

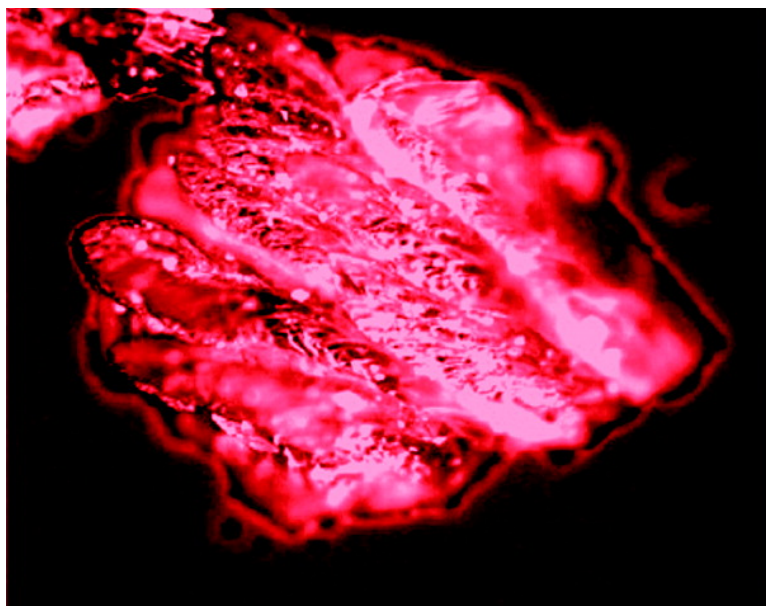
Communication

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## A Donor–Acceptor Molecular Dyad Showing Multiple Electronic Energy-Transfer Processes in Crystalline and Amorphous States

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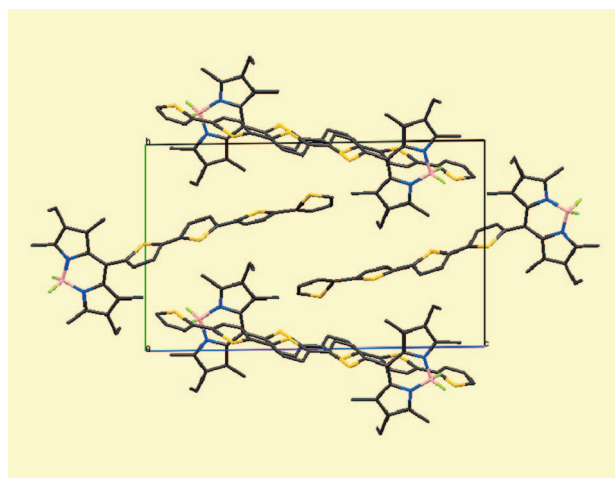
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Inspired by natural photosynthesis, a large number of artificial photoactive molecular dyads have been synthesized and studied. According to the composition of the light-active terminals and the molecular topology, a wide variety of physical and chemical processes have been observed and many important discoveries have been made with such molecules. Almost all of these studies refer to fluid solution at ambient temperature, where ultrafast transient spectroscopy can be used to determine rate constants and yields for the individual steps.<sup>1</sup> Only a few molecular dyads have been studied in glassy matrices at low temperature<sup>2</sup> or embedded in solid media.<sup>3</sup> This latter research encompasses photochromic materials.<sup>4</sup> Even fewer studies have involved crystalline molecular dyads,<sup>5</sup> despite their obvious relevance to the natural system, but we now describe a system that undergoes intramolecular energy transfer in the crystal.

