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FRET in Orthogonally Arranged Chromophores

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Dedicated to Prof. H. Nöth on the occasion of his 80th birthday

Keywords: FRET (Fluorescence Resonance Energy Transfer) / Fluorescence spectroscopy / Nitrogen heterocycles / Arenes / Photophysics

Perylene and benzoperylene carboxylic imides were arranged to form a bichromophoric dye with orthogonal electronic transition moments. Thus, exciton interactions between the two chromophores could be excluded, in spite of their proximity. However, quantitative Förster-type energy transfer proceeds between the chromophores indicated by a fluorescence quantum yield close to unity even with hypsochromic excitation. Applications are discussed.
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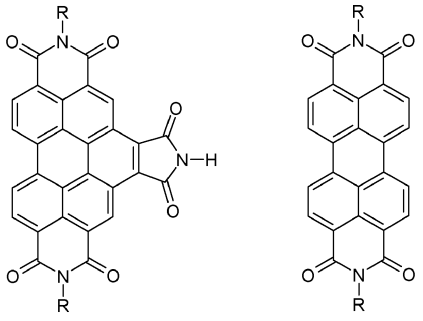
Introduction

Förster-type fluorescence energy transfer (FRET)[1] is gaining increasing interest in chemistry. FRET proved to be a powerful tool for the indication of the proximity of chemical structures. Such information is required for the investigation of molecular recognition. Thus, FRET systems are becoming of increasing importance in biochemistry and general analytics.[2] One may ask if there are limitations for the FRET process by the orientation of the components, because this would require special care for designing such systems.

Results and Discussion

Benzoperylene hexacarboxylic trisimides **1**[3] and perylene tetracarboxylic bisimides **2**[4] are ideal chromophores for the investigation of the influence of orientation on FRET, because there is only one electronic transition in the visible region,[5] both in absorption and fluorescence spectroscopy, and this is polarized along the N–N axis of **1** and **2**, respectively; dyads with **2** were developed[6] and further progressed. As a novel concept, we arranged both the transition moments of **1** and **2**, respectively, orthogonally in order to clarify if FRET can be switched off; compare.[7] To this end, an arrangement of the two chromophores with a stiff spacer has to be synthesized.



1 **2**

1, 2	R
a	$CH(C_6H_{13})_2$

Perylene anhydride carboxylic imide **3**[8] with the solubilizing long-chain *sec*-alkyl group[9] at the nitrogen atom was condensed with an excess amount of tetramethyl *p*-phenylene diamine to obtain amino dye **4**. The methyl groups of the phenyl spacer render the π systems of the chromophore and the spacer orthogonal and, thus, electronically decoupled; further decoupling is brought about by the fact that there are orbital nodes[10] in the HOMO and LUMO at the linking nitrogen atom of **2** and **4**, respectively. Amino derivative **4** was condensed with anhydride **5**[3] to obtain bichromophoric dye **6** (Scheme 1). The three solubilizing alkyl groups in **6** render the material soluble in spite of the accumulation of aromatics. The electronic transition moments both in **1** and **2** are parallel to the six-membered ring N–N-connection lines and, thus, are orthogonal in **6**; this was further verified by quantum chemical calculations[11] of a simplified derivative and is shown in Figure 1. The orthogonality remains independent from a rotation around the linking single bonds of the central *p*-phenylene unit in **6**.

