table 4.6 Fluorescence quantum yields and time constants with relative amplitudes obtained from the global analysis of the fluorescence time profiles of $R_{Br}$-MON, $R_{Br}$-POP and $R_{Br}$-OPE in the MeOH system.

<table>
<thead>
<tr>
<th>System</th>
<th>$\Phi_\text{fl}$</th>
<th>$\tau_{\text{fl}1}$</th>
<th>$\tau_{\text{fl}2}$</th>
<th>$\tau_{\text{fl}3}$</th>
<th>$\tau_{\text{fl}4}$</th>
<th>$\tau_{\text{fl}5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{Br}$-MON</td>
<td>0.32</td>
<td>31 ps (0.09)</td>
<td>3.75 ns (0.91)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{Br}$-POP</td>
<td>0.009</td>
<td>3.7 ps (0.29)</td>
<td>26 ps (0.48)</td>
<td>170 ps (0.18)</td>
<td>3.75 ns (0.05)</td>
<td></td>
</tr>
<tr>
<td>$R_{Br}$-OPE</td>
<td>0.004</td>
<td>0.11 ps (0.55)</td>
<td>1.35 ps (0.27)</td>
<td>7.2 ps (0.16)</td>
<td>73.2 ps (0.021)</td>
<td>420 ps (0.004)</td>
</tr>
</tbody>
</table>
the data (Table 4.6). The fast component of 30 ps can be safely ascribed to both vibrational and solvent relaxation of the excited state, whereas the second time constant is in good agreement with the lifetime obtained by TCSCP and can be attributed to the S₁ excited state decay.

The fluorescence decay of RBr-POP is remarkably faster than that of RBr-MON (Figure 4.16 and Figure 4.17) and cannot be reproduced with less than the sum of four exponential functions with time constant ranging from 3.7 ps to 3.75 ns (Table 4.6). The fluorescence dynamics of the multichromophoric system with an OPE scaffold are even faster (Figure 4.17). More than 90% of the total fluorescence decay occurs within the first 12 ps. The time constants obtained from the analysis of the fluorescence decays are summarized in the Table 4.6.

Transient absorption measurements. TA spectra measured with RBr-MON in MeOH at different time delays after excitation at 520 nm are shown in the Figure 4.18A. Directly after photoexcitation, the spectra consist of a broad positive band with a maximum at 470 nm and a negative band above 530 nm with two pronounced minima at 550 and 610 nm. The positive band can be assigned to excited-state absorption of RBr-NDI, whereas the negative bands originate from bleach of the S₁←S₀ transition and stimulated emission. During the first 10 ps, the negative signal around 550 nm is replaced by a positive band, while the stimulated emission and excited state absorption bands change just slightly, mainly by shifting. After that, some slow change of the shape and the intensity of the whole spectrum can be observed.
Figure 4.18 Transient absorption spectra measured at various time delays of $R_{Br}$-MON (A), $R_{Br}$-POP (B), $R_{Br}$-OPE (C) after 520 nm excitation and $R_{Br}$-OPE excited at 400 nm (D) in MeOH.
Figure 4.19 Decay-associated difference spectra of $R_{60}$-MON (A), $R_{60}$-POP (B), $R_{60}$-OPE (C) obtained upon global analysis of the TA data shown in Figure 4.18
The time evolution of the TA spectra was analyzed globally using four exponential functions with the lifetimes listed in Table 4.7. Figure 4.19A shows the resulting decay-associated difference spectra. The initial spectral dynamics is represented by two short time constants, $\tau_1$ and $\tau_2$, which have values very similar to those reported for the solvation dynamics in MeOH.$^{106}$

It is surprising to find that the prominent changes at early time delays can be observed only in the spectral region of the bleach (around 550 nm) and it should be stressed that the effect is perfectly reproducible. The underlying effect is most probably mainly structural relaxation of the Franck-Condon $S_1$ state with minor contributions from solvent relaxation. The latter is responsible for the shift of the TA bands, an idea supported by the good agreement of $\tau_1$ and $\tau_2$ (Table 4.7) with the initial decay component observed by time-resolved fluorescence spectroscopy (Table 4.6). The early structural reorganization seems to involve a vibrational mode that is Franck-Condon active for the excited state absorption around 550 nm but not for the other transitions. This is in line with the fact that the absorption and fluorescence spectra of $R_{Br}$-MON are not perfectly mirror image to one another.

The next time constant, $\tau_3$, can be attributed to the decay of the $S_1$ population. Since the TA set-up has a time-window of 1.8 ns, the magnitude of $\tau_3$ can be only estimated. However, the value found for $\tau_3$ is quite close to the fluorescence lifetime of 3.75 ns, which was measured by TCSPC (Table 4.6). Yet, the TA signal does not decay to zero and its shape becomes considerably different from that of $R_{Br}$-MON $S_1$ state after 1.7 ns, which points to the existence of a long-lived population. In order to determined the lifetime of this last state precisely, flash photolysis experiments have been performed (Figure...
4.20. The transients observed at various wavelengths after 532 nm excitation have a 200 ns lifetime which becomes substantially shorter in the presence of oxygen. It has therefore been ascribed to the triplet state of $R_{Br-MON}$.

The TA spectra recorded with $R_{Br-POP}$ are substantially different from those of monomeric $R_{Br-NDI}$ (Figure 4.18B). During the first 30 ps the negative bands above 530 nm are replaced by a broad band with a shape similar to the steady-state absorption of $R_{Br-NDI^-}$ measured spectroelectrochemically. After that, the whole spectrum shows a simultaneous, slow decay. A global analysis of the TA time profiles has been performed using four exponential functions with the time constants listed in Table 4.7 and the decay-associated difference spectra shown in Figure 4.19B.

The decay-associated difference spectra corresponding to $\tau_1$ can be attributed to the relaxation of the $R_{Br-NDI}$-localized $S_1$ state ($R_{Br-LSS}$). Indeed, this lifetime is in agreement with the shortest time
constant, $\tau_1$, measured by fluorescence up-conversion and can be partially assigned to the decay of the excited state by charge separation (CS). The second time constant, $\tau_2$, is very close to $\tau_{fl2}$ (Table 4.6) and reflects the replacement of the stimulated emission by a positive band around 610 nm and a rise of the signal intensity around 470 nm. This is attributed to the decay of the $R_{Br}$-LSS and the population of the charge separated state (CSS). The third time constant, $\tau_3$, accounts most probably for both CS as certified by the larger fluorescence time constant ($\tau_{fl3}$ in Table 4.6) and partial charge recombination (CR) of the CSS population. Finally, the spectrum associated with $\tau_4$ can be assigned to CR and was determined by laser flash photolysis (Figure 4.20). However, it is important to mention that the spectrum of the $R_{Br}$-NDI T$_1$ ($R_{Br}$-LTS) state overlaps with that of the CSS in the region between 400 and 470 nm (Figure 4.18A,B and Figure 4.19A,B). Thus some contribution of the $R_{Br}$-LTS state can in principle not be excluded. As has been stated earlier, the population of the triplet state occurs on the nanosecond scale. Taking into account that TCSPC and up-conversion experiments

<table>
<thead>
<tr>
<th>System</th>
<th>$\lambda_{ex}$</th>
<th>$\tau_1$</th>
<th>$\tau_2$</th>
<th>$\tau_3$</th>
<th>$\tau_4$</th>
<th>$\tau_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{Br}$-MON</td>
<td>520 nm</td>
<td>1.5 ps</td>
<td>17 ps</td>
<td>$\sim$ 2.4 ns</td>
<td>200 ns*</td>
<td></td>
</tr>
<tr>
<td>$R_{Br}$-POP</td>
<td>520 nm</td>
<td>1.7 ps</td>
<td>14 ps</td>
<td>175 ps</td>
<td>2.5 $\mu$s*</td>
<td></td>
</tr>
<tr>
<td>$R_{Br}$-OPE</td>
<td>520 nm</td>
<td>0.9 ps</td>
<td>7 ps</td>
<td>71 ps</td>
<td>270 ns</td>
<td>$&gt; 3$ ns</td>
</tr>
<tr>
<td></td>
<td>400 nm</td>
<td>4.6 ps</td>
<td>68 ps</td>
<td>217 ps</td>
<td>$&gt; 3$ ns</td>
<td></td>
</tr>
</tbody>
</table>
show that 95% of the $R_{Br}$-LSS population decay much faster than ISC, the contribution of the triplet state to the TA spectra can be considered to be negligible. A more detailed discussion on the nature of the long lived CSS together with a possible explanation of the extremely slow CR will be presented in the discussion section.

TA spectra measured with $R_{Br}$-OPE at different time delays upon 400 nm (OPE-LSS$\leftarrow$S$_0$) and 520 nm ($R_{Br}$-LSS$\leftarrow$S$_0$) excitation are shown in Figures 4.18C,D. These spectra are essentially identical and consist of a broad positive band above 450 nm, which increases in the first 10 ps and after that slowly decays almost to zero. The negative signal with a maximum at 408 nm, which originates from the bleach of the OPE-LSS$\leftarrow$S$_0$ transition, can be observed in both spectra. Its behavior is identical to the positive band. The TA data have been analyzed globally using four (for the sample excited at 400 nm) and five (520 nm excitation) exponential functions with the lifetimes listed in Table 4.7 (Figure 4.19C,D).

Upon 520 nm excitation, the build-up of a state with a positive band around 600 nm and a bleach of the OPE, which can be assigned to the $R_{Br}$-NDI/OPE CSS is populated with the first two lifetimes, $\tau_1$ and $\tau_2$. This is followed by a decay of the CSS population with $\tau_3$, $\tau_4$ and $\tau_5$ time constants. This decay can be attributed to CR to the ground state.

CS is much faster upon OPE-LSS$\leftarrow$S$_0$ excitation at 400 nm. The fluorescence up-conversion experiment reveals two ultrafast components, $\tau_{fl1}$ and $\tau_{fl2}$, which were probably missed in the TA data analysis. The subsequent CR is independent of the excitation wavelength (Table 4.7) and so are the residual spectra.
Discussion

The steady-state, time-resolved fluorescence and TA experiments evidence CS upon photoexcitation in the $R_{Br}$-NDI multichromophoric systems. Based on the Weller equation and the known redox potentials of $R_{Br}$-NDI, POP and OPE (Table 4.1), the driving force for photoinduced CS between $R_{Br}$-NDI/$R_{Br}$-NDI and $R_{Br}$-NDI/scaffold can be estimated (Table 4.8). The correction factor, C, which accounts for the electrostatic interaction between the resulting ionic components has been assumed to be -0.05 eV. All three cases are exergonic, and the most favorable situation is ET from the OPE to the $R_{Br}$-NDI.

In order to explain the nature of the exceptionally long-lived CSS populated in the $R_{Br}$-POP system, the following hypothesis can been brought forward. The energy level scheme is depicted in Figure 4.21. Population of the $R_{Br}$-LSS is followed by CS to the $R_{Br}$-NDI/$R_{Br}$-NDI CSS (process 1). In parallel CS to the POP/$R_{Br}$-NDI CSS is also possible, but if it occurs, it should not be the dominant pathway since the coupling among NDIs units is stronger then between NDI and POP. Process 1 can then be followed by a hole-transfer to the POP to

<table>
<thead>
<tr>
<th>Donor/Acceptor</th>
<th>$\Delta G_{CS}$/ eV</th>
<th>$\Delta G_{CR}$/ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{Br}$-NDI / $R_{Br}$-NDI</td>
<td>-0.13</td>
<td>-2.1</td>
</tr>
<tr>
<td>$R_{Br}$-NDI / POP</td>
<td>-0.28</td>
<td>-1.95</td>
</tr>
<tr>
<td>$R_{Br}$-NDI / OPE</td>
<td>-0.43</td>
<td>-1.80</td>
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</tbody>
</table>
populate the POP/$\text{RBr-NDI}$ CSS (process 2), which subsequently decays by CR (process 3). In the $\text{RBr-NDI/\text{RBr-NDI CSS}}$, the two unpaired electrons are in vicinity of two heavy atoms and experience a large spin-orbit coupling, which favors fast intersystem-crossing (ISC) to the triplet CSS ($\text{RBr-NDI/\text{RBr-NDI TCSS}}$). The singlet-triplet energy gap of this CSS is not known but it can be expected to be small (≤ 0.1 eV), as it is normally the case for CSS. After that, CR of $\text{RBr-NDI/\text{RBr-NDI TCSS}}$ to the ground state (process 4) is spin forbidden but CR to the $\text{RBr-LTS}$ (process 5) is not and thus occurs preferentially. The population of this state can then undergo CS to the lower-lying POP/$\text{RBr-NDI TCSS}$ (process 6). Another possibility might be that the POP/$\text{RBr-NDI TCSS}$ can be populated directly from the $\text{RBr-NDI/\text{RBr-NDI TCSS}}$.

The energy of the $\text{RBr-LTS}$ has not been determined experimentally in this work. It could be measured by phosphorescence in a low temperature matrix or triplet sensitization experiment. However, it can be expected to lie below $\text{RBr-NDI/\text{RBr-NDI CSS}}$.

**Figure 4.21** Energy levels scheme pertaining to the relevant CS and CR processes in the $\text{RBr-POP}$ system. LSS: local singlet state, LTS: local triplet state, CSS: charge separated state, TCSS: triplet charge separated state.
Figure 4.22 A - TA spectra at various time delay of $R_{Br}$-MON with 1 M 1-methylnaphthalene in MeOH, B - decay-associated difference spectra.

The long lifetime of the POP/$R_{Br}$-TCSS state can be explained by the spin-forbidden character of the CR to the ground state (process 7). Also, ISC to the singlet POP/$R_{Br}$-NDI CSS is not efficient for two reasons: i) the singlet state is higher in energy thus ISC is endergonic, and ii) spin-orbit coupling is weaker because only the negative charge is located on a $R_{Br}$-NDI, the hole being on the POP.

In order to obtain experimental support for the population of the $R_{Br}$-NDI LTS upon CR (process 5), the electron transfer (ET) quenching of $R_{Br}$-MON by a weak electron donor, 1-methylnaphthalene (MN, $E_{ox}=1.43$ V vs SCE in acetonitrile)\textsuperscript{41} has been investigated by TA (Figure 4.22A). The early spectra show the quenching of the S\textsubscript{1} state by MN and the formation of $R_{Br}$-MON$^*$ and MN$^{**}$ (absorbing above 650 nm)\textsuperscript{171} and then the decay of this ionic population. The residual
spectrum (Figure 4.22B) associated with $\tau_4$ has a positive band with a maximum at 440 nm and can be assigned to the T$_1$ state of $R_{Br}$-MON (Figure 4.18A and Figure 4.19A). Thus, the $R_{Br}$-MON$^\ast$/MN$^\ast\ast$ pair is energetically above the $R_{Br}$-LTS and CR to this state (equivalent to process 5) is operative.

For the multichromophoric system with an OPE scaffold, an ultrafast electron transfer between $R_{Br}$-NDI and OPE with the hole located on the latter has been observed, independent on the wavelength of excitation. This can be clearly seen by the presence of the OPE bleach around 410 nm and the broad absorption band of the $R_{Br}$-NDI$^\ast$ above 440 nm. From TA and fluorescence up-conversion experiments, the CS is faster when the OPE-LSS is populated. This can be rationalized by the fact that the OPE is surrounded by ten electron acceptors while a photoexcited $R_{Br}$-NDI “sees” only one OPE.

The CR occurs with the same three components independent on the excitation wavelength. This is further proof that the nature of the CSS is in the both cases the same. The decay-associated difference spectra associated with lifetimes of 70 and 220 ps show a pronounced negative signal from the OPE bleach and positive signal from $R_{Br}$-NDI$^\ast$. By contrast, the residuals associated with the long-lived component lacks the negative feature from OPE bleach. Thus, the last decay-associated spectrum can be due to $R_{Br}$-NDI/$R_{Br}$-NDI CSS. However, this is quite improbable because this state should be above the OPE/$R_{Br}$-NDI CSS and a long lifetime of this state would be difficult to justify. It is well known that the position and intensity of the local S$_1$←S$_0$ absorption band of OPE strongly depends on its degree of torsion. Planarization leads to an increase in oscillator strength and to a bathochromic shift due to improved conjugation. 51
Thus, another possible explanation for the lack of the OPE bleach might be an OPE/$R_{br}$-NDI CSS with a strongly distorted scaffold. The distorted scaffold could also be expected to decrease the delocalization of the hole in the OPE and thus to slow down CR.

The lifetime of the CSS between $R_{br}$-NDI and POP is much longer than that observed for $R_{br}$-NDI and OPE. This suggests that the triplet-state mechanism (processes 5 and 6 shown in Figure 4.21) is not operative in the $R_{br}$-OPE system. This is easily understood since CS for the latter occurs directly between $R_{br}$-NDI and the scaffold because of its substantially larger driving force and for this state a change of multiplicity is of minor importance.

**Conclusions**

Similar to $Y$-NDI, the multichromophoric systems build of $R_{br}$-NDI and POP or OPE show photoinduced electron transfer between NDI units and the scaffold with the hole in both cases located on the latter. The presence of a bromine atom leads to population of an extremely long-lived (2.5 µs, Table 4.7) CSS in the $R_{br}$-POP construct. Since OPE is much better an electron donor than $R_{br}$-NDI, charge separation between the NDI unit and the scaffold is extremely fast and independent of the energy of excitation in the case of $R_{br}$-OPE. This can be especially well seen by time-resolved fluorescence measurements, which reveal two lifetimes of 0.11 and 1.35 ps for the CS. However, the CR is not as slow in this case as has been observed for $R_{br}$-POP.

In the introduction, the importance of a long-lived CSS for the efficiency of photosystems has been discussed. The outstanding photophysical properties of the $R_{br}$-NDI systems make it attractive for potential applications in artificial photovoltaics.
4.3 Pink NDI artificial photosystems

The objective of this chapter is to present the photophysical properties of the core-substituted \( R_{\text{O}} \)-NDI with an alkoxy and an \( \text{iso} \)-propylamino-group attached to a POP and OPE scaffold (Figure 4.23). Compared to the halogenated red \( R_{\text{Br}} \)-NDI, the HOMO level of this chromophore is 0.2 eV higher and the gap between HOMO and LUMO is 0.1 eV smaller (Figure 4.3 and Table 4.1).\(^\text{131}\) The aim of the investigations was to evaluate the usefulness of these systems for building supramolecular n/p-heterojunctions with an oriented multicolored antiparallel redox gradient.

It has not been accented above that NDI units can be differently charged depending on the sidechain. As will be shown, this can affect the direction of the electron transfer. From the following data, steady-state and time-resolved fluorescence were measured with cationic \( R_{\text{O}} \)-NDIs systems, whereas the TA part additionally brings forward data

![Molecular structures of the \( R_{\text{O}} \)-MON (X=NH\text{3}\text{+} (cationic \( R_{\text{O}} \)-MON), X=(benzyloxy)carbonyl (neutral \( R_{\text{O}} \)-MON)), \( R_{\text{O}} \)-POP and \( R_{\text{O}} \)-OPE (R = \( R_{\text{O}} \)-MON)](image-url)
obtained for the neutral \( R_0 \)-OPE system. Unless explicitly mentioned, the cationic system is considered.

**Results**

*Steady-state measurements.* The absorption spectra of \( R_0 \)-MON, \( R_0 \)-POP and \( R_0 \)-OPE in MeOH are shown in the Figure 4.24. The band originating from the \( S_1 \rightleftharpoons S_0 \) transition has its maximum at 550 nm and is clearly red-shifted compared to halogenated \( R_B \)-NDI. Similar to the other compounds presented earlier, this band is slightly broadened in the multichromophoric \( R_0 \)-NDIs due to excitonic coupling between the NDI units.\textsuperscript{172, 173} The band with vibrational structure around 350 nm is observed for all three systems and originates from a \( \pi-\pi^* \) transition involving the NDI center. The features of the POP which correspond to the LSS-POP\(\rightleftharpoons S_0 \) transition can be seen at 320 nm in the \( R_0 \)-POP system. The origin of

![Figure 4.24 Normalized absorption and emission spectra of cationic \( R_0 \)-MON, \( R_0 \)-POP and \( R_0 \)-OPE in MeOH](image)
the additional absorption around 400 nm in the $R_0$-OPE is the LSS-OPE$\leftrightarrow$S$_0$ transition.

The fluorescence spectra obtained upon local NDI excitation are almost identical for monomeric and multichromophoric NDIs systems (Figure 4.24). The band, whose maximum is located at 595 nm, is a mirror-image of the absorption spectrum. The fluorescence quantum yield strongly varies for the investigated systems. The $R_0$-MON has much larger a fluorescence quantum yield than the multichromophoric NDIs systems (Table 4.9) indicating efficient quenching in $R_0$-POP and $R_0$-OPE systems.

**Time-resolved fluorescence measurements.** The fluorescence decay of the $R_0$-MON measured by TCSPC can be well reproduced a by monoexponential function with a lifetime of 10.5 ns (Table 4.9) (Figure 4.25). The fluorescence up-conversion experiment reveals an

<table>
<thead>
<tr>
<th>System</th>
<th>$\Phi_{fl}$</th>
<th>$\tau_{fl1}$</th>
<th>$\tau_{fl2}$</th>
<th>$\tau_{fl3}$</th>
<th>$\tau_{fl4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_0$-MON</td>
<td>0.57</td>
<td>11.7 ps (0.08)</td>
<td>10.5 ns (0.92)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_0$-POP</td>
<td>0.005</td>
<td>1.7 ps (0.58)</td>
<td>12 ps (0.33)</td>
<td>0.24 ns (0.2)</td>
<td>9 ns (0.09)</td>
</tr>
<tr>
<td>$R_0$-OPE</td>
<td>0.01</td>
<td>0.5 ps (0.33)</td>
<td>2.9 ps (0.45)</td>
<td>20.5 ps (0.2)</td>
<td>10 ns (0.02)</td>
</tr>
</tbody>
</table>

**Table 4.9** Fluorescence quantum yields and time constants with relative amplitudes obtained from the global analysis of the fluorescence time profiles of cationic $R_0$-MON, $R_0$-POP and $R_0$-OPE in MeOH (the $R_0$-OPE was excited at 400 nm, whereas $R_0$-MON and $R_0$-POP were excited at 469 nm for TCSPC and at 500 nm for fluorescence up-conversion measurements)
additional component of the fluorescence decays of 11.7 ps, which might be attributed to vibrational and solvent relaxation of the $R_0$-MON excited state in MeOH.\textsuperscript{106}

\textbf{Figure 4.25} Normalized fluorescence time profiles of cationic $R_0$-MON, $R_0$-POP and $R_0$-OPE in MeOH at 600 nm after 470 nm excitation and best fits to data

\textbf{Figure 4.26} Intensity-normalized early fluorescence decays of cationic $R_0$-MON, $R_0$-POP and $R_0$-OPE in MeOH at 600 nm and the best multiexponential fits. The wavelength of excitation is indicated in brackets
The fluorescence decay of the $R_O$-POP and $R_O$-OPE systems is much faster than that measured for $R_O$-MON and this can be seen especially well in the fluorescence up-conversion experiment (Figure 4.26). Four exponentials have been necessary to satisfactorily reproduce the experimental data (Table 4.9). The first three components of $R_O$-OPE fluorescence decay are too fast to be resolved by TCSPC, and therefore the dynamics of $R_O$-MON and $R_O$-OPE appear almost identical in Figure 4.25. The low fluorescence quantum yield and very fast fluorescence decay of multichromophoric $R_O$-NDIs systems point to a very efficient non-radiative deactivation pathway of the LSS.

