Synthesis and Characterization of Donor−Bridge−Acceptor Molecule Containing Tetraphenylbenzidine and Perylene Bisimide

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A novel donor acceptor dyad consisting of tetraphenylbenzidine (TPD) and perylene bisimide was synthesized by linking these moieties using a dodecyl spacer. HOMO and LUMO values of the dyad were aquired by cyclic voltammetry. Photophysical properties were studied by steady-state UV−vis and fluorescence spectroscopy. After selective excitation of the TPD moiety, a quenching of donor fluorescence and the appearance of acceptor fluorescence was observed. This proves nonradiative energy transfer from the donor to the acceptor group. The energy transfer was 4 times more efficient in DBA than in a mixture of D and A. The energy transfer efficiency in the dyad is also independent of the concentration, indicating intramolecular transfer mechanism. However, the direct excitation of the acceptor in the dyad exhibited reduced fluorescence emission of the acceptor, indicating electron transfer between the moieties. Thus, this DBA is an excellent model system for the study of energy- and electron-transfer processes in organic semiconductors.

Introduction

Energy-transfer and electron-transfer processes between a donor and an acceptor play a fundamental role in most of the applications such as OLEDS and solar cells as well as in basic biological process such as photosynthesis. Therefore, a systematic design and study of tailor-made donor−bridge−acceptor (DBA) model systems is required for understanding these key processes. Photoinduced energy transfer between donor and acceptor was studied as early as 1940.[1,2] The nonradiative energy transfer due to dipole−dipole interactions in donor−acceptor mixtures and bridged systems within a range of about 10 nm can be explained by Förster transfer. Here, the rate of energy transfer (k_T) is extremely dependent on the distance R between the moieties ($k_T \propto R^{-6}$). In the past, the energy transfer was mainly studied in basic organic moieties such as naphthalene−anthracene systems.[2] Further, intramolecular energy transfer was observed in DBA molecules containing anthracene and porphyrine linked by an oligothienyl spacer.[3,4] Photoinduced electron transfer was also reported in different types of donor acceptor systems. Picosecond dynamics of electron transfer in intramolecular exciplex systems of porphyrin−quinone dyads were investigated.[5] Further, electron tunneling could be identified as a main deactivation channel from a selective excited zinc porphyrine donor to gold porphyrine acceptor linked by an oligophenylene−ethynylene bridge.[6] Recently, model systems based on perylene bisimide and triphenylamine have been studied for electron transfer at the single molecule level. Fluorescence studies in these systems showed an electron transfer from D to A as well as a reverse electron transfer from A to D.[7] Furthermore, electron-transfer studies of dendrimers containing TPA and perylene bisimide derivatives have also been published.[8]

Here we report the synthesis, characterization, and photophysical studies of a novel DBA system carrying *N,N,N′,N′*-tetraphenylbenzidine (TPD) as donor and perylene bisimide (PI) as an acceptor. The donor and acceptor moieties were linked by a saturated C_{12} hydrocarbon bridge. It is a challenge for us to employ a TPD donor, especially because TPD derivatives are used as organic hole conductor materials in various applications. Furthermore, PI is well-known as a photostable dye suitable for applications in solar cells.[9] These chromophores have attracted attention on account of their intensive luminescence, light fastness and *n*-type semiconductor properties.[10] The main task was to functionalize the TPD and PI moieties unsymmetrically and to couple them suitably to get a soluble, well-defined DBA molecule. The DBA molecule is thoroughly characterized using spectroscopic analysis such as FTIR, NMR, etc. Using steady-state absorption and fluorescence measurements, we examined the energy- and electron-transfer processes. Time-resolved emission decay and lifetime measurements support both energy and electron transfer.

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(1) Förster, T. *Z. Naturforsch.* **1949**, *4a*, 321.
(2) For review: Speiser, S. *Chem. Rev.* **1996**, *96*, 1953
(3) Würthner, F.; Vollmer, M. S.; Effenberger, F. P.; Emele, P.; Meyer, D. U.; Pat, H.; Wolf, H. C. *J. Am. Chem. Soc.* **1995**, *117*, 8090.
(4) Vollmer, M.; Würthner, F.; Effenberger, F.; Emele, P.; Meyer, D. U.; Stümpfig, T.; Port, H.; Wolf, H. C. *Chem.−Eur. J.* **1998**, *4/2*, 260.
(5) Mataga, N. N.; Karen, A.; Okada, T. L. *J. Phys. Chem.* **1984**, *88*, 5138.
(6) Pettersson, K.; Wiberg, J.; Ljungdahl, T.; Martensson, J.; Albinsson, B. *J. Phys. Chem. A* **2006**, *110*, 319.

(7) Bell, T. B. M.; Stefan, A.; Masuo, S.; Vosch, T.; Lor, M.; Cotlet, M.; Hofkens, J.; Bernahrdt, S.; Müllen, K.; Auweraer, V. d. M.; Verhoeven, J. W.; De Schryver, F. C. *Chem. Phys. Chem.* **2005**, *6*, 942.
(8) Cotlet, M.; Masuo, S.; Lor, M.; Fron, E.; Auweraer, V. d. M.; Müllen, K.; Hofkens, J.; De Schryver, F. D. *Angew. Chem., Int. Ed.* **2004**, *43*, 6116. Qu, J.; Pschirer, N. J.; Liu, D.; Stefan, A.; De Schryver, F. C.; Müllen, K. *Chem.−Eur. J.* **2004**, *10*, 528.
(9) Tang, C. W. *Appl. Phys. Lett.* **1986**, *48*, 183.
(10) Würthner, F.; Chen, Z.; Dehm, V.; Stepanenko, V. *Chem. Commun.* **2006**, 1188.

