Chapter 2

Optical energy transport and interactions between the excitations in a coumarin – perylene bisimide dendrimer

ABSTRACT

Energy transfer properties of novel coumarin – perylene bisimide dendrimer are studied by means of steady state and time-resolved UV/VIS spectroscopy. At low donor excitation density fast (transfer rate \( \sim 10 \text{ ps}^{-1} \)) and efficient (quantum yield \( \sim 99.5\% \)) donor-acceptor energy transfer is observed. The random distributions of donor-acceptor orientations and distances result in non-exponential energy transfer kinetics. The energy transfer remains independent of excitation density up to densities corresponding to one absorbed photon per 10 dendrimer molecules. At higher excitation densities the transfer rate is found to increase due to excitation of multiple donors per dendrimer. Control of the donor-acceptor energy transfer rate is achieved by pre-excitation of the acceptor and monitored by pre-pump – pump – probe experiments, which show that the energy transfer rate can be decreased by a factor of two. The relative orientations of transition dipole moments in the donor and acceptor molecules are found to be one of the key factors determining the energy transfer dynamics at high excitation densities.

I. INTRODUCTION

Dendrimers are well-defined branched macromolecules with a high degree of order. The distinctive structure of dendrimers allows encapsulation of active components [1-4] which is an important issue in drug delivery [5, 6], catalysis of chemical reactions [7-10], surface modification [11-14], and molecular opto-electronics [15-17]. Over the last decade extensive studies of the optical properties and applications of dendrimers have been carried out. Kawa et al. [18, 19] have employed dendrimeric encapsulation to isolate lanthanide ions from the solvent, leading to a significant suppression of vibrational quenching of the lanthanide luminescence. Dendritic systems are considered as promising candidates for light harvesting and excitation energy transport [17, 20-29]. Efficient light harvesting in dendrimers is realized through a large number of donors branching around a single or a few acceptors. The distances between the donors and acceptors can be optimized for efficient dipole-dipole interaction and Förster energy transfer. In such systems a high UV/VIS absorptivity of a large number of donors is potentially beneficial for light harvesting when efficient energy transport takes place. This assures a high energy flux to the acceptor (or the core of the dendrimer) [17, 20-29].

A detailed model of donor-acceptor population dynamics based on a system of differential rate equations for a first generation dendrimer has been presented in [31]. For higher generation dendrimers, the light harvesting can be improved through the use of cascade systems containing several different chromophores [35-38]. Recently, novel energy harvesting and transfer related phenomena in dendrimers, such as photocatalysis [39, 40] and energy upconversion [41, 42], have been reported, highlighting the importance of a fundamental understanding of the ET mechanisms that take place in dendrimeric systems.

Due to the presence of multiple donors per dendrimer, more than one donor per dendrimer can be excited already at moderate excitation densities. This leads to interactions between the excitations, which potentially can either increase or decrease the ET efficiency. For example Neuwahl et al. [43], while measuring pump-probe spectra in a donor-acceptor type system at relatively high irradiation intensities, observed residual emission from the donor at delays, which are long compared to the energy transfer time. The phenomenon was explained by proposing, that once the acceptor is excited via excitation transfer from one donor molecule, ET from the other donors is prohibited. Later on, the effect of donor-acceptor ET restriction when the acceptor is excited was extensively studied by the group of De Schryver [29, 36, 37], attributing the phenomena to “exciton blockade”. In contrast, no change in the ET rate upon increasing excitation density was observed by Hania et al. in a coumarin-porphyrin dendrimer [31]. It was demonstrated that both the difference between the energy transfer rate constants to a singly and doubly excited acceptor states, and the rate of radiationless decay from such doubly excited states are the key parameters determining the overall ET dynamics at high excitation density conditions. A recent paper by Melnikov et al. [28] studies the phenomena of simultaneous emission from both donor, and acceptor chromophores in a peryleneimide-tetrylenediimide dendrimer at the single-molecule level. Though the “exciton blockade” effect would be the most straightforward explanation for the phenomena observed, the authors conclude that additional conditions are necessary, in particular – unfavorable donor-acceptor transition orientation and photobleaching of the donors with favorable orientations.

Here we present detailed studies of the ET properties of a first generation dendrimer composed of four equivalent coumarin donors surrounding a perylene bisimide based acceptor under both low and high excitation density conditions. Well defined properties of the coumarins (donor chromophores) and extensively studied perylene bisimide derivatives (acceptor chromophore) [44-46] as well as its high photostability, make this dendrimer an excellent model system for studying the interactions between the excitations. An additional advantage of this dendrimer as a model system for ET studies is the difference in the rates of various ET and energy relaxation processes, such as donor-acceptor ET, donor-donor energy hopping, relaxation of the acceptor from the higher excited states to the lowest excited state, and relaxation of both chromophores to the ground state.

Time-resolved fluorescence and intensity dependent pump-probe techniques are employed to study the excitation dynamics. In addition, control of donor-acceptor energy transfer is achieved through pre-excitation of the acceptor using multi-color pre-pump – pump – probe techniques. These experiments show that the energy transfer rate can be reduced by a factor of two. One of the key factors determining the ET rate at high excitation fluence is the relative orientation of the transition dipole moments in the donors and the acceptor, which exceeds the influence of spectral overlap changes in the dendrimer. In addition, by performing molecular dynamics (MD) simulations, we have studied the influence of the flexible nature of the dendrimer on the ET dynamics.

The chapter is organized as follows. After introducing the material and the experimental procedures in section II, we start with a discussion on the qualitative properties of the ET in the first generation coumarin–perylene bisimide dendrimer in section III.A. The ET dynamics
studied by time-resolved measurements at low excitation density are discussed in section III.B. Analytical considerations and experimental confirmation concerning interactions between excitations at high excitation densities are presented in sections III.C and III.D, respectively. Finally, in section III.E, the results of optical pre-pump – pump – probe experiments are presented, which allow distinctive investigation of the effect of an excited acceptor on the ET rate.