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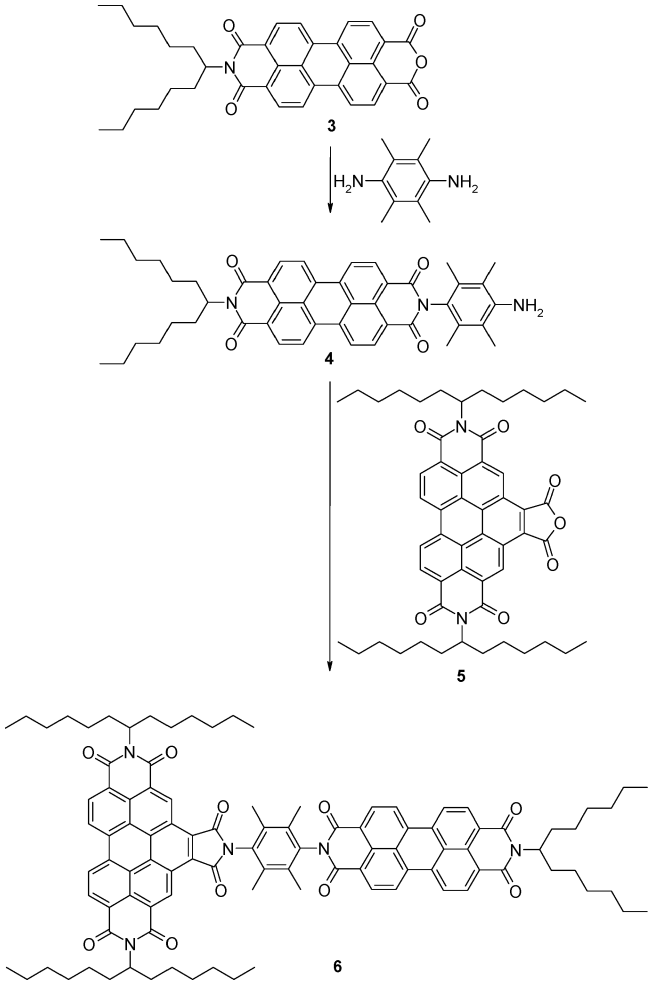

Scheme 1. Synthesis of bichromophoric dye **6**.

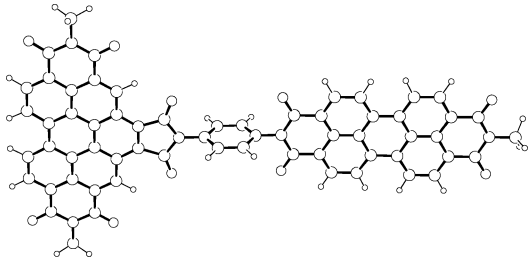

Figure 1. Arrangement of the chromophores in **6** verified by quantum chemical calculations of a simplified structure (see text). The electronic transition moments are parallel to the N–N-connection lines for each of the two chromophores and remain orthogonal even after torsion of the chromophores around the single bonds of the central unit.

The UV/Vis absorption spectra of two chromophores **1** and **2** in **6** are additive (see Figure 2). Exciton interactions are negligible for absorption, because the well-established vibrational pattern of the chromophore of **1** and **2**, respectively, remains unaltered (see Figure 2). Alterations in the spectra of **6** relative to those in the spectra of monochromophore **2** are even more precisely studied by means of Gaussian analysis[12] (see Figure 3 and Table 1).

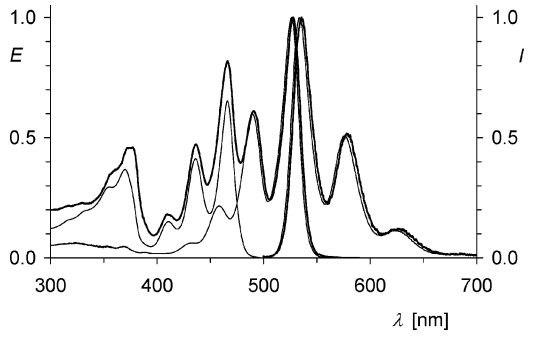

Figure 2. Absorption (thick line left hand) and fluorescence spectrum (thick line right hand) of **6** in chloroform. Thin lines from left to right: absorption spectra of **1a** and **2a** and fluorescence spectrum of **2a** in chloroform.

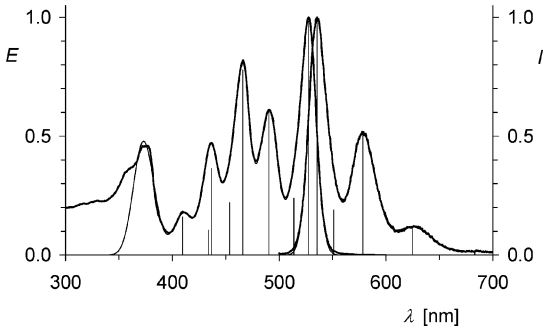

Figure 3. Gaussian analysis of the absorption (thick line left hand) and the fluorescence spectrum (thick line right hand) of **6** in chloroform (400–750 nm). Bars: positions and intensities of the Gaussian bands; thin lines: simulated spectra on the basis of the Gaussian analysis; see Table 1.