Experimental Section

Materials. The starting materials, perylenetetracarboxylic acid dianhydride, 1,12-dibromododecane, and 8-aminopentadecane, were purchased from Synthec/Synthon, Merck, Aldrich, and Fluka. THF was distilled from potassium benzophenone prior to use. Compounds **3** and **5** were synthesized according to published procedures.[11,12]

Instrumentation. ^{1}H NMR measurements were carried out by a Bruker Cryomagnet BZH 250/52 instrument with a field of 5.87 T, current of 54.80 A/1 D WIN NMR. Mass spectroscopic data were obtained from a FINNIGAN MAT 8500 instrument. FT−IR data were achieved by a Bio Rad DigiLab Division FTS 40/13130 instrument. For photochemical studies, a Hitachi model U 3000 spectrophotometer (UV−vis) and Shimadzu RF-5301 PC (fluorescence spectroscopy) were used. CV measurements were carried out by a three-electrode assembly microcell from E&G Princeton Applied research and a Potentiostat/Galvanostat model 263A.

Synthesis of *N*-[4-(12-Bromo-dodecyloxymethyl)phenyl]-*N,N′,N′*-triphenylbenzidine (4). In an anhydrous apparatus, *N*-[4-(hydroxymethyl)phenyl]-*N,N′,N′*-triphenylbenzidine (0.93 g, 1.8 mmol) was dissolved under argon in 10 mL of dried THF. A sodium hydride suspension (60%; 0.086 g, 2.16 mmol, 0.052 g of NaH) was added in portions under stirring followed by 1,2-dibromdodecane (2.36 g, 7.2 mmol). After 2 h of stirring, more NaH dispersion (0.086 g, 2.16 mmol NaH) and bromide (0.6 g, 1.8 mmol) were added. The mixture was heated for 5/1/2 h (60−65 °C) and filtered hot. The residue was washed with THF. The evaporation of the filtrate yielded an oil, which was purified by column chromatography (silica gel/*n*-hexane/ethyl acetate 20:1). A yellowish orange oil (0.9 g) was obtained. Yield: 0.9 g, 65.3%. ^{1}HNMR (250 MHz, CDCl$_3$): δ 1.17−1.80 (20H, m, (CH$_2$)$_{10}$), 3.32 (2H, m, ^3J = 6.94 Hz, CH$_2$Br), 3.42 (2H, m, ^3J = 6.63 Hz, CH$_2$O), 4.37 (2H, m, C$_{aryl}$−CH$_2$O), 6.95 (3H, m, ^3J = 6.93 Hz, ^3J = 7.60 Hz, C$_{aryl}$−H), 7.03 (12H, m, ^3J = 6.95 Hz, ^4J = 1.9 Hz, C$_{aryl}$−H), 7.18 (8H, m, ^3J = 8.23 Hz, ^4J = 1.9 Hz, C$_{aryl}$−H), 7.37 (4H, m, ^3J = 8.23 Hz, C$_{aryl}$−H). MS: *m/z* 764 (M$^+$, 85%), 766 (M$^+$isotope, 81%), 684 (41%); 597 (15%), 502 (base peak, 100%), 251 (79%). Elem. Anal. Calcd for C$_{49}$H$_{53}$N$_2$OBr (%): C, 76.85; H, 6.98; N, 3.66. Found: C, 76.88; H, 7.14; N, 3.19.

Synthesis of (1-Heptyloctyl)-perylene-3,4:9,10-tetracarboxylic bisimide (5). Perylene-3,4:9,10-tetracarboxylic monoanhydride monoimide (3.13 g, 8 mmol) and 8-aminopentadecane (2.91 g, 12.8 mg) were stirred in imidazole (30 g) and quinoline (5 mL) under argon (160 °C, 2h). The mixture was dissolved in THF and precipitated in 400 mL of a mixture of ethanol and 2N HCl (1:1). The precipitate was collected by vacuum filtration, treated with boiling aqueous K$_2$CO$_3$ solution (100 mL, 10%), washed with distilled water, and dried under a vacuum. The compound was purified by extractive recrystallization[20] and traces of *N,N′*-di(1-heptyloctyl)-perylene-3,4:9,10-tetracarboxylic bisimide were removed by extraction with hexane to yield a red solid (3.64 g, 77%). ^{1}H NMR (CDCl$_3$, 250 MHz): δ 0.81 (6H, t, ^3J = 6.95 Hz, CH$_3$ end groups), 1.28 (20H, m, methylene protons), 1.87 (2H, m), 2.21 (2H, m), 5.16 (1H, m, CH proton), 8.59 (1H, s, NH proton), 8.56 (8H, m, C$_{aryl}$−H). MS (EI) *m/z*: 600 [M$^+$]. IR (Si, ν (cm^{-1})): 3067, 2958, 2927, 2855, 1698, 1659, 1594, 1432, 1403, 1343, 1269, 1179, 810, 741, 655. Elem. Anal. Calcd for C$_{39}$H$_{40}$N$_2$O$_4$ (%): C, 77.97; H, 6.71; N, 4.66. Found: C, 77.84; H, 6,35; N, 5.01.