II. MATERIALS AND METHODS

The coumarin – perylene bisimide dendrimer (C4P) (Fig. 1c) consists of four coumarin subunits acting as energy donors and a single perylene bisimide core, which is connected to the donors via spacers. Model constituent compounds are also shown in Fig. 1 (a, b): two donors connected via a spacer (a) and a perylene bisimide acceptor with two spacers (b). The synthesis of C4P and constituent compounds was performed using an amide coupling methodology. The details of the synthesis are discussed in Ref. 47. Analytical data (1H and 13C NMR, MS (MALDI-TOF)) for the C4P and constituent compounds are in agreement with the structures shown. All optical experiments were carried out at room temperature under ambient air conditions with the compounds dissolved in chloroform in a 2 mm cuvette or a 0.1-0.5 mm flow cell.

Energy transfer dynamics in C4P was studied by means of time-resolved fluorescence and transient absorption (pump-probe) spectroscopy. In order to study interactions between excitations, pump-probe measurements were carried out at different excitation densities. In addition, pre-pump – pump – probe experiments, which potentially disclose a dependence of the ET dynamics on the population of acceptor sites, were performed.

Time and spectrally resolved (spectral resolution is ca. 0.6 nm) fluorescence measurements were performed using a streak camera system with a synchro-scan sweep unit (Hamamatsu). The sample was irradiated by a frequency-tripled (λ = 325 nm, τ = 120 fs) output of a tunable 76 MHz Ti:Sapphire laser (Mira 900, Coherent), which was pumped by an all-solid-state diode-pumped, frequency doubled Nd:YVO4 laser (Verdi, Coherent). A pulse picker was used to reduce the repetition rate to 1.9 MHz. In order to maintain low excitation density conditions, the pulse energy was attenuated to 1 pJ which corresponds to one photon absorbed per 10⁵ donor molecules per pulse. The time resolution of the experiments, as determined by recording scattered light from the excitation pulse, was 7 ps. In order to avoid population of the acceptor triplet states by multiple laser pulses and to ensure photostability of the sample, a 10⁻⁴ M solution of C4P in CHCl₃ was pumped along a 0.5 mm fused silica cell by a peristaltic pump. The absorption spectra of the samples measured before and after the time-resolved fluorescence experiments were identical, which indicates the absence of photodecomposition.

Pump-probe experiments were performed in a standard geometry using two independently tunable non-collinearly pumped optical parametric amplifiers (NOPAs) (Topas White, Light Conversion) as pump and probe sources. The NOPAs were pumped by a Ti:Sapphire laser/regenerative amplifier system (Hurricane, Spectra Physics) producing 120 fs, 800 nm pulses at 1 kHz repetition rate. The sample was excited at 325 nm, corresponding to the absorption maximum of the donor molecule. UV pulses at 325 nm were obtained by frequency doubling of the 650 nm signal wave of one of the NOPAs in a 0.15 mm BBO crystal and subsequent compression in a double-pass compressor based on two fused silica prisms. In addition to the pulse shortening, the compressor allows for spatial separation of the fundamental and second harmonic beams. The time resolution of pump-probe experiments, as measured by monitoring two-color two-photon absorption in a 100 µm
glass plate, was 70 fs. For the measurements of the dynamics of the pump-probe spectrum, white light in a 390-800 nm spectral range was generated in a 1 cm water cell. The time resolution in this case was lower because of the chirped white light, though it remained in the sub-picosecond range.

Pre-pump – pump – probe experiments were performed by pre-exciting acceptors with a high energy pre-pump pulse centered at \( \lambda_{\text{prep}} = 550 \text{ nm} \). Then, after a time delay, a pump pulse at \( \lambda_{\text{ex}} = 325 \text{ nm} \) wavelength corresponding to the maximum of the donor absorption, was applied. The third pulse centered at \( \lambda_{\text{pr}} = 325 \text{ nm} \) wavelength probed the photoinduced optical density changes in the C4P dendrimers. The delay between the pre-pump and pump pulses was variable in a 1 ns time window. Polarization of the pre-pump pulse was either parallel or perpendicular to the polarization of the pump pulse.

Molecular dynamic (MD) simulations were performed using the Langevin MD method with MM+ force field (Hyperchem 7.5) in a medium with a viscosity of chloroform (5.8 \( \times \) 10\(^{-4} \text{ N} \cdot \text{s} \cdot \text{m}^2 \)) at room temperature. Simulations were performed on a single dendrimer molecule with no solvent molecules present. Data was collected for 10 ns with 100 fs time-steps after 1 ns equilibration time, while atom positions were updated every 1 fs.

III. RESULTS AND DISCUSSION

A. Donor-acceptor ET in C4P: qualitative description

The realization of both, efficient light energy harvesting and transport, requires a rather weak interaction between donors and between donor and acceptor units as well as sufficient spectral overlap of donor and acceptor resonances, i.e. donor fluorescence and acceptor absorption. In order to estimate the interactions between the constituent parts of the C4P dendrimer, to confirm the occurrence of donor-acceptor ET, and to examine the ET properties qualitatively, we measured steady state absorption and fluorescence spectra of the model compounds and compared them with the ones, characteristic for the whole dendrimer.

Steady state absorption and fluorescence spectra of donor and acceptor constituents are presented in the top panel of Fig. 1. A simplified energy level diagram of C4P, which also shows a number of possible transitions, is shown in Fig. 2. The absorption spectrum of the donor molecule is dominated by a single band, centered at around 325 nm, which originates from the \( S_0 \rightarrow S_1 \) transition. The corresponding fluorescence spectrum consists of a band centered at 385 nm. The absorption spectrum of the acceptor molecule in the visible spectral region is characterized by a \( S_0 \rightarrow S_1 \) transition leading to an absorption band peaking at 584 nm featuring a vibronic progression, as well as by a \( S_0 \rightarrow S_2 \) transition resulting in an absorption band with a maximum at 455 nm. The fluorescence spectrum of the acceptor has a maximum at 620 nm and is a mirror image of the \( S_0 \rightarrow S_1 \) absorption band. As can be seen from the upper panel in Fig. 1, the \( S_0 \rightarrow S_2 \) absorption band of the acceptor overlaps partially with the fluorescence band of the donor enabling resonant ET. The fluorescence spectrum of the complete dendrimer (Fig. 1, lower panel), measured while exciting at the absorption maximum of the donors (325 nm), clearly shows the occurrence of donor-acceptor ET: the fluorescence of the donors is quenched significantly, while the fluorescence intensity of the acceptor is increased considerably.