The line positions and intensities of the bathochromic absorption of **6** and the fluorescence are very similar to the corresponding bands of **2a** indicating negligible interaction of the two chromophores in **6** (see Table 1). This demonstrates the exclusion of exciton interactions by orthogonality; compare ref.[7] The fluorescence quantum yield of **6** is close to 100% if bathochromic absorbing chromophore **2** is irradiated at 490 nm, as one may expect. Surprisingly, the fluorescence quantum yield is also close to 100% if hypsochromically absorbing chromophore **1** is irradiated at 435 nm. The fluorescence of chromophore **1** is completely quenched and only a bathochromic emission of chromophore **2** is observed. Thus, the energy transfer to chromophore **2** must proceed with a quantum yield close to 100%. This efficient energy transfer is surprising because of the rather stiff orthogonal arrangement of the two chromophores. Obviously, the orthogonal geometry of the two chromophores cannot prevent efficient energy transfer. Vibronic effects may be one reason, because the fluorescence lifetime of **1** and **2** is about 5 ns[4] and, therefore, much longer than the time scale of vibration. The bending of the C–N single bonds in **6** would break the orthogonal arrangement of the chromophores and could open a pathway for energy transfer.

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Table 1. Gaussian analysis of UV/Vis spectra in chloroform (400–750 nm).

Dye	**6** abs.	**1a** abs.	**6** flu.	**1a** flu.
λ_{max}(**1**)[a]	527.6	526.3	535.4	533.7
2 σ^2(**1**)[b]	0.125	0.123	0.149	0.147
E_{max}(**1**)[c]	0.984	0.984	0.989	0.990
λ_{max}(**2**)[a]	513.7	512.5	551.0	549.4
2 σ^2(**2**)[b]	0.082	0.085	0.085	0.082
E_{max}(**2**)[c]	0.239	0.25	0.189	0.180
λ_{max}(**3**)[a]	490.4	489.4	578.3	576.1
2 σ^2(**3**)[b]	0.280	0.268	0.253	0.250
E_{max}(**3**)[c]	0.607	0.586	0.506	0.497
λ_{max}(**4**)[a]	466.0	458.7	624.6	622.2
2 σ^2(**4**)[b]	0.185	0.526	0.441	0.420
E_{max}(**4**)[c]	0.779	0.212	0.118	0.111
λ_{max}(**5**)[a]	453.8	436.0	683.0	682.7
2 σ^2(**5**)[b]	0.133	0.127	0.169	0.233
E_{max}(**5**)[c]	0.221	0.022	0.013	0.012
λ_{max}(**6**)[a]	436.7	428.4	750.2	750.2
2 σ^2(**6**)[b]	0.286	0.252	1.246	1.246
ε_{max}(**6**)[c]	0.363	0.044	0.006	0.006
λ_{max}(**7**)[a]	433.6	412.2		
2 σ^2(**7**)[b]	0.899	0.777		
E_{max}(**7**)[c]	0.105	0.02		
λ_{max}(**8**)[a]	409.6			
2 σ^2(**8**)[b]	0.563			
E_{max}(**8**)[c]	0.161			
R[d]	0.023	0.017	0.033	0.016

[a] Calculated wavelength in nm. [b] Linewidth in 10^6 cm^{-2} (kK^2). [c] Calculated absorptivity for E_{max} = 1.00. [d] R = Residual, see equation below.

$$R = \sqrt{\int\left[\varepsilon(\lambda)_{calcd.} - \varepsilon(\lambda)_{exp.}\right]^2 d\lambda \;/\; \int\left[\varepsilon(\lambda)_{exp.}\right]^2 d\lambda}$$

Conclusions

These results are important for the design of molecular optical devices, because the handling of the energy of optical excitation will become one central problem for such a technology.