Synthesis of *N*-[12-N(4-benzyloxy)-*N,N′,N′*-triphenyl benzidine) dodecyl]-*N′*-(1-heptyloctyl)-perylene-3,4:9,10-tetracarbox-

(11) Bolink, H. J.; Arts, C.; Krasnikov, V.; Malliaras, G. G.; Hadziiouannou, G. *Chem. Mater.* **1997**, *9*, 1407.
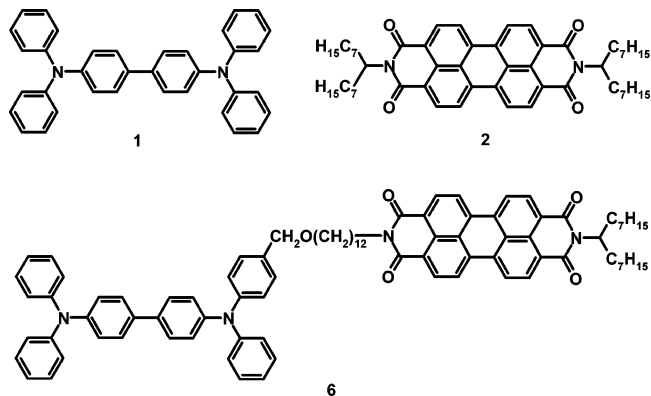(12) Kaiser, H.; Lindner, J.; Langhals, H. *Chem. Ber.* **1991**, *124*, 529.

Figure 1. Chemical structures of *N,N,N′,N′*-tetraphenylbenzidine (TPD 1), *N,N′*-bis(1-heptyloctyl)]-perylene-3,4:9,10-tetracarboxylic bisimide (PI 2), and *N*-[12-N(4-benzyloxy)-*N,N′,N′*-triphenyl benzidine) dodecyl]-*N′*-(1-heptyloctyl)-perylene-3,4:9,10-tetracarboxylic bisimide (DBA 6).

ylic bisimide (DBA 6). 4 (1 g, 1.305 mmol), *N*-(1-heptyloctyl)-perylene-3,4:9,10-tetracarboxylic bisimide **5** (0.81 g, 1.305 mmol), and potassium carbonate (1.8 g, 13.05 mmol) were dissolved in 5 mL of dried DMF and 10 mL of dried THF under argon by stirring. After 2 h, a small amount of potassium iodide and 5 mL of methylethylketone were added. The reaction was slowly heated to 75 °C. After 18 h of stirring, 100 mg of diimide (**5**) was added and stirred for 2 h at 75 °C. The mixture was filtered hot by a büchner funnel and washed with chloroform until the filtrate was colorless. The filtrate was evaporated on silica gel and purified by column chromatography (Kieselgel 60), first with *n*-hexane and afterward with a slowly increasing part of ethyl acetate with an *n*-hexane/ester ratio from 1:20 to 1:5. Yield: 0.5 g of a dark reddish solid (0.389 mmol, 29.8%). ^{1}HNMR (250 MHz, CDCl$_3$): δ 0.75(6H, m, CH$_3$), 1.15−1.83 (42H, m, methylene), 2.18 (2H, m, CH$_2$) 3.42 (2H, m, OCH$_2$), 4.12 (2H, m, >NCH$_2$), 4.87 (2H, m, C$_{aryl}$−CH$_2$O), 5.12 (1H, m, >N−CH<), 7.06 (23H, m, C$_{aryl}$−H), 7.36 (4H, m, ^3J = 8.20 Hz, C$_{aryl}$−H), 8.53 (8H, m, C$_{aryl}$−H). MS: *m/z* 1285 (M + 1, 1%), 784 (7%), 768 (8%); 531 (70%), 502 (base peak). IR (KBr, ν (cm^{-1})): 2924 and 2855 (s, CH$_2$ and CH$_3$), 1697 (vs, O=C−N). UV−vis (in CHCl$_3$, 1 × 10^{-5} M; ε (L mol^{-1} cm^{-1}): 80 400 (at 525 nm), 34 100 (at 308 nm). Elem. Anal. Calcd for C$_{88}$H$_{92}$N$_4$O$_5$ (%): C, 82.21; H, 7.21; N, 4.36. Found: C, 81.70; H, 8.45; N, 4.02.

Results and Discussion

Synthesis. The individual donor **1** (TPD) and the acceptor **2** model compounds (Figure 1) were synthesized according to previously reported procedures.[13,14]

To obtain soluble, unsymmetrically substituted perylene bisimide derivative **5**, we started the synthesis with the opening of one of the anhydride groups in the perylene-3,4:9,10-tetracarboxylic dianhydride to form the monopotassium salt (Scheme 1). The ring is closed again to get the unsymmetrical monoanhydride monoimide.[12] As the imide group is stable against basic and acidic reactions, only the anhydride group reacts with 8-aminopentadecane, forming a swallow-tail-substituted product **5**. In contrast to most perylene bisimide derivatives, these swallow-tail-substituted perylene bisimides are highly soluble in organic solvents.[14]

(13) Schmitz, C.; Thelakkat, M.; Schmidt, H. W. *Adv. Mater.* **1999**, *11*, 821.
(14) Langhals, H.; Demmig, S.; Potrawa, T. *J. Prakt. Chem.* **1991**, *333*, 733.

Scheme 1. Synthesis of Unsymmetrically Substituted Perylene Bisimide Derivative, *N*-(1-Heptyloctyl)-perylene-3,4:9,10-tetracarboxylic Bisimide 5[a]
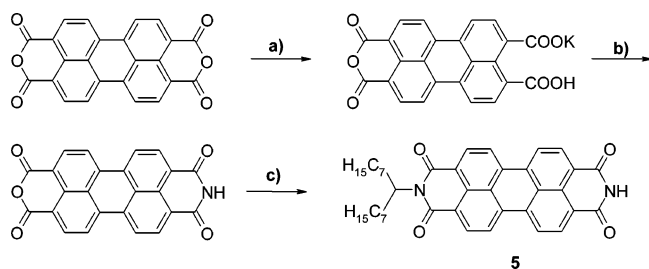
[a] (a) KOH, H₂0; AcOH; (b) NH₃, H₂0; (c) 8-aminodecane, imidazole, quinoline, 160 °C.