The absorption spectrum of the dendrimer (lower panel of Fig. 1) is red shifted by ca. 100 cm\(^{-1} \) with respect to the weighted sum of absorption spectra of donors and acceptor with spacer, indicating that donor-acceptor interaction is rather weak. The weakness of the interaction allows for a description of the ET dynamics in terms of the dipole-dipole Förster
energy transfer theory. A more detailed analysis of the changes in the C4P absorption spectrum due to attachment of different constituents is presented in Ref. [47].

Figure 1. Top panel: absorption and fluorescence spectra of donor (absorption – dotted line, fluorescence – dashed-dotted line) and acceptor (absorption – solid line, fluorescence – dashed line) constituents. The chemical structure of the constituent compounds is shown in the insets: two donors attached to a spacer (a) and acceptor with two spacers attached (b). Bottom panel: absorption and fluorescence spectra of the C4P dendrimer (absorption – solid line, fluorescence – dashed line). The chemical structure of the C4P dendrimer is shown in inset (c). All absorption data are presented in absolute units of optical density. Spectra are measured in a 2 mm cell, at concentration of 10⁻⁴ M for all compounds. Fluorescence spectra are scaled to match the maxima of corresponding absorption bands.

Finally, the linear donor and acceptor spectra shown in Fig. 1 overlap partially. This makes selective excitation of donor molecules impossible. Nevertheless, by taking into account that the dendrimer is composed of four donors and a single acceptor, we estimate that the selectivity toward donor excitation is still about 85% at 325 nm.

For more evident verification of the ET, time-resolved fluorescence measurements were performed. The experiments reveal a single-exponential decay of excitations for both constituent parts of the dendrimer with decay time constants of 2.1 ns and 6.7 ns for the donor and acceptor model compounds (Fig. 1a and b), respectively (results are not shown). The decay time constants obtained are close to those reported for similar dyes [48, 49], indicating that the chemical modifications of the chromophores does not alter the photophysical properties of the compounds considerably. In addition, the measured fluorescence quantum yield for both, coumarin and side-branch model compound (Fig. 1a) is found to be 70%, indicating that the spacer doesn’t affect the fluorescence efficiency of the donors. The measured emission quantum yields for the acceptor model compound (Fig. 1b) and for the whole dendrimer (Fig. 1c) are 92% and 85%, respectively, showing that the
influence of the incorporation of the acceptor in the dendrimer on the emission efficiency of the acceptor is rather low.

![Energy transfer diagram](image)

**Figure 2.** Energy transfer diagram showing the ET processes where one donor per dendrimer is excited (boxed part) and where two donors per dendrimer are excited (full diagram).

![Normalized fluorescence dynamics](image)

**Figure 3.** Normalized fluorescence dynamics observed for C4P at wavelengths $\lambda_{pr} = 385$ nm (dashed line) and $\lambda_{pr} = 620$ nm (solid line), corresponding to the maxima of the fluorescence spectra of the donor and the acceptor, respectively. Excitation wavelength is $\lambda_{ex} = 325$ nm. The system response function is shown by the dotted line. All the signals are normalized to their maxima.

The fluorescence kinetics in a 100 ps time window after excitation of the dendrimer at 325 nm is shown in Fig. 3. The wavelengths 385 nm and 620 nm correspond to the fluorescence maxima of donor and acceptor units, respectively. After deconvolution of the instrumental response, the fluorescence of the dendrimer at 385 nm is found to decay, while the fluorescence at 620 nm features a delayed formation, both with the time constant of about 10 ps. The observed precursor-successor relationship points towards rather efficient (estimated quantum yield is 99.5%) donor-acceptor ET. It appears that the growth of fluorescence of the acceptors is slightly faster than the decay of fluorescence of the donors, which, most likely, originates from direct excitation of ca. 15% of the acceptor molecules. About 4% of the fluorescence of the donor units decays with a time constant of 2.1 ns. Since the 2.1 ns decay time coincides with the excitation lifetime of the side-branch model
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compounds (Fig. 1a) and the long-timescale emission spectrum matches the emission of donors or side-branches, it is most likely that the slow emission component originates from residual, disconnected, donor molecules.

A simple, qualitative, diagram of ET in C4P at low excitation energies is depicted in the boxed area of Fig. 2. First, an incoming photon excites the donor from S$_0$ to S$_1$. Subsequently ET from donor to acceptor takes place resulting in a S$_2$ excited acceptor state, which decays rapidly via a non-radiative S$_2$→S$_1$ transition to the S$_1$ state on a ~100 fs time scale. Finally, the acceptor decays radiatively from S$_1$ to S$_0$ leading to the fluorescence observed.

B. ET at low excitation density

As noted in the previous section, the interaction between the donor and acceptor chromophores of the dendrimer is weak; therefore the donor-acceptor ET rate constant can be estimated using the Förster dipole-dipole ET model [50]:

$$ (k_{ET})^{-1} = (k_D)^{-1} \frac{R_{DA}}{R_0}^6, \quad (1) $$

where $R_{DA}$ is the donor – acceptor distance, $k_{ET}$ and $k_D$ are the rate constants for the energy transfer and the donor decay, respectively, and $R_0$ is the Förster radius:

$$ R_0^6 = C \frac{\kappa^2 \phi_D}{N_A n^2} J. \quad (2) $$

$J = \int_0^\infty I_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda$ in this equation represents the overlap integral of donor fluorescence $I_D(\lambda)$ and acceptor absorption denoted by the extinction coefficient $\varepsilon_A(\lambda)$, $\kappa^2$ is an orientational factor, $\phi_D$ is the fluorescence quantum yield (QY) of a separate donor, $N_A$ is Avogadro’s number, $n$ is the refractive index of the medium, and $C = 9000 \cdot \ln(10)/(128\pi^5) \approx 0.53$ [50].

