

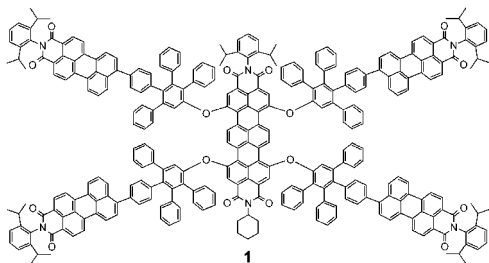
Intramolecular Förster Energy Transfer in a Dendritic System at the Single Molecule Level

Roel Gronheid,[†] Johan Hofkens,^{*,†} Fabian Köhn,[†] Tanja Weil,[‡] Erik Reuther,[‡] Klaus Müllen,^{*,‡} and Frans C. De Schryver^{*,†}

Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, 3001 Heverlee, Belgium, and Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany

Received October 31, 2001

In the past decades a vast amount of information has been collected on the photophysical processes of natural and artificial light-harvesting complexes.^{1–3} Three features of these complexes play a key role in the efficient collection of incident light for conversion into chemical energy: (1) large absorption cross-section of the complex due to a large number of chromophores with high extinction coefficients and varying spatial orientation and (2) energy hopping of the exciton along the chromophores at the rim of the complex, until eventually (3) efficient and uni-directional energy transfer (ET) of the exciton from a chromophore at the rim to the chromophore in the center of the complex takes place. This chromophore acts as the energy sink from which light-driven reactions may occur. We report here on the photophysics at the single-molecule level of a dendritic molecule (**1**) that was designed to display these three features. Its synthesis will be published elsewhere.⁴



The dendrimer consists of a terylenediimide (TDI) unit acting as the energy sink in the center of the molecule and four peryleneimide (PI) units as energy donors on the periphery. These chromophores were chosen because of their photostability, their high extinction coefficients at convenient absorption wavelengths ($\lambda_{\max} = 495$ nm ($\epsilon = 35,000$ L·mol⁻¹·cm⁻¹) and $\lambda_{\max} = 673$ nm ($\epsilon = 85,500$ L·mol⁻¹·cm⁻¹) for PI⁵ and TDI, respectively), and their high fluorescence quantum yields ($\phi_f \sim 1$ for both chromophores in toluene), and because the emission of PI matches the absorption of TDI very well (overlap integral $J = 3.7 \times 10^{-13}$ M⁻¹·cm³, also see Supporting Information). This provides an optimal basis for efficient intramolecular Förster ET⁶ (the distance of the chromophores in **1** is ~ 14 Å, which is well within the Förster radius of ~ 60 Å⁷ for this donor–acceptor pair).⁸ Ensemble measurements in toluene indicate very efficient ET as the fluorescence lifetime of PI is reduced to ~ 5 ps⁹ for **1** compared to 4.2 ns for free PI.

Single-molecule spectroscopy provides an ideal technique to investigate energy hopping as well as ET in dendritic systems.¹⁰ No information is lost by ensemble averaging. In this way a more detailed picture of physical parameters is obtained, for instance multimodal distributions can be revealed.¹¹ Furthermore, in multi-

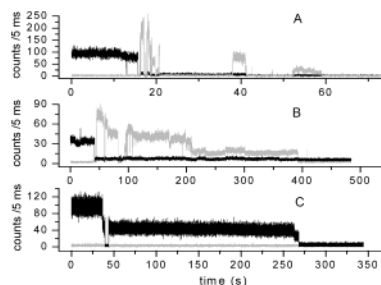


Figure 1. Exemplary fluorescence traces for single molecules of **1**. The TDI (black) and PI emission channels (gray) are depicted.

chromophoric systems, upon continuous irradiation the chromophores of the parent molecule are bleached in a stepwise fashion. When measurements are performed on a large number of molecules, insight into the role of the various chromophores in the dendritic system is obtained. In this way the interactions between the chromophores can be studied in a more detailed way than is possible by means of bulk measurements.

Single molecule measurements were performed at ambient temperature using a confocal microscope. All measurements were performed on films of Zeonex, a polynorbornene, in which molecules of **1** were embedded. In the first set of experiments, the PI units at the rim of the dendrimer were excited with 488 nm light (cw). Fluorescence was collected, guided through a hybrid beam-splitter, and detected with two ADPs. In front of one APD a 700 nm longpass filter was placed, to exclusively detect fluorescence from the TDI chromophore. In front of the other APD a 600 nm shortpass filter was placed so only emission from PI was observed.

At the start of all traces of **1** (49 molecules studied), TDI emission is observed exclusively (Figure 1). This demonstrates that Förster-type ET from PI to TDI occurs very efficiently. In 70% of the molecules, emission of PI comes up after the TDI chromophore has bleached first (Figure 1A,B). In 30% of the traces the molecule remains inactive after emission from the TDI chromophore has ceased (Figure 1C).¹²

Emission spectra at the single molecule level confirm the above conclusions (also see Supporting Information). All molecules initially show TDI emission spectra ($\lambda_{\max} \sim 680$ nm and a second peak at $\lambda \sim 745$ nm). For type A, after bleaching of the TDI emission typical PI emission ($\lambda_{\max} \sim 550$ nm and a second peak at $\lambda \sim 590$ nm) is observed.