N-[4-(12-Bromo-dodecyloxymethyl)phenyl]-*N,N′,N′*-triphenylbenzidine **4** was prepared by Williamson ether synthesis from the corresponding hydroxy functionalized *N*-[4-(hydroxymethyl)phenyl]-*N,N′,N′*-triphenylbenzidine **3** and 1,-12-dibromododecane. By heating **4** in dry DMF with the unsymmetrical perylene bisimide, *N*-(1-heptyloctyl)-perylene-3,4:9,10-tetracarboxylic bisimide **5**, in presence of K₂CO₃, we could obtain the target molecule **6** in 30% yield (see Scheme 2).The DBA molecule **6** was thoroughly characterized using FT−IR, ¹H NMR, and MS methods. Figure 2 shows the ¹H NMR spectrum of **6**. Thus, eight aryl protons belonging to the perylene moiety appear as multiplet at 8.52 ppm (similar to those in perylene diimide **5**) and four additional aryl protons at 7.36 ppm could be assigned to the biphenyl part connected to nitrogen atoms in TPD. Finally, the rest of the 23 aryl protons of TPD were observed in the range 6.91−7.21 ppm. The characteristic signals of the dodecyl spacer, similar to those in **4**, could also be identified. Thus, the typical signals of the single N−CH proton at 5.12

ppm, two TPD−CH₂O protons at 4.37 ppm, two >N−CH₂ methylene protons at 4.12 ppm, and two CH₂−O protons in the dodecyl group at 3.42 ppm were confirmed. The 24 protons of methylene groups of the 1-heptyl-octyl residue and the 20 protons of the dodecyl spacer appear between 1.15 and 2.18 ppm. The six CH₃ protons appear as a triplet at 0.75 ppm.

MS shows a very weak (M + 1) peak at 1285, a base peak at 502 (*m/z* of TPD−CH₂⁺) and a series of other fragments, which can be assigned to perylene and alkyl fragments. Additionally, the asymmetric imide carbonyl vibration at 1697 cm⁻¹ was present in FT−IR.

Photophysical Properties. The primary condition for energy transfer is the spectral overlap of the donor emission and acceptor absorption. This is obvious in Figure 3, in which the emission spectrum of **1** (measured in a 1×10^{-5} M solution in CHCl₃ at an excitation wavelength of 349 nm) and absorption spectrum of **2** (measured in a 1×10^{-5} M solution in CHCl₃) are depicted. The transitions require us to follow the Franck−Condon principle, and the vibrational deactivation of the excited donor singlet state must be faster than the energy transfer. The spectral overlap is then proportional to the resonance donor emission and acceptor absorption transition. Nonradiative energy transfer according to the equation D* + A → D + A* on the basis of a suitable dipole−dipole interaction (Förster transfer) or electron exchange (Dexter transfer) between donor and acceptor can be then assumed.[1,15]

The steady-state UV−vis spectra of donor **1**, acceptor **2**, and DBA **6** were recorded in 1×10^{-5} M solutions in CHCl₃ (Figure 4). Perylenbisimide **2** exhibits its typical $S_0 \rightarrow S_1$ transition in the range of 400−550 nm ($\lambda_{max} = 525$ nm) with well-resolved vibronic structure that can be attributed to