MD simulations give an average distance between the donor and acceptor molecules of $\langle R_{DA} \rangle = 1.5$ nm. The simulations of the dendrimer geometry show that rotation is rather free around the bonds adjacent to the amide carbonyls. However, the timescale of the structural fluctuations ranges from tens to hundreds of picoseconds. Specifically, donor-acceptor distance autocorrelation decay could be fitted with two exponents with time constants of 56 and 1550 ps. Thus, even the fastest fluctuations are expected to be several times slower than the donor-acceptor ET. Consequently, for the present experiments, a solution of dendrimers can be treated as an ensemble of rigid molecules with static structural variations. Assuming a static random distribution of orientations [51] between the transition dipole moments of the donor and acceptor units leads to an orientational factor $\kappa^2 = 0.845^2 \cdot 2/3$ [52]. Using the bulk value of the refractive index of chloroform $n = 1.45$, the donor-acceptor distance $\langle R_{DA} \rangle = 1.5$ nm, the donor fluorescence lifetime $\tau_D = 2.1$ ns and the measured quantum yield $\phi_D = 70\%$, and the overlap integral $J = 2.33 \cdot 10^{14} M^{-4} cm^{-1} nm^4$, estimated from the experiments, we obtain an ET time constant $k_{ET}^{-1} = 15$ ps.

As it is evident from Eq. 1, the ET rate constant is extremely sensitive to variations of the distance between donor and acceptor units, which, because of the flexible nature of the dendrimer mentioned above, can be distributed over quite a wide range. In addition, donor-acceptor dipole orientations are not completely random, so the estimated $\kappa$ value is not precise. Another limiting factor for the precision of the calculated ET rate is the finite size of the perylene bisimide and coumarin molecules: The Förster ET model is applicable for point dipoles separated by a specific distance, and can substantially fail in describing energy transfer processes when the distance between the chromophores becomes similar to the size
of the chromophores [53-57]. In the case of C4P, the donor and acceptor chromophores are relatively large compared to the distances between them, thus an extended dipole approach in calculating the ET rate would be more relevant. Given these limitations the ET rate constant (15 ps) calculated here is in a very good agreement with that determined experimentally from the time resolved fluorescence measurements.

Although the time resolved fluorescence measurements confirm efficient ET in C4P, the time resolution of the streak camera (ca. 7 ps) is insufficient for a detailed examination of the ET dynamics. Time and frequency resolved pump-probe experiments with a sub-100 fs time resolution were employed to characterize the ET dynamics more quantitatively. The dendrimers were excited at the wavelength corresponding to the maximum of the donor absorption. Experiments were carried out at a relatively low excitation density corresponding to one photon absorbed per 30 dendrimer molecules.

The pump-probe trace measured at probe wavelengths of 325 nm, corresponding to bleaching of the $S_0 \rightarrow S_1$ donor absorption band and to $S_1 \rightarrow S_n$ photoinduced absorption in the acceptor, is presented in the lower panel of Fig. 4. The bleaching dynamics of the $S_0 \rightarrow S_1$ absorption band in the acceptor at 590 nm is shown in the upper panel of Fig. 4. The pump-probe dynamics of the other bands of the acceptor (bleaching at 470 nm and photoinduced absorption above 680 nm) correlate well with the bleaching dynamics of the $S_0 \rightarrow S_1$ band.

The band in the vicinity of 590 nm has been chosen for the monitoring the occupation of the acceptor $S_1$ state in all experiments, because of its strong response, thus giving the best signal-to-noise ratio. Although the experiments are performed with a much higher time resolution, the interpretation of the dynamics observed in the pump-probe experiments is not as straightforward as it is for time resolved fluorescence experiments. The complexity arises from the spectral overlap of pump-probe signals originating from the different photoinduced features in the donor and acceptor units. For instance, in the case of probing at 325 nm (Fig. 4, lower panel) bleaching of the donor band is observed directly after excitation. As a result of ET from the donor to the acceptor this bleaching decays, and evolves into photoinduced
absorption caused by excited acceptor molecules (see the following section for more details). From the magnitudes of the initial photoinduced bleaching and the photoinduced absorption measured at later times we estimate a ratio of 0.4 between the contributions of donor and acceptor units to the pump-probe signal. Since after ET from the donor to the acceptor the internal conversion \( S_2 \rightarrow S_1 \) is very fast (not quite resolvable at the time resolution available), the formation of the photoinduced absorption depicted in the lower panel of Fig. 4 reflects the ET dynamics from the donor to the acceptor.

Figure 5. Pump-probe signal at probe wavelength \( \lambda_{\text{pr}} = 590 \) nm recalculated from Fig. 4, as explained in the text (dots), single-exponential fit to the data (dashed line) and curve simulated by using Eq. 3 (solid line). The inset shows the distribution of donor-acceptor distances used in Eq. 3.

The analysis of pump-probe transients, such as the ones shown in Fig. 4, confirms a precursor-successor relationship as observed in the time resolved fluorescence experiments and reveals that ET proceeds on a sub-10 ps timescale. However the dynamics measured show a, evidently, non-exponential character resulting from the flexible nature of C4P molecules. In general, the orientation of a donor molecule with respect to the acceptor also affects the ET rate, however to a lesser extent. Taking only variations of the donor-acceptor distance into account, the ET dynamics \( N(t) \) can be modeled in the following way:

\[
N(t) = \int_0^\infty \frac{1}{\sigma \sqrt{2\pi}} \exp\left(-\frac{(r-1)^2}{2\sigma^2}\right) \cdot \exp\left(-\frac{k_{\text{eff}}t}{r^6}\right) dr.
\]  

