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Energy Transfer Rates and Pathways of Single Donor Chromophores in a Multichromophoric Dendrimer Built around a Central Acceptor Core

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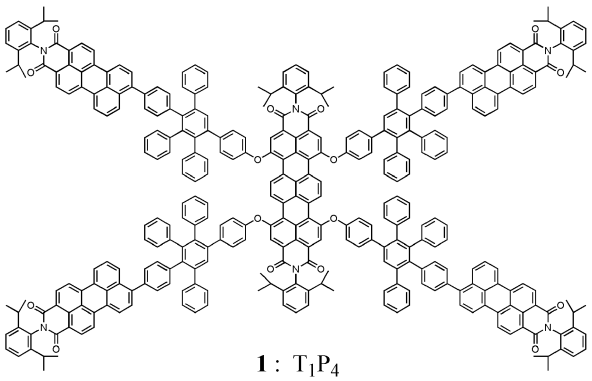
Single-molecule spectroscopy of multichromophoric aggregates is continuously generating new insights into electronic excitation energy transfer, a process which is crucial for the functioning of light-harvesting complexes[1] and conjugated polymers.[2] Recently, such studies have been extended to a new class of structurally well-defined light-harvesting arrays which exhibit efficient energy transfer with an energy gradient.[3] The fluorescent polyphenylene dendrimer shown below (T_1P_4) consists of 4 peripheral perylene-monoimides (P) which serve as energy donors and a central terrylenediimide (T) which is the energy acceptor.[3] Time-resolved fluorescence measurements of T_1P_4 in solution have indicated the presence of two FRET-related (FRET: fluorescence resonance energy transfer) energy transfer processes at 4 and 22 ps.[4] In single-molecule experiments of T_1P_4 the rise-time of the acceptor emission was monitored. The corresponding distribution was peaked at 19 ps and had a width of 20 ps.[5] The rise-time was interpreted to reflect the average energy transfer rate of a collection of donors to a single acceptor. In the following we will demonstrate that confocal imaging in combination with frequency selective single-molecule spectroscopy at low temperature[6,7] gives direct access to energy transfer rates of single donors within T_1P_4.



1: T_1P_4

Thin polymer films (zeonex) containing T_1P_4 at low concentrations were spin-coated onto glass cover slides. The samples were transferred into an optical cryostate which allowed confocal imaging of single molecules between room and liquid helium temperatures.[7] To record single-dendrimer emission spectra, the samples were excited at 488 nm (Ar-Ionlaser), or by the output of a tunable ring dye-laser (525−545 nm; line width: ∼2 GHz). The circular polarized dye-laser was also employed to measure fluorescence excitation spectra.

In single-molecule fluorescence spectroscopy at room temperature it has been found that selective excitation at 488 nm leads to highly efficient directional energy transfer from P to T from which emission then occurs.[5] Similarly, at low temperature ($T = 1.4$ K, $\lambda_{exc} = 488$ nm) the vast majority of fluorescence emission spectra of single T_1P_4 dendrimers does not show any contribution from P emission and is dominated by the sharp and intense purely electronic zero-phonon line (ZPL) of T.[8] Typically, the emission lines are subject to spectral diffusion, i.e., the emission spectra are randomly fluctuating by up to several nm as a function of time.[8]

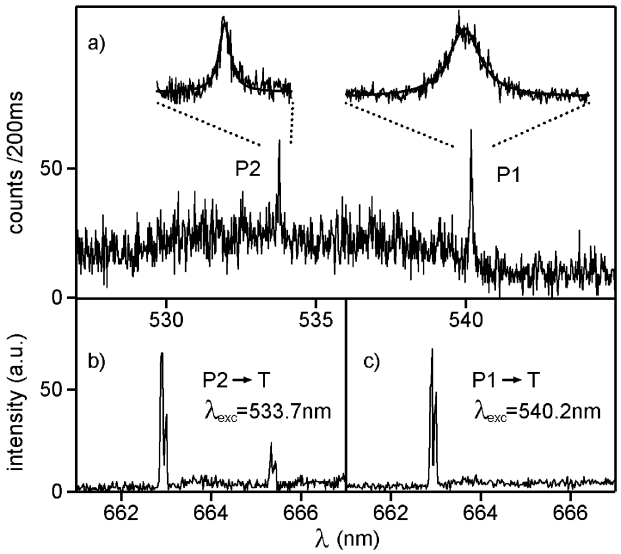


Figure 1. (a) Fluorescence excitation spectrum of a single T_1P_4 dendrimer at 1.4 K ($\lambda_{em} > 620$ nm, $I \approx 50$ W/cm^2). The enlarged part shows Lorentzian profiles fitted to the zero-phonon lines of the two donor chromophores P1 and P2. (b, c) High-resolution emission spectra of the same single dendrimer after excitation at $\lambda_{exc} = 533.7$ nm (P2) and $\lambda_{exc} = 540.2$ nm (P1), respectively.