Dye **6** is of interest for many other applications, because of the broad light absorption in the visible region and the high fluorescence quantum yield even in the presence of atmospheric oxygen. Such a combination of properties is both of importance for the application as laser dyes and for fluorescent planar solar collectors[13] and may even be useful for the calibration of fluorescence spectrometers.[14]

Experimental Section

General: IR spectra were recorded with a Perkin–Elmer 1420 Ratio Recording Infrared Spectrometer, FT 1000. UV/Vis spectra were measure with a Varian Cary 5000 and Bruins Omega 20. Fluorescence spectra were acquired with a Perkin–Elmer FS 3000 (totally corrected). NMR spectra were recorded with a Varian Vnmrs 600 (600 MHz). Mass spectrometry was performed with a Finnigan MAT 95.

***N*-(4-Amino-2,3,5,6-tetramethylphenyl)-*N*-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic Bisimide (4):** Perylene-3,4,9,10-tetracarboxylic-3,4-anhydride-9,10-(1-hexylheptylimide)[8] (**3**, 300 mg, 523 μmol), 2,3,5,6-tetramethyl-1,4-phenylene diamine (129 mg, 785 μmol), and imidazole (30 g) with the exclusion of moisture and air (argon atmosphere) was heated at 105 °C for 4 h, cooled, quenched while still warm with an acetic acid/2-N HCl (1:1, 200 mL), collected by vacuum filtration (D4 glass filter), washed with distilled water, dried in air at 110 °C for 16 h, and purified by MPLC chromatography [silica gel, chloroform/ethanol (10:1), flux 30 mL min^{-1}]. Yield: 146 mg (39%) dark-red solid. M.p. >300 °C. R_f (silica gel, chloroform/ethanol, 100:1) = 0.10. IR (KBr): $\tilde{\nu}$ = 3435.8 (s), 2926.5 (m), 2856.9 (w), 1698.5 (s), 1660.9 (s), 1594.0 (s), 1578.3 (m), 1507.3 (w), 1458.4 (w), 1432.7 (w), 1405.0 (m), 1347.1 (m), 1329.4 (s), 1253.1 (m), 1175.3 (w), 1108.2 (w), 963.6 (w), 854.3 (w), 840.2 (w), 811.8 (w), 749.0 (w), 722.6 (w), 672.0 (w), 585.8 (w) cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.83 [t, ^3J(H,H) = 7.1 Hz, 6 H, 2 CH_3], 1.23–1.34 (m, 16 H, CH_2), 1.85–1.89 (m, 2 H, β-CH_2), 2.07 (s, 6 H, 2 CH_3), 2.23–2.28 (m, 8 H, β-CH_2/2 CH_3), 5.17–5.22 (m, 1 H, α-CH), 8.67–8.77 (m, 8 H, arom. CH) ppm. ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 14.0, 14.2, 15.1, 22.6, 26.9, 29.2, 31.8, 32.4, 54.8, 123.1, 123.3, 123.4, 126.5, 126.8, 129.6, 130.1, 131.2, 132.0, 134.5, 135.1, 163.4, 163.6, 164.6 ppm. UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 459 (0.23), 491 (0.61), 527 (1.00) nm. Fluorescence ($CHCl_3$): λ_{max} = 536, 578 nm. Fluorescence quantum yield ($CHCl_3$, λ_{ex} = 489 nm, E_{489nm} = 0.277 cm^{-1}, reference: **2a** with Φ = 1.00): 0.53. MS (DEI+/70 eV): *m*/*z* (%) = 719 (100) [M]$^+$, 538 (19), 537 (18), 505 (7), 391 (8), 147 (26). HRMS: calcd. for $C_{47}H_{49}N_3O_4$ 719.3723; found 719.3653 (Δ = –7.0 mmu).