In this equation it is assumed that the donor-acceptor distances have a normal distribution with standard deviation \( \sigma \ll 1 \) [51], and \( k_{\text{eff}} \) is the “effective” ET rate corresponding to that of the mean donor-acceptor distance \( \langle R_{DA} \rangle \). We assume that for every donor-acceptor distance \( r = R/\langle R_{DA} \rangle \) the dynamics are mono-exponential with rate constants determined by the distances only. The combined dynamics is then obtained by integrating over the range of donor-acceptor distances \( r \). We used Eq. 3 to fit the experimental data presented in the top panel of Fig. 4. In order to emphasize the non-exponentiality of the dynamics, a normalized pump-probe signal subtracted from unity is plotted in Fig. 5 on a logarithmic scale. By fitting the experimental data we obtain \( \sigma = 0.105 \) and \( k_{\text{eff}}^{-1} = 7 \) ps. The spreading, \( \sigma \), of the distances is in agreement with the range of donor-acceptor distances determined from the molecular dynamics simulations.
C. Analytical description of ET dynamics in C4P at high excitation density

Experiments at low excitation density, as presented in the previous sections, give a consistent picture and understanding of the ET processes in C4P. One important aspect of the ET dynamics, namely the consequences of multiple excitations on a single C4P dendrimer, has so far not been addressed. Therefore, we have performed pump-probe experiments with high excitation densities (more than 1 photon per dendrimer absorbed). However, before turning to the data, a simple rate model describing ET processes at high excitation densities based on the diagram shown in Fig. 2 will be considered, first taking only the effects of multiple donor excitation into account, and later also discussing the effects of excitation induced spectral changes. The diagram shown in Fig. 2 reads as follows: first the acceptor is excited via the process described in the previous sections (boxed area); second, before this excited \( S_1 \) state decays, another excitation from the second donor reaches the acceptor (right side) and the acceptor is excited from \( S_1 \) to some higher state \( S_n \); third, rapid relaxation of the acceptor back to the \( S_1 \) state takes place on a sub-100 fs timescale. As a result, the excitation energy from an additionally excited donor may easily be dissipated nonradiatively. Assuming that ET to an acceptor in the \( S_0 \) and \( S_1 \) states proceeds with rate constants \( k_{ET} \) and \( k_{ET}^{*} \), respectively (as in Fig. 2), one can distinguish two interesting extreme cases: \( k_{ET} \gg k_{ET}^{*} \) and \( k_{ET} \ll k_{ET}^{*} \). The first case can be considered as an “ET blockade”: Only the energy of one of the excited donors is transferred initially to the acceptor, while the remaining excitation energy is temporarily stored on the other donors (assuming long radiative donor decay times as is the case here) until the acceptor relaxes to the \( S_0 \) state. This would be a desirable situation for energy harvesting, since the superfluous absorbed photon energy would be stored until the acceptor is ready to accept a new energy packet. The second case provides “enhanced ET” to the excited acceptor, i.e. overall ET speed-up with increasing excitation density. In this case, however, the excess energy absorbed by the donors is lost through non-radiative \( S_n \rightarrow S_1 \) decay on the acceptor.

The excitation dynamics in C4P, including the interaction of multiple excitations, can be described by a system of differential rate equations [31]:

\[
\begin{align*}
\frac{dN_j}{dt} &= -j(k_D + k_{ET})N_j + (j+1)k_D N_{j+1} + k_A N_j^* \\
\frac{dN_j^*}{dt} &= (j+1)k_{ET} N_{j+1} - (k_A + j(k_D + k_{ET}^*))N_j^* + (j+1)(k_D + k_{ET}^*)N_{j+1}^*
\end{align*}
\]

(4)

where the generation terms have been omitted. The index \( j = 1\ldots4 \) in this set of equations represents the number of excited donor molecules on a single dendrimer. \( N_j \) is the number of dendrimers with non-excited acceptor and \( j \) excited donors, whereas \( N_j^* \) represents the number of dendrimers with an excited acceptor and again with \( j \) excited donors. Note that for C4P only four donors are attached to the acceptor which is taken into account by putting \( N_5 = N_5^* = 0 \). \( k_D \) and \( k_A \) in Eq. 4 are the donor and acceptor relaxation rates, respectively. \( k_{ET} \) and \( k_{ET}^* \) are the rates of ET from the donor to the acceptor in the ground state and in the first excited state, respectively.

By describing ET dynamics in this way, it is assumed that the \( S_n \rightarrow S_1 \) relaxation in this system is much faster than the ET itself and the donor-donor ET is negligible. The first assumption is based on the observation that after excitation of the \( S_2 \) state, a nearly instantaneous formation of the \( S_1 \) population of the acceptor is observed on the timescale of our experiments. The second assumption is reasonable since the donor-donor overlap integral \( J \) in Eq. 2) is approximately two orders of magnitude smaller, while the donor-donor
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Distances are of the same order as donor-acceptor distances. In addition, the anisotropy decay was measured for coumarin and biscoumarin (the side-branch model compound) using 325 nm light for pump and probe. The anisotropy in coumarin was decaying mono-exponentially, with a time constant of 81 ps, governed by the rotational motion of the coumarin molecules only. The same measurement for biscoumarin revealed a mono-exponential decay as well, with a 93 ps time constant. In this case the anisotropy is decaying at a slightly lower rate due to the restricted motion of the interconnected coumarins. If fast donor-donor ET were present in the biscoumarin, we would expect a faster biexponential decay of anisotropy, as it is observed in multichromophoric systems when donor-donor energy hopping is present [58, 59].

The probability of singlet-singlet annihilation in donors when multiple donors are excited cannot be completely excluded, although no fast (on a 100 ps timescale) pump-probe dynamics was observed in biscoumarin at high excitation densities (>1 photon per biscoumarin), so we may safely assume that on the donor-acceptor ET timescale, singlet-singlet annihilation is negligible even at high excitation densities. Another process which we neglect in our model is the possibility of triplet formation in the coumarins. Since the triplet formation yields in coumarins usually are of the order of several percent [60], their formation rates are of the order of at least several nanoseconds and have therefore no influence on the picosecond timescale of donor-acceptor ET dynamics.