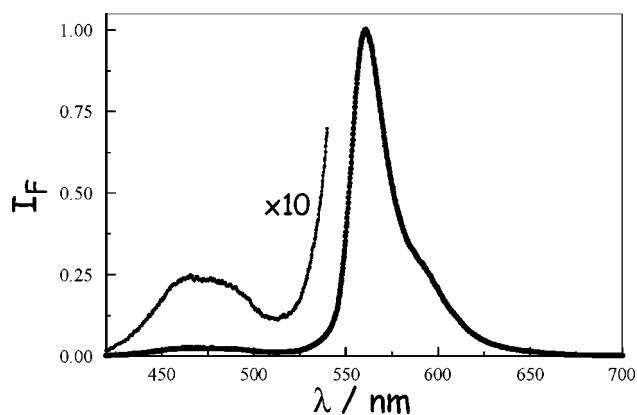
The target dyad, BOD-T4, comprises a boron dipyrromethene (BODIPY) dye equipped with a tetrameric oligo-thiophene residue (T4) sited at the meso position. Crystalline samples were obtained by slow evaporation of petroleum ether into a saturated toluene solution. Single crystal X-ray diffraction indicates that the two subunits are held at an almost perpendicular geometry, with near-orthogonality for two independent molecules in the asymmetric unit (Figure 1). The structure also reveals that each thiophene group adopts the expected antiarrangement, except for the terminal ring that is twisted markedly out-of-plane in one molecule; this molecule shows concerted ring-flip disorder for the other thiophene rings.

Initially, BOD-T4 was dissolved in a sucrose octaacetate glass at room temperature. The absorption spectrum shows the separate transitions localized on the two subunits (see Supporting Information) with the BODIPY and T4 units, respectively, exhibiting maxima at 540 and 393 nm. There is no evidence for self-aggregation of the sample. In contrast, dispersing BOD-T4 in a compacted KBr disk leads to extensive self-association as evidenced by a pronounced absorption band centered at 603 nm. Excitation into the T4 unit of BOD-T4 in the glass results in weak fluorescence centered at 465 nm that can be attributed to the singlet-excited state centered on T4 and much stronger fluorescence at 560 nm attributable to the BODIPY dye (Figure 2). Comparison with an isolated T4 reference compound shows that the T4-based fluorescence in BOD-T4 is quenched by 95% while the fluorescence lifetime decreases from 800 to 30 ps.

The fluorescence–excitation spectrum recorded for emission from the BODIPY unit confirms that fluorescence quenching is due to intramolecular electronic energy transfer from T4 to BODIPY. The rate constant is  $3.3 \times 10^{10} \text{ s}^{-1}$ . It is likely that this process includes a contribution from Förster-type dipole–dipole energy



**Figure 1.** Crystal packing and molecular structure of BOD-T4, showing the anti-arrangement of the thiophene units: sulfur, yellow; carbon, gray; hydrogen, pale gray; nitrogen, blue; boron, red; fluorine, green.

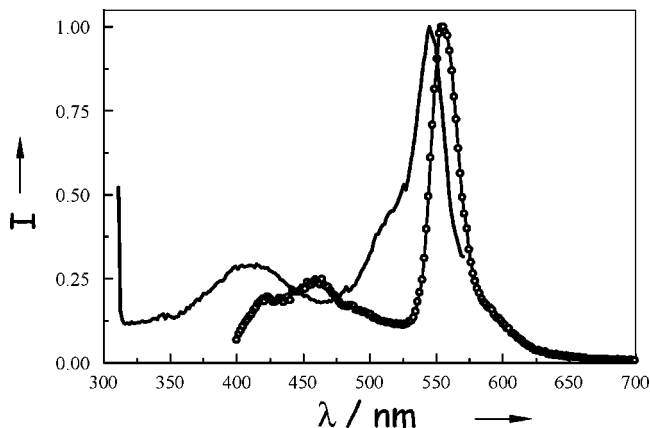


**Figure 2.** Fluorescence spectrum recorded for BOD-T4 in a sugar glass at 20 °C following excitation into the T4 unit.

transfer in view of the large overlap integral ( $J_F = 1.5 \times 10^{-13} \text{ mol}^{-1} \text{ cm}^6$ ) and close positioning ( $R_{CC} = 9.3 \text{ \AA}$ ) of the reactants, but the orientation factor ( $\kappa^2 = 0.06$ ) is kept small by the almost perpendicular alignment of the transition dipole moments. Consequently, the rate constant for Förster-type energy transfer is calculated to be only  $3 \times 10^9 \text{ s}^{-1}$ ; this is too low to account for the experimental observation, although it is recognized that care needs to be taken in applying Förster theory to short separations.<sup>6</sup> We conclude, therefore, that Dexter-type electron exchange dominates the energy-transfer process, as was observed earlier for certain meso-substituted BODIPY-based dyads in fluid solution.<sup>7</sup>