Scheme 2. Synthesis of DBA 6 From Unsymmetrically Functionalized Donor and Acceptor Moieties.[a]
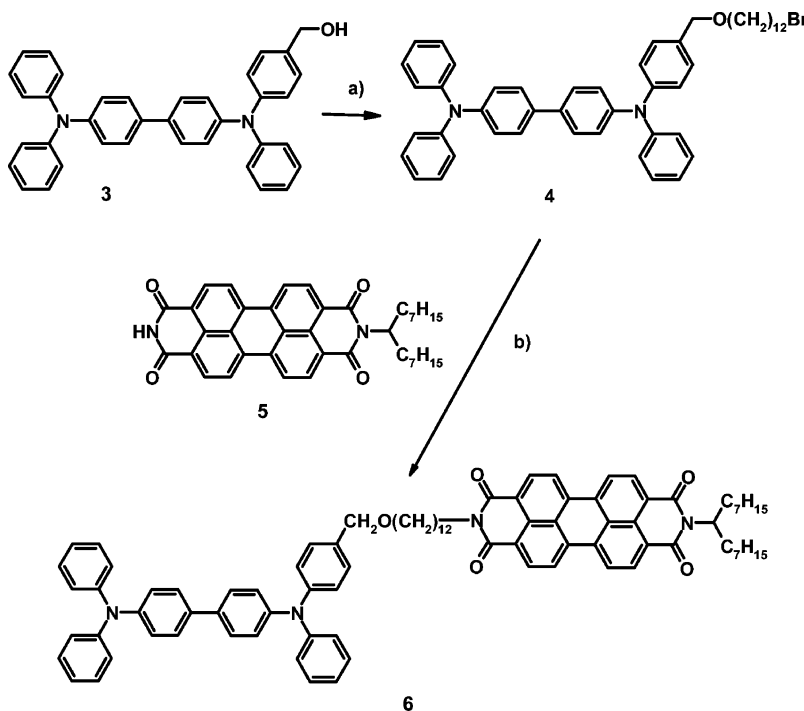
[a] Reagents and conditions: (a) 1,12-dibromododecane, K₂CO₃/MEK; and (b) in DMF/75 °C.
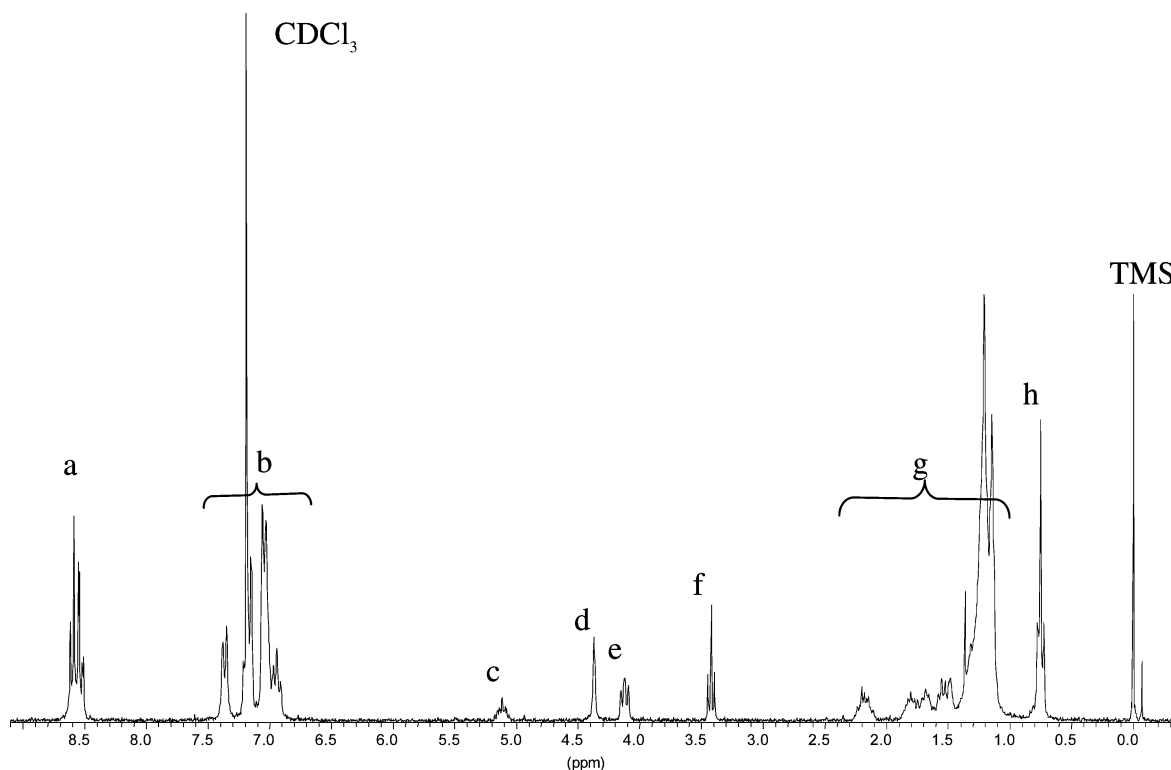
Figure 2. ^{1}H NMR Spectrum of **6** measured in CDCl$_3$: (a) 8H from perylene unit; (b) 27H from TPD unit; (c) 1H from >N−CH (single proton of heptyl-octyl rest); (d) 2H CH$_2$ (TPD); (e) 2H from >N−CH$_2$−(dodecyl spacer); (f) 2H from OCH$_2$−(dodecyl spacer); (g) 44H from methylene units; (h) 6H from CH$_3$ groups.
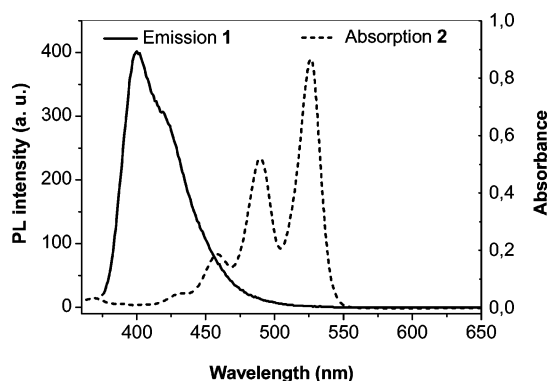

Figure 3. Emission spectrum of donor **1** at an excitation wavelength of 349 nm and the absorption spectrum of **2**, both measured in 1×10^{-5} M solutions in CHCl$_3$.
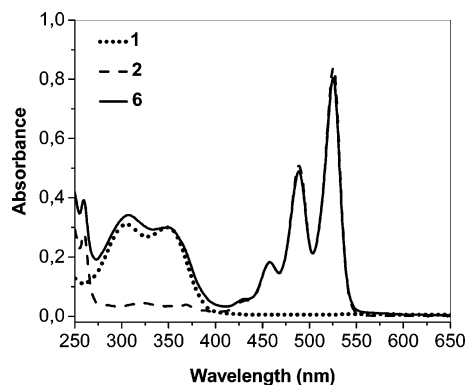

Figure 4. UV−vis spectra of donor **1**, acceptor **2**, and DBA **6**, recorded in 1×10^{-5}M solutions in CHCl$_3$.