*Transient absorption measurements.* TA spectra of the $R_O$-MON consist of two positive bands with maxima around 550 and 670 nm which can be assigned to the excited state absorption of the $R_O$-MON (Figure 4.27A). The broad negative signal between 550 and 650 nm is due to bleach of the ground state and stimulated emission. In the first 30 ps, the negative band originating from the bleach vanishes in a similar way to what was observed for $R_{RR}$-MON. In parallel to this, the stimulated emission and excited state absorption signal change only insignificantly. After that, the whole spectrum slowly changes shape and decays with a lifetime which can not be reliably determined from these TA measurements. TCSPC reveals that the fluorescence decays in 10.5 ns and this time constant can be attributed to population of the triplet state. The lifetime of the $R_{RR}$-MON triplet state has been determined by flash photolysis experiment and equals to 2 µs. All lifetimes obtained from the global analysis of the time evolution of the $R_O$-MON TA signal are listed in Table 4.10.
Figure 4.27 Transient absorption spectra measured with the cationic $R_0$-MON (A), $R_0$-POP (B), $R_0$-OPE (C) after 550 nm excitation and of $R_0$-OPE (D) after 400 nm excitation in the MeOH
The TA spectra of \( R_0 \)-POP and \( R_0 \)-OPE measured after local singlet state (LSS) \( R_0 \)-NDI excitation at 550 nm are almost identical to one another but distinct from those of \( R_0 \)-MON just described (Figure 4.27B,C). During the first 10 ps the features of the local excited singlet state (LSS) absorption of the \( R_0 \)-NDI are replaced by broad positive bands, which can be assigned to the CSS absorption. The identical shape of the CSS absorption in both multichromophoric systems despite different scaffolds suggests that the latter does not

**Table 4.10** Time constants obtained from the global analysis of the TA and flash photolysis* data for \( R_0 \)-MON, \( R_0 \)-POP and \( R_0 \)-OPE in MeOH after excitation at different wavelengths (cationic \( R_0 \)-MON, \( R_0 \)-POP and \( R_0 \)-OPE were measured in MeOH, neutral \( R_0 \)-OPE in DMF). The numbers in parenthesis refer to Figure 4.52

<table>
<thead>
<tr>
<th>System</th>
<th>( \lambda_{\text{ex}} )</th>
<th>( \tau_1 )</th>
<th>( \tau_2 )</th>
<th>( \tau_3 )</th>
<th>( \tau_4 )</th>
<th>( \tau_5 )</th>
<th>( \tau_6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_0 )-MON</td>
<td>550 nm</td>
<td>1.5 ps</td>
<td>12 ps</td>
<td>( \sim 10 ) ns</td>
<td>2 ( \mu )s*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( R_0 )-POP</td>
<td>550 nm</td>
<td>1.1 ps</td>
<td>9.4 ps</td>
<td>81 ps</td>
<td>450 ps</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cationic</td>
<td>550 nm</td>
<td>1.9 ps</td>
<td>12 ps</td>
<td>95 ps</td>
<td>( \sim 1 ) ns</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( R_{B+} )-OPE</td>
<td>400 nm</td>
<td>0.2 ps</td>
<td>8 ps</td>
<td>60 ps</td>
<td>260 ps</td>
<td>( &gt;2 ) ns</td>
<td></td>
</tr>
<tr>
<td>neutral</td>
<td>550 nm</td>
<td>0.5 ps</td>
<td>3.6 ps</td>
<td>136 ps</td>
<td>500 ps</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( R_{B+} )-OPE</td>
<td>400 nm</td>
<td>0.2 ps</td>
<td>0.4 ps</td>
<td>2.4 ps</td>
<td>19 ps</td>
<td>150 ps</td>
<td>( &gt;1 ) ns</td>
</tr>
</tbody>
</table>
participate in the CS process and, thus, upon 550 nm excitation, electron transfer occurs between two $\text{RO-NDI}$ units. The subsequent observation wavelength independent decay of the total TA signal to zero can be attributed to CR to the ground state.

TA spectra of both, $\text{RO-POP}$ and $\text{RO-OPE}$ excited at 550 nm, were analyzed globally using four exponential function. The obtained lifetimes are listed in the Table 4.10 and the decay-associated difference spectra are represented in Figure 4.28.

In addition, the TA spectra of the $\text{RO-OPE}$ system after 400 nm excitation have been measured, and were found to be substantially

Figure 4.28 Decay-associated difference spectra of the cationic $\text{RO-POP}$ (A) and $\text{RO-OPE}$ (B) in MeOH excited at 550 nm
different from those measured after 550 nm excitation (Figure 4.27D). Excitation at 400 nm leads to population of the OPE-LSS and, but to a lesser extent, also the \( R_0 \)-NDI-LSS. The very early TA spectra exhibit a negative band at 400 nm which can be assigned to the OPE bleach, while the broad positive band with indented shape originates from the \( R_0 \)-NDI\(^*\) absorption. Within the first picoseconds, the intensity of the positive band and the bleach at 400 nm decays partially, and the TA signal in the 550 nm region turns negative. These changes were ascribed to the decay of the OPE-LSS population by CS between OPE and \( R_0 \)-NDI. After 1.8 ns, the bleach at 400 nm has completely vanished, whereas the bands due to \( R_0 \)-NDI\(^*\) absorption can still be observed. This points to CS between two \( R_0 \)-NDI units being operative additionally.

Global analysis of the TA spectra required the sum of not less than five exponential functions (Figure 4.29 and Table 4.10). Based on the decay-associated difference spectra, the shortest time constant, \( \tau_1 \), can be assigned to CS from the OPE-LSS to the OPE\(^*\)/\( R_0 \)-NDI\(^*\) CSS. Since a part of the 400 nm bleach recovers with the same time constant, one could conclude that a fraction of the OPE\(^*\)/\( R_0 \)-NDI\(^*\) CSS population forms the \( R_0 \)-NDI\(^*\)/\( R_0 \)-NDI\(^*\) ion pair on a similar time scale. The \( \tau_2 \) component can also be attributed to CS and partial conversion to \( R_0 \)-NDI\(^*\)/\( R_0 \)-NDI\(^*\). The decay-associated difference spectrum associated with \( \tau_3 \) does not indicate changes of the OPE signal intensity, thus it can be assigned to CS from the NDI-LSS directly populated upon 400 nm excitation to \( R_0 \)-NDI\(^*\)/\( R_0 \)-NDI\(^*\). The last two lifetimes, \( \tau_4 \) and \( \tau_5 \), can be attributed to the CR of the OPE\(^*\)/\( R_0 \)-NDI\(^*\) and \( R_0 \)-NDI\(^*\)/\( R_0 \)-NDI\(^*\) CSS respectively.
The lack of electron transfer between the RO-NDI unit and the OPE scaffold in cationic RO-OPE upon excitation at 550 nm was quiet surprising. The cyclic voltammetry reveals that the oxidation potential of OPE is 150 mV below that of RO-NDI.\textsuperscript{131} This suggests that other RO-OPE systems measured under different conditions could provide access to the OPE•+/RO-NDI•- CSS. To test this hypothesis, TA measurements of the neutral RO-OPE in $N,N$-dimethylformamide (DMF) have been performed.

The TA spectra of neutral RO-OPE in DMF after 400 nm excitation (Figure 4.30B) are very similar to those measured for cationic RO-OPE in MeOH excited at the same wavelength (Figure 4.27D). The global analysis of the TA data reveals only small difference in the CSS lifetimes (Table 4.10), which originate probably from the non-protic nature of DMF.

Contrary to the cationic RO-OPE, the TA spectra of the neutral RO-OPE in DMF measured upon RO-NDI excitation at 550 nm contain a
weak negative band at 400 nm (Figure 4.30A). This feature can be assigned to the bleach of the OPE-LSS←S₀ and points to an involvement of the OPE unit in the CS. The small amplitude of this negative band suggests a relatively poor yield of the OPE•*/NDI•*-CS.

In order to get experimental insight in the reason which induces the reorganization of the energy levels and leads to population of the CSS between R₀-NDI and OPE scaffold, TA measurements with the cationic R₀-OPE in DMF have been performed upon 550 nm excitation (Figure 4.31). Because of the poor solubility, the TA
spectra are perturbed by strong scattering of the pump light. However, the quality of the TA spectra was sufficient to distinguish two broad absorption bands between 400-550 nm and between 570-750 nm, similar to those observed for cationic RO-OPE in MeOH after 550 nm excitation.

The absence of a negative signal around 400 nm from the OPE scaffold clearly indicates that the OPE is not involved in the electron transfer process. Consequently, for cationic RO-OPE in DMF, as well as in MeOH after 550 nm excitation, the charge separation takes place between two RO-NDI units and does not depend on the solvent.

**Discussion**

The behavior of RO-NDIs is very similar to Y-NDIs and R_{βα}-NDIs systems described before. A strong decrease in the fluorescence quantum yield and fluorescence lifetime is observed for multichromophoric systems compared to the monomer. In order to
estimate the feasibility of electron transfer between two $R_0$-NDIs or between $R_0$-NDI and the scaffold, the Weller equation has been used (see Chapter 2.3). The oxidation and reduction potentials were taken from cyclic voltammetry experiments (Table 4.1), and the obtained $\Delta G_{CS}$ and $\Delta G_{CR}$ between different units in the $R_0$-POP and $R_0$-OPE constructs are listed in Table 4.11.

**Table 4.11** Energetics of the photoinduced electron transfer between different units in the multichromophoric $R_0$-NDIs systems

<table>
<thead>
<tr>
<th>Donor/Acceptor</th>
<th>$\Delta G_{CS}$/eV</th>
<th>$\Delta G_{CR}$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_0$-NDI / $R_0$-NDI</td>
<td>-0.25</td>
<td>-1.95</td>
</tr>
<tr>
<td>$R_0$-NDI / POP</td>
<td>-0.25</td>
<td>-1.95</td>
</tr>
<tr>
<td>$R_0$-NDI / OPE</td>
<td>-0.58</td>
<td>-1.80</td>
</tr>
</tbody>
</table>

For the $R_0$-POP system, the CS between two chromophoric units is energetically equivalent to CS between $R_0$-NDI and the scaffold and thus both are possible. The TA experiment confirms formation of the radical anion $R_0$-NDI$^\bullet$, while the location of the hole can not be determined unambiguously. The experimental results suggest that symmetry-breaking CS between two $R_0$-NDIs (pathway 1 in Figure 4.32) occurs simultaneously with CS between the scaffold and $R_0$-NDI (pathway 2). Additionally, electron hopping and thus exchange between these states is possible. The CR (pathway 3 and 4) happens on the subnanosecond time scale (Table 4.10).

It is interesting to note that although the triplet state is populated in the $R_0$-MON, it plays no role in the multichromophoric systems. This is because CS is much faster than ISC. Furthermore, the rate of ISC
in the CSS is not enhanced by a heavy atom, in clear contrast to the 
R_{h\text{-NDI}} systems discussed earlier.

In the R_{O\text{-OPE}} system, electron transfer between the OPE scaffold 
and R_{O\text{-NDI}} is energetically slightly more favorable than symmetry-
breaking CS and thus expected to occur preferentially. Clear 
evidence for OPE^{*+}/R_{O\text{-NDI}}^{*-} CS is present after excitation of the 
OPE chromophore (pathway 7). By contrast, exciting the R_{O\text{-NDI}} 
unit at 550 nm, only the R_{O\text{-NDI}}^{*+}/R_{O\text{-NDI}}^{*-} CSS (pathway 5) 
contributes to the TA spectra of cationic R_{O\text{-OPE}} and it also is the 
dominant contribution in the spectra of neutral R_{O\text{-OPE}}. The reason 
for the predominance of the symmetry-breaking CS in opposition to 
the free energies of these reactions most likely stems from factors like 
the solvation energy, electrostatic interaction between the charged 
moieties, coupling between proximal NDIs, kinetic effects, etc. which 
might override the small difference in oxidation potentials.

For neutral R_{O\text{-OPE}}, both pathways, 5 and 6 are operative after 550 
nm excitation, although the former prevails. That the two CSS are 
very close in energy can also be inferred from the fact that the R_{O\text{-}}
OPE•*/NDI•- CSS can populate the NDI•*/NDI•- CSS after 400 nm excitation of $R_0$-OPE (pathway 8). Finally, CR in the $R_0$-OPE systems via pathways 9 and 10 repopulate the ground state with the lifetimes listed in Table 4.10.

Conclusions

The photophysical properties of the multichromophoric $R_0$-NDIs systems with POP and OPE scaffold have been investigated in order to predict their behavior in supramolecular zipper architectures. The exchange of the bromo atom by the alkoxy group leads to an increase in $\Delta G_{CS}$ between two $R_0$-NDIs and a decrease of $\Delta G_{CS}$ between $R_0$-NDI and the scaffolds. Thus, the energy levels of the different CSS become very close.

Contrary to the expectation, the $R_0$-OPE system shows only symmetry-breaking CS upon $R_0$-NDI excitation. By TA experiments, it has been shown that minor structural changes of $R_0$-NDI (exemplified by the variation of the sidechain) result additionally in population of the OPE•*/$R_0$-NDI•- CSS.

Although the $R_0$-POP and $R_0$-OPE show photoinduced electron transfer (mainly between two $R_0$-NDIs), these systems are not favorable building blocks for the n/p-heterojunctions architecture, since they do not provide the required spatial separation of the charges (electron on the NDI and hole on the scaffold).152, 174
4.4 Green PDI artificial photosystems

Similar to NDIs, perylene diimides (PDI) systems attract a lot of attention due to their outstanding photochemical properties.\textsuperscript{175-178} Introducing substituents on the diimide core makes it possible to tune the photophysical properties of the molecule namely the energy of their HOMO and LUMO levels, their absorption and fluorescence band and the fluorescence quantum yield.\textsuperscript{179} In many cases, the fluorescence quantum yield of core-substituted PDIs is almost unity and accompanied by a long lifetime of the singlet excited state.

The $G$-PDI with pyrrolidin substituents in 1 and 7 position (Figure 4.53) has properties that are remarkably similar to those of chlorophyll $a$.\textsuperscript{180} Wasielewski and co-workers extensively studied this system and showed its promising properties for photovoltaics.\textsuperscript{181, 182} In particular, the photoexcitation of the cofacial dimer with two $G$-PDIs linked via the imide groups through a xanthene spacer leads to

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.33.png}
\caption{Molecular structure of the $G$-MON and $G$-POP ($R = G$-MON)}
\end{figure}
photoinduced symmetry-breaking electron transfer between two chromophoric units.\textsuperscript{182}

In this chapter, the photophysical properties of a multichromophoric system consisting of \( G \)-PDIs covalently attached to a POP scaffold (Figure 4.33) will be presented and compared with the NDIs systems shown above.

\textbf{Results}

\textit{Steady-state measurements.} The absorption spectra of \( G \)-MON and \( G \)-POP are depicted in the Figure 4.34. The lowest energy broad band originates from the \( S_1 \leftarrow S_0 \) transition polarized along the long molecular axis and has a strong charge transfer character according to Wasielewski and co-workers.\textsuperscript{180} For \( G \)-MON, the shape of this band strongly depends on the concentration of the dye in solution. For low concentrations, the maximum is located at 700 nm while at

![Figure 4.34](image)

\textbf{Figure 4.34} Intensity-normalized absorption and fluorescence spectra of the \( G \)-MON and \( G \)-POP in MeOH
Chapter 4

this wavelength only a shoulder is observed in concentrated samples. At higher concentrations, the maximum is found 870 cm$^{-1}$ further to the blue. This speaks in favor of aggregate formation in MeOH. The second band with a maximum at 440 nm does not depend on the chromophore concentration. The $G$-POP system’s absorption bands are substantially broader than those of the $G$-MON and the maximum is found at 660 nm, like for the concentrated $G$-MON samples.

The fluorescence spectra of $G$-MON and $G$-POP have identical shape and peak around 770 nm. A fluorescence quantum yield of 0.005 and 0.0006 was determined for micromolar $G$-MON and $G$-POP solutions in MeOH. Previously, Wasielewski and co-workers found that $G$-MON has a fluorescence quantum yield of 0.35 and 0.28 in toluene and 2-methyltetrahydrofuran, respectively. The much smaller fluorescence quantum yield observed here points to efficient exciton coupling of the dyes in MeOH solution (see Chapter 2.2).

*Time-resolved fluorescence measurements.* The fluorescence decay of $G$-MON and $G$-POP in MeOH after 440 nm excitation have been registered at 700 nm (*Figure 4.35*). A monoexponential function convolved with a Gaussian function has been used for the mathematical analysis of $G$-POP fluorescence decay. The determined lifetime of 0.2 ps reveals ultrafast decay of fluorescence signal. For the $G$-MON, the experimental data can be well reproduced by a biexponential function with 0.15 and 2.5 ps lifetimes. However, due to the weak fluorescence signal, the signal to noise ratio for both investigated systems was very low, and the obtained lifetimes should be considered as approximate. The ultrafast fluorescence decays in both the systems are in agreement with the very small quantum yield
determined by steady-state experiments and indicate the presence of a very efficient non-radiative deactivation pathway.

**Transient absorption measurements.** TA spectra of G-MON and G-POP in MeOH measured upon 700 nm excitation are represented in Figure 4.36. A concentration of 0.1 mM of G-MON was used for the TA experiment in order to have the same conditions as for fluorescence up-conversion measurements. It is important to mention

**Figure 4.35** Fluorescence decay of the G-MON and G-POP at 700 nm in MeOH after 440 nm excitation

<table>
<thead>
<tr>
<th>System</th>
<th>$\tau_1$</th>
<th>$\tau_2$</th>
<th>$\tau_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-MON</td>
<td>0.3 ps</td>
<td>5.2 ps</td>
<td>650 ps</td>
</tr>
<tr>
<td>G-POP</td>
<td>0.3 ps</td>
<td>6.8 ps</td>
<td>270 ps</td>
</tr>
</tbody>
</table>

**Table 4.12** Time constants obtained from the global analysis of the TA data of G-MON and G-POP in the MeOH after 700 nm excitation
that at this concentration the steady-state spectrum reveals the presence of aggregated G-MON. The TA spectra of G-MON at early time delays consists of a broad negative signal with two pronounced maxima at 650 and 700 nm, which originate from the bleach of the ground state absorption of free and aggregated G-MON (Figure 4.36A). Another negative band with maximum at 440 nm has the same origin. Several positive bands are located above 750 nm, below 410 nm and in region between 460 and 560 nm. In the first half a picosecond after excitation an intensification of the positive and the

Figure 4.36 TA spectra at different time delays of the G-MON (A) and G-POP (B) in MeOH after 750 nm excitation
negative bands is observed. During the following ca. 10 ps, the positive band above 750 nm vanishes and the bleach and positive band between 460 and 560 nm strongly changes shape. Finally, the total intensity of the TA signal decays to zero.

The dynamics of the TA signal at different wavelength were analyzed globally by a sum of three exponential functions (Figure 4.37A and Table 4.12). Based on the decay-associated difference spectra, the fastest lifetime of 0.3 ps can be assigned to the population of the CSS between two G-MON dyes in the aggregate (see below). The lifetime of 5.2 ps originates from CR. The decay-associated difference spectra

**Figure 4.37** Decay-associated difference spectra of G-MON (A) and G-POP (B) in MeOH. Note that the red and green spectra are not mirror-images of each other
associated with the 630 ps component does not show absorption above 750 nm, the maximum of the negative bleach signal is at 700 nm and the positive band between 460 and 560 nm is broader than that of the CSS. Thus, it can be attributed to the excited state absorption of free G-MON.

TA spectra at different time delays of G-POP in MeOH are shown in Figure 4.36B. Contrary to G-MON, the spectra of the multichromophoric system consist of a negative signal with a maximum at 650 nm and the second peak at 700 nm, which is not very pronounced. However, the positive bands have the same shape as the early TA spectra of G-MON. Global analysis of the TA dynamics, reveals an ultrafast rising component of 0.3 ps, which can be ascribed to symmetry-breaking CS between two G-PDI units in the G-POP. The subsequent decay of the TA signal is simultaneous over the observation window and can be reproduced by two lifetimes of 6.8 and 270 ps. Unlike G-MON, the decay-associated difference spectrum associated with the longest lifetime has positive contributions above 750 nm, and can be as well attributed to a CR process.

Discussion

Introducing two pyrrolidin substituents in the bay positions of PDI core leads to a shift of the absorption bands to the near-infrared region. To estimate the energy levels of the possible CSS, the Weller equation has been used (see Chapter 2.3) with $E_{ox1}(G$-PDI) = +0.68 V and $E_{red1}(G$-PDI) = -0.76 V (Table 4.13). The obtained $\Delta G_{CS}$ reveals that CS between two G-PDI units is energetically preferable to CS between G-PDI and the scaffold.
The steady-state, time-resolved fluorescence and TA measurements indicate ultrafast population of the $G$-$PDI^*/G$-$PDI^•$ CSS in both, $G$-MON and $G$-POP with rate constant of (0.3 ps)$^{-1}$. This value and the shape of the CSS are in excelled agreement with those published earlier (Figure 4.38).\(^{182}\) The main feature of the symmetry-breaking CSS between two G-PDIs, the absorption band at 750 nm, has been observed in both, $G$-MON and $G$-POP systems (Figure 4.36A,B). The strongly ragged shape of this band is due to technical peculiarities of the TA set-up and is artificial.

**Table 4.13** Energetics of the photoinduced electron transfer between different units in the multichromophoric $G$-PDIs systems

<table>
<thead>
<tr>
<th>Donor/Acceptor</th>
<th>$\Delta G_{CS}$/eV</th>
<th>$\Delta G_{CR}$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G$-$PDI / G$-$PDI$</td>
<td>-0.31</td>
<td>-1.39</td>
</tr>
<tr>
<td>$G$-$PDI / POP$</td>
<td>-0.04</td>
<td>-1.66</td>
</tr>
</tbody>
</table>

Figure 4.38 TA spectra of $G$-MON (---) and its cofacial dimer (----) in toluene after 400 nm excitation. The inset shows the simulated TA spectrum of the $G$-$PDI^*/G$-$PDI^•$ CSS based on spectroelectrochemistry\(^{182}\)
The subpicosecond photoinduced charge separation in the \( G \)-MON system occurs between two dyes which form aggregates and are thus located in close proximity to each other. Aggregate formation in MeOH is evident by the change of the absorption spectrum and strong quenching of the fluorescence. The CR can be described with one exponential with a 5.2 ps lifetime, which is much shorter than those found for the cofacial dimers.\(^{182}\) This difference can be explained by variety in the samples structure (distance and relative orientation) and the solvent. Additionally, the TA spectra of \( G \)-MON reveal the features of excited state absorption of the free dye which as well in good agreement with those reported.\(^{182}\) The global analysis reveals that the excited state of the \( G \)-MON decays with 630 ps. From the \( S_1 \) state energy and the energy gap law using Siebrand’s parameters (see Chapter 2.2), a non-radiative rate constant of \((500 \text{ ps})^{-1}\) is calculated for \( G \)-MON, reasonably close to the 630 ps determined experimentally. The reason for the absence of this lifetime in the time-resolved fluorescence decay, however, is not clear. One of the possible explanations can be that due to the weak fluorescence intensity and the poor signal to noise ratio, this contribution to the fluorescence decay was missed.