If \( k_A << k_{ET} \) and \( k_D << k_{ET} \), which is evidently the case for C4P (see section III.A), the dynamics of the total population of excited donors and acceptors can, according to the Eq. 4, be expressed as:

\[
\frac{dN_D}{dt} = \sum_{j=1}^{4} \left( \frac{dN_j}{dt} + \frac{dN_j^*}{dt} \right) = -k_{ET} \sum_{j=1}^{4} jN_j -k_{ET}^* \sum_{j=1}^{4} jN_j^* ,
\]

\[
\frac{dN_A}{dt} = \sum_{j=1}^{4} \frac{dN_j^*}{dt} = k_{ET} \sum_{j=1}^{4} jN_j ,
\]

where \( N_D \) and \( N_A \) are the total numbers of excited donors and acceptors, respectively. Equation 5.2 shows that the dynamics of excitations in acceptors does not depend on \( k_{ET}^* \), permitting the study of the effects caused only by the excitation of multiple donors in the same dendrimer. In the case of an “ideal” dendrimer, for which the donor molecules are selectively excited, the number of acceptor molecules contributing to the signal is

\[
N_{A_{1>>>t}} = \sum_{j=0}^{4} N_j \bigg|_{j=0}
\]

while the contribution of a single dendrimer to the overall signal can be expressed as

\[
\frac{dN_A}{dt} \bigg|_{t=0} = \frac{1}{N_{A_{1>>>t}}} \sum_{j=1}^{4} jN_j \bigg|_{j=0} k_{ET} .
\]

Equation 6 demonstrates non-linearity of the ET dynamics at high excitation densities, i.e. the population of dendrimers with an excited acceptor evolves in time depending on how many donors are excited on a single dendrimer. The right hand side of Eq. 6 is relevant to the acceptor population growth rate constant at \( t = 0 \). In the case of low excitation density it is simply equal to \( k_{ET} \). At high excitation densities where multiple donors are excited on a dendrimer \( (N_2, N_3 \text{ and/or } N_4 > 0) \) the observed dynamics would, based solely on the number of excited donors, speed up.
Apart from the number of excited donors, a change of spectral properties of the acceptor which occurs as a consequence of the ET process may also influence the ET dynamics. According to Eq. 4 under high excitation density conditions, when multiple donors in the dendrimer are excited and when internal conversion \((S_n \rightarrow S_1)\) in the acceptor is much faster than the ET itself, ET can be understood in a sequential way (see diagram presented in Fig. 2). If no structural changes occur in the dendrimer during the first step of ET (static distribution of donor-acceptor distances), the rate constant of the second ET step would be determined by the spectral properties only, which in Eq. 2 are taken into account by an overlap integral \(J\). Consequently, the effect of spectral changes on the ET rate can be accounted for by evaluating the differential overlap integral of donor fluorescence and photoinduced acceptor absorption:

\[
\Delta J = J^* - J = \int_{0}^{\infty} F_D(\lambda) \cdot \Delta \varepsilon_A(\lambda) \cdot \lambda^4 \cdot d\lambda.
\]

\(J^* = \int_{0}^{\infty} F_D(\lambda) \cdot \varepsilon_A^*(\lambda) \cdot \lambda^4 \cdot d\lambda\) in Eq. 7 is the overlap integral of donor fluorescence with the absorption of the acceptor in the \(S_1\) energy state, and \(\varepsilon_A^*(\lambda)\) is the extinction coefficient of the excited acceptor. As one can see from Eq. 7 the sign of \(\Delta \varepsilon_A(\lambda)\) or, in other words, the sign of the optical density changes in the spectral region of the donor fluorescence determines the sign of the change of ET rate, assuming that other factors, such as donor-acceptor distance \(R_{DA}\) and the geometrical factor \(\kappa\), remain unchanged. The first assumption seems to hold, since, as discussed in the previous section, the dendrimer geometry hardly changes on the ET timescale. The second assumption might not be accurate since it is not guaranteed that the orientation of the \(S_0 \rightarrow S_2\) and \(S_1 \rightarrow S_n\) transition dipoles in the acceptor are the same. If these are different, then one has to include different geometrical factors for the different transitions in evaluating Eq. 7. Neglecting this point for the moment, Eq. 7 states that the ET from the donor to the excited acceptor is faster than to the non-excited acceptor when \(\Delta \varepsilon_A(\lambda) > 0\), and slower when \(\Delta \varepsilon_A(\lambda) < 0\).

In order to estimate the ET rate from donor to excited acceptor, as it is formally described by Eq. 7, we measured a transient absorption spectrum of dendrimers at a delay of 30 ps following the excitation with 325 nm light. At this delay the majority of excitations reach the acceptor so the measured spectrum represents the photoinduced optical density changes upon population of the \(S_1\) state of the acceptor. To exclude orientational effects, the measurement was performed in a magic angle configuration. The pump – probe spectrum presented in Fig. 6 is found to be in good agreement with the spectra reported in literature [24-26]. It exhibits a bleaching of the spectral region corresponding to the absorption bands of the acceptor, as well as photoinduced absorption bands on the blue (below 420 nm) and red (above 690 nm) sides of the spectrum. Since the spectrum of the white light used as a probe did not extend below 390 nm, the changes induced in the 315-405 nm spectral region were measured using a single wavelength probe.

From the data in Fig. 6, we estimate a positive differential overlap integral \(\Delta J \approx 10^{-14} \text{ M}^{-1} \text{ cm}^3 \text{ nm}^4\), which predicts an additional speed-up of the ET process. Estimating \(J^*\) to be \(3.4 \cdot 10^{14} \text{ M}^{-1} \text{ cm}^4 \text{ nm}^4\), the time constant of ET from a donor to an excited acceptor is \(k_{ET}^* = 4.9\) ps, which is nearly half that of the ET time constant from donor to the non-excited acceptor. As shown in Eq. 5.2, the dynamics of excitations in acceptors is not influenced by the spectral changes in excited acceptors, while the excitation decay in donors, according to Eq. 5.1, would experience a speed-up at high excitation density. However, as discussed in the previous section, the absorption bleaching of donors overlaps with the photoinduced absorption of acceptors, so the observations of the donor signal alone are impossible. In addition, the second term in Eq. 5.1 is comparable with the first one only at
high excitation density, so the donor population dynamics depends only partially on the spectral properties of the excited acceptor.