breathing vibrations of the perylene skeleton.[10] On the other hand, TPD shows its absorption bands in the range of 250−400 nm (λ_{max} = 349 nm). Thus, absorption of compounds **1**
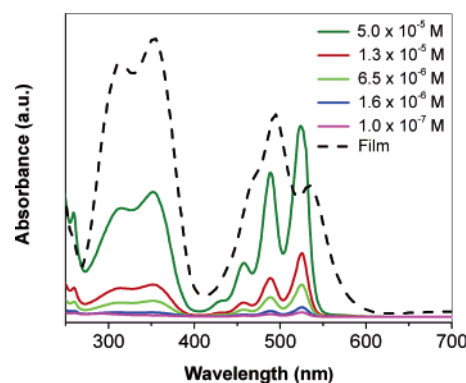

Figure 5. UV−vis spectra of DBA **6** in CHCl$_3$ recorded at different concentrations of 5.0×10^{-5} M to 1×10^{-7} M. For comparison, the absorption spectrum of the highly aggregated state in film is also given.

and **2** do not have any considerable overlap, which makes them suitable for selective excitation and energy-transfer studies. The absorption spectrum of DBA **6** results from the linear addition of the characteristic absorption bands of both TPD **1** and perylene bisimide **2**, indicating no charge transfer in the ground state.

Additionally, UV−vis spectra of DBA were recorded at different concentrations (1×10^{-7} M to 5×10^{-5} M) in chloroform in order to understand the aggregation properties of perylene bisimide (Figure 5). For comparison, the absorption spectrum of **6** in highly aggregated form (in thin film) is also given.[10] The intensities of vibronic transitions (for the $S_0 \rightarrow S_1$ transition) for the whole range of concentrations do not vary considerably, whereas in the film, the absorption

(15) Klessinger, M.; Michl, J. *Excited States and Photochemistry of Organic Molecules*; Verlag Chemie: Weinheim, Germany, 1995; p 288.
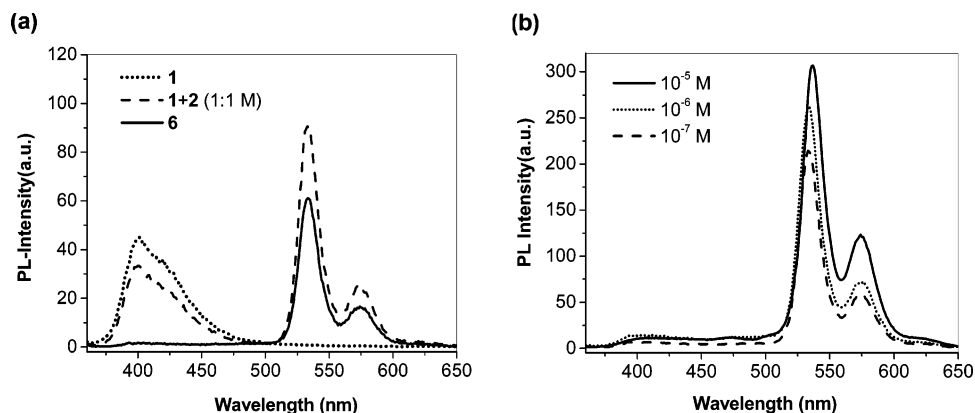
(a)

(b)

Figure 6. (A) Fluorescence spectra of donor **1,** DBA **6**, and a 1:1 molar mixture of **1** and **2** in CHCl$_3$ at a 1×10^{-7} M concentration and (B) fluorescence spectra of DBA **6** at different concentrations of 1×10^{-5} M to 1×10^{-8} M. All the samples were excited at 349 nm, the absorption maximum of the donor.

peaks are shifted to higher wavelengths and the intensity of vibronic transitions change dramatically. Thus, aggregation effects can be excluded at concentrations up to 5×10^{-5} M. Consequently, absorption and photoluminescence measurements will not be perturbed by interactions between molecules in dilute solutions in a measurement range up to this concentration.

The influence of linking D and A on the energy-transfer process from D to A can be investigated by comparing the fluorescence spectra of DBA and a blend of D and A with that of D. Therefore, fluorescence spectra of donor **1**, DBA **6**, and a 1:1 molar mixture of **1** and **2** in CHCl$_3$ were recorded at 1×10^{-7} M concentrations (Figure 6A). All the samples were selectively excited at 349 nm, the absorption maximum of the donor. The donor **1** exhibits a broad emission in the range of 350−500 nm, and this emission is completely quenched in the DBA molecule. Instead, the characteristic emission due to acceptor − almost a mirror image of the $S_0 \rightarrow S_1$ transitions − can be observed in DBA, which clearly proves an efficient energy transfer from donor to acceptor moiety in DBA. An emission due to a direct excitation of the acceptor moiety at 349 nm under the same conditions is almost negligible. On comparison for the same concentration, the 1:1 mixture of donor and acceptor (where the moieties are not linked together) exhibits only a partial energy transfer. The fluorescence quenching of the donor in DBA is about 96%, whereas it is only 26% in a 1:1 mixture if the fluorescence intensities are compared with that of pure donor emission in **1**. This is a clear evidence for the efficient energy transfer in the DBA system. The time-resolved measurements of decay of donor emission and the evolution of subsequent acceptor emission in DBA confirms the energy transfer.[16] It is also interesting to note that the intensity of emission of A in DBA is less than that in the mixture. This can be explained by the presence of some additional efficient deactivation channels, such as charge transfer, in DBA.