***N*^{2},*N*^{3}-Bis(1-hexylheptyl)-*N*^{1}-[*N*-(1-hexylheptyl)-*N*′-(2,3,5,6-tetramethylphenyl-4-yl)perylene-3,4:9,10-tetracarboxylic Bisimide]benzo[*ghi*]perylene-2,3:8,9:11,12-hexacarboxylic Trisimide (6):** Compound **4** (264 mg, 367 μmol), *N*^{1},*N*^{2}-bis(1-hexylheptyl)benzo[*ghi*]-perylene-2,3,8,9,11,12-hexacarboxylic-2,3;8,9-bisimide-11,12-anhydride[3] (**5**, 311 mg, 367 μmol), and imidazole (15 g) were allowed to react as was described for **4** and purified by column separation (silica gel 60), where byproducts were firstly eluted with chloroform and bichromophore **6** collected with chloroform/methanol (25:1). Yield: 85 mg (15%), bright-red powder. M.p. >300 °C. R_f ($CHCl_3$/methanol, 25:1) = 0.8. IR: $\tilde{\nu}$ = 3077.6 (w), 2951.6 (s), 2923.1 (s), 2854.3, (s), 1774.3 (w), 1701.7 (s), 1659.8 (s), 1626.4 (w), 1593.1 (s), 1579.3 (m), 1521.9 (w), 1506.5 (w), 1456.8 (m), 1432.5 (w), 1415.4 (w), 1404.3 (s), 1363.3 (s), 1335.7 (s), 1316.5 (s), 1272.2 (w), 1250.0 (m), 1203.1 (w), 1173.8 (m), 1122.5 (w), 1016.3 (w), 962.8 (w), 944.8 (w), 850.6 (m), 808.4 (s), 767.4 (w), 745.1 (s), 723.9 (w), 660.4 (w), 644.0 (w), 584.4 (w) cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, 25.0 °C): δ = 10.6 (br. d, ^3J = 20.4 Hz, 2 H), 9.47 (d, ^3J = 8.5 Hz, 2 H), 9.22 (br. d, ^3J = 15.6 Hz, 2 H), 8.83 (d, ^3J = 7.8 Hz, 2 H), 8.73 (d, ^3J = 8.1 Hz, 2 H), 8.70 (br. d, ^3J = 6.8 Hz, 4 H), 5.36–5.27 (m, 2 H), 5.19 (tt, ^3J = 5.8 and 9.4 Hz, 1 H), 2.40–2.30 (m, 4 H), 2.29 (s, 6 H), 2.28–2.22 (m, 2 H), 2.20 (s, 6 H), 1.98–1.91 (m, 4 H), 1.90–1.83 (m, 2 H), 1.44–1.20 (div. m, 48 H), 0.83 (t, ^3J = 6.9 Hz, 6 H), 0.82 (t, ^3J = 6.9 Hz, 12 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25.0 °C): δ = 167.1, 162.8, 135.4, 135.0, 134.4, 134.1, 133.5, 132.9, 132.1, 130.3, 130.2, 129.6, 128.4, 127.8, 127.5, 126.9, 126.5, 125.4, 124.2, 123.6, 123.4, 123.2, 55.3, 54.8, 32.4, 31.8, 31.8, 29.7, 29.2, 29.2, 27.0, 26.9, 22.6, 15.9, 15.4, 14.0 ppm. UV/Vis ($CHCl_3$): λ_{max} (E_{rel}): 527 (100), 491 (61), 466 (82), 436 (47), 410 (19), 374 (46) nm. Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 535 (100), 577 (36) nm. Fluorescence quantum yield ($CHCl_3$, $\lambda_{excit.}$ = 435 nm, E = 0.138 cm^{-1}, ref.[5] perylene-3,4,9,10-tetracarboxylic tetramethyl ester with Φ = 100%): 100%. MS (DEP/EI): *m*/*z* (%) = 1550 (100) [M]$^+$. MS (FAB$^+$): calcd. for $C_{101}H_{108}N_5O_{10}$ 1550.8096; found 1550.8094 (Δ = –0.2 mmu). $C_{101}H_{107}N_5O_{10}$ (1551.0): calcd. C 78.21, H 6.95, N 4.52; found C 77.40, H 7.26, N 4.67.

Synthesis of 6 by Microwave Irradiation: Compound **4** (150 mg, 208 μmol), **5**[3] (100 mg, 118 μmol), and quinoline (6 mL) were heated with stirring at 210 °C for 5 h by microwaves (200 W Dis-

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coverer from CEM) and isolated as was described before. Yield: 65 mg (36%). For spectroscopic data see above.

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