The decay of the CSS in the \( G \)-POP system is biexponential. The short lifetime of 6.8 ps is very close to the one found in \( G \)-MON and can be attributed to CR between two PDI units located in close proximity to each other. The decay-associated difference spectrum associated with the longer lifetime of 270 ps has a slightly different shape in the region above 750 compared to the 6.8 ps component. It can be assigned to the decay of the CSS between \( G \)-PDI and POP scaffold. However, the lifetime of this state should not be longer than those attributed to CSS between two \( G \)-PDI, since it should be followed by hole hopping from POP to \( G \)-PDI. Another and more
probable possibility might be that this lifetime corresponds to the decay of the CSS between two G-PDI units which are located at large distance from each other, in an extreme case on different ends of the scaffold. The biexponential decay can reflect a wide distribution of distances between the charges.

Conclusions

Similar to the NDI systems shown above, the G-PDI monomeric and multichromophoric systems undergo photoinduced electron transfer. The investigation reveals that the CS occurs between to G-PDI units. The population of this CSS is ultrafast and shows good agreement with CS in the cofacial G-PDI dimer measured previously. The CR is as well very fast with an inverse rate constant of approximately 6 ps for both, G-MON and G-POP. However, G-POP has an additional lifetime of 270 ps with a very small amplitude, which was attributed to the decay of the CSS between either G-PDI and scaffold, or between two G-PDIs located far from each other (for example on different ends of the POP).

The short-lived CSS is not optimal for photovoltaic applications, since the efficiency of the devices depends on the splitting efficiency between electron and hole. Moreover, the G-PDI systems with a POP scaffold does not reveal the spatial distribution of the charges necessary for n/p-heterojunctions. Thus, a different scaffold is necessary in order to use G-PDI for this type of artificial photosystems.
General conclusions

The photophysical properties of several multichromophoric systems have been investigated in order to explore their potential for photovoltaic applications. The choice of chromophores was dictated by the aim to build a directed redox gradient via fine tuning of the HOMO levels. Additionally, the presented chromophores absorb in different spectral regions to better match the spectrum of sunlight and hence improve the harvesting properties. They have a planar structure and tend to self-organize. These supramolecular architectures present one of the few air-stable molecular n-semiconductors available.

In order to understand the behavior of the multichromophoric systems, the photophysical properties of the chromophores themselves have been characterized. All of them, with exception of G-PDI, show nanosecond $S_1$ state lifetimes and fair fluorescence quantum yields. For the red and pink monomeric NDI an additional long-lived triplet state population has been established.

In the multichromophoric systems, photoexcitation leads to electron transfer, the nature of which strongly depends on the chromophore as well as on the system’s scaffold. In general, the CS is fast or even ultrafast (Table 4.14) and involves the backbone, which means that the electron and hole are separated in distinct channels, as needed in the $n/p$-heterojunctions. In addition, symmetry-breaking CSS between two NDIs or PDIs is evident from the TA spectra in some cases.

In case of the $R_0$-NDI system, the influence of the sidechain on the CS process was shown by exchange of a cationic to a neutral protecting group. Excitation of the NDI in the neutral $R_0$-OPE leads
to CS between the NDI and the scaffold while in the cationic system it leads solely to $R_0$-NDI••$/R_0$-NDI•• ion pairs. It should be reminded that the steady-state spectra and redox potentials are unaltered by the modification of the sidechain. The cationic $R_0$-NDI is also distinct from the other NDIs in that it shows excitation wavelength dependence of the CS: Excitation of the OPE leads to ET from the backbone to the $R_0$-NDI, whereas excitation of the $R_0$-NDI itself leads to symmetry breaking CSS. The $R_{Br}$-OPE does not show this feature presumably because the free energy of the reaction including the OPE is much bigger in this case. Indeed, in the $R_0$-POP system charge transfer to the backbone and to another NDI are according to the Weller equation thermodynamically indifferent.

The PDI system shows only symmetry breaking CS owing to the extremely efficient coupling between the PDI units that could be evidence from the study of the dimer.

It is important to mention that the driving force for the different possible CS processes calculated on basis of the Weller equation is not sufficient to predict with accuracy the observations. For example, in $R_0$-OPE system the CSS between $R_0$-NDI••$/OPE•$ is energetically below the $R_0$-NDI••$/R_0$-NDI•• CSS. However experimental data show, that only the $R_0$-NDI••$/R_0$-NDI•• CSS is populated in cationic $R_0$-OPE. The dynamic behavior is not directly governed by the driving force, which is a thermodynamic property. Hence, the functionality of a given electron donor/acceptor system cannot be predicted from the redox potentials and ultrafast spectroscopy is indispensable.

In general, the lifetime of the CSS is of the order of nanoseconds with an extreme of 2.5 µs for the $R_{Br}$ system (Table 4.15). This longevity
can be explained by the triplet character of the CSS. The complex TA
dynamics shows the involvement of triplet states and a cascade of CS
and CR processes that finally lead to the population of the triplet R-
NDI$^\bullet$/POP$^{\bullet\bullet}$ state.

Based on the obtained results, it is possible to conclude that the
systems presented in this chapter have outstanding properties which
can be further explored in the field of the photovoltaic. Most
favorable qualities are found for $Y$- and $R_B$-NDI multichromophoric
systems.
Table 4.14 Summary of the CS time constants obtained from time-resolved fluorescence and TA measurements (the excited unit is indicated in parentheses)

<table>
<thead>
<tr>
<th>System</th>
<th>λ_{ex}</th>
<th>τ1</th>
<th>τ2</th>
<th>τ3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-POP</td>
<td>400 nm</td>
<td>4.1 ps</td>
<td>37 ps</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Y-NDI)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R_{Br}-POP</td>
<td>520 nm</td>
<td>3.7 ps</td>
<td>26 ps</td>
<td>170 ps</td>
</tr>
<tr>
<td></td>
<td>(R_{Br}-NDI)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R_{Br}-OPE</td>
<td>520 nm</td>
<td>0.9 ps</td>
<td>7 ps</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(R_{Br}-NDI)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>500 nm</td>
<td>0.11 ps</td>
<td>1.35 ps</td>
<td>7.2 ps</td>
</tr>
<tr>
<td></td>
<td>(OPE)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R_{O}-POP</td>
<td>550 nm</td>
<td>1.7 ps</td>
<td>12 ps</td>
<td>240 ps</td>
</tr>
<tr>
<td></td>
<td>(R_{O}-POP)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R_{O}-OPE</td>
<td>550 nm</td>
<td>1.9 ps</td>
<td>12 ps</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(R_{O}-POP)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>400 nm</td>
<td>0.5 ps</td>
<td>2.9 ps</td>
<td>20.5 ps</td>
</tr>
<tr>
<td></td>
<td>(OPE)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G-POP</td>
<td>750 nm</td>
<td>0.3 ps</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(G-PDI)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4.15 Summary of the time constant of CR obtained from TA measurements (the excited unit is indicated in parentheses)

<table>
<thead>
<tr>
<th>System</th>
<th>$\lambda_{ex}$</th>
<th>$\tau_1$</th>
<th>$\tau_2$</th>
<th>$\tau_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-POP</td>
<td>400 nm (Y-NDI)</td>
<td>190 ps</td>
<td>&gt; 3 ns</td>
<td></td>
</tr>
<tr>
<td>RBr-POP</td>
<td>520 nm (RBr-NDI)</td>
<td>175 ps</td>
<td>2.5 µs</td>
<td></td>
</tr>
<tr>
<td>RBr-OPE</td>
<td>520 nm (RBr-NDI)</td>
<td>71 ps</td>
<td>270 ps</td>
<td>&gt; 3 ns</td>
</tr>
<tr>
<td></td>
<td>400 nm (OPE)</td>
<td>68 ps</td>
<td>217 ps</td>
<td>&gt; 3 ns</td>
</tr>
<tr>
<td>RO-POP</td>
<td>550 nm (RO-POP)</td>
<td>81 ps</td>
<td>450 ps</td>
<td></td>
</tr>
<tr>
<td>R\text{O}-OPE</td>
<td>550 nm (R\text{O}-POP)</td>
<td>93 ps</td>
<td>1 ns</td>
<td></td>
</tr>
<tr>
<td></td>
<td>400 nm (OPE)</td>
<td>260 ps</td>
<td>&gt; 2 ns</td>
<td></td>
</tr>
<tr>
<td>G-POP</td>
<td>750 nm (G-PDI)</td>
<td>6.8 ps</td>
<td>270 ps</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 5

Self-organized photosystems

The history of photovoltaics begun with the discovery made by W. Adams and R. Day in 1876, which was considered to be “scientifically of the most far-reaching importance.” Experimentally, they showed the formation of an electrical current in a selenium sample simply by exposing it to light. The efficiency of the light conversion was very small, but it revealed that sun light can be converted into electricity by a solid material without heating or moving parts.

The demonstration of the first silicon-based single p/n-junction solar cell, which had a light conversion efficiency of 6 %, was a breakthrough discovery in the field of photovoltaics. The device was designed in such a way that electron rich (n) and electron poor
(p) materials of doped silicon were in contact with each other. By photoexcitation, the electrons of the semiconductor could reach the conduction band and move freely, creating a photocurrent. This and other cells made of inorganic semiconducting materials (for example gallium arsenide, cadmium telluride, copper indium, etc.) belong to the class of inorganic solar cells which are currently commercialized and widely used.\textsuperscript{186} However, single layer $p/n$-junction solar cells have a limited efficiency, since just a narrow part of the solar spectrum can be used in the energy conversion and the rest is lost in heat. Shockley and Queisser estimated that for a semiconductor with a 1.1 eV band gap (the band gap of silicon), a maximal efficiency of 30\% can be achieved at room temperature.\textsuperscript{187} Introducing additional layers with a different band gap might slightly improve the theoretically possible efficiency, and so a two-layer cell can reach 42\%, a three-layer cell 49\%, and a theoretical infinity-layer cell 68\% efficiency.\textsuperscript{188} Practically, the highest efficiency was shown for a triple-junction solar cell exposed to concentrated light of 240 suns (one sun is about the amount of light that typically hits Earth on a sunny day) which reached 40.7\%.\textsuperscript{189, 190} At the same time, the fabrication of this multi-junction cell is extremely costly and, thus, economically unattractive.\textsuperscript{144}

In parallel to inorganic solar cells, the field of organic photovoltaics has been actively developed.\textsuperscript{191-193} The main difference between the organic semiconductors and their inorganic counterparts lies in the nature of the optically excited state. Photoexcitation of the organic semiconductors does not lead directly to electron/hole separation, but rather to formation of an exciton where the electron is located on the LUMO, and hole on the HOMO of the same molecule. The exciton binding energy is typically around 500 meV, whereas it is just a few meV in the case of inorganic semiconductors.\textsuperscript{194} One of the main
challenges in organic photovoltaics is to dissociate the exciton before it recombines back to the ground state. In 1986, Tang and co-workers introduced the first organic bilayer heterojunction solar cell (Figure 5.1A), which consisted of two organic semiconductor layers with electron-donor and electron-acceptor character, respectively.\(^{195}\) The photoinduced electron transfer process, which occurs at the interface between these two layers, lead to exciton dissociation, i.e. spatial separation of the charges.

Since an exciton dissociation proceeds just at the interface between donor and acceptor semiconductors, the concept of bulk p/n-heterojunction (BHJ) (Figure 5.1B) has been proposed. In this type of organic solar cells, the donor and acceptor materials can be either co-deposited\(^{196}\) or blended\(^{197, 198}\) together. An increase of the donor-acceptor contact area greatly improves the exciton dissociation yield. However, the morphology of BHJ cells leads to a high probability of the separated electron to meet a hole before it reaches the electrode and this causes a significant limitation of the device.

Charge transport and exciton diffusion play a key role in the solar cell performance. In order to improved both these properties, the supramolecular p/n-heterojunction (SHJ) approach has been proposed (Figure 5.1C). In this type of organic photovoltaics, donor

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**Figure 5.1** Schematical representation of the bilayer heterojunction (A), bulk n/p-heterojunction (B) and supramolecular n/p-heterojunction (C) organic solar cells. D: donor, A: acceptor
and acceptor are organized on a molecular level in such a way that electron and hole have separate transport channels. Over the last years, numerous SHJs have been reported. Most of these supramolecular architectures consist of one type of donor and one type of acceptor assembled with high precision by π-stacking, hydrogen bonds or electrostatic interactions into perpendicular or parallel lines with respect to the electrode.

The charge mobility in the SHJ architecture can be further improved by introducing an antiparallel redox gradient, which guides electrons and holes in opposite directions. For example, numerous covalently linked donor-acceptor triads, tetrads and pentads have been synthesized for realizing multi-step electron-transfer processes. The aim is to achieve highly efficient population of a long-lived charge separation state (CSS). Figure 5.2A sketches how the fullerene-porphyrin-ferrocene triad 1 and boron dipyrrin thiol 2 self-assemble as monolayer on a gold surface. Excitation of 2 leads to efficient energy transfer from 2 to the porphyrin unit of 1. This is followed by electron transfer from the excited porphyrin to the fullerene and then from ferrocene to the porphyrin, leaving the electron and hole at the very ends of the triad, separated far from each other. Consequently, this CSS has a lifetime of several microseconds.

Majima and co-workers showed long-range electron transport through a modified DNA assembled on a gold surface (Figure 5.2B). The redox gradient in this system was formed by the strong electron acceptor naphthaleneimide (NI) covalently attached to the DNA, and by the adenine (A) and guanine (G) bases. Photoexcitation of NI leads to population of the NI•/A•• CSS. Subsequent electron transfer with the G bases and eventually the Au
Figure 5.2  Schematic representation of selected architectures of supramolecular p/n-heterojunction solar cells with a redox gradient (see text for details)\textsuperscript{152}
electrode leads to a cathodic photocurrent. Hole mobility along the DNA sequence stems from electron hopping among the A and G bases, as indicated in Figure 5.2B.

The paramount importance of the redox gradient for the overall SHJ efficiency has also been proved by Guldi and co-workers. They introduced a supramolecular assembly composed of four photoactive layers, namely anionic fullerene dendrimers 3, cationic porphyrins 4, anionic zinc porphyrins 5 and cationic ferrocenes 6 on an ITO surface (Figure 5.2C). The final ITO-3-4-5-6 system was 100 times more active than the system consisting of just two layers of 3 and 4. The direction of the redox gradient clearly was a key feature since the efficiency of the light conversion was worse in situations where the order of the deposited layers was inverted.

An elegant approach to assemble photoactive molecules according to their redox potential in highly organized layers via a coordination network has been suggested by Thompson and co-workers. Layers of the dithiolated zinc porphyrin 7, dithiolated porphyrin 8 and diphosphonated viologen 9 were self-assembled on top of each other via coordination to copper 12, zirconium 11 and the link 10 with thiol and a phosphonate groups (Figure 5.2D). Upon photoexcitation of porphyrin units 7 and 8, CS occurs with the hole located on 7 and the electron on 9. The complete cascade shows an outstanding charge-separation quantum yield of 4%. This value was much smaller for systems consisting of just two layers (7 and 9 or 8 and 9).

In all the systems introduced above, the chromophores were chosen in such a way that their optical energy gaps would be different. An additional strong enhancement of the light conversion in the SHJ architecture is thereby attained since the set of functional chromophores absorb light all over the visible spectrum. By this, the
losses of sun energy are minimized and the total device efficiency improved.

Matile and co-workers were the first who reported a multicolor SHJ with a redox gradient on a conductive surface. P-oligophenyl (POP) and oligophenylethynyl (OPE) rods with covalently attached core-substituted NDIs were self-organized layer-by-layer into a multicomponent zipper assembly on gold by π-stacking, hydrogen bonds and electrostatic interactions between the chromophores (Figure 5.5). In this structure, electron conducting NDI stacks were aligned parallel to the hole conducting rods in agreement with the idea lying behind the SHJ approach. The redox gradient in the electron transporting channels was formed by the \( N \)-NDI, \( Y \)-NDI and \( R_{Br} \)-NDI sequence, which harvests light in the region between...
350 and 580 nm. OPE and POP rods create a minimalist redox gradient in the hole transporting channel. The Au-$N^\ominus$-($Y^\ast$-$Y^\ominus$)$_m$-($R_{Br^\ast}$-$R_{Br^\ominus}$)$_n$- architecture with $N$-NDI and $Y$-NDI attached to the POP and $R_{Br^\ast}$-NDI to the OPE scaffold was shown to generate more photocurrent than a unicolored $Y$ or $R_{Br^\ast}$-zipper architecture.\textsuperscript{129, 130, 208} Also, the same architecture but without redox gradient in the hole transporting channel (the $N$-NDI, $Y$-NDI and $R_{Br^\ast}$-NDI was linked to the POP rod) showed a reduced photocurrent generation, indicating the dramatic importance of both, hole and electron redox gradient for efficient charge separation over a long distance.\textsuperscript{153}

The zipper assembly of the core-substituent NDIs attached to the scaffold is a very powerful way to construct multicolor SHJ with a redox gradient. However, the amount of synthetic work and time necessary for realization of this architecture makes it economically unprofitable.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.4.png}
\caption{Schematical representation of the multicolor SOSIP architecture with redox gradient on the ITO conductive surface constructed from $Y$-NDI (yellow), $R$-NDI (red) and $B$-NDI (blue) building blocks\textsuperscript{209}}
\end{figure}
As alternative to zipper architecture, Matile and co-workers suggested another approach to build oriented SHJ incorporating an antiparallel redox gradient from core-substituent NDIs. Self-organizing surface-initiated polymerization (SOSIP) allowed to assemble monomeric NDIs in well-organized channels on the transparent conductive indium tin oxide (ITO) surface. The ring-opening disulfide exchange links NDIs units covalently in a controlled, fast and simple way. As example Figure 5.4 represents SOSIP architecture with redox gradient in the channel which suppose to transport electrons and holes in different directions.\textsuperscript{209, 210} Constructing rods containing different NDIs, will allow to have SOSIPs with separate channels for electron and hole transport.

In this chapter, the ultrafast excited-state dynamics in three different SOSIP architectures will be presented. The aim is to detect photoinduced electron transfer in these systems and understand its origin. First, the photophysics of the monochrome yellow SOSIP assembled on ITO from Y-NDI will be discussed. After that, the results obtained with more sophisticated SOSIP architectures constructed from various NDIs will be shown.
5.1 Yellow SOSIP architecture

The \( Y\)-SOSIP architecture has been designed and assembled in the group of Prof. Matile. \( Y\)-NDI propagators were self-organized by ring-opening surface-initiated polymerization on top of non-substituted \( N\)-NDI initiators deposited on ITO (Figure 5.5).\(^{209}\) In addition, a disorganized solution-polymerized \( Y\)-SOSIP’ architecture has been realized on ITO with the same type of \( Y\)-NDI propagator (\( Y\)-NDIp) in order to compare its properties with the \( Y\)-SOSIP architecture. Electrochemical experiments revealed that upon photoexcitation, the \( Y\)-SOSIP architecture generates about 5 times more photocurrent than the disorganized \( Y\)-SOSIP’ system. That speaks in favor of a strong influence of the fluorophore organization

![Figure 5.5](image)

**Figure 5.5** Structure of \( Y\)-NDIp (A), \( Y\)-NDIss (B) and of the \( Y\)-SOSIP architecture (C) deposited on ITO surface (Boc: \( t\)-Butoxycarbonyl)
on the overall efficiency of the SHJ device. To better understand the photoinduced processes in Y-SOSIP and Y-SOSIP’, ultrafast spectroscopy has been applied to them and to the monomeric disulfide Y-NDIss in MeOH (Figure 5.5).

Results and Discussion

Steady-state measurements. The absorption spectra of Y-SOSIP on ITO consist of a band with a maximum at 477 nm which corresponds to the S₁←S₀ Y-NDI transition (Figure 5.6). This band is much broader, the maximum 400 cm⁻¹ red shifted and it has a pronounced tail in comparison with Y-NDIss in MeOH as typical for polymers.²¹¹ The second band around 360 nm is due to a π-π* transition and as well subject of strong broadening. The observed changes arise from the interaction between the stacked Y-NDI chromophores. Also, in Y-SOSIP the NDIss units are not surrounded by solvent molecules.

Figure 5.6 Normalized absorption and fluorescence spectra of the Y-SOSIP on ITO and Y-NDIss in MeOH
but embedded in the polymer which has a different refractive index. This might contribute to the spectral shifts. The absorbance of the investigated SOSIP architecture at 477 nm was around 0.2, corresponding to the organization of approximately 170 $Y$-NDI layers.\textsuperscript{209}

As has been mentioned earlier, $Y$-SOSIP and $Y$-SOSIP' were assembled on a thin ITO plate and it was not possible to measure their fluorescence spectra or to determine the fluorescence quantum yield with our set-ups.

\textit{Time-resolved fluorescence measurements.} The early fluorescence dynamics of $Y$-SOSIP and $Y$-SOSIP' after 400 nm excitation are displayed in Figure 5.7. Due to a more pronounced surface inhomogeneity of the disorganized $Y$-SOSIP', its fluorescence decay is more noisy than that of $Y$-SOSIP. A three exponential function convolved with a Gaussian function was used to reproduce the time
trace of Y-SOSIP. The obtained lifetimes are listed in Table 5.1. The time profile of Y-SOSIP' has not been analyzed quantitatively, however, it overlaps well with that measured with Y-SOSIP (Figure 5.7), pointing to very similar fluorescence dynamics. All three fluorescence lifetimes are in a good agreement with those found by TA measurement (see below) and can be attributed to the decay of the locally excited-state population.

The fluorescence dynamics of Y-NDIss in MeOH solution has been measured by fluorescence up-conversion and TCSPC. Analysis of the fluorescence decay reveals three lifetimes of 1.3 ps, 87 ps and 1.4 ns. They coincide well with those found by TA. The fastest component corresponds to a rise with an amplitude of 0.10, the others to the fluorescence decay with relative amplitudes of 0.21 and 0.79, respectively (Table 5.1). The faster decay component, $\tau_{fl2}$, does not have a correspondence in the fluorescence decay of Y-MON (see Table 4.2). It might be assigned to vibrational cooling, since the fluorophore was excited with excess energy but this process is usually significantly faster than 80 ps in MeOH solution. Alternatively, it might reflect the excited state proton transfer, but in this case it

**Table 5.1** Fluorescence quantum yields and lifetimes with relative amplitudes obtained from analysis of the fluorescence time profile measured with Y-NDIss in MeOH and Y-SOSIP on ITO upon 400 nm excitation

<table>
<thead>
<tr>
<th>System</th>
<th>$\Phi_{fl}$</th>
<th>$\tau_{fl1}$</th>
<th>$\tau_{fl2}$</th>
<th>$\tau_{fl3}$</th>
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</thead>
<tbody>
<tr>
<td>Y-NDIss</td>
<td>0.05</td>
<td>1.3 ps</td>
<td>87 ps</td>
<td>1.4 ns</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-0.1)</td>
<td>(0.21)</td>
<td>(0.79)</td>
</tr>
<tr>
<td>Y-SOSIP</td>
<td>0.8 ps</td>
<td>6.3 ps</td>
<td>55 ps</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0.34)</td>
<td>(0.61)</td>
<td>(0.05)</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.8 A - TA spectra measured with Y-NDIss in MeOH at various time delays after 400 nm excitation, B - decay-associated difference spectra obtained from a global fit analysis

Figure 5.9 A - TA spectra measured with Y-SOSIP on ITO at various time delays after 400 nm excitation, B - decay-associated difference spectra obtained from a global fit analysis
should be also present in \( Y \)-MON (see Chapter 4.1). Comparison of the \( Y \)-MON and \( Y \)-NDI\(\text{s} \) structure shows that the main difference lies in the disulfide group and \( \tau_{fl2} \) might be associated with cleavage of the S-S bond. However, such a chemical modification should not effect the fluorescent part of \( Y \)-NDI\(\text{s} \). Finally, it might be a feature of \( Y \)-NDI\(\text{s} \) aggregates, but no evidence for aggregation has been found in steady-state experiments.

