

Bichromophoric Perylene-3,4-dicarboxylic Imides: Highly Intense and Light-fast Fluorescent Dyes

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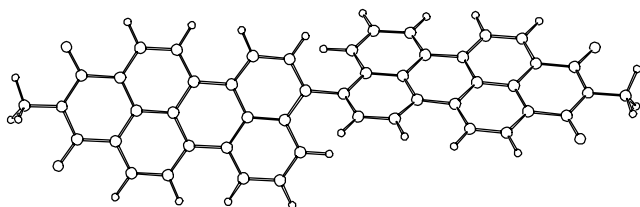
Dedicated to Prof. Dr. F. Vögtle on the Occasion of his 60th Birthday

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Abstract. Perylene-3,4-dicarboxylic imides **1a–c** with molar absorptivities of about $30\,000\ \text{l mol}^{-1}\ \text{cm}^{-1}$ form bichromophoric fluorescent dyes **4a–c** by the coupling in the

positions 9 and 9' with molar absorptivities of nearly $100\,000\ \text{l mol}^{-1}\ \text{cm}^{-1}$ forced by exciton interactions.

Perylene-3,4-dicarboxylic imides **1** [1] are a novel class of highly photostable [2] fluorescent dyes and beat with their lightfastness even the extremely photostable perylene dyes [3] **2**. Further advantages are their comparably small, rectangle-like absorption band, which causes brilliant colour-shades, and the higher solubility compared to **2**. However, the molar absorptivity of **1** of about $30\,000\ \text{l mol}^{-1}\ \text{cm}^{-1}$ is appreciably less than that of **2** (about $90\,000\ \text{l mol}^{-1}\ \text{cm}^{-1}$). We tried to increase [4] the absorptivity of **1** by means of the exciton effects of two identical chromophores which have to be brought close together, but must be electronically decoupled. A linkage of **1** *via* the positions 9 and 9' is therefore suitable because steric interactions of the *peri*-protons in the positions 10 and 10' turns the chromophores out of plane. Indeed, an inter-chromophore torsion angle of 62° was obtained by a quantum mechanic AM1 calculation [5–7] of **4d** which indicated a nearly orthogonal orientation with a slight preference towards *s-trans*; see formula 1.



Formula 1 Calculated structure (AM1) of the bichromophoric bisimide **4d**

The starting materials for the synthesis of **4** are perylene-3,4-dicarboxylic anhydride [8] and the perylene-3,4-dicarboxylic imides [1] **1**, respectively. The latter were

brominated [1] and coupled to **4**. Simple reaction conditions and the standard-reagents nickel(0)/zinc in DMF [9, 10] were therefore preferred and yielded 50% of pure **4** (compare ref. [11]). Nearly no by-products were formed, and the rest was non-converted starting material which can be used for further reactions. Two derivatives of **4** with the solutizing long-chain *sec*-alkyl substituent (“swallow-tail” [12] substituent) at the nitrogen atoms and one derivative with the 3,5-di-*tert*-butylphenyl substituent [13] were prepared. All derivatives exhibit very similar properties except their solubilities.

The differences between the UV/Vis-spectra of **1** and **4** are remarkable; see figure 1. There is a striking bathochromic shift of the absorption of **4** which is certainly caused by the electronic interaction of the π -systems. The exciton interaction forms an additional band which amplifies the absorption because of the weak exciton