From the emission spectra it can be inferred that also at low temperature the excitation energy is transferred efficiently from the P donors to the T acceptor. To determine the transfer rate for single donors within an isolated T_1P_4 dendrimer, we have measured fluorescence excitation spectra in the wavelength range of the donor absorption. In a typical experiment the dye laser wavelength was first tuned to 535 nm and a fluorescence image is recorded at detection wavelengths $\lambda > 620$ nm. Using this procedure, we excite the P chromophores via their phonon sidebands and select those molecules which quantitatively transfer their excitation energy to T. The spectral selection within a given dendrimer is achieved by scanning the laser wavelength at the location of a fluorescent spot in the image. In Figure 1a the fluorescence excitation spectrum of a spatially isolated dendrimer is shown at $T = 1.4$ K. In this case two narrow lines are observed which correspond to the purely electronic zero-phonon transitions of two distinct P chromophores

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(P1, P2). As one dendrimer is decorated by four P chromophores, four excitation lines should be observed ideally. It is well-known that phenomena such as inhomogeneous broadening, spectral diffusion, and polarization issues can lead to a varying number of lines in an excitation spectrum measured over a limited wavelength range (525−545 nm).[7] Additionally, in a small fraction of dendrimers part of the P chromophores may have photobleached. Thus far the number of sharp lines observed was between 0 and 4 for various dendrimer molecules studied.

The energy transfer from P to T can be treated as an energy relaxation process which causes line broadening of the P excitation spectrum. To extract the line widths, we have fitted Lorentzian profiles to the excitation spectra in Figure 1a. It is seen that the line profiles are well approximated by Lorentzians, a fact which holds true for all excitation spectra analyzed. By varying the excitation intensities over 1 order of magnitude (8−80 W/cm^2), we verified that the line shapes were not power broadened. From the fitting, line widths of $\Delta\nu_1 = 94.5 \pm 2.5$ GHz and $\Delta\nu_2 = 36.0 \pm 2.5$ GHz were obtained for the excitation spectra in Figure 1a. In addition to energy transfer, contributions from natural lifetime, dephasing, and (fast) spectral diffusion to the line width have to be considered. For another, structurally closely related polyphenylene dendrimer carrying 4 P chromophores (no T acceptor) and a bichromophore, where 2 P chromophores are linked by a benzil spacer, we have found that in a zeonex film the low power line widths of the lowest energy transitions (no broadening by energy transfer) are given by the width of the laser line (∼2 GHz). As this number gives only an upper limit to the actual line widths, we assume that in T_1P_4 the P → T energy transfer contribution to the line width is the dominating one. Under these conditions the energy transfer rate or time can be simply related to the line width: $\tau_{ET} = (2\pi\ \Delta\nu)^{-1}$. Applying this equation, we calculate energy transfer times of 1.7 ± 0.05 ps (P1) and 4.5 ± 0.35 ps (P2).

P1 is the donor with the longest absorption wavelength (Figure 1a) because to the red of its ZPL the signal height is given by the background, i.e., no phonon sideband contribution from another chromophore. Therefore, energy can only be transferred toward T, as the thermal energy at 1.4 K is much smaller than the energy difference between P1 and P2. The situation is different for P2. Although the P−P energy transfer rate should on average be clearly smaller than the P−T rate, there could be 3-D geometries[3] of the dendrimer where two P chromophores come so close spatially that the two energy transfer processes can compete. Hence, besides P2 → T the energy transfer pathway for P2 could also be: P2 → P1 → T. In the following, we will exclude this possibility for the case considered here.

In addition to the excitation spectra of P we have also measured emission spectra after selective excitation into the zero-phonon transitions of P1 and P2 (Figure 1b,c). Interestingly, the emission spectra are different, although both P donors transfer their excitation energy eventually to the same single T acceptor. We have carefully checked the validity of the experimental result by repeatedly recording emission spectra at the two excitation wavelengths. Excitation at 540.2 nm (P1) reproducibly gives a T emission line around 663 nm (Figure 1c). A closer look indicates spectral diffusion, because the line shows a splitting of approximately 0.1 nm. Excitation at 533.7 nm (P2) yields the same split emission line at ∼663 nm (Figure 1b). In addition, however, now a second emission line appears which is shifted to the red by ∼2.4 nm. As a single T acceptor is involved, again spectral diffusion must be responsible for this phenomenon. Obviously, the energy transfer P2 → T activates a conformational degree of freedom (a so-called two-level system[9]) which leads to fluctuations of the transition energy of T. As the energy difference between the two spectral positions is fairly large, the two-level system is supposed to be spatially close to T. Since the corresponding degree of freedom is not activated for P1 → T, we conclude that P2 transfers its energy directly to T and not via P1.

By analyzing a limited number of donor excitation spectra of several dendrimers, we thus far have found transfer times in the range of 2−20 ps. From these data a preliminary average transfer time of 4−5 ps can be computed. This number is smaller than the mean acceptor rise time (19 ps) measured for the same system.[5b] The difference may be attributed to the limited time resolution of the rise time measurements. The variations of energy transfer rates for different donors within a given dendrimer can be caused by some conformational flexibility of the dendrimer leading to a distribution of relative orientations and distances between the donors and the acceptor. Additionally, the spectral overlap between donor emission and acceptor absorption spectra, which is directly proportional to the transfer rate, varies for each pair. It is surprising, however, that the low-temperature energy transfer times are very much in the same range as the room-temperature values, taking into account that the spectral overlap integral is temperature dependent for systems with weak-to-intermediate electron−phonon coupling.[2b,10] Preliminary estimates for T_1P_4 in zeonex indicate that the spectral overlap on average drops by a factor of 10 when going from room temperature to 1.4 K. Therefore, there may be an additional non-Förster type through-bond contribution to the energy transfer because of non-negligible π-overlap between the dendrimer arms and the chromophores.[11]

In summary, we have shown that frequency-selective high-resolution spectroscopy at low temperature allows the elucidation in great detail of complex energy transfer processes in individual multichromophoric assemblies. A key feature of our approach is that the donors as well as the acceptor can be interrogated. This suggests that investigation of transfer rate fluctuations caused by spectral shifts of either the donor and/or acceptor and controlled modifications of the energy flow in such systems should be undertaken.

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