**Figure 6.** Transient absorption spectrum of the C4P dendrimer at 30-ps after excitation with $\lambda_{ex} = 325$ nm (solid line) and fluorescence spectrum of the donor molecules (dashed line, same as displayed in figure 1). Filled circles represent transient absorption data at 30 ps obtained using fixed probe wavelengths. The change in optical density, $\Delta OD$, has been rescaled to match a concentration of $10^{-4}$ M excited molecules in a 2 mm cell to facilitate comparison to the absorption and fluorescence spectra of figure 1 (the actual concentration in the experiment was $10^{-6}$ M excited molecules in a 2 mm cell).

### D. ET at high excitation density: experimental results

Before performing high excitation density experiments we studied the photodegradation of the dendrimers in order to estimate the acceptable excitation intensities for the actual experiments. The photostability was tested by irradiating a stirred solution of C4P in chloroform at $\lambda_{ex} = 325$ nm (absorption peak of the donors) or $\lambda_{ex} = 525$ nm (absorption peak of the acceptors) while monitoring optical density changes (pump – probe signal) at $\lambda_{pr} = 590$ nm after 30 ps delay. This test is sensitive to photodegradation of the donors or the acceptors and to the detachment of the donors from the acceptors. The tests involved absorption of about 1000 photons per dendrimer. At low excitation density (1 photon per 30 dendrimers per pulse absorbed) no observable photodegradation was observed, independent of the excitation wavelength used. At high excitation density (1 photon per dendrimer per pulse absorbed), excitation in the visible region did not lead to observable photodamage, while UV excitation ($\lambda_{ex} = 325$ nm) caused photodamage of 50% of the dendrimer molecules after 125 photons per dendrimer were absorbed. This result implies that multiple excitations are responsible for photodamage of the dendrimers. In order to minimize the influence of photodecomposition on pump – probe data, the experiments at high excitation density conditions were performed while keeping the total number of absorbed photons per single dendrimer molecule below 5, which corresponds to ca. 3% of photodecomposed dendrimers.

Since the determination of the excitation density in absolute units is not straightforward, we have checked the linearity of the dependence of number of excited donors on the number of photons per pulse. Since only a single excitation transferred from the donor to acceptor
contributes to the fluorescence, we use the measurement of the dependence of fluorescence quantum yield on the incoming number of photons per pulse for the verification of the excitation density. The ratio between the fluorescence quantum yield at any donor excitation density $\phi$ with the fluorescence quantum yield at the low excitation density limit $\phi_0$ can be expressed as:

$$\frac{\phi}{\phi_0} = \frac{\sum_{j=1}^{4} N_j}{\sum_{j=1}^{4} jN_j} \bigg|_{j=0},$$  

where the same approach was used as in the derivation of Eq. 6. Here we define quantum yield of a chromophore as the number of emitted photons per absorbed photon. In Fig. 7 a simulation obtained by taking into account the number of dendrimers with an excited acceptor at various photon fluxes (8) is plotted together with the measured ratio. A very good match between the calculated curve and the experimental data demonstrates that effects originating from two-photon absorption by solvent and dendrimers and from the spatial distribution of light intensity do not play a crucial role, validating the absolute excitation densities estimated for the experiments.

![Figure 7](image_url)

**Figure 7.** Scaled fluorescence quantum yield of C4P dendrimers versus the excitation density using $\lambda_{ex} = 325$ nm (dots). The solid line shows a simulation based on Eq. 8 (see text for details).

Pump-probe transients were measured at excitation densities ranging form 1/100 to 2 photons absorbed per pulse per C4P molecule. The dendrimers were excited at 325 nm, while optical density changes were probed at 590 nm. Typical examples, measured at low (1 photon per 30 C4P molecules absorbed) and high (1 photon per 1 C4P molecule absorbed) excitation density, are shown in Fig. 8. In the case of high excitation density (1 photon per C4P), the estimated percentage of multiply excited dendrimers with two, three, and four excited donors is 29%, 10%, and 2.5%, respectively. In the case of low excitation density (1 photon per 30 C4P), less than 2% of the excited dendrimers experience multiple excitations.

The data clearly show that the formation of the photoinduced acceptor absorption speeds up at high excitation density, thereby confirming the anticipated acceleration of the ET upon multiple donor excitations. The solid lines in Fig. 8 are the calculated formation curves using the model described by Eq. 4. The modeling was carried out taking into account the effect of
variation of the dendrimer geometry on the ET rate. A set of pump-probe traces was calculated for an ensemble of various dendrimer geometries, using a set of $k_{ET}$ and $k_{ET}^*$ values, generated using the distribution of donor-acceptor distances with $\sigma = 0.1$ and the effective ET time $k_{\text{eff}}^{-1} = 7$ ps calculated previously. Though $k_{ET}^*$ is almost irrelevant in this case, the value estimated in the previous section $(k_{ET}^*)^{-1} = 4.9$ ps was used. The solutions acquired were averaged for the ensemble to achieve the dynamics of donor and acceptor populations in a bulk solution. Note, that no further fitting procedures were performed after the determination of the effective ET rate and the distribution of donor-acceptor distances. Very good agreement between the measured and calculated traces suggests reasonable relevance of the model for this system. The determining factor which leads to the increase of the ET rate is the occurrence of the multiple donor excitations in the dendrimer. As discussed in the previous section, the results are almost independent on the value $k_{ET}^*$, and we will therefore return to this rate constant using more dedicated experiments in the next section.

**Figure 8.** Pump-probe transients measured at $\lambda_p=590$ nm with excitation densities corresponding to one photon absorbed per 1 dendrimer (open circles) and one photon absorbed per 30 dendrimers (filled circles). Solid lines show the simulated population dynamics obtained using Eq. 4 (for details see text).