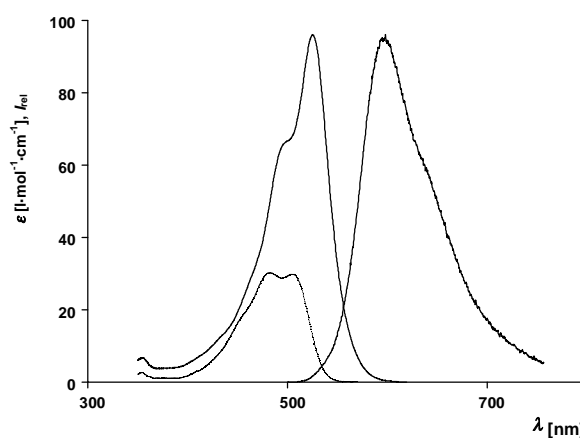
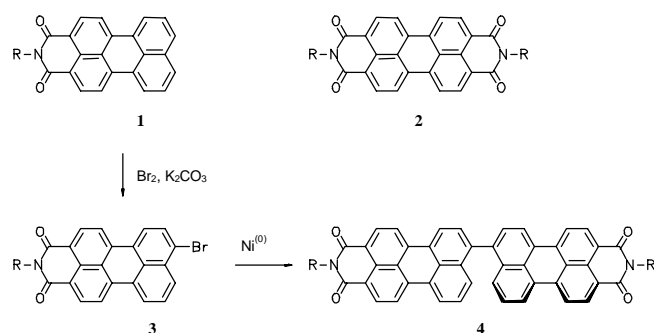


Fig. 1 UV/Vis-absorption (color coordinates $x = 0.3902$, $y = 0.2926$, $Y = 58.07$, 2° , normlight C at $T_{\text{min}} = 0.1$) and fluorescence spectrum of the bichromophoric bisimide **4a** in chloroform compared with the imide **1a** (lower left).



1 – 4	R
a	CHC(C ₆ H ₁₃) ₂
b	CHC(C ₉ H ₁₉) ₂
c	2,5-di- <i>t</i> -C ₄ H ₉ C ₆ H ₄
d	CH ₃

Scheme 1

coupling. The molar absorptivity of **4** with nearly 100 000 l mol⁻¹ cm⁻¹ thus reaches more than the three-fold value of **1** instead the twofold; the dye **4** can therefore compete with **1**.

The dyes **4** exhibit an pronounced orange fluorescence in solution: 80% fluorescence quantum yield was found in chloroform which is about the same as for **1** [14]. This verifies that the single-bond between the chromophores is of no importance for any fluorescence quenching processes by flexibility.

One can thus suppose that the concept for the increase of the molar extinction which is demonstrated here is a more general principle.

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Experimental

IR-spectra: IFS 45, Bruker. – UV/Vis-spectra: OMEGA 20, Bruins Instruments. – Fluorescence spectra: FS 3000, Perkin Elmer; total spectral correction according to [15]. – NMR-Spectra: VXR 400S, Varian. – Mass spectra: SN 1B, Varian MAT.

Table 1 Bichromophoric dyes **4a–c**

4	Yield (%)	R_f^a	λ_{\max}^b	ϵ^c	λ_{\max}^d	ϕ^e (%)
a	51	0.84	525.3	96000	592	80
b	43	0.92	527.0	96600	592	77
c	46	0.18	528.0	94000	590	81

a) Silica gel, chloroform; b) Absorption maximum in chloroform in nm; c) Molar absorptivity; d) Fluorescence maximum in chloroform in nm; e) Fluorescence quantum yield

9,9'-Bis-[N-(1-hexylheptyl)-perylene-3,4-dicarboxylic-imide] (**4a**)