The slowest fluorescence lifetime, \( \tau_{fl3} \), is shorter in comparison with that found for \( Y \)-MON (2.1 ns, see Chapter 4.1). The fluorescence quantum yield is as well smaller for \( Y \)-NDI\(\text{s} \) than for \( Y \)-MON. These changes in the photophysical properties probably originate from the different sidechains.

**Transient absorption measurements.** TA spectra measured at different time delays after 400 nm excitation of \( Y \)-NDI\(\text{s} \) in MeOH are depicted in Figure 5.8A. At early time delays, the spectra consist of a positive band centered around 550 nm, which can be attributed to excited state absorption and a negative band at 480 nm, that can be assigned to the bleach and stimulated emission. The decay of the initial excited state absorption band is accompanied by a rise of another positive band at 400 nm.

The dynamics of the TA signal measured with \( Y \)-NDI\(\text{s} \) at different wavelengths were analyzed globally using a three exponential function. The obtained decay-associated difference spectra are shown in Figure 5.8B. The first lifetime, \( \tau_1 \), represents early spectral dynamics due to solvent and vibrational relaxation (Table 5.2). The origin of \( \tau_2 \) is probably the same as for \( \tau_{fl2} \) since this lifetimes are very similar and is unclear. On a longer time scale, the bands originating from absorption of the \( S_1 \) state and from stimulated emission decay with \( \tau_3 \) in agreement with the time-resolved fluorescence. This last
lifetime was assigned to the lifetime of the $S_1$ state. Since $Y$-NDIss does not undergo any photochemical reaction and the ground-state bleach decays only partially with $\tau_3$, the positive bands present around 400 nm and above 500 nm at long pump probe time delays must originate from triplet-triplet absorption of the lowest triplet state. However, the triplet state does not play a relevant role in the photophysics of the SOSIP architecture as will be discussed later.

The TA spectra of $Y$-SOSIP on ITO were measured upon 400 nm excitation (Figure 5.9A). The spectra contain a broad positive band between 480 and 760 nm with a maximum at 550 nm and a negative band around 470 nm. Already after the first few picoseconds, the shape of the positive band with a maximum at 550 nm changes and the negative band vanishes. This points to the population of an intermediate state, which decays thereafter on a nanosecond time scale.

The TA time profiles of $Y$-SOSIP at different wavelengths were analyzed globally using a four exponential function. The decay-associated difference spectra are presented in Figure 5.9B and the lifetimes are listed in Table 5.2. The spectra associated with the first two time constants, $\tau_1$ and $\tau_2$, are similar to each other, showing a

Table 5.2 Time constants obtained from the global fit analysis of the TA data for $Y$-SOSIP and $Y$-SOSIP’ architecture assembled on ITO

<table>
<thead>
<tr>
<th>System</th>
<th>$\tau_1$</th>
<th>$\tau_2$</th>
<th>$\tau_3$</th>
<th>$\tau_4$</th>
</tr>
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<tr>
<td>$Y$-NDIss</td>
<td>4.8 ps</td>
<td>70 ps</td>
<td>1.3 ns</td>
<td></td>
</tr>
<tr>
<td>$Y$-SOSIP</td>
<td>0.7 ps</td>
<td>8.3 ps</td>
<td>74 ps</td>
<td>&gt; 2 ns</td>
</tr>
<tr>
<td>$Y$-SOSIP’</td>
<td>1 ps</td>
<td>10 ps</td>
<td>86 ps</td>
<td>&gt; 2 ns</td>
</tr>
</tbody>
</table>

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maximum at 550 nm due to absorption of the locally excited state, and a minimum at 480 due to stimulated emission. These two time constants coincide very well with those found by time-resolved fluorescence and can thus be ascribed to the decay of the locally excited state upon charge separation (CS).

The decay-associated difference spectra associated with the two longest time constants, $\tau_3$ and $\tau_4$, are also similar to each other and exhibit a broad band with two maxima, one at 510-550 nm and the other around 630 nm. This band can be attributed to a charge-separated state (CSS).

The absorption spectra of $\text{Y-NDI}^{**}$ and $\text{Y-NDI}^*$ have been measured by performing TA experiments with $\text{Y-MON}$ in the presence of the electron donor N,N-dimethylaniline (DMA) and the electron acceptor tetranitromethane (TNM), respectively, and are presented in Figure 4.11 in Chapter 4.1. The $\text{Y-NDI}^*$ spectrum is dominated by a positive band around 490 nm with a weaker shoulder at $\sim$625 nm. The $\text{Y-NDI}^{**}$ radical cation has a very broad absorption band above 480 nm with a not very pronounced maximum at 570 nm.

Since the only possible electron donor in the $\text{Y-SOSIP}$ architecture is another $\text{Y-NDI}$ unit (the side chain proved to be innocent in the $\text{Y-NDI}_{\text{iss}}$ system), the CSS should consist of a $\text{Y-NDI}^{**}/\text{Y-NDI}^*$ pair resulting from photoinduced symmetry-breaking CS. In order to have further support for this interpretation, the hypothetical TA spectrum of the $\text{Y-NDI}^{**}/\text{Y-NDI}^*$ CSS was elaborated by adding the TA spectrum of $\text{Y-NDI}^{**}$ to that of $\text{Y-NDI}^*$. Figure 5.10 compares this hypothetical CSS spectrum with the TA spectrum of $\text{Y-SOSIP}$ recorded at long time delays. The agreement between the two spectra is very good except for the region below 450 nm, where the bleach of
the $S_1 \leftarrow S_0$ absorption is dominating. This discrepancy can be accounted for by the shift of the $S_1 \leftarrow S_0$ band observed in the steady-state absorption when going from the monomeric $Y$-NDI in solution to the $Y$-SOSIP polymerized on the ITO surface (Figure 5.6). Thus, it is reasonable to also expect a shift in the absorption bands of the $Y$-NDI cation and anion in the $Y$-SOSIP architecture with respect to liquid solution.

The fact that CS as well as CR dynamics are characterized by two time constants reflects most likely a distribution of time constants, due to a variety of relative geometries and distances between two $Y$-NDIs units. The 74 ps time constant could be ascribed to the CR of two adjacent $Y$-NDI$^\ddagger$/$Y$-NDI$^\ddagger$. On the other hand, charge hopping to nearby $Y$-NDIs leads to an enhanced spatial separation of the charges and thus to a longer lifetime of the CSS. Such process could be responsible for the slowest part of the CR dynamics.

**Figure 5.10** Comparison of the TA spectra measured with $Y$-SOSIP at long time delay and a composite of the spectra of $Y$-NDI$^\ddagger$ cation and $Y$-NDI$^\ddagger$ anion measured with $Y$-MON in the presence of a electron donor and acceptor, respectively (see Chapter 4.1)
The TA spectra measured with Y-SOSIP’ at various time delays after 400 nm excitation are remarkably more noisy than those measured with Y-SOSIP, although the measurements were performed under identical conditions. The difference in surface quality are at the origin of this discrepancy. Nevertheless, the same spectral features can be recognized, the sharp band with its maximum at 550 nm transforms into a broad band located between 480 and 700 nm without clear maxima.

Comparison of the TA time profiles at 495 and 550 nm for Y-SOSIP and Y-SOSIP’ architectures shows that the dynamics of the two architectures coincide well (Figure 5.11). A global analysis as well reveals that the CS and CR processes in the two samples occur on the same time scale and do not dependent on the organization of the Y-NDIiss units (Table 5.2).

Figure 5.11 Decay of the TA intensity at 495 (A) and 550 nm (B) for Y-SOSIP and Y-SOSIP’ architectures
Conclusions

The results presented in this chapter demonstrate the successful implementation of the home-made translational sample holder in our TA and fluorescence up-conversion set-up, which allowed us for the first time to address solid samples. Despite of the weak signal, the spectra are well reproducible and can be readily analyzed in the common way. As expected, the quality of the sample surface is of paramount importance for such type of experiments.

The ultrafast measurements reveal that the origin of the photocurrent generation in the $Y$-SOSIP and $Y$-SOSIP’ architectures is symmetry-breaking CS between two $Y$-NDI units. The TA and fluorescence up-conversion show that CS occurs with an average time constant of about 6 ps independent on the organization of the $Y$-NDI units on the ITO surface. Moreover, the time constant for CR was found to be the same for both systems in the measured time window. Hence, the local structure of $Y$-SOSIP and $Y$-SOSIP’ are indistinguishable and the difference in photocurrent generation observed electrochemically might be due to either i) better overall electron and hole mobility in the whole of the $Y$-SOSIP architecture or ii) longer lived CSS which can not be seen by our TA set-up due to the limited time window.
5.2 Yellow/non-colored SOSIP architecture

In this chapter the photophysical properties of more complex SOSIP architectures, which consist of two different types of NDIs, will be discussed. By ring-opening surface-initiated polymerization $Y$-NDI and $N$-NDI (non-substituted NDI) propagators were aligned on a molecular level in supramolecular channels, each of which was composed of only one type of NDIs.\textsuperscript{210} $N$-NDI is a strong electron acceptor and can form channels for transporting electrons whereas $Y$-NDI has the HOMO and LUMO levels located energetically above...
those of \(N\)-NDI (Figure 4.3) and, thus, can act as electron donor and channel for holes in the \(N\)-NDI/\(Y\)-NDI assembly.

Two different SOSIP architectures, \(1N-1Y\)-SOSIP and \(1N-6Y\)-SOSIP have been prepared in the group of Prof. Matile (Figure 5.12). The difference between them lies in the length of the alkyl chain on the \(Y\)-NDI propagator. In the case of the \(1N-6Y\)-SOSIP architecture, the \(Y\)-NDI and \(N\)-NDI channels reside further apart from each other than in the \(1N-1Y\)-SOSIP. The photocurrent generation by \(1N-1Y\)-SOSIP measured in a wet setup analogue to dye-sensitized solar cells, has much higher an efficiency than \(1N-6Y\)-SOSIP. Using ultrafast spectroscopical methods, the origin of the photocurrent and reasons for the different behavior of these two systems will be explored.

Results and Discussion

Steady-state measurements. The absorption spectra of \(1N-1Y\)-SOSIP and \(1N-6Y\)-SOSIP architectures display two bands with maxima around 480 and 370 nm (Figure 5.13). The absorption band around 480 nm stems from the \(S_1 \rightarrow S_0\) transition of \(Y\)-NDI, whereas the band at 370 nm with several maxima corresponds to the \(S_1 \rightarrow S_0\) transition of \(N\)-NDI overlapping with the \(S_n \rightarrow S_0\) transitions of \(Y\)-NDI.

Time-resolved fluorescence measurements. The fluorescence dynamics of both SOSIP architectures was measured by fluorescence up-conversion. Two different excitation wavelengths, 390 nm for populating the local excited state (LES) of \(N\)-NDI and 490 nm for populating the LES of \(Y\)-NDI, were used and the fluorescence emission of \(Y\)-NDI was registered at 530 nm. Three- and four-exponential functions convolved with a Gaussian function have been used to reproduce the fluorescence time profiles (Table 5.3). The
**Figure 5.13** Normalized absorption spectra of 1N-1Y-SOSIP and 1N-6Y-SOSIP assembled on an ITO surface

**Figure 5.14** Intensity-normalized fluorescence decays of 1N-1Y-SOSIP and 1N-6Y-SOSIP on ITO after excitation at 390 nm (A) and 490 nm (B) monitored at 530 nm. The solid lines represent the best fits to the data.
fluorescence dynamics of 1N-1Y-SOSIP and 1N-6Y-SOSIP after excitation at 490 nm are indistinguishable (Figure 5.14B). The obtained lifetimes can be attributed to the decay of the Y-NDIs LES, which obviously does not depend on the space between the NDIs channels.

The fluorescence decay after excitation at 390 nm is faster for both systems. The 0.5 ps and 3.5 ps lifetimes have the most important contribution to the total fluorescence decay while the longer lifetimes have only insignificant amplitudes. Notably, the amplitude of the 0.5 ps lifetime is higher for 1N-1Y-SOSIP than for 1N-6Y-SOSIP.

**Transient absorption measurements.** TA measurements of the SOSIP architectures were as well performed at two different excitation wavelengths. The spectra of 1N-1Y-SOSIP and 1N-6Y-SOSIP after 490 nm excitation are very similar to one another (Figure 5.15). For

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**Table 5.3** Time constants obtained from the analysis of the fluorescence decays of 1N-1Y-SOSIP and 1N-6Y-SOSIP on ITO excited at different wavelength and registered at 530 nm

<table>
<thead>
<tr>
<th>System</th>
<th>λ&lt;sub&gt;ex&lt;/sub&gt;</th>
<th>τ&lt;sub&gt;fl1&lt;/sub&gt;</th>
<th>τ&lt;sub&gt;fl2&lt;/sub&gt;</th>
<th>τ&lt;sub&gt;fl3&lt;/sub&gt;</th>
<th>τ&lt;sub&gt;fl4&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1N-1Y-SOSIP</td>
<td>390 nm</td>
<td>0.5 ps</td>
<td>3.5 ps</td>
<td>26 ps</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.68)</td>
<td>(0.3)</td>
<td>(0.02)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>490 nm</td>
<td>1.3 ps</td>
<td>12 ps</td>
<td>84 ps</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.25)</td>
<td>(0.47)</td>
<td>(0.29)</td>
<td></td>
</tr>
<tr>
<td>1N-6Y-SOSIP</td>
<td>390 nm</td>
<td>0.5 ps</td>
<td>3.9 ps</td>
<td>16 ps</td>
<td>103 ps</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.41)</td>
<td>(0.39)</td>
<td>(0.16)</td>
<td>(0.04)</td>
</tr>
<tr>
<td></td>
<td>490 nm</td>
<td>1.3 ps</td>
<td>12 ps</td>
<td>84 ps</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.25)</td>
<td>(0.47)</td>
<td>(0.29)</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.15 TA spectra measured with 1N-1Y-SOSIP (A) and 1N-6Y-SOSIP (B) at different time delays after 490 nm excitation

Figure 5.16 Decay-associated difference spectra of 1N-1Y-SOSIP (A) and 1N-6Y-SOSIP (B) obtained from global analysis of the TA data shown in the Figure 5.15
the global analysis of the TA dynamics at different wavelengths, a two-exponential function was used, the obtained decay-associated difference spectra are shown in Figure 5.16 and the lifetimes are listed in Table 5.4. At early time delays, the TA spectra consist of a broad positive band with a pronounced maximum at 550 nm which transforms within the first 20 ps into a broad band without clear maximum. Based on previous results, the band peaking at 550 nm can be attributed to Y-NDI LES absorption. The 11 ps time constant coincides with that found by time-resolved fluorescence stems from the decay of the LES population upon CS. The lifetime of 1.3 ps found by time-resolved fluorescence was presumably missed due to the mediocre sample quality, which caused the TA spectra to be rather noisy. Since the samples were excited at 490 nm, the observation window of the TA is restricted to 510 - 760 nm, the short wavelength spectral region is dominated by artifacts from scattered pump light. Figure 5.17 compares the decay-associated difference spectra previously obtained for the Y-NDI•+/Y-NDI• CSS in a Y-SOSIP architecture (Figure 5.9) with those of the CSS of 1N-1Y-SOSIP and 1N-6Y-SOSIP. In all the spectral region, the decay-

Table 5.4 Lifetimes obtained from a global analysis of TA decays at different wavelengths with 1N-1Y-SOSIP and 1N-6Y-SOSIP architectures after excitation at 390 and 490 nm

<table>
<thead>
<tr>
<th>System</th>
<th>$\lambda_{ex}$</th>
<th>$\tau_1$</th>
<th>$\tau_2$</th>
<th>$\tau_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1N-1Y-SOSIP</td>
<td>390 nm</td>
<td>45 ps</td>
<td>1500 ps</td>
<td></td>
</tr>
<tr>
<td></td>
<td>490 nm</td>
<td>12 ps</td>
<td>580 ps</td>
<td></td>
</tr>
<tr>
<td>1N-6Y-SOSIP</td>
<td>390 nm</td>
<td>10 ps</td>
<td>90 ps</td>
<td>&gt; 2 ns</td>
</tr>
<tr>
<td></td>
<td>490 nm</td>
<td>11 ps</td>
<td>520 ps</td>
<td></td>
</tr>
</tbody>
</table>
associated difference spectra overlap very well. We can thus assume that in both investigated SOSIP systems, photoinduced symmetry-breaking CS between two \(Y\)-NDIs takes place upon 490 nm excitation. The CSS decays with a time constant of 530 ps back to the ground state.

Thermodynamically, the CS between \(Y\)-NDI and \(N\)-NDI is more favorable than symmetry-breaking CS between two \(Y\)-NDI units.

Table 5.5 Energetics of the photoinduced electron transfer between different units in the 1\(N\)-1\(Y\)-SOSIP and 1\(N\)-6\(Y\)-SOSIP systems

<table>
<thead>
<tr>
<th>Donor/Acceptor</th>
<th>(\Delta G_{CS} / \text{eV})</th>
<th>(\Delta G_{CR} / \text{eV})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Y)-NDI / (Y)-NDI</td>
<td>-0.29</td>
<td>-2.29</td>
</tr>
<tr>
<td>(Y)-NDI* / (N)-NDI</td>
<td>-0.74</td>
<td>-1.84</td>
</tr>
<tr>
<td>(Y)-NDI / (N)-NDI*</td>
<td>-1.54</td>
<td>-1.84</td>
</tr>
</tbody>
</table>

Figure 5.17 Comparison of the decay-associated difference spectra associated with \(\tau_3\) in \(Y\)-SOSIP (assigned to the \(Y\)-NDI* / \(Y\)-NDI* CSS) and with \(\tau_2\) in 1\(N\)-1\(Y\)-SOSIP and 1\(N\)-6\(Y\)-SOSIP after 490 nm excitation.
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Using the Weller equation and the redox potential determined for individual \( Y \)- and \( N \)-NDIs, the driving force for photoinduced CS between two \( Y \)-NDIs equals -0.29 eV, compared to \( \Delta G_{CS} = -0.74 \) eV for \( Y\text{-NDI}^{\bullet\bullet}/N\text{-NDI}^{\bullet\bullet} \) (Table 5.5). In light of this, the obtained result that only the \( Y\text{-NDI}^{\bullet\bullet}/Y\text{-NDI}^{\bullet\bullet} \) CSS is populated in both SOSIP architectures upon 490 nm excitation is quiet surprising. The absorption spectrum of \( N\text{-NDI}^{\bullet\bullet} \) is known and has specific features at 480, 620 and 690 nm in the visible spectral region\(^{156}\) and, thus, would be certainly detectable in case that CS between \( Y\)-NDI and \( N\)-NDI took place.

The TA spectra of 1\( N\)-1\( Y \)-SOSIP after 390 nm excitation are given in Figure 5.18A. Due to experimental problems (shift of time zero), the features and the decay of the LES of \( N\)-NDI and \( Y\)-NDI, which according to the fluorescence up-conversion results happens biexponentially with time constants of 0.5 and 3.5 ps (Table 5.3), were not resolved. The earliest TA spectra of 1\( N\)-1\( Y \)-SOSIP show several maxima at 480, 540 (shoulder), 620 and 690 nm. As the band decays, all these maxima apparently shift to longer wavelengths. Global analysis reveals two distinct populations decaying with 45 and ca. 1500 ps, respectively (Table 5.4). The decay-associated difference spectra associated with the fast decaying population perfectly agrees with the absorption spectrum of \( N\text{-NDI}^{\bullet\bullet} \) published by Wasielewski and co-workers (Figure 5.19A).\(^{156}\) The decay-associated difference spectra of the second, slower decaying population has the same aspect, but is bathochromically shifted by 430 cm\(^{-1}\). Figure 5.20 demonstrates that a very good agreement exists between this spectrum and the spectrum of \( Y\text{-NDI}^{\bullet\bullet} \) obtained by electron transfer between \( Y\)-MON and DMA in solution (see Chapter 4.1).
Figure 5.18 TA spectra measured with 1N-1Y-SOSIP (A) and 1N-6Y-SOSIP (B) at different time delays after 390 nm excitation.

Figure 5.19 Decay-associated difference spectra of 1N-1Y-SOSIP (A) and 1N-6Y-SOSIP (B) obtained from global analysis of the TA data shown in Figure 5.18.
The TA spectra of 1N-6Y-SOSIP excited at 390 nm are shown in the Figure 5.18B. A three-exponential function was used in the global fit analysis of the TA decays at different wavelengths. The decay-associated difference spectra reveal the presence of three different populations. The band with a maximum at 550 nm represents LES absorption of Y-NDI. The excitation energy is in principle sufficient to populate the LES of N-NDI, which absorbs around 610 nm, but it is not observed, probably due to the very fast decay. Instead, the decay-associated difference spectra reflecting the absorption of N-NDI•- and Y-NDI•- can be clearly identified. The shape of the spectra of both radical anions is in good agreement with that previously found by ourselves and others. The spectrum of N-NDI•- has several maxima, namely at 480, 540, 620 and 690 nm and decays with 90 ps,
whereas the spectrum of $Y$-NDI$^\cdot$ has peaks at 490 and 610 nm and disappears on a time scale longer than 2 ns.

According to Figure 5.20, the radical anion of $Y$-NDI$^\cdot$ is present in both 1N-1Y-SOSIP and 1N-6Y-SOSIP systems after excitation at 390 nm — the decay-associated difference spectra coincide very well with the spectrum of $Y$-NDI$^\cdot$ obtained previously. Notable, the spectra of the $Y$-NDI$^{\cdot+}$/Y-NDI$^\cdot$ CSS are much broader (Figure 5.20). This might be explained in two ways — either the positive charge stays on $Y$-NDI$^{\cdot+}$ but in this case the missing of its spectral features in the TA spectra is unclear, or the positive charge is located somewhere else. It is important to mention that presence of $N$-NDI$^{\cdot+}$ seems highly improbable since oxidation of $N$-NDI is energetically unfavorable. Thus, only ITO might act as hole acceptor. It is commonly known, that the working function of ITO is $\sim 4.6$ eV and varies with surface quality.213, 214 As a consequence the Fermi level of ITO lies in between the HOMO and LUMO levels of $N$-NDI when calculated against vacuum.210

**Conclusions**

Ultrafast spectroscopical experiments reveal that in both bicolor SOSIP systems ultrafast charge transfer processes take place upon photo-excitation. By varying the excitation wavelength, the nature of the CS can be tuned.

The fluorescence experiments provide information about the CS. The low signal to noise ratio of the TA data hides the details of this process and the analysis yields only an average CS lifetime. Yet, the TA data unravels the nature of the CSS.
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After 490 nm excitation, both, 1N-1Y-SOSIP and 1N-6Y-SOSIP show the same fluorescence dynamics and TA spectra as Y-SOSIP meaning that N-NDI is not involved in the photochemical processes and CS takes place between two Y-NDI units.