**E. Control of the ET rate: pre-pump – pump – probe experiment**

From the previous section it can be seen that the effect of a high excitation density on the ET dynamics is complex because the ET rate is influenced by multiple factors such as the number of excited donors, changes in the spectral response, and the transition dipole orientation in the excited acceptor. As can be seen from Eq. 6, with an increase in the number of excited donor molecules, the ET rate should increase independent of the conditions in which the acceptor molecule persists. In order to separate the effects of the magnitude of the ET rate constant for transfer to the excited state from those due to multiple donor excitations we performed pre-pump – pump – probe experiments in which the acceptor is pre-excited to the $S_1$ state using an intense 550 nm pulse. The delay between pre-pump and pump pulses should be as short as possible, to ensure a fixed orientation and geometry of the dendrimer. On the other hand, the solvent needs to relax after the intense pre-pump pulse, which requires some time. To meet both conditions satisfactory, the pre-pump – pump delay was set to 10 ps.
The results of the pre-pump – pump – probe experiments are shown in Fig. 9. In all cases a negative signal, corresponding to photoinduced bleaching induced in the donor molecules, is observed directly after excitation. With an increase of the delay between the pump and probe pulses the signal grows and saturates at a certain positive value. These dynamics are due to significant photoinduced absorption at 325 nm of the $S_1$ excited acceptor. The bleaching signal at 325 nm observed at low pre-pump power and in the conventional pump-probe experiments, becomes overshadowed by the photoinduced absorption of the acceptor in the $S_1$ state resulting from donor-acceptor ET. Eventually, the photoinduced absorption is expected to decay with a time constant of 6.7 ns (lifetime of the $S_1$ excited state of the acceptor).

![Figure 9](image-url)

**Figure 9.** Pre-pump – pump – probe transients measured at $\lambda_{pr}=325$ nm for various pre-pump pulse energies. The pre-pump polarization is parallel to the pump polarization. The polarization of the probe is set at the magic angle with respect to those of the pre-pump and pump pulses.

Another observation from the data shown in Fig. 9 is that the positive pump – probe signal at longer delays (>30 ps) decreases with increasing pre-pump pulse energy. This results from the fact that more acceptors are already excited upon increasing the pre-pump energy. Pre-excited acceptors do not contribute to the pump – probe signal even if excitation from the donors reach these acceptors, since, as discussed above, higher lying excited states ($S_n$ in Fig. 2) are short lived and the acceptor returns to the $S_1$ state on a sub-100 fs timescale. In contrast, the initial negative part of the pump-probe signal increases with increasing pre-pump pulse energy. This originates from the fact that the acceptor has both, a weak linear (Fig. 1) and a photoinduced (Fig. 6) absorption at 325 nm. Since the pre-excitation pulse excites a significant fraction of acceptors, the number of acceptors which contribute to the photoinduced absorption in subsequent pump – probe measurements is significantly diminished. This leads to the larger relative contribution of the donor bleaching.

Pre-excitation of the acceptor molecules not only changes the amplitude and sign of the pump – probe signal, but indeed also influences the donor-acceptor ET rate. Independent of pre-pump, pump, and probe pulse polarizations, the ET rate is found to decrease with increasing pre-pump pulse energy. In particular: $k_{ET}$ decreases from ca. $7 \text{ ps}^{-1}$, in the absence of the pre-pump, to $14 \text{ ps}^{-1}$, when a pre-pump pulse is applied with an energy corresponding to approx. 2 photons per dendrimer per pulse. This result contradicts the previous estimation of the $k_{ET}$ value (4.9 ps). The most likely explanation for the...
disagreement with the excited state rate constant estimated from the overlap integral (Eq. 7) is the difference between the orientations of the $S_0 \rightarrow S_2$ (ET to the acceptor in ground state) and $S_1 \rightarrow S_n$ (ET to the pre-excited acceptor) transition dipole moments. If these are not parallel, then one should take the relative orientations into account when evaluating the integral in Eq. 7. Effects of unfavorable donor/acceptor $S_0 \rightarrow S_1$ orientations on the energy transport in dendrimers have previously been observed in single molecule experiments by Melnikov et al. [28]. Polarization selective pump-probe experiments indeed have shown that the relative orientations of the $S_0 \rightarrow S_2$ and $S_1 \rightarrow S_n$ transition dipole moments of the acceptor are close to perpendicular, therefore we expect that the overlap integral is altered severely by the inclusion of a wavelength dependent orientational factor $\kappa(\lambda)$, leading to a negative value, and hence to the observed significant “ET blockade”. One interesting consequence of this is that pre-excitation, at least at low excitation densities when no multiply excited dendrimers are present, enables substantial control for the energy transfer rate.

IV. SUMMARY AND CONCLUSIONS

This chapter presents a detailed study of the ET properties of a first generation coumarin-perylene bisimide dendrimer. At low donor excitation intensity fast and efficient (quantum yield – ca. 99.5%) donor-acceptor energy transfer is observed. Based on a Förster dipole-dipole resonant ET model the initial energy transfer time constant is estimated to be of the order of 7 ps, which is in good agreement with experimental observations. Frequency resolved pump-probe measurements reveal a non-exponential behavior of the ET dynamics, which is found to result from variations of the donor-acceptor distances due to conformational disorder. Taking this disorder into account gives an effective ET time constant of 7 ps and a distance distribution with a standard deviation of ca. 10%, consistent with the results of MD simulations.

High excitation densities lead to more than one excited donor per dendrimer. The simple rate equation model presented here predicts speeding up of the ET with an increase in excitation density arising mainly from the increased number of excited donors per dendrimer. It has been shown by pre-pump – pump – probe experiments that the ET rate decreases depending on the number of pre-excited acceptors. The observed decrease is in strong contradiction with the behavior predicted by using the usual overlap integral approach. The origin of this discrepancy lies in the simplicity of calculation of the overlap integral which does not take the relative transition dipole moment orientations into account. This is a particularly bad approach for C4P dendrimers, since the relevant transition dipole moments ($S_0 \rightarrow S_2$ and $S_1 \rightarrow S_n$) are found to be nearly perpendicular to each other. This causes a sign change of the differential overlap integral and strongly suppresses the ET to the excited acceptor state, i.e. leads to “ET blockade” phenomena.

REFERENCES

51. A detailed distribution of both the orientations of the transition dipole moments of the donor and acceptor molecules, as well as of the dipole-acceptor distances may be obtained from the MD calculations. In our MD calculations, however, we did not include any solvent molecules and used a rather simple force field model (MM+). We therefore chose to take a more qualitative approach by using average values only, rather than detailed distributions.