Nickel chloride (NiCl₂·2H₂O, 202 mg, 0.85 mmol) was dissolved in DMF (3.7 ml) and degassed with argon. Triphenylphosphine (900 mg, 3.43 mmol) was added, and after warming (50 °C) zinc powder (60 mg, 0.92 mmol) was added with stirring. **1a** (500 mg, 0.85 mmol) was added after a red-brown solution had formed. The mixture was stirred at 50 °C for 4 h, evaporated and purified by column separation (silica gel, chloroform; **4c** by chloroform/ethanol 10:1). Yield 220 mg (51%) of **4a**, *m.p.* >250 °C. – R_f (silica gel, CHCl₃): 0.84. – IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ = 2926 (m, C-H), 2856 (m, C-H), 1693 (s, C=O), 1654 (s, C=O), 1592 (s), 1572 (s), 1351 (s), 1245 (w), 812 (m). – UV (CHCl₃): $\lambda_{\max}(\epsilon)$ = 525.3 (96000), 500 (sh, 67200), 473.6 (sh, 37000). – Fluorescence (CHCl₃): $\lambda_{\max}(I_{\text{rel}})$ = 592 nm (1), 617 (sh, 0.66). – Fluorescence quantum yield ($c = 4.0 \times 10^{-7}$ mol/l in CHCl₃, reference *N,N'*-di-(1-hexylheptyl)-perylene-3,4:9,10-bis-(dicarboximide) (**2a**) with $\phi = 100\%$, $\lambda_{\text{excit.}} = 490$ nm) = 80%. – ¹H NMR (CDCl₃): δ/ppm = 8.60 (m, br, 4H), 8.59 (d, 2H, $J = 8.1$ Hz), 8.50 (d, 2H, $J = 8.3$ Hz), 8.46 (d, 2H, $J = 6.8$ Hz), 8.44 (d, 2H, $J = 8.3$ Hz), 7.72 (d, 2H, $J = 7.8$ Hz), 7.56 (d, 2H, $J = 8.3$ Hz), 7.41 (dd, 2H, $J_1 = 7.3$ Hz, $J_2 = 8.3$ Hz), 5.21 (m, 2H, CH-N), 2.31–2.25 (m, 4H, CH₂), 1.91–1.85 (m, 4H, CH₂), 1.38–1.24 (m, 32H, CH₂), 0.82 (t, 12H, CH₃). – ¹³C NMR (CDCl₃): δ/ppm = 165.16 (CO), 164.13 (CO), 140.39, 136.81, 136.60, 133.71, 132.00, 131.24, 129.99, 129.69, 129.61, 129.18, 128.31, 127.35, 126.65, 123.77, 123.13, 122.04, 121.25, 120.51, 120.38, 54.51 (CH-N), 32.47 (CH₂), 31.80 (CH₂), 29.28 (CH₂), 27.01 (CH₂), 22.62 (CH₂), 14.05 (CH₃). – MS (70 eV): m/z (%) = 1005 (M⁺, 29), 1004 (38), 987 (11), 824 (13), 823 (25), 822 (14), 642 (22), 641 (67), 640 (100), 639 (13), 321 (17) (M⁺–C₂₆H₅₂).
C₇₀H₇₂N₂O₄ Calcd.: C 83.63 H 7.23 N 2.79 (1005.3) Found: C 84.06 H 7.31 N 2.68.

9,9'-Bis-[N-(1-nonyldecyl)-perylene-3,4-dicarboxylic-imide] (**4b**)

Preparation procedure exactly according to **4a**: Yield 43% of **4b**, *m.p.* > 250 °C. – R_f (silica gel/CHCl₃): 0.92. – IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ = 2923 cm⁻¹ (s, C-H), 2852 (s, C-H), 1693 (s, C=O), 1653 (s, C=O), 1592 (s), 1572 (s), 1350 (s), 1290 (m), 1245 (m), 811 (m), 753 (m). – UV (CHCl₃): $\lambda_{\max}(\epsilon)$ = 527 nm (96600), 500 (sh, 66900), 465 (sh, 30000). – Fluorescence (CHCl₃): $\lambda_{\max}(I_{\text{rel}})$ = 592 nm (1), 619 (sh, 0.63). – Fluorescence quantum yield ($c = 0.32 \times 10^{-6}$ mol/l in CHCl₃, reference *N,N'*-di-(1-hexylheptyl)-perylene-3,4:9,10-bis-(dicarboximide) (**2a**) with $\phi = 100\%$, $\lambda_{\text{excit.}} = 494$ nm) = 77%. –