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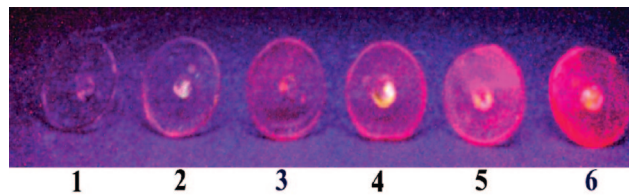


**Figure 3.** Fluorescence (circles) and excitation (solid line) spectra recorded from a single crystal of BOD-T4.

Fluorescence from the BODIPY unit is also quenched when compared to that from an isolated reference compound.<sup>8</sup> The fluorescence quantum yield is reduced from 0.76 to 0.24 while the fluorescence lifetime is decreased from 4.6 to 1.2 ns. Laser flash photolysis studies show transient formation of the  $\pi,\pi^*$  triplet state localized on the BODIPY dye, which has a lifetime of 14  $\mu$ s in the glass at 20 °C. Since the triplet state is barely detectable in the reference compound,<sup>9</sup> fluorescence quenching is attributed to singlet–triplet energy transfer in which the triplet state associated with T4 is populated as a short-lived intermediate. This process, for which the rate constant is ca.  $6.1 \times 10^8 \text{ s}^{-1}$ , will be followed by rapid triplet–triplet energy transfer from T4 to BODIPY, with the latter triplet lying at rather low energy<sup>10</sup> and acting as the drain for photonic energy in the system. Each of the three intramolecular energy-transfer steps occurs with an efficiency >75%, those involving the triplet manifold are assigned to electron exchange. An alternative mechanism, often important for orthogonal geometries,<sup>11</sup> whereby fast intersystem crossing occurs in a charge-separated state is considered to be unlikely in the nonpolar environment employed in this work.

Fluorescence from a single crystal of BOD-T4 is easily detected (see Supporting Information). The emission spectrum contains contributions from both BODIPY and T4 units, with the former being predominant (Figure 3). The excitation spectrum, when compared to the absorption spectrum recorded for a single crystal of BOD-T4, is indicative of incomplete energy transfer from T4 to the BODIPY unit. Nonetheless, ca. 70% of photons absorbed by the T4 unit within the crystal are transferred to BODIPY. The rate constant for energy transfer was found by time-resolved fluorescence spectroscopy to be  $7.8 \times 10^9 \text{ s}^{-1}$ . The fluorescence quantum yield for the BODIPY unit in the single crystal is ca. 0.4 while the excited-singlet state lifetime is 3.0 ns. Although this latter lifetime approaches that found for the BODIPY reference compound in solution, it is apparent that the excited-singlet state of the BODIPY unit is quenched within the crystal. The rate constant for this latter step, which is again attributed to singlet–triplet electron exchange, was found by laser flash photolysis to be ca.  $1.2 \times 10^8 \text{ s}^{-1}$ .