After 390 nm excitation, on the other hand, the features of both radical anions Y-NDI•⁻ and N-NDI•⁻ are apparent in the TA spectra and they decay independently with very distinct lifetimes. There is, however, no evidence for the radical cations of any of the NDIs. The reason for this might be that the positive charge gets trapped by the ITO. Although the nature of the CS states is the same for 1N-1Y-SOSIP and 1N-6Y-SOSIP, fluorescence and TA data shows that the increase of the length of the alkyl chain on the Y-NDI propagator leads to a slow down of CS and CR.
5.3 Yellow/blue SOSIP architecture

In this chapter the photophysical properties of other bicolored systems assembled by Matile and co-workers will be presented, 1B-1Y-SOSIP and 1B-6Y-SOSIP (Figure 5.21). The pair of Y- and B-NDIs were chosen for constructing separate electron and hole transporting channels due to their appropriate photophysical properties (Figure 5.21B). The HOMO and LUMO levels of Y-NDI are below those of B-NDI and, thus can accept electrons from B-NDI. Contrary to the systems consisting of Y- and N-NDIs described

![Figure 5.21](image)

**Figure 5.21** A - Molecular structure of the Y-NDI and B-NDI propagators, used for construction 1B-1Y-SOSIP (R = CH₃) and 1B-6Y-SOSIP (R = C₆H₁₃) architecture (yellow color represents the Y-NDI building blocks and blue — B-NDI), B - structure of the 1B-RY-SOSIP deposited on ITO surface

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in Chapter 5.2, Y-NDI acts as channel for transporting electrons in the 1B-1Y-SOSIP and 1B-6Y-SOSIP architectures. Figure 5.21A demonstrates the molecular structures of the propagators used for constructing the 1B-1Y-SOSIP and 1B-6Y-SOSIP architectures. The distance between the channels can be varied by the length of the peripheral alkyl group R- attached to the Y-NDI propagator. In the 1B-1Y-SOSIP system the channels of different NDIs are supposed to be closer to each other than in 1B-6Y-SOSIP.

Photocurrent generation experiments revealed that the contribution of B-NDIs to the total current is substantially smaller than that of Y-NDIs. A decrease of the distance between the channels causes an increasing contribution of B-NDI. The aim of this investigations is to discover the origin of the photocurrent generation by spectroscopical methods in both, 1B-1Y-SOSIP and 1B-6Y-SOSIP system. Additionally, the 1B-xY-SOSIP will be compared to 1N-xY-SOSIP architectures presented in the previous chapter.

Results and Discussion

Steady-state measurements. The absorption spectra of 1B-1Y-SOSIP and 1B-6Y-SOSIP consist of a broad band with a maximum at 630 nm which originates from the S_1 ← S_0 transition of B-NDI. This transition is slightly red shifted in comparison with monomeric B-NDI in MeOH solution. The second band centered around 470 nm is due to the S_1 ← S_0 transition of Y-NDI and notably more intensive in the 1B-6Y-SOSIP architecture. The strong absorption band around 360 nm arises from both B- and Y-NDI. The whole spectrum of 1B-1Y-SOSIP is red shifted in comparison with 1B-6Y-SOSIP probably due to different NDIs organization.
Time-resolved fluorescence measurements. The fluorescence dynamics of 1B-1Y-SOSIP and 1B-6Y-SOSIP after 450 nm excitation monitored at 650 nm (fluorescence from B-NDI) are depicted in Figure 5.23. They were analyzed by a three exponential function convolved with a Gaussian function (Table 5.6). Direct excitation of B-NDIs was experimentally impossible. Therefore, the wavelength of excitation was chosen in such a way that Y-NDI LES was populated. It is important to mention, that the fluorescence signal from Y-NDI was very weak and could not be recorded.

The fast time constant, $\tau_{f1}$, has a negative amplitude and can be explained by energy transfer to the B-NDI via the trivial and/or non-trivial mechanisms (see Chapter 2.3), since the fluorescence spectrum of Y-NDI partially overlaps with the absorption band of B-NDI (Figure 5.22). The other two lifetimes are as well very fast and
can be assigned to the decay of the B-NDI LES via CS. Evidence for this assignment will be shown later.

It is noteworthy that all three fluorescence lifetimes of 1B-6Y-SOSIP are approximately twice as long as those found for 1B-1Y-SOSIP system (Table 5.6).

**Figure 5.23** Intensity-normalized fluorescence decays of 1B-1Y-SOSIP and 1B-6Y-SOSIP on ITO after excitation at 450 nm monitored at 650 nm. The solid lines represent the best fits to the data points

**Table 5.6** Fluorescence lifetimes with corresponding amplitudes obtained from the analysis of the fluorescence decays of 1B-1Y-SOSIP and 1B-6Y-SOSIP on ITO excited at 450 nm and registered at 650 nm

<table>
<thead>
<tr>
<th>System</th>
<th>$\tau_{f1}$</th>
<th>$\tau_{f2}$</th>
<th>$\tau_{f3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1B-1Y-SOSIP</td>
<td>0.7 ps</td>
<td>7 ps</td>
<td>26 ps</td>
</tr>
<tr>
<td></td>
<td>(-0.63)</td>
<td>(0.73)</td>
<td>(0.27)</td>
</tr>
<tr>
<td>1B-6Y-SOSIP</td>
<td>1.4 ps</td>
<td>11 ps</td>
<td>60 ps</td>
</tr>
<tr>
<td></td>
<td>(-0.75)</td>
<td>(0.61)</td>
<td>(0.59)</td>
</tr>
</tbody>
</table>
Figure 5.24 TA spectra measured with 1B-1Y-SOSIP (A) and 1B-6Y-SOSIP (B) at different time delays after 650 nm excitation

Figure 5.25 Decay-associated difference spectra of 1B-1Y-SOSIP (A) and 1B-6Y-SOSIP (B) obtained from global analysis of the TA data shown in Figure 5.24
Transient absorption measurements. The TA spectra measured with 1B-1Y-SOSIP and 1B-6Y-SOSIP upon 650 nm excitation shown in Figure 5.24 are very similar to each other. At early time delays the feature of the B-NDI LES, a broad positive band with maximum at 570 nm, is clearly seen. Due to the strong scattered light, the region where B-NDI’s bleach and stimulated emission are situated can not be exploited. After a few picoseconds the LES of B-NDI modifies into a broad band centered approximately at 490 nm. The shape of this band is in good agreement with that previously attributed to the B-NDI*/B-NDI• CSS.22, 98, 139 After that, the positive band with a maximum at 490 nm changes shape and simultaneously a negative band at 470 nm from Y-NDI ground-state bleach appears.

The temporal evolution of the TA signal at different wavelength for B-1Y-SOSIP and 1B-6Y-SOSIP after 650 nm excitation were analyzed globally using a three exponential functions. The obtained decay-associated difference spectra are very similar for both systems, however the lifetimes are distinct (Figure 5.25 and Table 5.7). The fastest lifetime, \( \tau_1 \), represents the decay of the B-NDI LES through

<table>
<thead>
<tr>
<th>System</th>
<th>( \lambda_{\text{ex}} )</th>
<th>( \tau_1 )</th>
<th>( \tau_2 )</th>
<th>( \tau_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1N-1Y-SOSIP</td>
<td>500 nm</td>
<td>0.6 ps</td>
<td>14 ps</td>
<td>1.2 ns</td>
</tr>
<tr>
<td></td>
<td>650 nm</td>
<td>3.2 ps</td>
<td>40 ps</td>
<td>2.8 ns</td>
</tr>
<tr>
<td>1N-6Y-SOSIP</td>
<td>500 nm</td>
<td>1.5 ps</td>
<td>28 ps</td>
<td>860 ps</td>
</tr>
<tr>
<td></td>
<td>650 nm</td>
<td>4.6 ps</td>
<td>60 ps</td>
<td>670 ps</td>
</tr>
</tbody>
</table>
ultrafast CS between two B-NDI units. This lifetime is in good agreement with the 4 ps found for electron transfer in B-NDI multichromophoric systems in MeOH solution.\textsuperscript{98,172} After that, the B-NDI•/+Y-NDI•-CSS is populated by an electron transfer from B-NDI• to a Y-NDI unit, which is energetically more favorable. The Weller equation reveals that the driving force for CS between two B-NDI units equals to -0.2 eV, whereas it amounts to -0.47 eV for CS between Y- and B-NDIs (Table 5.8). The spectral features of Y-NDI•-* can not be clearly distinguished since B-NDI•+ as well contributes to the TA signal. However, the involvement of the Y-NDI in the CS is additionally supported by the appearance of the Y-NDI bleach signal at 450 nm (B-NDIs neither absorb nor emit in this spectral region).

The TA spectra measured with 1B-1Y-SOSIP and 1B-6Y-SOSIP at different time delays upon 500 nm excitation are as well very similar to each other (Figure 5.26). They consist of a negative signal centered at 640 nm originating from B-NDI bleach and stimulated emission, and broad positive bands above 600 nm and below 700 nm. In the early spectra, the negative band becomes more negative and

Table 5.8 Energetics of the photoinduced electron transfer between different units in the 1B-1Y-SOSIP and 1B-6Y-SOSIP systems

<table>
<thead>
<tr>
<th>Donor/Acceptor</th>
<th>ΔGCS / eV</th>
<th>ΔGCR / eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-NDI / Y-NDI</td>
<td>-0.29</td>
<td>-2.29</td>
</tr>
<tr>
<td>B-NDI / B-NDI</td>
<td>-0.24</td>
<td>-1.79</td>
</tr>
<tr>
<td>Y-NDI* / B-NDI</td>
<td>-1.11</td>
<td>-1.53</td>
</tr>
<tr>
<td>Y-NDI / B-NDI*</td>
<td>-0.5</td>
<td>-1.53</td>
</tr>
</tbody>
</table>

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Figure 5.26 TA spectra at different time delays of 1B-1Y-SOSIP (A) and 1B-6Y-SOSIP (B) at different time delays after 500 nm excitation

Figure 5.27 Decay-associated difference spectra of 1B-1Y-SOSIP (A) and 1B-6Y-SOSIP (B) obtained from global analysis of the TA data shown in Figure 5.26
the positive bands modify in shape. After that, the whole spectrum decays to zero.

A global fit analysis has been performed using a three-exponential function. The decay-associated difference spectra are represented in Figure 5.27 and the lifetimes are listed in Table 5.7. The shortest time constant, $\tau_1$, is responsible for the intensification of the $B$-NDI bleach signal directly after photoexcitation of $Y$-NDI and, thus, can be attributed to CS between the $Y$- and $B$-NDIs units. In parallel, the fraction of $B$-NDIs, which got excited via EEH undergo symmetry-breaking CS. Based on the previous results, the time constant of this process can be estimated to be as well very short and probably overlaps with $\tau_1$. The decay-associated difference spectrum associated with $\tau_2$ is similar to that assigned to the $B$-NDI$^{\bullet\bullet}/B$-NDI$^{\bullet}$ CSS$^{98, 172}$ except for the red-shift observed already for the steady-state spectra. Due to energetic considerations (Table 5.8), the $B$-NDI$^{\bullet\bullet}/B$-NDI$^{\bullet}$ CSS is followed by population of the longer lived $B$-NDI$^{\bullet\bullet}/Y$-NDI$^{\bullet}$ CSS which finally decays with $\tau_3$.

The only difference between the TA spectra of 1B-1Y-SOSIP and 1B-6Y-SOSIP systems after 500 nm excitation are the lifetimes of the CS and CR process. Probably due to a smaller distance between donor and acceptor channels, the CS occurs faster in the 1B-1Y-SOSIP system. Additionally, the CSS lives longer in such a system which affects the overall SOSIP efficiency.

**Conclusions**

Using spectroscopical methods it has been shown that in the 1B-1Y-SOSIP and 1B-6Y-SOSIP architectures an ultrafast CS between $Y$- and $B$-NDI units takes place independent on the wavelength of excitation. This behavior is highly favorable for constructing SHJ
devices, since electron and hole are clearly separated. Even those B-NDIs which firstly undergo symmetry-breaking, CS later donate an electron to Y-NDI units.

Only a difference in the temporal behavior of 1B-1Y-SOSIP and 1B-6Y-SOSIP architectures has been found. Although the same intermediates are involved, CS is always faster in the 1B-1Y-SOSIP system than in its longer sidechain congener. At the same time the CR seems to be faster in the second system, however the lifetimes are not very distinct and the apparent difference might be due to low signal intensity. Altogether, it is possible to conclude that probably both factors, fast CS and slow CR crucially influence on the overall system efficiency and make the 1B-1Y-SOSIP architecture better suited for the envisaged applications.
General conclusions

In this chapter three different SOSIP architectures deposited on an ITO surface have been introduced. In order to study these samples, a special translational sample holder has been developed. Although the quality of the spectra strongly depends on the sample surface quality, the obtained results are reliable and reproducible and their quality is in many cases comparable to liquid solution spectra. The data obtained for the individually investigated NDIs allowed to establish features of states and to identify them.

First, it has been shown that the origin of the photocurrent in the one colored Y-SOSIP architecture is symmetry-breaking CS between Y-NDI units. The TA spectra clearly represented the Y-NDI**/Y-NDI*-CSS appearance and its shape is in excelled agreement with those found in solution.

Two colored SOSIP architectures consisting of the N-/Y-NDI and Y-/B-NDI pair have been investigated. In the first system, Y-NDI is supposed to act as electron donor whereas in the second system it acts as electron acceptor. Both systems should therefore have separate electron and hole transporting channels. However, this turned out to be true only for the 1B-xY-SOSIP architectures, where independently of the excitation wavelength, CS between the distinct NDIs takes place.

Contrary to this, CS in the 1N-xY-SOSIP systems depends on whether the N- or Y-NDI LES is photoprepared. Excitation of Y-NDI yields symmetry-breaking charge separation between two Y-NDIs although electron transfer from Y-NDI to N-NDI is energetically preferred. The spectral features of N-NDI* radical anion, which are easily traceable, are absent from the TA data.
Surprisingly, after excitation of $N$-NDI, the signatures of the radical anions of both NDIs, $N$-NDI$^-$ and $Y$-NDI$^-$, are evident in the TA spectra of $1N$-$xY$-SOSIP. The location of the hole remains unclear but assumed to be the ITO electrode.

The Table 5.9 and Table 5.10 summarize the time constants of CS and CR process obtained from fluorescence up-conversion and TA experiments of the investigated SOSIP systems.

An influence of the distance between the channels is clearly observed for the $1B$-$xY$-SOSIP where CS was found to be faster when donor and acceptor are closer to each other, as expected from theoretical considerations.

In agreement with the assignment to symmetry breaking CS between two alike NDIs, no effect of the length of the sidechain is present in the $1N$-$xY$-SOSIP. Indeed, the lifetimes associated with CS are identical after excitation of the $Y$-NDI chromophore. The dynamics after $N$-NDI excitation are rather complex but no striking difference between $1N$-$1Y$-SOSIP and $1N$-$6Y$-SOSIP is present in the time-resolved fluorescence or absorption data.
**Table 5.9** Summarized CS time constants obtained from time-resolved fluorescence and TA measurements of different SOSIP architectures (the excited NDI is indicated in parentheses)

<table>
<thead>
<tr>
<th>System</th>
<th>$\lambda_{ex}$</th>
<th>$\tau_1$</th>
<th>$\tau_2$</th>
<th>$\tau_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y$-SOSIP</td>
<td>400 nm</td>
<td>0.8 ps</td>
<td>6.3 ps</td>
<td>55 ps</td>
</tr>
<tr>
<td>1$N$-$1Y$-SOSIP</td>
<td>390 nm (N-NDI)</td>
<td>0.5 ps</td>
<td>3.5 ps</td>
<td>26 ps</td>
</tr>
<tr>
<td></td>
<td>500 nm (Y-NDI)</td>
<td>1.3 ps</td>
<td>12 ps</td>
<td>84 ps</td>
</tr>
<tr>
<td>1$N$-$6Y$-SOSIP</td>
<td>390 nm (N-NDI)</td>
<td>0.5 ps</td>
<td>3.9 ps</td>
<td>16 ps</td>
</tr>
<tr>
<td></td>
<td>500 nm (Y-NDI)</td>
<td>1.3 ps</td>
<td>12 ps</td>
<td>84 ps</td>
</tr>
<tr>
<td>1$B$-$1Y$-SOSIP</td>
<td>500 nm (Y-NDI)</td>
<td>7 ps</td>
<td>26 ps</td>
<td></td>
</tr>
<tr>
<td></td>
<td>650 nm (B-NDI)</td>
<td>3.2 ps</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1$B$-$6Y$-SOSIP</td>
<td>500 nm (Y-NDI)</td>
<td>11 ps</td>
<td>60 ps</td>
<td></td>
</tr>
<tr>
<td></td>
<td>650 nm (B-NDI)</td>
<td>4.6 ps</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5.10 Summarized time constant of CR obtained from TA measurements of different SOSIP architectures (the excited NDI is indicated in parentheses, the superscripts indicate the nature of the CSS: \( \alpha \zeta \) — CR of \( X\text{-NDI}^{*+}/Z\text{-NDI}^{*} \) CSS with \( y = Y\text{-NDI}, \ n = N\text{-NDI}, \ b = B\text{-NDI} \) )

<table>
<thead>
<tr>
<th>System</th>
<th>( \lambda_{ex} )</th>
<th>( \tau_1 )</th>
<th>( \tau_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Y\text{-SOSIP} )</td>
<td>400 nm</td>
<td>74 ps (^{39})</td>
<td>&gt; 2 ns (^{39})</td>
</tr>
<tr>
<td>1N-1Y-SOSIP</td>
<td>390 nm (N-NDI)</td>
<td>45 ps (^{hole\text{-}n})</td>
<td>1.5 ns (^{hole\text{-}y})</td>
</tr>
<tr>
<td>1N-6Y-SOSIP</td>
<td>500 nm (Y-NDI)</td>
<td>580 ps (^{39})</td>
<td></td>
</tr>
<tr>
<td>1B-1Y-SOSIP</td>
<td>500 nm (Y-NDI)</td>
<td>90 ps (^{hole\text{-}n})</td>
<td>&gt; 2 ns (^{hole\text{-}y})</td>
</tr>
<tr>
<td>1B-6Y-SOSIP</td>
<td>650 nm (B-NDI)</td>
<td>14 ps (^{bb})</td>
<td>1.2 ns (^{by})</td>
</tr>
<tr>
<td>1B-1Y-SOSIP</td>
<td>650 nm (B-NDI)</td>
<td>40 ps (^{bb})</td>
<td>2.8 ns (^{by})</td>
</tr>
<tr>
<td>1B-6Y-SOSIP</td>
<td>500 nm (Y-NDI)</td>
<td>28 ps (^{bb})</td>
<td>0.86 ns (^{by})</td>
</tr>
<tr>
<td>1B-6Y-SOSIP</td>
<td>650 nm (B-NDI)</td>
<td>60 ps (^{bb})</td>
<td>0.67 ns (^{by})</td>
</tr>
</tbody>
</table>
Chromophores which fluoresce in the near-infrared (NIR) spectral region and interact with biological macromolecules are highly needed for numerous applications in chemistry, biology and medicine.\textsuperscript{215-219} First of all, it was shown that the single molecule detection efficiency of NIR dyes is significantly better than for visible dyes, even though the NIR dye possessed a smaller quantum yield and shorter fluorescence lifetime.\textsuperscript{220} The improved detection efficiency mainly comes from the lower background signal upon excitation with NIR light, which is not absorbed by other fluorophores present in the investigated system or by fluorescence impurities in the solvent blank. Another advantage of long excitation wavelengths is that IR light is more gentle than visible
light and causes less damage to biological tissue what is crucial for live-cell imaging applications. Consequently, designing and testing NIR fluorescence probes has become an important issue.

The [4]helicene cations (HelR) presented in this chapter (Figure 6.1) have been synthesized for the first time in the group of Prof. Lacour.221-225 These compounds emit in the NIR region and belong to the class of intrinsically chiral aromatic molecules called helicenes. The configuration of HelR is highly stable because of strong steric repulsions between the methoxy substituents and the large degree of rigidity brought by the two nitrogen atoms in conjugation.222, 226

Due to its chiral nature, HelR can be used for exploring recognition mechanisms occurring in biological systems. These mechanisms are extremely important and play a crucial role in numerous fundamental stereoselective processes such as, e.g., protein-DNA interaction, enzymatic catalysis, drugs metabolism and antibody activity. However, studies of the effect of chirality on naturally abundant substances are complicate due to difficulties in the synthesis of the unnatural enantiomer. One of the approaches to overcome this difficulty is to use the information about interaction of a given biological macromolecule with a small chiral chromophore in vitro in order to predict its behavior in vivo.
HelR are expected to interact with biological macromolecules due to their extended aromaticity. Moreover, several other molecules from the helicene family have been shown to specifically bind to DNA. For example, the \((P)\)-enantiomer of helicene bearing a protonated amino group displays structural selectivity for binding to DNA as it discriminates between right-handed B-DNA and left-handed Z-DNA.\(^{227}\) DNA-binding properties have also been revealed with 5,8-bis(aminomethyl)-1,12-dimethylbenzo[c]-phenanthrene and N-methyl-5-azahelicenium salts.\(^{228, 229}\) Since it is commonly established that a positive charge on an aromatic molecule enhances its binding ability to DNA,\(^{230-232}\) HelR is expected to efficiently bind to DNA.

Aggregation and self-assembly are common properties of helicenes. Heterocyclic helicenes assemble into hexagonal phases consisting of hollow-centered helical columns.\(^{233, 234}\) A similar helical columnar liquid-crystalline structure is typical for other materials such as DNA,\(^{235}\) poly(\(\gamma\)-benzyl-L-glutamate),\(^{236}\) and xanthan.\(^{237}\) Enantiopure helicenamidate was grafted on silica nano-particles and the pattern showed the ability to aggregate and de-aggregate in different aromatic solvents.\(^{238}\) The stereoisomers of a cyclic alkyne with three helicene units self-aggregate in organic solvents. The conformation of the helicene units plays an important role for the aggregation.\(^{239}\)

In addition to the properties mentioned above, helicenes have been intensively studied due to their photochromic\(^{240, 241}\) and nonlinear optical properties.\(^{242-245}\) In spite of the strong interest in this class of molecules, photophysical investigations, apart from basic absorption and emission spectroscopy,\(^{228, 234, 246, 247}\) are still very scarce.\(^{248, 249}\)

This chapter is divided into two parts. The first part presents a detailed photophysical investigation of the HelR shown in Figure 6.1. The aim is to characterize these new, promising chiral NIR

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fluorescent probes. Since aggregate formation always dramatically changes the photophysical properties of the dyes, special attention is devoted to the photophysical properties of the HelR aggregates.

The second part is dedicated to the interaction of different enantiopure forms of HelR with right-handed double strand DNA. Evidence for binding is given by different methods. Additionally, the binding geometry is determined using linear dichroism (LD) spectroscopy. The investigated compounds have different substituents at the nitrogen atoms and their influence on the binding ability is discussed.

The photophysical properties of HelR (Figure 6.1) in organic solvents is substantially different from those in aqueous solutions due to aggregation and will thus be discussed separately for clarity.