Furthermore, we studied the influence of the concentration of DBA on this energy-transfer process by exciting different concentrations of DBA in CHCl$_3$ at 349 nm (Figure 6B). For a broad range of concentration from 1×10^{-5} M to 1×10^{-7} M, there is more than 95% fluorescence quenching of

donor in all cases. This confirms a complete energy transfer from donor to acceptor in such dilutions. On the other hand, we found that for a mixture of donor and acceptor, the energy-transfer efficiency depends on the concentration. The higher the concentration, the more efficient the energy transfer in a mixture (not shown in the figure). Even for the highest concentration of 1×10^{-5} M solution, the fluorescence quenching in the mixture was only partial. This indirectly indicates that the energy transfer in DBA at high dilutions may be of an intramolecular nature. Here we have to note that there are no aggregation effects in DBA at this concentration range (see Figure 5).

This observation is quantified by recent photoluminescence measurements.[16] The energy-transfer efficiencies in DBA determined using different methods such as (i) decrease in donor lifetime, (ii) decrease in donor fluorescence intensity, and (iii) increase in acceptor fluorescence intensity lie close to >90%. We also found that the fluorescence lifetime of pure donor, donor in the presence of acceptor, and donor in DBA decreases from 0.85 to 0.57 ns and finally to extremely short values of even below 80 ps, respectively. Thus, the linkage of D and A has a drastic influence on energy-transfer dynamics in DBA.

However, in competition with energy transfer, a possible photoinduced electron transfer in such a system cannot be excluded. It causes a substantial or even complete quenching of local donor fluorescence.[17] In steady-state photoluminescence (PL) measurements, a charge-transfer band was not observed. To study the influence of linkage on the emission properties of the acceptor, we measured and compared fluorescence spectra of **2**, **6**, and a 1:1 mixture of **1** and **2** in CHCl$_3$ at the same concentration (Figure 7). All the samples were directly excited at $\alpha \lambda_{max}$ of the acceptor of 525 nm. Here, the free acceptor has the highest emission intensity, followed by that of the mixture and finally by the DBA molecule. The PL intensity of A decreased only to 88.2% in the mixture, whereas it was drastically reduced to 44.7%. This strong decrease in PL intensity of A in DBA can be attributed to some alternative quenching processes, the major contender being the charge-transfer process that is possible in this system.

(16) Scharf, C.; Peter, K.; Bauer, P.; Jung, C.; Thelakkat, M.; Köhler, J. *Chem. Phys.* **2006**, *328*, 403.

(17) Oevering, H.; Verhoeven, J. W.; Paddon-Row, M. N.; Warman, J. M. *Tetrahedron* **1989**, *45*, 4751.
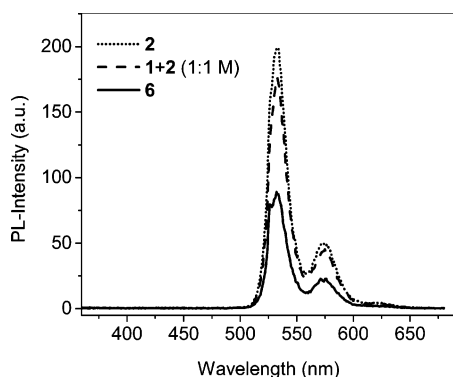
Figure 7. Steady-state fluorescence spectra of acceptor **2**, DBA **6**, and a 1:1 molar mixture of **1** and **2** in CHCl₃ at 1×10^{-8} M at an excitation wavelength of 525 nm.
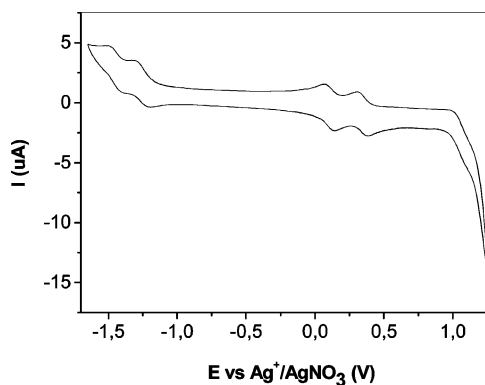

Figure 8. CV of **6** measured in CH₂Cl₂ solution containing 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte. The measurements were carried at a glassy carbon microelectrode against Ag/AgNO₃ as the reference electrode. Each measurement was calibrated with ferrocene.

This is again supported by time-resolved measurements of fluorescence lifetimes and intensities of D, A, and DBA in solution.[16] Interestingly, we found that the fluorescence lifetime of the acceptor emission of DBA in toluene, τ_A^{DBA} (= 1.70 ± 0.08 ns), deviates significantly from τ_A (= 3.9 ns) obtained for free A in the same solvent. This discrepancy in the fluorescence lifetimes of pure A and A in DBA hints at an additional quenching process in DBA that occurs with a rate constant of 0.33 ns⁻¹ and a quenching efficiency of 0.57. It is interesting to note that this additional quenching process was not observed in the donor−acceptor mixtures, where we found about the same fluorescence lifetime for the acceptor as for a pure acceptor solution.

This is in perfect agreement with the observation made in steady-state PL measurements. The decrease in emission intensity from the mixture to the DBA is again due to the linkage of the two moieties in DBA, which enhances the charge-transfer efficiency. This also explains the decreased emission observed for DBA compared to the blend in Figure 6A. A back energy transfer from acceptor to donor can be excluded because of energetic conditions.