The intensity traces of type A and B also show that upon photobleaching of the TDI chromophore, the PI chromophores start to emit. Thus, the photoproduct of TDI is not a quencher for this emission. Several intensity steps in the PI emission may be observed, corresponding to one by one bleaching of the PI chromophores. A striking feature from the fluorescence traces is that no emission of the PI chromophores is observed during the

[†] Katholieke Universiteit Leuven.

[‡] Max-Planck-Institut für Polymerforschung, Mainz.

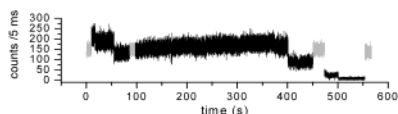


Figure 2. Fluorescence trace upon alternating excitation of a single molecule of **1** with $\lambda_{\text{exc}} = 633$ nm (gray) and $\lambda_{\text{exc}} = 514$ nm (black).

short (ms range; Figure 1A at 13 s) or long (s-range; Figure 1C at 41 s) off periods of the TDI chromophore. It is generally accepted that the short off periods correspond to the chromophore in its triplet-excited state.¹³ This demonstrates that ET from PI occurs to the ground state as well as to the triplet state of TDI. Such Förster ET from a singlet-excited state to a triplet state has recently been demonstrated for single-excited PI to triplet PI at the single molecule level.^{10,14} Long off periods have previously been reported.¹⁰ Although their origin is still unknown, it is clear that the intermediate that causes them quenches the PI emission. Let us now concentrate on the features that are observed in the traces of type C. They display stepwise bleaching of the TDI emission, upon excitation of the PI chromophores (Figure 1). Three explanations come to mind. (1) Twisting of the chromophore.¹⁵ Such twisting should be accompanied by shifts in the emission spectrum. Spectral jumps and bleaching steps were however not simultaneously observed. (2) Rotation of the entire dendrimer molecule. We regard this explanation as unlikely because it occurs too often for such big molecules in a rigid polymer matrix. Moreover the emission intensity always decreases whereas rotation of the entire molecule should lead to increases as well as decreases of the intensity with (almost) equal probability. (3) Bleaching of PI prior to bleaching of TDI. Evidence for the latter explanation comes from three experiments.

First, upon excitation at 633 nm (in the absorption band of TDI) no stepwise bleaching is observed. This is in agreement with (3), but not with (1) or (2). Second, upon excitation at 488 nm, the polarization of the emitted light does not change after a step in the intensity of the TDI emission has occurred (Figure S3, Supporting Information). This falsifies mechanism (2) as this would lead to a change in polarization.

In the third experiment the setup is modified to excite the same molecule with 514 or 633 nm light. First the intensity of the TDI emission upon excitation of TDI (633 nm) is measured. Then the excitation source is changed to 514 nm and PI is excited until a step in the intensity occurs. The excitation source is changed back and the intensity of the TDI emission upon excitation of TDI is measured again. This is repeated until full bleaching at either excitation wavelength occurs. In Figure 2, a typical example is given for a trace of type B for **1**. It is clear from this figure that the intensity of the emission at $\lambda_{\text{exc}} = 633$ nm does not change after an intensity jump at $\lambda_{\text{exc}} = 514$ nm has occurred. This proves that the intensity jump at 514 nm is not caused by a reorientation of the molecule. Five intensity levels at $\lambda_{\text{exc}} = 514$ nm are observed, corresponding to 4, 3, 2, 1, and 0 active PI chromophores, respectively. Small changes in intensity after changing the excitation source are due to refocusing.

The third experiment gives definite proof that the stepwise bleaching of TDI emission is caused by deterioration of the PI chromophores. This is an unexpected result because most of the time the excitation energy is located on the chromophore from which emission occurs (i.e., TDI). Therefore, it was anticipated that TDI would generally photoreact first. If bleaching of PI occurs prior to bleaching of TDI, this also means that in such cases the triplet state is not involved in bleaching. Given the efficient ET, it is unlikely that (slow) triplet formation occurs at a donor chromophore. Bleaching from the singlet-excited state in this system is most likely not caused by photooxidation, which is corroborated

by the observation that upon removal of oxygen stepwise bleaching still occurs (results not shown). To the best of our knowledge, this is the first time that photobleaching from the singlet-excited state is demonstrated at the single-molecule level.¹⁶

Bleaching of PI and TDI, thus, are competing processes and the five chromophores may bleach in any order (see also Figure S2, where first a PI bleaches, next the TDI, and after that the rest of the PIs). Stepwise bleaching of the TDI emission (Figure 1C) is caused by photoreaction of the PI chromophores, whereas bleaching of the TDI emission followed by PI emission (Figure 1A,B) is caused by photoreaction of the TDI chromophore.

Acknowledgment. We thank the FWO, the Flemish Ministry of Education for their support through GOA/1/96 and GOA/1/2001, the EC through the TMR Sisitomas, the European Science Foundation through SMARTON, the VW-Stiftung, and the support of DWTC (Belgium) through IUAP-IV-11. J.H. thanks the FWO for a postdoctoral fellowship.