The absorption spectra of HelR in organic solvents consist of two bands in the visible region with maxima at 617 nm and around 425 nm, respectively (Figure 6.2). The fluorescence spectra of the investigated molecules show a broad band with maximum around 670 nm. No significant solvatochromism can be observed with the set of solvents used even though they span a sizable range of polarity. As

Table 6.1 Absorption, $\lambda_a$, and fluorescence, $\lambda_f$, maxima of the HelR dyes in various solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>HelMe $\lambda_a$ / nm</th>
<th>HelPr $\lambda_a$ / nm</th>
<th>HelOH $\lambda_a$ / nm</th>
<th>HelMe $\lambda_f$ / nm</th>
<th>HelPr $\lambda_f$ / nm</th>
<th>HelOH $\lambda_f$ / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>614</td>
<td>617</td>
<td>615</td>
<td>678</td>
<td>677</td>
<td>680</td>
</tr>
<tr>
<td>MeOH</td>
<td>615</td>
<td>617</td>
<td>617</td>
<td>664</td>
<td>663</td>
<td>673</td>
</tr>
<tr>
<td>EtOH</td>
<td>617</td>
<td>618</td>
<td>618</td>
<td>663</td>
<td>662</td>
<td>672</td>
</tr>
<tr>
<td>PoOH</td>
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<td>619</td>
<td>621</td>
<td>664</td>
<td>663</td>
<td>672</td>
</tr>
<tr>
<td>ACN</td>
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<td>617</td>
<td>617</td>
<td>671</td>
<td>668</td>
<td>678</td>
</tr>
<tr>
<td>DMSO</td>
<td>625</td>
<td>625</td>
<td>627</td>
<td>683</td>
<td>677</td>
<td>690</td>
</tr>
<tr>
<td>THF</td>
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<td>620</td>
<td>621</td>
<td>668</td>
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<td>678</td>
</tr>
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<td>DCM</td>
<td>616</td>
<td>617</td>
<td>619</td>
<td>658</td>
<td>656</td>
<td>672</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>616</td>
<td>617</td>
<td>621</td>
<td>662</td>
<td>658</td>
<td>679</td>
</tr>
</tbody>
</table>
expected, the shape of the spectra does not depend on the enantiomeric form, however variation of substituents leads to small spectral shifts: in most solvents, the absorption and emission maxima of HelMe and HelPr are almost identical, whereas those of HelOH, especially for emission, are red shifted by at most 20 nm (450 cm$^{-1}$) (Table 6.1).

Figure 6.2 Absorption and fluorescence spectra of (rac)-HelMe in various solvents
TDDFT calculations of HelR in the gas phase predict the first electronic transition to be at 530 nm and to be due to a HOMO-LUMO one-electron transition (Table 6.2). Figure 6.3 shows that this transition involves a slight decrease of electron density at the R substituents and an increase at the oxygen atoms of the methoxy groups. This first transition has thus some charge transfer character. This could explain why its energy calculated in the gas phase is substantially larger than that measured in solution. Unfortunately, because of their ionic nature, the absorption spectrum of the HelR dyes cannot be measured in weakly or non-polar solvents. According to the calculations, the absorption band observed around 425 nm should be due to two transitions of similar intensity but with a rotatory strength of opposite sign. This prediction agrees very well with the circular dichroism (CD) spectra of HelMe, that show one band at 407 nm with the same sign as that of the 625 nm band, and one band at 456 nm with opposite sign (Figure 6.19).
Table 6.2 Parameters obtained from TDDFT calculations of HelR dyes in the gas-phase (\textit{a} - energy, \textit{b} - transition dipole moment, \textit{c} - rotatory strength (P-form) in atomic units)

<table>
<thead>
<tr>
<th></th>
<th>HelMe</th>
<th>HelPr</th>
<th>HelOH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_1 \leftrightarrow S_0$ transition</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_a$ (eV)</td>
<td>2.35</td>
<td>2.35</td>
<td>2.34</td>
</tr>
<tr>
<td>HOMO-LUMO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu_b$ (D)</td>
<td>$\mu_y = -3.16$</td>
<td>$\mu_y = -5.55$</td>
<td>$\mu_y = -3.45$</td>
</tr>
<tr>
<td></td>
<td>$\mu_z = -0.50$</td>
<td>$\mu_z = -0.60$</td>
<td>$\mu_z = -0.55$</td>
</tr>
<tr>
<td>$R_c$ (a.u.)</td>
<td>$3.9 \cdot 10^{-4}$</td>
<td>$1.2 \cdot 10^{-4}$</td>
<td>$1.8 \cdot 10^{-4}$</td>
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<tr>
<td>$S_2 \leftrightarrow S_0$ transition</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$E_a$ (eV)</td>
<td>2.72</td>
<td>2.77</td>
<td>2.73</td>
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<tr>
<td>HOMO-1-LUMO</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$\mu_x$ (D)</td>
<td>$\mu_x = 2.30$</td>
<td>$\mu_x = 2.28$</td>
<td>$\mu_x = 2.30$</td>
</tr>
<tr>
<td>$R_c$ (a.u.)</td>
<td>$-1.2 \cdot 10^{-3}$</td>
<td>$-1.1 \cdot 10^{-3}$</td>
<td>$-1.1 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>$S_3 \leftrightarrow S_0$ transition</td>
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<td></td>
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</tr>
<tr>
<td>$E_a$ (eV)</td>
<td>2.88</td>
<td>2.88</td>
<td>2.84</td>
</tr>
<tr>
<td>HOMO-2-LUMO</td>
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<td></td>
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<tr>
<td>$\mu_y$ (D)</td>
<td>$\mu_y = 2.64$</td>
<td>$\mu_y = 2.50$</td>
<td>$\mu_y = 2.69$</td>
</tr>
<tr>
<td></td>
<td>$\mu_z = -0.90$</td>
<td>$\mu_z = -0.88$</td>
<td>$\mu_z = -0.90$</td>
</tr>
<tr>
<td>$R_c$ (a.u.)</td>
<td>$5.4 \cdot 10^{-4}$</td>
<td>$5.5 \cdot 10^{-4}$</td>
<td>$5.0 \cdot 10^{-4}$</td>
</tr>
</tbody>
</table>
The fluorescence dynamics of HelR in different organic solvents were recorded at 670 nm after 395 nm excitation and are represented in Figure 6.4. In most cases, the fluorescence time profiles could be well reproduced by a mono-exponential function convolved with the instrument response function (IRF). The obtained time constants, $\tau_{fl}$, are listed in Table 6.3. In order to reproduce the fluorescence decay of all three dyes in CHCl$_3$ and of HelOH in DCM, the sum of two exponential decays convolved with the IRF was required. Measurements of fluorescence decays at different wavelengths (670, 690 and 780 nm) revealed an increasing contribution of the short-lived component at longer wavelengths (Figure 6.5). Moreover, the relative amplitude associated with the shorter lifetime increased markedly with increasing HelR concentration. These two decay components might be attributed to two different species.

Although the shape of the absorption spectrum of HelR in CHCl$_3$ is independent of concentration, a noticeable red shift of the
Figure 6.5 Intensity-normalized fluorescence time profiles at different wavelengths measured with (rac)-HelPr in chloroform at 670 nm after 395 nm excitation ($a_1$ and $a_2$ are the relative amplitudes of the $\tau_1 = 4.7$ ns and $\tau_2 = 14.8$ ns components)

Figure 6.6 Normalized absorption and fluorescence spectra at various concentrations of (rac)-HelPr in chloroform. The inset shows a close-up of the maxima
fluorescence band is observed with increasing dye concentration (Figure 6.6). It is worth mentioning that the origin of this shift is not reabsorption since the maximum absorbance did not exceed 0.3. The concentration dependence suggests that an HelR excimer or excited aggregate is most probably responsible for the red-shifted emission with the shorter lifetime. Unfortunately, the spectra associated with the two decay components overlap too much to allow for an observation of precursor-successor kinetics, as expected in such a case, and to permit an unambiguous assignment. Excimer formation is typical of many aromatic hydrocarbons, but contrary to what is observed here, the excimer band is usually much more red-shifted compared to that of the monomer and the lifetime is substantially longer. The cationic nature of the HelR dyes is probably responsible for the small stabilization of the excimer and for its presence in medium polarity solvents only. In more polar solvents, the difference of solvation energy between excimer and monomers most probably surpasses the excimer stabilization energy. Finally, the short excimer lifetime might arise from the fact that the main deactivation pathway of the excimer is dissociation and not fluorescence, as it is usually the case.

The determined fluorescence quantum yield, $\Phi_f$, allows to calculate the radiative, $k_r$, and non-radiative, $k_{nr}$, rate constants of HelR in different solvents (see Chapter 2). $k_r$ is around 0.01-0.015 ns$^{-1}$ and essentially solvent independent, whereas $k_{nr}$ varies substantially (Table 6.3). No evident relationship between $\tau_f$ or $k_{nr}$ and a solvent property or solvatochromic scale (Lippert-Mataga, $E_T(30)$, Kamlet-Taft) can be recognized. However, if only alcohols are considered, a substantial increase of the fluorescence lifetime of all three HelR dyes with increasing alcohol alkyl chain length can be observed. As the hydrogen-bond donating properties of the alcohols is also decreasing
Table 6.3 Fluorescence quantum yield, $\Phi_{fl}$, and time constants obtained from analysis of the fluorescence decays of HelR dyes (the non-radiative rate constant, $k_{nr}$, has been calculated with the shortest lifetime in aqueous solution and the longest lifetime in DCM and CHCl$_3$; the radiative rate constant, $k_r$, is essentially solvent independent and equals to 0.01-0.015 ns$^{-1}$)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\Phi_{fl}$</th>
<th>$\tau_{fl}$</th>
<th>$k_{nr}$</th>
<th>$\Phi_{fl}$</th>
<th>$\tau_{fl}$</th>
<th>$k_{nr}$</th>
<th>$\Phi_{fl}$</th>
<th>$\tau_{fl}$</th>
<th>$k_{nr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBS</td>
<td>1.9</td>
<td>1.3</td>
<td>0.75</td>
<td>2.6</td>
<td>1.6</td>
<td>0.6</td>
<td>1.6</td>
<td>1.2</td>
<td>0.85</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>1.9</td>
<td>1.3</td>
<td>0.75</td>
<td>2.5</td>
<td>2.0</td>
<td>0.5</td>
<td>1.6</td>
<td>1.1</td>
<td>0.86</td>
</tr>
<tr>
<td>D$_2$O</td>
<td>2.2</td>
<td>2.0</td>
<td>0.49</td>
<td>3.2</td>
<td>2.5</td>
<td>0.39</td>
<td>2.1</td>
<td>1.8</td>
<td>0.54</td>
</tr>
<tr>
<td>MeOH</td>
<td>5.2</td>
<td>4.3</td>
<td>0.22</td>
<td>7.6</td>
<td>5.6</td>
<td>0.17</td>
<td>3.5</td>
<td>2.8</td>
<td>0.34</td>
</tr>
<tr>
<td>EtOH</td>
<td>7.0</td>
<td>5.3</td>
<td>0.17</td>
<td>9.6</td>
<td>6.7</td>
<td>0.13</td>
<td>4.4</td>
<td>3.3</td>
<td>0.29</td>
</tr>
<tr>
<td>PeOH</td>
<td>8.9</td>
<td>6.2</td>
<td>0.15</td>
<td>11.8</td>
<td>7.7</td>
<td>0.12</td>
<td>5.9</td>
<td>4.1</td>
<td>0.25</td>
</tr>
<tr>
<td>ACN</td>
<td>5.0</td>
<td>4.2</td>
<td>0.23</td>
<td>7.6</td>
<td>5.5</td>
<td>0.17</td>
<td>3.5</td>
<td>2.9</td>
<td>0.33</td>
</tr>
<tr>
<td>DMSO</td>
<td>4.0</td>
<td>3.0</td>
<td>0.32</td>
<td>6.3</td>
<td>4.0</td>
<td>0.23</td>
<td>3.1</td>
<td>2.1</td>
<td>0.46</td>
</tr>
<tr>
<td>THF</td>
<td>7.5</td>
<td>5.5</td>
<td>0.18</td>
<td>10.5</td>
<td>7.0</td>
<td>0.13</td>
<td>4.3</td>
<td>3.2</td>
<td>0.50</td>
</tr>
<tr>
<td>DCM</td>
<td>17.2</td>
<td>11.3</td>
<td>0.07</td>
<td>20.5</td>
<td>12.0</td>
<td>0.06</td>
<td>5.5</td>
<td>3.1</td>
<td>0.14</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>11.3</td>
<td>5.8</td>
<td>0.06</td>
<td>14.4</td>
<td>4.7</td>
<td>0.06</td>
<td>4.0</td>
<td>2.7</td>
<td>0.15</td>
</tr>
</tbody>
</table>
in the same order, this dependence points to the possible involvement of hydrogen-bond assisted non-radiative deactivation. However, the even shorter lifetime observed in the non-protic DMSO and ACN clearly points to the role of other parameters.

In addition to this variation with the solvent, Table 6.3 also reveals that the R substituent has a clear influence on $\tau_{fl}$ and that this effect originates from $k_{nr}$, which increases in the order R= Pr, Me, (CH$_2$)$_2$OH in all organic solvents. The shorter lifetime with HelOH possibly arises from hydrogen-bond interaction with the solvent, whereas the difference between HelMe and HelPr is not clear and might originate from the different counter-ions (BF$_4^-$ with HelMe, Cl$^-$ with HelPr).

The transient absorption spectra of all HelR in ethanol are very similar to each other and display a positive structured band in 360 - 540 nm region, which originates from excited state absorption (Figure 6.7A). The broad negative band above 540 nm originates from both the bleach of the $S_1 \rightarrow S_0$ transition and stimulated emission. The slight difference in shape between the steady-state absorption spectrum and the bleach signal is due to overlap with the excited state absorption. The initial spectral dynamics occurring within the first 10 ps leads to a narrowing of the excited state absorption at 540 nm, a blue-shift of the positive band around 380 nm, and the appearance of new small positive features at 420 nm and 520 nm. Almost identical spectra have been recorded with excitation of the dyes at 600 nm. However, the early spectral dynamics are slightly different. This is reasonable taking into account that by exciting at 400 nm and 600 nm, different electronic state are populated.
Figure 6.7 TA spectra measured at different time delays with (rac)-HelPr in EtOH (A) and in aqueous buffer solution (B) after 400 nm excitation.

Figure 6.8 Decay-associated difference spectra obtained from the global analysis of TA spectra measured with (rac)-HelPr in EtOH (A) and in aqueous buffer solution (B) after 400 nm excitation.
The time evolution of the TA signal after 400 nm excitation over the whole measured spectral region can be reproduced globally by a sum of three exponential functions decaying to zero (Figure 6.8). The first two lifetimes, $\tau_1$ and $\tau_2$, can be attributed to internal conversion and/or vibrational relaxation. The longest lifetime, $\tau_3$, whose value was fixed to that of the TCSPC measurement, describes the decay of the whole signal on a nanosecond time scale. The extrapolated decay to zero of the whole TA signal indicates that intersystem-crossing (ISC) to the triplet state is not a significant deactivation pathway of the S$_1$ population. If it were the case, the TA spectra would show the a new long-lived absorption band and the decay of the S$_1$ population would result only in a partial recovery of the ground-state population. Thus, the main deactivation pathway of the S$_1$ excited state of HelR in organic solvents are fluorescence and internal conversion. However, for an unambiguous assignment additional nanosecond flash photolysis experiments would be required.

**[4]Helicene cation derivatives in aqueous solutions**

The absorption spectra of HelR in water, heavy water and aqueous buffer solution (PBS) show a band around 610 nm with a shoulder at 580 nm. This band is substantially broader than that in organic solvents. The second band around 420 nm is 700 cm$^{-1}$ blue-shifted relative to ACN (Figure 6.2). The shape of the absorption spectra varies with HelR concentration (Figure 6.9). The intensity of the 420 nm band and the contribution of the 580 nm shoulder increase with growing dye concentration. As will be discussed later, this shoulder stems from aggregates formed in aqueous solutions.

The emission spectra of the investigated compounds in aqueous solution display a broad band with a maximum between 677 and 680 nm depending on the R substituents, which is nearly mirror-image to
the first absorption band (Figure 6.2). Both, the position of the maximum and the shape of the band are the same in water, heavy water and aqueous buffer solution. As expected, the enantiomers and racemic mixtures of each compound have the same fluorescence quantum yield, but it is substantially smaller than that in organic solvents (Table 6.3). Going from water to deuterated water, the fluorescence quantum yield increases by a factor of about 1.3 indicating the involvement of intermolecular hydrogen bonds in the non-radiative relaxation of the excited state.\textsuperscript{253-257} This agrees as well with the increase of the fluorescence quantum yield observed in alcohols on going from MeOH to PeOH, i.e. on decreasing the hydrogen-bond donating ability of the solvent.

The fluorescence quantum yield does not depend on the concentration of HelR and varies within the limits of experimental error around 0.026, 0.019, and 0.016 for HelPr, HelMe and HelOH, respectively. This is distinct with many other dyes, such as, for
example, those of the xanthene family, for which aggregation leads to a strong decrease of the fluorescence quantum yield.\textsuperscript{258-260}

Contrary to the fluorescence quantum yield, the fluorescence decay in aqueous solutions changes dramatically with HelR concentration (Figure 6.10). A biexponential function convolved with the IRF was required to satisfactorily reproduce the fluorescence dynamics. The obtained time constants are listed in Table 6.3. The biphasic nature of the decay indicates the presence of two emitting species. The contribution of the long-lived component to the fluorescence kinetics increases with HelR concentration. Thus, the long lifetime can be attributed to aggregated and the short lifetime to non-aggregated HelR.
The increase of the monomeric lifetime on going from water to D$_2$O confirms the role of hydrogen-bonds in the non-radiative deactivation of the S$_1$ state. Most probably, the hydrogen-bonding interactions occur at the oxygen atom of the methoxy groups. The coupling with the solvent should become stronger in the S$_1$ state because of the increase of the electron density at the oxygens atoms associated with the charge transfer character of the S$_1$←S$_0$ transition (Figure 6.3). Such an increase of the hydrogen-bonding interaction upon excitation has been shown to strongly favor hydrogen-bond assisted non-radiative deactivation.$^{253-257}$

Further evidence of aggregation in aqueous solution can be obtained from the decay of the fluorescence anisotropy, which, as it occurs via reorientational motion, depends on the size of the chromophore.$^{158}$ Figure 6.11 shows the anisotropy decays of (rac)-HelMe measured by fluorescence up-conversion in PBS and EtOH, which have a similar viscosity of $\sim$1 cP at room temperature. The poor signal to

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**Figure 6.11** Time profiles of the fluorescence polarization anisotropy at 650 nm measured with (rac)-HelMe in aqueous buffer solution and ethanol upon 400 nm excitation and best fits
noise (S/N) ratio of these data is due to the very small anisotropy of the fluorescence upon 400 nm excitation as illustrated in Figure 6.12. The initial anisotropy of 0.03 measured in the time-resolved measurements agrees with that found in the fluorescence excitation anisotropy spectrum of (rac)-HelPr in methyl-methacrylat-butyl-methacrylat (PMMA) film. This small value arises from the angle between the transition dipole moment and that responsible for absorption at 400 nm. This value points to an angle of 50°, whereas TDDFT calculations predict an angle of 90° between the S₁ ← S₀ and S₂ ← S₀ dipoles and of 30° between the S₁ ← S₀ and S₃ ← S₀ transition dipole. The difference is not so large considering that vibronic coupling can lead to mixing of the electronic states. On the other hand, Figure 6.12 shows that the fluorescence anisotropy upon excitation in the first transition band is close to the maximum of 0.4 for parallel transition dipoles.

**Figure 6.12** Excitation anisotropy and absorption spectra of (rac)-HelPr in polymer film
The dye concentration was higher than for TCSPC and steady-state experiments, and therefore the aggregate form predominates in aqueous solution. Despite the small S/N ratio, both anisotropy time profiles can be reproduced with a monoexponential function decaying to zero.

Table 6.4 summarizes the initial anisotropy, $r_0$, and anisotropy decay time, $\tau_a$, of HelR in different environments obtained from the fit. The measurements confirm the slower anisotropy in aqueous solution. Thus, the anisotropy decay time in EtOH can be ascribed to the diffusional reorientation of the monomeric dye and the long decay time in aqueous solution to that of the aggregate. The size of this aggregate cannot be directly determined from this time constant as the latter not only depends on the volume but also on the shape of the rotator.\(^{158}\)

The TA spectra of HelR in aqueous solution (Figure 6.7B) are very similar to those measured in organic solvents. The concentration of HelR was around 0.3 mM and, thus, the fraction of the aggregates was significant. The global analysis of the TA signal evolution at different wavelengths reveals a tri-phasic decay with picosecond and nanosecond components (Figure 6.8B). The first two time constants,
\[ nM \rightleftharpoons A, \quad \text{with} \quad K_e = \frac{[A]}{[M]^n} \] (eq. 6.1)

where \( n \) is the number of molecules in the aggregate and \( K_e \) is the equilibrium constant for the aggregation of enantiopure dyes.

Taking into account that the total dye concentration is \( [\text{HelR}] = [M] + n[A] \), the relationships between the concentration of each form and \( [\text{HelR}] \) are:
\[ \text{HelR} = [M] + nK_e [M]^n \]  
(eq. 6.2a)

\[ \text{HelR} = ([A]/K_e)^{1/n} + n[A] \]  
(eq. 6.2b)

The contributions of the short and long decay component of the fluorescence dynamics, i.e. the amplitude multiplied by the lifetime, are proportional to the concentration of monomeric, [M], and aggregated, [A], HelR respectively. In order to extract \( K_e \) and \( n \), the dependence on the total dye concentration was analyzed with eq. 6.2 (Figure 6.13, Table 6.5). An aggregation number of 2 has been found for all HelR dyes except for the (M)- and (P)-HelPr. This indicates that for all but these two, a simple dimerization is taking place. However, it is important to mention that the fluorescence time profiles measured with different HelR concentrations cannot be

<table>
<thead>
<tr>
<th>Compound</th>
<th>n</th>
<th>2m</th>
<th>( K_e )</th>
<th>( K_r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M)-HelMe</td>
<td>2</td>
<td></td>
<td>5.7\times10^5</td>
<td></td>
</tr>
<tr>
<td>(P)-HelMe</td>
<td>2</td>
<td></td>
<td>5.5\times10^5</td>
<td></td>
</tr>
<tr>
<td>(rac)-HelMe</td>
<td>2</td>
<td></td>
<td></td>
<td>1\times10^4</td>
</tr>
<tr>
<td>(M)-HelPr</td>
<td>1.6</td>
<td></td>
<td>230</td>
<td></td>
</tr>
<tr>
<td>(P)-HelPr</td>
<td>1.5</td>
<td></td>
<td>260</td>
<td></td>
</tr>
<tr>
<td>(rac)-HelPr</td>
<td>2</td>
<td></td>
<td></td>
<td>3.1\times10^4</td>
</tr>
<tr>
<td>(M)-HelOH</td>
<td>2</td>
<td></td>
<td>4.5\times10^5</td>
<td></td>
</tr>
<tr>
<td>(P)-HelOH</td>
<td>2</td>
<td></td>
<td>4.7\times10^5</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.5 Homochiral, \( K_e \), and heterochiral, \( K_r \), aggregation equilibrium constant, and aggregation number, \( n \) and \( m \)
perfectly reproduced using two global time constants. Indeed individual analysis of each profiles results in slightly different lifetimes. Therefore, the formation of larger aggregates cannot be excluded.