Both energy-transfer steps occurring in the crystal are assigned to intramolecular processes because of the relatively large edge-to-edge separation (i.e., >5 Å) between BODIPY and T4 units and their near orthogonal arrangement. There are no significant ring-stacking interactions in the crystal, the centroid–centroid distances



**Figure 4.** Observed fluorescence from vapor deposited films of BOD-T4 on a glass disk under UV irradiation ( $\lambda > 350 \text{ nm}$ ): 1 = blank; 2–6 = increasing sublimation times.

all being >4.1 Å for essentially parallel rings; the closest of these correspond to pyrrole rings having interplanar spacings of ca. 3.6 Å and dihedral angles of ca. 8°, but the rings have almost no overlap when viewed perpendicular to their mean planes (see Supporting Information). The incidence of ring-flip disorder, low crystal density of  $1.279 \text{ g cm}^{-3}$ , and lack of ring stacking indicate a loose packing of the molecules. The Förster rate constant for intramolecular energy transfer from T4 to BODIPY is calculated as  $1.2 \times 10^9 \text{ s}^{-1}$ , on the assumption that Förster theory can be applied to very short separation distances.<sup>6</sup> This computed rate is well below the measured value and points to the dominance of electron-exchange in this dyad. The slow rates of through-bond electron exchange found in the crystal relative to amorphous media are attributed to the more rigid environment enforcing an orthogonal geometry.

Finally, so as to produce a means by which to incorporate BOD-T4 into a simple opto-electronic device, attention was turned to films generated by vacuum sublimation. Careful sublimation of thin films of BOD-T4 leads to slides that are strongly fluorescent (Figure 4) but that clearly display electronic energy transfer. Increasing the amount of deposited material causes a progressive increase in fluorescence intensity but this saturates once a certain amount of BOD-T4 has condensed onto the substrate due to aggregation of BODIPY units.

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**Supporting Information Available:** Crystal packing arrangement and absorption and triplet absorption spectra in the solid state. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) (a) Gust, D.; Moore, T. A.; Moore, A. L. *Pure Appl. Chem.* **1998**, *70*, 2189–2200. (b) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435–461. (c) Holten, D.; Bocian, D.; Lindsey, J. S. *Acc. Chem. Res.* **2002**, *35*, 57–65.
- (2) (a) Wasielewski, M. R.; Johnson, D. G.; Svec, W. A.; Kersey, K. M.; Minsek, D. W. *J. Am. Chem. Soc.* **1988**, *110*, 7219–7221. (b) Harriman, A.; Heitz, V.; Ebersole, M.; van Willigen, H. *J. Phys. Chem.* **1994**, *98*, 4982–4989.
- (3) Otsubo, T.; Aso, Y.; Takimiya, K. *J. Mater. Sci.* **2002**, *12*, 2565–2575.
- (4) Van Gemert, B.; Bergomi, M.; Knowles, D. *Mol. Cryst. Liq. Cryst. Sci. Technol.* **1994**, *A246*, 67–73.
- (5) Leroy-Lhez, S.; Baffreau, J.; Perrin, L.; Levillain, E.; Allain, M.; Blesa, M.-J.; Hudhomme, P. *J. Org. Chem.* **2005**, *70*, 6313–6320.
- (6) (a) Wong, K. F.; Bagchi, B.; Rossky, P. J. *J. Phys. Chem. A* **2004**, *108*, 5725–5763. (b) Füchel, B.; Köhn, A.; Harding, M. E.; Diezemann, G.; Hinze, G.; Baschè, T.; Gauss, J. *J. Chem. Phys.* **2008**, *128*, 074505.
- (7) Kim, T. G.; Castro, J. C.; Loudet, A.; Jiao, J. G.-S.; Hochstrasser, R. M.; Burgess, K.; Topp, M. R. *J. Phys. Chem. A* **2006**, *110*, 20–27.
- (8) Harriman, A.; Mallon, L. J.; Ulrich, G.; Ziessel, R. *ChemPhysChem* **2007**, *8*, 1207–1214.
- (9) Harriman, A.; Mallon, L. J.; Goeb, S.; Ziessel, R. *Phys. Chem. Chem. Phys.* **2007**, *9*, 5199–5201.
- (10) Harriman, A.; Rostron, J. P.; Cesario, M.; Ulrich, G.; Ziessel, R. *J. Phys. Chem. A* **2006**, *110*, 7994–8002.
- (11) van Willigen, H.; Jones, G., II; Farahat, M. S. *J. Phys. Chem.* **1996**, *100*, 3312–3316.

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