^1H NMR (CDCl_3): δ/ppm = 8.58 (m, br, 6H), 8.50 (d, 2H, J = 8.4 Hz), 8.46 (d, 2H, J = 6.8 Hz), 8.44 (d, 2H, J = 8.3 Hz), 7.72 (d, 2H, J = 7.7 Hz), 7.55 (d, 2H, J = 8.4 Hz), 7.49 (dd, 2H, J_1 = 7.5 Hz, J_2 = 8.4 Hz), 5.21 (m, 2H, CH-N), 2.27 (m, 4H, CH_2), 1.87 (m, 4H, CH_2), 1.36–1.21 (m, 56H, CH_2), 0.84 (t, 12H, CH_3). – ^{13}C NMR (CDCl_3): δ/ppm = 165.14 (C=O), 164.16 (C=O), 140.39, 136.79, 136.60, 133.71, 132.01, 131.24, 129.99, 129.69, 129.61, 129.18, 128.31, 127.35, 126.64, 123.77, 123.12, 121.98, 121.28, 120.51, 120.38, 54.51 (CH-N), 32.47 (CH_2), 31.88 (CH_2), 29.71 (CH_2), 29.61 (CH_2), 29.57 (CH_2), 29.29 (CH_2), 27.04 (CH_2), 22.66 (CH_2), 14.09 (CH_3). – MS (70 eV): m/z (%) = 1173 (M^+ , 82), 1172 (85), 1156 (M^+ –OH, 10), 1155 (M^+ – H_2O , 11), 908 (24), 907 (M^+ – $\text{C}_{19}\text{H}_{38}$, 44), 906 (28), 641 (73), 640 (M^+ – $\text{C}_{38}\text{H}_{76}$, 100), 321 (18).
 $\text{C}_{72}\text{H}_{60}\text{N}_2\text{O}_4$ Calcd.: C 83.92 H 8.24 N 2.39
 (1173.6) Found: C 83.84 H 8.26 N 2.37.

9,9'-Bis-[N-(2,5-di-tert-butylphenyl)-perylene-3,4-dicarboxylic-imide] (**4c**)

Preparation procedure exactly according to **4a**: Yield 46% of **4c**, $m.p.$ > 250 °C. – R_f (silica gel, CHCl_3): 0.18. – IR (KBr): ν/cm^{-1} = 2959 cm^{-1} (m, C-H), 2867 (w, C-H), 1705 (s, C=O), 1666 (s, C=O), 1592 (s), 1571 (s), 1355 (s), 1245 (m), 811 (m). – UV (CHCl_3): λ_{max} (ϵ) = 528 nm (94000), 502.3 (sh, 65100), 472 (sh, 34600). – Fluorescence (CHCl_3): λ_{max} (I_{rel}) = 590.3 nm (1), 616 (sh, 0.69). – Fluorescence quantum yield (c = 0.42×10^{-6} mol/l in CHCl_3 , reference *N,N'*-di-(1-hexylheptyl)-perylene-3,4:9,10-bis-(dicarboximide) **2a** with ϕ = 100%, $\lambda_{\text{excit.}}$ = 494 nm) = 81%. – ^1H NMR (CDCl_3): δ/ppm = 8.70–8.38 (m, 12H), 7.79–7.73 (m, 2H), 7.61–7.44 (m, 8H), 7.06 (t, 2H, J = 2.2 Hz), 1.34 (s, 9H, CH_3), 1.32 (s, 9H, CH_3). – ^{13}C NMR (CDCl_3): δ/ppm = 164.89 (CO), 164.87 (CO), 164.83 (CO), 164.82 (CO), 150.03, 149.99, 143.82, 140.49, 140.47, 140.42, 140.40, 137.31, 137.30, 137.23, 137.22, 137.10, 137.09, 137.01, 137.00, 133.62, 133.05, 133.03, 131.94, 131.84, 130.27, 130.19, 129.59, 129.55, 129.49, 129.31, 129.28, 129.19, 129.16, 128.76, 128.73, 128.25, 128.22, 128.20, 127.82, 127.80, 127.39, 127.36, 126.91, 126.83, 126.17, 123.97, 123.41, 123.33, 123.25, 121.63, 121.58, 121.56, 121.52, 120.51, 120.43, 120.40, 35.55, 35.54, 34.25, 34.23, 31.78 (CH_3), 31.75 (CH_3), 31.26 (CH_3), 31.24

(CH_3). – MS (70 eV): m/z (%) = 1018 (7), 1017 (M^+ , 8), 1000 (M^+ –OH, 4), 962 (29), 961 (75), 960 (M^+ – C_4H_9 , 100), 451 (11).

$\text{C}_{72}\text{H}_{60}\text{N}_2\text{O}_4$ Calcd.: C 85.01 H 5.95 N 2.75
 (1017.2) Found: C 84.19 H 6.19 N 2.63.

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