In racemic mixtures, heterochiral aggregates, $A_{\pm}$, can be formed additionally:

$$pM_+ + mM_- \rightleftharpoons A_{\pm}, \text{ with } K_r = \frac{[A_{\pm}]}{[M_+]^p[M_-]^m} \text{ (eq. 6.3)}$$

In this case, the total concentration of HelR in aqueous solution equals $[HelR] = [M_+] + [M_-] + n_+ [A_+] + n_- [A_-] + (p + m)[A_{\pm}]$. This equation can be simplified since the homochiral aggregates $A_+$ and $A_-$ have within experimental error the same aggregation constants, $K_e$, and aggregation number, $n$ (Table 6.5). Assuming furthermore that $p = m$, the experimental data obtained for racemic mixtures of HelR can be analyzed using eq. 6.4.

$$[HelR] = 2[M] + 2nK_e [M]^n + 2mK_r [M]^{2m} \text{ (eq. 6.4)}$$

The fit of the experimental data using eq. 6.4 was successful for HelMe and HelPr, but did not yield physically realistic values for HelOH. Most probably, the suggested model is too simplistic for this dye. For example, interactions between homochiral aggregates of opposite chirality, that have been neglected here, might be significant with HelOH.

The determined aggregation constant, $K_r$, and aggregation number, $m$, reveals that the heterochiral aggregates are dimers and that $K_r$ is substantially larger than that for homochiral dimers, $K_e$ (Table 6.5). This difference in the aggregation constant between enantiopure and
Figure 6.14 Normalized calculated absorption spectra of aggregated, A, and monomeric, M, form of (P)-HelR, +, and (rac)-HelR, +-, in aqueous buffer solution.

racemic aggregates reveals that heterochiral complexes are more stable than homochiral ones. This is a common property for chiral systems and has been reported for other homochiral and heterochiral complexes. Two helicenium of opposite chirality can form a more compact dimer than two molecules of the same chirality, favoring stabilizing intermolecular interactions. The bulky propyl groups probably minimize these interactions between homochiral HelPr dyes. Because of this, dimers without a well-defined geometry might be formed, leading to an apparent $n$ value of 1.5. With two HelPr of
opposite chirality, this problem might be just small enough to enable the formation of a more stable dimer with a better defined geometry.

The changes in the absorption spectra observed for different HelR concentrations originate from differences in the spectra of monomeric and aggregated dyes. Since the relative concentration of each form is known from the fluorescence decays, their individual absorption spectra can be calculated. Figure 6.14 shows normalized spectra of the monomeric HelR, and of its heterochiral and homochiral aggregates in aqueous solution. Since the obtained absorption spectra of \( \Lambda^- \) and \( \Lambda^+ \) are identical, only the latter is shown. The results are corroborated by the fact that the calculated spectra of the monomeric dyes are the same for enantiopure and racemic HelR solutions.

For all HelR dimers, a splitting of the first absorption band around 600 nm and a strong red shift of the second band around 430 nm are evident. In the case of HelMe and HelOH, the calculated absorption spectra of the homo- and heterochiral aggregates have almost identical shape and the energy gap between the two maxima of the 600 nm absorption band is approximately 940 cm\(^{-1}\). On the other hand, for the HelPr the spectra of homo- and heterochiral aggregates differ from each other in position of the maxima and in the splitting energy of 600 nm band.

According to Kasha exciton theory,\(^ {12} \) dye molecules can form dimers in different ways: parallel to each other face-to-face (H-aggregates), in a parallel end-to-end arrangement (J-aggregates) or in a skew way (see Chapter 2.2). They can be distinguished by the effect of the aggregation on the absorption spectrum. The splitting of the absorption band observed for HelR dimers points to a skew orientation of the aromatic moieties relative to each other. Additionally, the dimer’s lowest excited state has approximately the
same energy as that of the monomer, as apparent from the 600 nm absorption band, which coincides well for monomer and dimer, and from the very similar fluorescence spectra of both monomer and dimer. The radiative rate constant of the dimer is substantially smaller than that of the monomer as reflected by the difference of fluorescence lifetimes (Table 6.3), while both forms have the same fluorescence quantum yield. In order to get more insight into the structure of these dimers, quantum chemical calculations need to be performed.

Conclusions

In this chapter, the photophysical properties of new synthesized NIR dyes have been presented. The data points towards aggregation as an important feature of HelR in aqueous solution. This aggregation dramatically changes the fluorescence lifetime and anisotropy decay. Other photochemical properties, such as spectral shape of the absorption and fluorescence quantum yield are not affected so strongly. Thus, only a thorough investigation by time-resolved fluorescence spectroscopy allowed to differentiate monomeric and aggregated forms. Aggregation does not take place in the set of organic solvents chosen, leading to a lack of their spectral fingerprints in absorption and emission and to monoexponential fluorescence decays.

Owing to a fluorescence quantum yield varying in the range 0.01-0.2, these compounds could be applicable as NIR probe dyes. Apart from their aggregation in aqueous solution, the photophysical properties of these helicenes are relatively insensitive to solvent properties, the exception being a decrease of the fluorescence quantum yield and lifetime with increasing hydrogen-bond donating ability of the solvent. This feature, together with their chirality and relative
hydrophobicity could make these dyes useful for probing biological biomolecules such as nucleic acids and proteins.

Double helical DNA macromolecules carry the genetic information used in the development and functioning of all living organisms. It is a long fairly rigid polymer consisting of two antiparallel helices, that hold tightly together via hydrogen bonds and \( \pi \)-stacking interaction between nucleotides (Figure 6.15A). The nucleotide units consist of a sugar and one out of four different nucleobases (also called bases): adenine (A), cytosine (C), guanine (G) and thymine (T). The bases are complementary with respect to their hydrogen bonding sites and form AT and CG base pairs (Figure 6.15B).

In nature, the doubled strand DNA can be found in three different conformations, called A-, B- and Z-conformations.\(^\text{263}\) A- and B-DNA

![Figure 6.15 A - Structure of the B-DNA, B - molecular structures of the nucleic acid base pairs and location of the major or minor grooves (dashed lines indicate hydrogen bonds between the bases)](image)
are right-handed and are the most common conformations. They differ from each other by their sugar conformation (C2’-endo for B-DNA and C3’-endo for A-DNA), their diameter, twist and tilt angle. B-DNA is a compact cylinder with the bases centered on the helical axis and two clearly distinguished grooves, the minor and major grooves.

Generally, the A-conformation is typical for RNA, whereas for DNA it occurs under non-physiological conditions, e.g. in partially dehydrated samples. In cells, A-DNA may be produced in hybrid pairings of DNA and RNA strands, as well as in enzyme-DNA complexes. In comparison with B-DNA, the strands arrangement of the A-DNA results in a smaller minor groove and a larger major groove. Also, the angle between the base pair axis and the long DNA axis is no longer 90° like for B-DNA, but around 20°.

Z-DNA is a seldom DNA conformation of left-handed orientation. Transformation of B-DNA into Z-DNA occurs most readily in segments with specific sequences, favored largely by alternations of deoxycytidine and deoxyguanosine residues and involves upside down “flipping” of the base pairs. As a result, the backbone follows a zigzag path. The structure becomes slightly thinner and elongated with a single narrow groove that corresponds to the minor groove of B-DNA.

Chirality is intrinsically present in the DNA structure, both at the molecular and at the supramolecular level. It plays a crucial role in the DNA functionality since it guides interaction of DNA with other chemical species, such as proteins, enzymes, drugs or metal complexes. However, getting deeper insight into the molecular mechanisms involved in these specific interactions is very challenging. For example, protein-DNA interaction has been studied thoroughly,
and some proteins clearly show preference for a certain DNA helicity, yet the contribution of chirality in this interaction is unclear. As has been mentioned earlier, the main strategy to study specific interaction is via chiral organic dyes, which bind to DNA. Additionally, molecules which are able to bind strongly and specifically to DNA are of high importance due to the possibility to use them in therapeutical applications, medical diagnostics and genetic screening. For example, by DNA-drug interaction the replication and gene transcription can be suppressed leading to destruction of tumor cells or infected tissue.

Over the last decades, interaction of numerous drugs with different DNA sequences and conformations have been intensively studied. I would like to concentrate only on examples of chiral dyes, which show stereoselectivity for DNA.

Studies carried out with the DNA binding anticancer drug daunorubicin, which naturally exist as (P)-enantiomer and with its synthetic (M)-stereoisomer clearly show distinct behavior with B- and Z-DNA. (P)-Daunorubicin binds selectively to B-DNA, whereas (M)-daunorubicin (WP900) selects left-handed Z-DNA. Additional substituents can be introduced into planar polycyclic aromatic hydrocarbons which usually efficiently bind to DNA, in order to introduce chirality. For example, piperazinecarbonyloxyalkyl derivatives of anthracene and pyrene show small preferential binding of their (S)-enantiomers to B-DNA. Numerous monomeric and linked polyamides have been used to elucidate the influence of chirality on binding abilities. For this group of molecules, the (R)-enantiomer has in general a strongly enhanced binding affinity to B-DNA. Other molecules, which belong to the helicene group are as
well often used for examine chiral selectivity and were presented in detail earlier in this chapter.

Due to high importance of DNA-metal interaction, a colossal number of organometallic complexes was investigated in nuclear acid environment. It has been shown that enantioselectivity of DNA binding and appearance of undesired effects such as toxicity or mutagenicity strongly depend on chirality of these complexes. For example, the (R,R)-isomer of platinum complexes with 1,2-diaminocyclohexane and other ligands is less toxic and a more efficient anticancer drug than the (S,S)-isomer. Additionally, chiral selectivity of numerous other metal complexes with iron, rhodium, ruthenium and osmium has been used as tool for probing different DNA conformations.

In general, the binding molecules can be split into two big groups, those which bind by intercalation and those which stick to the minor or major DNA groove. In intercalation mode, the dye is inserted between two base pairs in the double helix in a parallel manner to the neighboring base pairs (Figure 6.16A). Since the distance between DNA base pairs is small, intercalates are mostly small planar
aromatic molecules. The intercalation mode very often induces a lengthening and unwinding (reducing the helical twist) of the DNA helix. Moreover, the base pairs can be tilted by several degrees from their usual arrangement (perpendicular to the long DNA axis) after dye intercalation.

The spectrum of molecules which bind on the groove, is much broader and includes molecules of various geometries. Compared to intercalation, groove binding perturbs the DNA structure to a smaller extend (Figure 6.16B). The size of the grooves allows the molecules to fit in with little distortion of the duplex structure. It is possible to distinguish minor and major groove binding. It is often presumed, that small molecules interact with the minor groove, whereas large dyes tend to recognize the major groove due to steric reasons. The binding on the minor groove is stabilized by the strong electronegative potential of the AT base pairs. Alternatively, the amino group of guanine in GC base pairs generate a steric barrier for binding to the minor groove.

A better understanding of the functionality of DNA binding agents requires to establish their binding mode. However, only a few methods such as X-ray crystallography, multidimensional NMR, and circular and linear dichroism provide information about the binding geometry. In this chapter, the overall picture of the interaction between DNA and intrinsically chiral HelR dyes will be presented. The influence of the substituents on the aromatic ring on the binding abilities, binding geometry and chiral selectivity will be discussed.
Results

*Steady-state experiments.* As has been shown in Chapter 6.1, the absorption spectra of HelR (Figure 6.1) in aqueous solution display three pronounced bands which do not depend on the chirality of the dye, but slightly shift for different substituents R. Significant changes

![Absorption spectra](image)

![Fluorescence spectra](image)

**Figure 6.17** Absorption and fluorescence spectra of 5 µM (P)-HelPr with different concentration of base pairs sspDNA (upon addition of sspDNA the volume of the solution increases by 3%)
in the absorption spectra arise upon addition of salmon sperm DNA (sspDNA) which consist in a decreased absorbance, changes in spectral shape and band position (Figure 6.17). The shoulder at 580 nm becomes more pronounced, the band around 430 nm broadens, the one around 615 nm narrows and both undergo a hypsochromic shift. These effects were observed with all investigated HelR samples irrespective of whether they were racemic or enantiopure.

Simultaneously with the changes in the absorption spectrum, significant alterations of the fluorescence spectrum appear after addition of salmon sperm DNA (Figure 6.17). When considering on a wavenumber scale, the spectrum becomes narrower, shifts hypsochromically and its intensity increases. At a certain DNA concentration, the intensity of the fluorescence stops to rise.

**Table 6.6** Fluorescence quantum yields, $\Phi_{fl}$, of the free and DNA-bound forms of HelR

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Phi_{fl}$ (free)</th>
<th>$\Phi_{fl}$ (bound)</th>
<th>Contrast</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M)-</td>
<td>0.014</td>
<td>0.061</td>
<td>4.4</td>
</tr>
<tr>
<td>HelMe</td>
<td>(P)-</td>
<td>0.018</td>
<td>0.064</td>
</tr>
<tr>
<td>(rac)-</td>
<td>0.019</td>
<td>0.085</td>
<td>4.4</td>
</tr>
<tr>
<td>(M)-</td>
<td>0.026</td>
<td>0.095</td>
<td>3.7</td>
</tr>
<tr>
<td>HelPr</td>
<td>(P)-</td>
<td>0.026</td>
<td>0.088</td>
</tr>
<tr>
<td>(rac)-</td>
<td>0.026</td>
<td>0.1</td>
<td>3.8</td>
</tr>
<tr>
<td>(M)-</td>
<td>0.016</td>
<td>0.06</td>
<td>3.7</td>
</tr>
<tr>
<td>HelOH</td>
<td>(P)-</td>
<td>0.016</td>
<td>0.05</td>
</tr>
<tr>
<td>(rac)-</td>
<td>0.016</td>
<td>0.06</td>
<td>3.7</td>
</tr>
</tbody>
</table>
indicating that all HelR present in solution are bound to DNA. The fluorescence quantum yield, $\Phi_f$, determined for free and DNA bound HelR are listed in Table 6.6, its contrast amounts to approximately 4, depending on the system.
It is important to mention that all DNA titration experiments were performed at very low HelR concentration (1 - 6 µM) in order to minimize the amount of dimers in solution. Assuming that at the beginning of the titration experiment HelR is only present as

**Figure 6.19** CD spectra of 17 µM (M)-HelMe with and without sspDNA in aqueous solution. The dotted line represents the CD spectrum of 0.65 mM sspDNA

**Figure 6.20** CD spectra recorded for different concentrations of (M)-HelMe in the presence of 0.65 mM sspDNA
monomer and that all fluorophores are bound to DNA after saturation of the fluorescence signal, the ratio of free and bound HelR at different DNA concentrations can be determined from the absorption spectra (Figure 6.18). As expected, the ratio of HelR bound to DNA grows with increasing DNA concentration in solution.

The interaction of HelR with DNA can also be detected by circular and linear dichroism experiments (see Chapter 3.2). The CD spectra of HelR change upon addition of sspDNA due to coupling of the HelR electric transitions dipole with those of the nucleobases (Figure 6.19). The maximum of the bands is red shifted and the rotational strength of the positive bands increases (except for the band at 615 nm), whereas the negative bands become less intense. In the UV spectral region the bands of sspDNA overlap with those of HelR.

**Figure 6.21** LD spectra of racemic and enantiopure HelMe \([(M)\text{-HelMe}] = 45 \, \mu\text{M}, [(P)\text{-HelMe}] = 56 \, \mu\text{M} \text{ and } [(rac)\text{-HelMe}] = 86 \, \mu\text{M}] \text{ with } 60 \, \mu\text{M ctDNA in aqueous solution.}
Figure 6.20 represent the CD spectra of (M)-HelMe with sspDNA at different ratios. The intensity of the CD signals increases linearly with dye concentration, whereas the shape of the spectra remains unaltered.

LD spectra were recorded with all investigated systems. The presence of signal confirms that the dyes interact with DNA. Figure 6.21 shows the LD spectrum of the flow oriented racemic and enantiopure HelMe with ctDNA. For HelMe and all the other investigated HelR, the LD spectra consist of three negative peaks.
around 615 nm, 460 nm and 310 nm, which originate from the HelR and a very intense peak at 257 nm, which comes from the ctDNA. Figure 6.22 shows that increasing the HelR concentration leads to changes in intensity and shape of the LD spectra. The shoulder at 580 nm becomes more pronounced and the weak signal at 400 nm disappears (Figure 6.22B).

**Time-resolved fluorescence measurements.** In order to have a reasonable TCSPC signal, a much higher dye concentration (20 - 30 µM) was used than in the steady-state titration experiments discussed so far. Hence, the contribution of aggregated HelR was much higher. Upon addition of sspDNA, the fluorescence decays of the different HelR enantiomers and racemic mixture change significantly (Figure 6.23). The fluorescence dynamics becomes longer with increasing sspDNA concentration. The sets of kinetics with different sspDNA ratio were
analyzed for each HelR system including enantiopure and racemic mixtures. Although a two exponential function reproduces well each trace separately, a global analysis of the fluorescence decays with different sspDNA concentration failed (Figure 6.23). As will be discussed later, both HelR monomer and dimer bind to DNA, thus four fluorescent species are present in solution and a four-exponential decay is expected. However, the fluorescence lifetimes of each species cannot be resolved in a reliable way. Analysis of the fluorescence dynamics indicates that the excited state lifetime of the free monomer ($\tau_{fl} = 1.6$ ns for HelPr (Table 6.3)) is easily distinguishable from the longer lifetimes associated with the HelR monomer bound to DNA as well as from free and DNA bound HelR dimers, but the latter three forms have very similar lifetimes.

Even higher concentrations of HelR (90 - 100 µM) were used for the fluorescence polarization anisotropy (FPA) measurements, whereas the HelR/sspDNA ratio was kept at 1/60. Figure 6.24 represents the

Figure 6.24 Fluorescence polarization anisotropy decays measured with (M)-HelMe at 650 nm with and without sspDNA upon 400 nm excitation and the best fits
FPA decay measured with (M)-HelMe with and without sspDNA after excitation at 400 nm. As has been discussed earlier, the poor signal to noise ratio of the anisotropy decays originates from the very small (0.025-0.03) initial anisotropy. A monoexponential function with a lifetime of 200 ± 50 ps reproduces the anisotropy decay of (M)-HelMe in aqueous solution, whereas in presence of DNA, at least two exponential functions are needed to reproduce the FPA decay. In the latter case, the first lifetime around 110 ± 30 ps can be ascribed to diffusional reorientation of the free dye in solution. The second lifetime is much longer (> 10 ns) than our time window and can not be determined precisely. It can be attributed to the slow tumbling of the DNA-bound HelR.

Discussion

Evidence of binding. The strong changes in the absorption, fluorescence and CD spectra of HelR upon addition of DNA (Figure 6.17 and 6.19) together with the increase of fluorescence quantum yield and lifetime (Figure 6.23) unambiguously point to the binding of the HelR chromophores to DNA. Additionally, the LD signal from HelR in solution with DNA clearly indicates their interaction. Finally, the strong slow down of the fluorescence anisotropy decay is one more indication of the interaction between HelR and DNA. A similar slowing down has been reported for other dyes which bind to biological macromolecules.99

The decrease of the extinction coefficient of HelR upon binding to DNA (Figure 6.17) points to a significant decrease of its radiative rate constant, $k_r$. Unfortunately, $k_r$ of the HelR bound to DNA can not be directly calculated from the fluorescence decay, since four fluorescent species (monomer and dimer HelR, both either free or
bound to DNA), three of which have very similar $S_1$ state lifetimes, contribute to the total decay. In Chapter 6.1 it has been shown that $k_r$ of HelR is not very sensitive to environmental changes (but essentially solvent independent, see Table 6.3), thus the observed decrease of $k_r$ probably arises from slight geometrical alteration of the dyes.

It is important to notice that the shape of the LD spectra measured at different DNA/dye ratios differ from each other (Figure 6.22B). These differences can be due to the fact that either i) monomeric HelR has at least two different binding modes to DNA or ii) HelR dimers interact as well with the nucleic acid. The appearance of the shoulder at 580 nm in the LD spectra (the main feature of HelR dimers) speaks in favor of interaction of HelR dimers with DNA. Thus, both HelR monomers and dimers bind to DNA and the experimentally observed LD signal consists at least of two contributions. However, it is not clear if the dimers bind to DNA directly or if dimerization takes place between a free monomer and one which is already bound to DNA.

In contrast to other molecules which have several DNA binding modes, no changes in the CD spectra with increasing HelR concentration were observed (Figure 6.20). This lack of changes can be explained by very similar CD spectra of monomer and dimer bound to DNA, which are consequently almost indistinguishable. Another possibility might be that the range of concentration chosen is not sufficient.

**Binding geometry.** Analysis of the sign and relative amplitude of the LD signal provides information about the orientation of the bound molecule (see Chapter 3.2). Figure 6.25 represents the LD signal spectra of the samples with very low concentration of HelR in order to
minimize the amount of LD signal originating from bound dimers. The LD\textsuperscript{r} amplitude of the HelR transitions are more negative than that of the DNA at 260 nm. The same has been previously observed for other molecules bound to DNA, for example for cyanine oxazole yellow (YO) dyes,\textsuperscript{304} ruthenium polypyridyl complexes,\textsuperscript{305} phenothiazinium\textsuperscript{306} and acridine dyes. Two possible explanations can be suggested. First, dye intercalation can tilt the bases of the DNA and second, the DNA becomes stiffer at the binding sites and thus better oriented in the flow. Comparison of the LD\textsuperscript{r} amplitudes of DNA (at 260 nm) with and without HelR reveals their similarity, which is probably coincidental (Figure 6.25). Indeed, Figure 6.21 demonstrates that the LD signal of DNA is significantly more intense in presence of HelR. This difference can be due to changes in DNA flow orientation upon interaction with HelR. It can also originate

**Figure 6.25** Absorption spectrum of (\textit{M})-HelMe and reduced linear dichroism (LD\textsuperscript{r}) spectra of ctDNA and the (\textit{M})-HelMe/ctDNA complex.
from the overlap of the absorption bands of HelR and DNA, since the dye transition might contribute with either positive or negative sign, depending on the binding geometry. Clearly, the LD_r signal of DNA can not be directly used for the determination of the orientational parameter S.

Since the relative orientation of the transition dipole moments of the HelR are known from the TDDFT calculations (see Chapter 6.1), the parameter S and the angles between the orientational axis of DNA and the transition dipole moments of the dye can be calculated from a set of linear equations and the obtained LD_r values.

**Figure 6.26** represent the orientation of the three transition dipole moments of HelR at 415, 465 and 615 nm. From TDDFT calculations the transition dipole moments at 615 nm and at 415 nm are located in the same plane and have an angle of approximately 28° between each other. The transition dipole moment at 465 nm is perpendicular to both, the 615 and 415 nm transition. From eq. 3.20, the experimental LD_r signal can be expressed through the angles between the DNA flow, \( \vec{D} \), and the respective transition dipole...
where $\alpha$ is the angle between the DNA flow and the 465 nm transition dipole moment ($\mathbf{\mu}_{465}$), $\beta$ the angle between the flow and the 615 nm transition dipole moment ($\mathbf{\mu}_{615}$), $\gamma$ the angle between the flow and the 415 nm transition dipole moment ($\mathbf{\mu}_{415}$) and $S$ is the orientation parameter. The system of eq. 6.5 has four unknown (the angles $\alpha$, $\beta$, $\gamma$ and the parameter $S$). In order to find the binding geometry (i.e. to determine the angles between the DNA flow and the HelR transition dipole moments), one unknown has to be represented via the others. The following mathematics allows to express $\cos \gamma$ as a function of $\cos \alpha$ and $\cos \beta$.