Supporting Information Available: Experimental details, ensemble absorption, and emission spectra of **1**, consecutive fluorescence emission spectra for a single molecule displaying both TDI and PI emission, and a simultaneous polarization and intensity trace (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) For some recent references see e.g.: (a) Timpmann, K.; Ellervee, A.; Pullerits, T.; Ruus, R.; Sundstrom, V.; Freiberg, A. *J. Phys. Chem. B* **2001**, *105*, 8436–8444. (b) Trinkunas, G.; Herek, J. L.; Polivka, T.; Sundstrom, V.; Pullerits, T. *Phys. Rev. Lett.* **2001**, *86*, 4167–4170.
- (2) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40–48 and references therein.
- (3) For some earlier examples on artificial light-harvesting complexes see: (a) Devadoss, C.; Bharathi, P.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 9635–9644. (b) Wagner, R. W.; Johnson, T. E.; Lindsey, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 11166–11180.
- (4) (a) Weil, T.; Reuther, E.; Müllen, K. *J. Org. Chem.* Submitted for publication. (b) Weil, T.; Reuther, E.; Müllen, K. *Angew. Chem.* accepted.
- (5) Gensch, T.; Hofkens, J.; Herrmann, A.; Tsuda, K.; Verheijen, W.; Vosch, T.; Christ, T.; Basché, T.; Müllen, K.; De Schryver, F. C. *Angew. Chem., Int. Ed.* **1999**, *38*, 3752–3756.
- (6) (a) Maus, M.; De, R.; Lor, M.; Weil, T.; Mitra, S.; Wiesler, U.-M.; Herrmann, A.; Hofkens, J.; Vosch, T.; Müllen, K.; De Schryver, F. C. *J. Am. Chem. Soc.* **2001**, *123*, 7668–7676. (b) Weil, T.; Wiesler, U. M.; Herrmann, A.; Bauer, R.; Hofkens, J.; De Schryver, F. C.; Müllen, K. *J. Am. Chem. Soc.* **2001**, *123*, 8101–8108.
- (7) This value is obtained assuming $\kappa^2 = 2/3$, although this assumption is arbitrary for **1**, the Förster radius is >40 Å for any value of $\kappa^2 > 0.05$.
- (8) Recently intermolecular Förster ET was shown at the single-molecule level by Lee et al. (Lee, M.; Tang, J.; Hochstrasser, R. M. *Chem. Phys. Lett.* **2001**, *344*, 501–508), while examples exist of intramolecular Förster ET in biological systems, e.g.: (a) Ha, T.; Enderle, Th.; Ogletree, D. F.; Chemla, D. S.; Selvin, P. R.; Weiss, S. *Proc. Natl. Acad. Sci.* **1996**, *93*, 6264–6268. (b) Deniz, A. A.; Dahan, M.; Grunwell, J. R.; Ha, T.; Faulhaber, A. E.; Chelma, D. S.; Weiss, S.; Schultz, P. G. *Proc. Natl. Acad. Sci.* **1999**, *96*, 3670–3675.
- (9) Schweitzer, G.; Jordens, S.; Lor, M.; De Belder, G.; Weil, T.; Reuther, E.; Müllen, K.; De Schryver, F. C. Submitted for publication.
- (10) Hofkens, J.; Maus, M.; Gensch, T.; Vosch, T.; Cotlet, M.; Köhn, F.; Herrmann, A.; Müllen, K.; De Schryver, F. C. *J. Am. Chem. Soc.* **2000**, *122*, 9278–9288.
- (11) (a) Yu, J.; Hu, D. H.; Barbara, P. F. *Science* **2000**, *289*, 1327–1330. (b) Köhn F.; Hofkens J.; De Schryver F. C. *Chem. Phys. Lett.* **2000**, *321*, 372–378.
- (12) Some exceptional cases (<5%) show simultaneous emission from the PI and TDI chromophores. We ascribe this to a small fraction of conformational isomers for which emission can compete with ET.
- (13) Veerman, J. A.; Garcia-Parajo, M. F.; Kuipers, L.; van Hulst, N. F. *Phys. Rev. Lett.* **1999**, *83*, 2155–2158.
- (14) Hofkens, J.; Schroeyers, W.; Loos, D.; Cotlet, M.; Köhn, F.; Vosch, T.; Maus, M.; Herrmann, A.; Müllen, K.; Gensch, T.; De Schryver, F. C. *Spectrochim. Acta, A* **2001**, *57*, 2093–2107.
- (15) Hofkens, J.; Vosch, T.; Maus, M.; Köhn, F.; Cotlet, M.; Weil, T.; Herrmann, A.; Müllen, K.; De Schryver, F. C. *Chem. Phys. Lett.* **2001**, *333*, 255–263.
- (16) In contrast, self-sensitized photooxidation was recently proposed as the operating mechanism for photobleaching of terylene in single-molecule experiments: Christ, T.; Kulzer, F.; Bordat, P.; Basché, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 4192–4195.

JA017442A