Electrochemical Properties. To elucidate the energetic conditions for energy and electron transfer in dilute solutions,
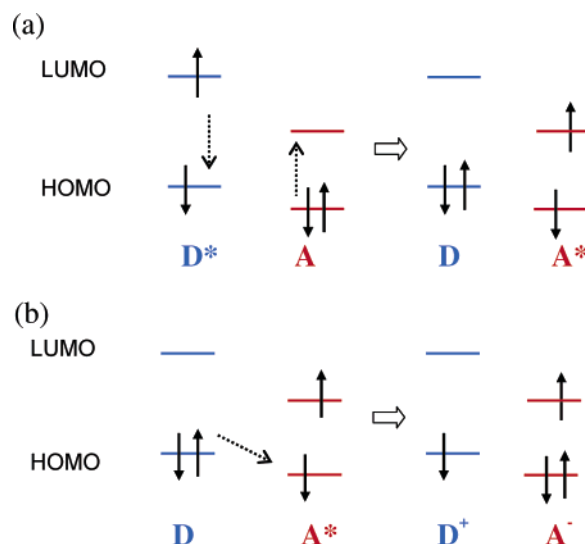

Figure 9. (A) Energy transfer from donor to acceptor after excitation of the donor at 349 nm and (B) one possible channel of electron transfer and fluorescence quenching of acceptor after direct excitation of acceptor at 525 nm.

we also determined the HOMO/LUMO values of all three compounds, **1**, **2**, and **6**, using cyclic voltammetry (CV). The measurements were carried out at a glassy carbon microelectrode in dichlormethane solutions containing 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte and Ag/AgNO₃ as the reference electrode. Each measurement was calibrated with ferrocene (Fc),[18] with the measured $E_{1/2}^{FC}$ = −0.162 V vs Ag/AgNO₃. Oxidation and reduction potentials were obtained as an average value between each anodic and corresponding cathodic potential: $E_{1/2}^{red/ox}$ = $1/2(E_{pc} + E_{pa})$. HOMO and LUMO energy levels were estimated on the basis of the reference energy level of ferrocene (4.8 eV below the vacuum level[18]) according to E^{HOMO}/E^{LUMO} = 4.8 + ($E_{1/2} - E_{1/2}^{FC}$) eV below the vacuum level. These HOMO/LUMO values do not represent any absolute solid-state or gas-phase ionization potentials but can be used to compare different compounds relative to one another.

The donor **1** shows two oxidation peaks corresponding to 0.30 and 0.55 V vs Fc, which results in a HOMO value of 5.10 eV (on the basis of the HOMO energy level of ferrocene as 4.8 eV). Similarly, the acceptor **2** exhibits an oxidation at 1.23 V and two reduction peaks at −1.09 and −1.29 V vs Fc. This gives a HOMO value of 6.03 eV and a LUMO value of 3.71 eV for compound **2**. Figure 8 shows the CV traces for the oxidation and reduction of DBA **6**. It exhibits oxidation peaks at 0.27, 0.51, and 1.21 V vs Fc. The first two oxidations are due to TPD moiety and the last one can be assigned to perylene bisimide unit, in agreement with the values measured for **1** and **2** under the same conditions. The corresponding HOMO energy values determined are 5.07 and 6.01 eV for donor and acceptor moieties in DBA, respectively. Additionally, the reduction peaks due to ac-

Table 1. Redox Potentials and HOMO/LUMO Values of 1, 2, and 6 Measured in Solution Cyclic Voltammetry; Fc: Ferrocene and $E_{1/2}^{Fc}$ = −0.162 V vs Ag/AgNO3

compd	E_{ox1} (V vs Fc)	E_{ox2} (V vs Fc)	E_{ox3} (V vs Fc)	HOMO (eV)	E_{red1} (V vs Fc)	E_{red2} (V vs Fc)	LUMO (eV)
1	0.30	0.55		5.10			
2	1.23			6.03	−1.09	−1.29	3.71
6	0.27	0.51	1.21	5.07	−1.09	−1.30	3.71

ceptor moiety appears at −1.09 and −1.30 V vs Fc (same as in **2**). This results in a LUMO value of 3.71 eV for the acceptor unit in DBA. Thus, the donor and acceptor units in **6** have similar HOMO/LUMO values as in free **1** and **2**, respectively. All the redox potentials and HOMO/LUMO values are given in Table 1. The LUMO of the TPD moiety lies much higher than the LUMO of perylene bisimide group and therefore could not be observed under our measurement conditions (up to −2.5 eV).

Thus, these energy values fulfill the energetic conditions required for the proposed energy transfer (from donor to acceptor on excitation of the donor) as well as the electron transfer between them (on direct excitation of the acceptor moiety) as schematically shown in Figure 9. In Figure 9a, the energy is transferred from the excited D to A, which could be observed as the PL quenching of D and a simultaneous emission from A. Figure 9b depicts one of the possible channels of concurring charge-transfer processes after the direct excitation of A.

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(18) Thelakkat, M.; Schmidt, H. W. *Adv. Mater.* **1998**, *10*, 219.

Conclusions

To conclude, we synthesized a novel DBA dyad in which tetraphenylbenzidine (TPD) as donor and perylene bisimide (PI) as an acceptor were linked by a saturated C_{12} hydrocarbon bridge. The selective excitation of the donor leads to a highly efficient energy transfer (>90%) to the acceptor in DBA. The donor emission was quenched and a simultaneous acceptor emission was observed. In DBA, nonradiative energy transfer can be assumed to be of an intramolecular nature. The concentration-dependent studies of DBA and a mixture of donor and acceptor make clear that any intermolecular energy transfer in DBA is negligible. However, competitive charge transfer cannot be excluded. This competing electron transfer from excited acceptor is also more efficient in DBA than in a mixture of D and A.