Let's introduce the cartesian coordinate system $XYZ$ in such a way that $\mathbf{\mu}_{465}$ is along the $z$-axis and $\mathbf{\mu}_{615}$ is along the $y$-axis (Figure 6.26). In this case, $\mathbf{\mu}_{415}$ lies in the $xy$-plane with an angle of $28^\circ$ between $\mathbf{\mu}_{415}$ and $\mathbf{\mu}_{615}$ (for simplicity $30^\circ$ will be used in the calculations). The DNA flow, $\mathbf{D}$, has the three vector components

$\mathbf{D} = \begin{pmatrix} d_x \\ d_y \\ d_z \end{pmatrix}$

and, for simplicity, the length of this vector is chosen to be 1, i.e. $|\mathbf{D}| = \sqrt{d_x^2 + d_y^2 + d_z^2} = 1$. 

\begin{align*}
LD_{415}^r &= \frac{3}{2} \cdot S \cdot (3 \cdot \cos^2 \gamma - 1) \\
LD_{465}^r &= \frac{3}{2} \cdot S \cdot (3 \cdot \cos^2 \alpha - 1) \\
LD_{615}^r &= \frac{3}{2} \cdot S \cdot (3 \cdot \cos^2 \beta - 1)
\end{align*}
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The vectors $\vec{M}^{465}$, $\vec{M}^{615}$ and $\vec{M}^{415}$ have the coordinates (see Figure 6.26)

$$
\vec{M}^{465} = \begin{pmatrix}
0 \\
0 \\
0
\end{pmatrix}, \quad \vec{M}^{615} = \begin{pmatrix}
0 \\
m_{x}^{615} \\
0
\end{pmatrix} \quad \text{and} \quad \vec{M}^{415} = \begin{pmatrix}
m_{x}^{415} \\
m_{y}^{415} \\
0
\end{pmatrix}.
$$

The angle $\delta$ between two vectors $\vec{k}$ and $\vec{m}$ of arbitrary length is given by

$$
\cos \delta = \frac{\vec{k} \cdot \vec{m}}{|k| \cdot |m|} \quad \text{(eq. 6.6)}
$$

with the length of the vector $|k| = \sqrt{k_{x}^2 + k_{y}^2 + k_{z}^2}$.

Using eq. 6.6, the angle between the two vectors $\vec{M}^{465}$ and $\vec{D}$ equals

$$
\cos \alpha = \frac{0 \cdot d_{x} + 0 \cdot d_{y} + m_{x}^{465} \cdot d_{z}}{\sqrt{(0^2 + 0^2 + (m_{x}^{465})^2) \cdot (d_{x}^2 + d_{y}^2 + d_{z}^2)}} = \frac{m_{x}^{465} \cdot d_{z}}{m_{x}^{465}} = d_{z} \quad \text{(eq. 6.7)}
$$

and the angle $\beta$ between the vectors $\vec{M}^{615}$ and $\vec{D}$ is

$$
\cos \beta = \frac{0 \cdot d_{x} + m_{y}^{615} \cdot d_{y} + 0 \cdot d_{z}}{\sqrt{(0^2 + (m_{y}^{615})^2 + 0^2) \cdot (d_{x}^2 + d_{y}^2 + d_{z}^2)}} = \frac{m_{y}^{615} \cdot d_{y}}{m_{y}^{615}} = d_{y} \quad \text{(eq. 6.8)}
$$

Determination of the angle $\gamma$ is a little bit lengthier. Since the angle between $\vec{M}^{415}$ and $\vec{M}^{615}$ is $30^\circ$, eq. 6.6 gives

$$
\cos 30^\circ = \frac{m_{x}^{415} \cdot 0 + m_{x}^{415} \cdot m_{y}^{615} + 0 \cdot 0}{\sqrt{(m_{x}^{415})^2 + (m_{y}^{615})^2 + 0^2) \cdot (0^2 + (m_{y}^{615})^2 + 0^2)}} = \frac{m_{x}^{415}}{\sqrt{(m_{x}^{415})^2 + (m_{y}^{415})^2}}.
$$
Rearranging yields $m_x^{415} = \frac{1}{\sqrt{3}} m_y^{415}$. Hence, the angle between $\vec{M}^{415}$ and $\vec{D}$ equals

$$\cos \gamma = \frac{\frac{1}{\sqrt{3}} m_y^{415} \cdot d_x + m_y^{415} \cdot d_y + 0 \cdot d_z}{\sqrt{\left(\frac{1}{\sqrt{3}} m_y^{415}\right)^2 + (m_y^{415})^2 + 0^2 \cdot (d_x^2 + d_y^2 + d_z^2)}} = \frac{1}{2} \cdot (d_x + \sqrt{3} \cdot d_y)$$

(eq. 6.9)

From eq. 6.7, 6.8 and 6.9, $\cos \gamma$ can be expressed as a function of $\cos \alpha$ and $\cos \beta$,

$$\cos \gamma = \frac{1}{2} \cdot (\sqrt{1 - \cos^2 \beta} - \cos^2 \alpha + \sqrt{3} \cdot \cos \beta)$$

(eq. 6.10)

Inserting eq. 6.10 into eq. 6.5 gives

$$\begin{cases}
LD_{415}^r = \frac{3}{2} \cdot S \cdot \left(\frac{3}{4} \cdot (\sqrt{1 - \cos^2 \beta} - \cos^2 \alpha + \sqrt{3} \cdot \cos \beta)^2 - 1\right) \\
LD_{465}^r = \frac{3}{2} \cdot S \cdot (3 \cdot \cos^2 \alpha - 1) \\
LD_{615}^r = \frac{3}{2} \cdot S \cdot (3 \cdot \cos^2 \beta - 1)
\end{cases}$$

Now the system of equations contains three unknown parameters: $S$, $\cos \alpha$ and $\cos \beta$. Rearranging to

$$\frac{3}{4} \cdot S^3 + \frac{LD_{465}^r}{2} \cdot S - \frac{1}{3} \cdot LD_{615}^r \cdot (LD_{465}^r + LD_{615}^r) - \frac{1}{9} \cdot (2 \cdot LD_{415}^r - LD_{615}^r + \frac{LD_{465}^r}{2})^2 = 0$$

and inserting the measured $LD^r$ values at the respective wavelengths yields $S = 0.034$ and, finally, all the angles
$\alpha = 69^\circ$

$\beta = 89^\circ$, and

$\gamma = 60^\circ$.

On the basis of the obtained angles, groove binding can be proposed for HelR (Figure 6.27). This is in fact anticipated for monomer HelR since it is non-planar and quite a big molecule compared to common DNA intercalates. Moreover, the strong variation in LD$^r$ amplitudes for the different transition dipole moments is incompatible with an intercalating binding mode.$^{13}$

Groove binding is the most probable interaction of HelR dimers with DNA as well. However, it cannot be precisely calculated because of the difficulties related to the overlap of the bands of monomeric and dimeric HelR.
Chiral selectivity. The chiral recognition of HelR to double strand DNA can be characterized by the binding constant $K$ for the following equilibrium, where $M$ is HelR

$$M + DNA \rightleftharpoons M \cdot DNA$$

The data represented in Figure 6.18 were analyzed using the McGhee and von Hippel model (see Chapter 3.2). The best fits describing the dependence of $r/[\text{HelR}]$ on $r$ using eq. 3.9 are shown in Figure 6.28. The determined binding constant, $K$, and the number of base pairs covered by a bound dye, $n$, are listed in Table 6.7.

The binding constants show that HelR are stereo-selective in binding to DNA. For all investigated dyes, the ($M$)-enantiomer interacts more efficiently with DNA than the ($P$)-enantiomer. Taking into account that the salmon sperm DNA used for the experiments is of right-handed B-form, this effect can be explained by enantiomeric
Table 6.7 DNA binding constant, \( K \), and the number of base pairs covered by a bound dye, \( n \), obtained for \((M)\)- and \((P)\)-enantiomer of HelR

<table>
<thead>
<tr>
<th>Compound</th>
<th>( n )</th>
<th>( K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HelMe ((M))</td>
<td>1.6</td>
<td>( 3.7 \cdot 10^5 )</td>
</tr>
<tr>
<td>HelMe ((P))</td>
<td>1.7</td>
<td>( 1.6 \cdot 10^5 )</td>
</tr>
<tr>
<td>HelPr ((M))</td>
<td>1.7</td>
<td>( 1 \cdot 10^5 )</td>
</tr>
<tr>
<td>HelPr ((P))</td>
<td>1.9</td>
<td>( 0.8 \cdot 10^5 )</td>
</tr>
<tr>
<td>HelOH ((M))</td>
<td>1.6</td>
<td>( 3.3 \cdot 10^4 )</td>
</tr>
<tr>
<td>HelOH ((P))</td>
<td>1.7</td>
<td>( 2.8 \cdot 10^4 )</td>
</tr>
</tbody>
</table>

discrimination, which leads to specific interaction between DNA and the \((M)\)-enantiomer.

The nature of the substituent R at the N atoms of HelR plays an important role in the binding ability (Figure 6.18, Table 6.7). The binding constant is the highest for \( R = \text{methyl} \) and slightly smaller for propyl. For \(-\text{(CH}_2\text{)}_2\text{-OH}\) groups, although having almost the same size as propyl groups, the binding constant is significantly smaller. Such a behavior might be explained by the difference in polarity of the \(-\text{(CH}_2\text{)}_2\text{-OH}\) and the propyl group. The hydrophobic propyl group avoids exposure to water and the molecule prefers to interact with DNA whereas the hydrogen bonds between the hydroxyl groups and water molecules increase the solvation energy of HelOH.

The racemic mixture of HelPr and HelOH does not behave like a 1:1 mixture of independent \((M)\)- and \((P)\)-chromophores. If this would be the case, the curve in Figure 6.18 corresponding to the racemic mixture would lie between those of \((M)\)- and \((P)\)-solutions. Instead
the amount of bound \((\text{rac})\)-HelR is bigger compared to enantiopure helicenes. Thus, it is obvious that dimers, the concentration of which is higher in the racemic than in the enantiopure solution, bind to DNA with a binding constant higher than that of monomeric dyes. However, an exact determination of the binding constant of dimer HelR to DNA is complicated by the overlap of the bands and has not been done.

Compared to other DNA binding molecules, HelR has quite good binding constant. It is almost one order of magnitude higher than those shown for 2,2,2-trifluoro-1-(9-anthryl)ethanol,\textsuperscript{507} piperazinecarbonyloxy-2-propyl derivatives,\textsuperscript{279} the anticancer drug Daunorubicin,\textsuperscript{278} 5,8-bis(aminomethyl)-1,12-dimethylbenzo[c]-phenanthrene\textsuperscript{229} and others.\textsuperscript{272, 286} However, it can not compete with the strongest binding molecules such as Hoechst 33258\textsuperscript{285} and Dervan’s polyamides.\textsuperscript{280, 283} The enantioselectivity of HelR to DNA \((K_M/K_P \approx 1.5)\) is rather poor in comparison with other chiral binding probes but can be clearly recognized.

**Conclusions**

All the methods used in the present work evidence the binding of HelR to DNA. The binding can be clearly seen as changes of the absorption, CD and fluorescence spectra, as an increasing fluorescence quantum yield and in the elongation of the FPA lifetime. The substituents on the N atoms strongly affect the binding ability of the dye. The highest binding constant was found for HelMe with the smallest hydrophobic substituent. The strong difference between the binding constant of HelPr and HelOH shows that the size of the substituents is not the only important factor. The hydroxyl group lowers the binding ability of the HelOH by almost one order of magnitude in comparison with the propyl group.
The (M)-enantiomer shows stereoselectivity for all investigated HelR. This indicates the presence of specific interactions between DNA and (M)-HelR. The LD experiments show that both, monomeric and dimeric HelR interact with DNA and that for both of them the way of binding is groove binding.

A favorable feature of HelR is the increasing quantum yield upon binding to DNA. Thus the dye-DNA complexes are better visible by fluorescence spectroscopy. This makes HelR promising candidates for biochemical sensor technologies.
General conclusions

This chapter presented a detailed investigation of the photophysical properties of [4]helicene dyes — new synthesized intrinsically chiral NIR fluorescence probes. HelR are promising NIR dyes with fluorescence quantum yield of up to 0.2, a reasonable value for this wavelength range. More importantly, the fluorescence quantum yield increases upon interaction with DNA.

Hydrogen bonding with the solvent and aggregation in aqueous solution were shown to determine the photophysics of the investigated HelR. Dimerization of helicenes has so far been largely overlooked in the literature but has been proven to be important for the fluorescence lifetime. From the data collected, a skew orientation between the chromophores can be anticipated in the dimer.

The obtained results evidence that the chirality of HelR dyes is of paramount importance for their behavior - the dimerization constant between two unlike enantiomers is substantially higher than that of the homodimer and the binding constant to DNA differs for the two enantiomers. The \( (M) \)-enantiomer of all studied HelR interacts with B-DNA more efficiently than the \( (P) \)-enantiomer. As continuation, their interaction with other DNA conformations, such as A- and Z-DNA should be examined.

The LD experiments show that HelR bind on the groove of the DNA, and hence it is might be interesting to investigate the sensitivity of the binding abilities to the nature of the base pairs. For this purpose, the DNA consisting only of either AT or CG base pairs can be used, and the HelR binding constant to such sequences compared.
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Apart from DNA, HelR can be expected to show selectivity for protein surfaces. Recently, a biotin-HelR construct has been synthesized successfully in the group of Prof. Lacour and enantiopure samples are available. Biotin is known to intercalate at specific sites of avidin, a medium-size protein.\textsuperscript{308} In the case of chiral selectivity, it can be anticipated that the \((M)\)- and \((P)\)-enantiomer will show distinct solvation dynamics since one probes the close protein surface while the other is further apart. Such studies are currently underway in our laboratory.
Chapter 7

Concluding remarks

The data presented in this work illustrates the power of ultrafast time-resolved spectroscopy to study a broad field of phenomena. Completely distinct tasks, such as the investigation of electron or energy transfer, aggregate formation, and interactions of dye with surrounding molecules have been addressed. Additionally, time-resolved spectroscopy provides characteristics of molecules by their spectral and temporal fingerprints. In certain cases, only the temporal features were sufficient to draw conclusions.

Transient absorption technique is especially useful to detect electron transfer since it does not rely on the chromophores to be fluorescent. However, without the information from ultrafast fluorescence, it
would not have been possible to unravel the complicated dynamics that result from relaxation process occurring in parallel to the ultrafast electron transfer and excitation energy transfer processes in many cases. The unique power of linear dichroism to detect interaction and to determine binding geometries was indispensable for the study of [4]helicene derivatives.

The obtained results highlight the power of NDI multichromophoric systems in a photovoltaic application, namely for constructing supramolecular n/p-heterojunction for solar cells. The photophysics of several NDI monomers and of assemblies of NDIs attached on different scaffolds has been thoroughly investigated. The main features of NDIs multichromophoric systems is that they act at the same time as antenna (harvesting optical energy) and as reaction center (undergoing charge separation), contrary to other multichromophoric systems presented in the literature. Using NDI cores and by slight chemical modifications, access to all the visible sunlight at high extinction coefficients is provided.

The first prototypes of supramolecular n/p-heterojunction solar cells constructed from NDIs showed promising results. The one- and two-colored SOSIP architectures assembled on ITO undergo very fast electron transfer between different NDIs and have subsequent long lived charge separated states. It is obvious that numerous parameters such as the type of NDIs, the distance between them, NDI sequence, etc. can change the efficiency of the electron transfer and charge separation characteristic of these architectures. Thus, one part of future work will be to combine different NDIs to yield efficient solar cells.

The binding on the groove of double strand DNA results in an increase of their fluorescence quantum yield, and thus makes them better visible. Also their other photophysical properties suggest them as potential near infrared fluorescence probes with a broad applicability in chemistry, biology and medicine. Aggregation of helicenes significantly alters their photophysical behavior. Variation of the substituents on the helicene core opens the door to other dyes with specific properties. Already now the helicene-biotin construct is used for probing the surface of proteins.
A.1 Absorption spectra of $R_{Cl}$-NDI and $B$-NDI radical ions

The oxidation and reduction of $R_{Cl}$-NDI and $B$-NDI (Figure 4.3) in dichloromethane (DCM) has been performed using a spectro-

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{absorption_spectra.png}
\caption{Absorption spectra of $R_{Cl}$-MON with 0.1 M Bu$_4$N(ClO$_4$) in DCM at room temperature measured during electro oxidation (A) and reduction (B) process (light grey curve correspond to $R_{Cl}$-MON and black to the final product)}
\end{figure}
electrochemical cell (see Chapter 3.2). The changes in absorption spectra are shown in Figure A.1 and A.2.
A.2 Résumé de la Thèse

Les données présentées dans ce travail illustrent la puissance de la spectroscopie ultra rapide résolue dans le temps pour étudier un large champ de phénomènes. Des tâches totalement distinctes, telles que la recherche de transfert d’électron ou d’énergie, la formation d’agrégats et les interactions d’un colorant avec les molécules environnantes, ont été abordées. La spectroscopie résolue dans le temps fournit des informations sur les caractéristiques moléculaires de par leurs empreintes spectrales et temporelles. Dans certains cas, seules les données temporelles permettent d’accéder à des conclusions. La technique d’absorption transitoire est spécialement utile pour détecter le transfert d’électron puisqu’elle ne se fonde pas sur la fluorescence des chromophores. Cependant, sans l’information de la spectroscopie de fluorescence ultra rapide, il n’aurait pas été possible de démêler les dynamiques complexes qui résultent de processus de relaxation se produisant en parallèle, dans de nombreux cas, à des processus ultra rapides de transfert d’électron et d’énergie d’excitation. Le pouvoir unique du dichroïsme linéaire de détecter les interactions moléculaires et de déterminer les géométries de liaison a été indispensable pour l’étude des dérivés de [4]hélicène.

Les résultats obtenus mettent en valeur le pouvoir des systèmes NDI multichromiques dans une application photovoltaïque, plus exactement pour la construction d’hétérojonctions supramoléculaires n/p pour des cellules solaires. La photophysique de plusieurs monomères et assemblages de NDI attachés sur différents échafaudages a été pleinement examinée. La principale caractéristique des systèmes multichromophoriques de NDI est qu’ils agissent en même temps que l’antenne (récoltant de l’énergie optique) et que le centre réactionnel (effectuant la séparation de charges),
contrairement aux autres systèmes multichromophoriques présentés dans la littérature. L'utilisation des noyaux NDI pour accéder à toute la lumière visible du soleil avec de hauts coefficients d’extinction a été atteinte, par de légères modifications chimiques.

Les premiers prototypes d’hétérojonctions n/p supramoléculaires pour des cellules solaires construits à partir des NDI ont montré des résultats prometteurs. Les architectures SOSIP colorées une et deux fois, assemblées sur de l’ITO, subissent des transferts d’électrons très rapides entre les différents NDI et ont des états de transfert de charge à long temps de vie. Dans cette thèse, il est montré que de nombreux paramètres tels que le type de NDI et la distance entre eux peuvent changer la nature des processus de transfert d’électron et par-dessus tout, l’efficacité de ces architectures.

La recherche de dérivés intrinsèquement chiraux de [4]hélicène a mis en évidence leur interaction stéréo-sélective avec des molécules biologiques. La fixation sur rainure de l’ADN double brin donne lieu à une augmentation de leurs rendements quantiques de fluorescence et ainsi, les rend plus visibles. A part ça, leurs autres propriétés photophysiques laissent penser qu’ils pourraient être des sondes fluorescentes prometteuses, dans le proche IR, avec une large applicabilité en chimie, biologie et médecine. L’agrégation des hélicènes, dont la preuve a été démontrée dans cette thèse, modifie de façon significative leur comportement photophysique.
Abbreviations

ACN  acetonitrile
ADP  adenosine diphosphate
ATP  adenosine triphosphate
BHJ  p/n-heterojunction
BS   beamsplitter
CCD  charge-coupled device
CD   circular dichroism
CHCl₃ chloroform
CPM  cross phase modulation
CR   charge recombination
CS   charge separation
CSS  charge-separated state
DADS decay associated difference spectra
DCM  dichloromethane
DFG  difference frequency generation
DMA  N,N-dimethylaniline
DMF  dimethylformamide
DMSO dimethyl sulfoxide
DNA  deoxyribonucleic acid
EDTA ethylenediaminetetraacetic acid
EEH  energy hopping
EET  excitation energy transfer
ESA  excited state absorption
ET   electron transfer
**Abbreviations**

EtOH ethanol  
FES free energy surface  
FPA fluorescence polarization anisotropy  
FRET Förster type energy transfer  
FWHM full width at half maximum  
GSB ground state bleach  
GVD group velocity dispersion  
HelR [4]helicene derivatives  
HOMO highest occupied molecular orbital  
HR hollow retroreflector  
IC internal conversion  
IRF instrument response function  
ISC intersystem crossing  
ITO indium tin oxide  
IVR intramolecular vibrational energy redistribution  
LD linear dichroism  
LES locally excited state  
LSS localized S\textsubscript{1} state  
LTS localized T\textsubscript{1} state  
LUMO lowest unoccupied molecular orbital  
MeOH methanol  
MN 1-methylnaphthalene  
MO molecular orbital  
NDI naphthalene diimide  
NIR near infrared  
NOPA non-collinear OPA  
OKE optical Kerr effect  
OPA optical parametric amplifier
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>OPE</td>
<td>oligophenylethynyl</td>
</tr>
<tr>
<td>OTTLE</td>
<td>optically transparent thin layer electrochemical cell</td>
</tr>
<tr>
<td>PBS</td>
<td>phosphate buffered saline</td>
</tr>
<tr>
<td>PDI</td>
<td>perylene diimide</td>
</tr>
<tr>
<td>PeOH</td>
<td>1-pentanol</td>
</tr>
<tr>
<td>PES</td>
<td>potential energy surface</td>
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<tr>
<td>PET</td>
<td>photoinduced electron transfer</td>
</tr>
<tr>
<td>PMT</td>
<td>photomultiplier tube</td>
</tr>
<tr>
<td>POP</td>
<td>$\rho$-octiphenyl</td>
</tr>
<tr>
<td>RC</td>
<td>reaction center</td>
</tr>
<tr>
<td>RNA</td>
<td>ribonucleic acid</td>
</tr>
<tr>
<td>SADS</td>
<td>species associated difference spectra</td>
</tr>
<tr>
<td>SE</td>
<td>stimulated emission</td>
</tr>
<tr>
<td>SFG</td>
<td>sum frequency generation</td>
</tr>
<tr>
<td>SHG</td>
<td>second harmonic generation</td>
</tr>
<tr>
<td>SOSIP</td>
<td>self-organizing surface-initiated polymerization</td>
</tr>
<tr>
<td>SVD</td>
<td>singular value decomposition</td>
</tr>
<tr>
<td>TA</td>
<td>transient absorption</td>
</tr>
<tr>
<td>TCSPC</td>
<td>time-correlated single photon counting</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TNM</td>
<td>tetranitromethane</td>
</tr>
<tr>
<td>TRES</td>
<td>time resolved emission spectra</td>
</tr>
<tr>
<td>TTA</td>
<td>triplet-triplet absorption</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>VC</td>
<td>vibrational cooling</td>
</tr>
<tr>
<td>VR</td>
<td>vibrational relaxation</td>
</tr>
<tr>
<td>WL</td>
<td>white light</td>
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