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An approach to novel NIR dyes utilising α-effect donor groups☆

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This paper is dedicated to the memory of Professor M. Matsuoka

Abstract

Light-fast and strongly fluorescent NIR dyes have been obtained by the core-substitution of perylene bisimides with joined nitrogen donor groups. Emission has been recorded beyond 1100 nm. Complete Gaussian analyses were successful both for the absorption and fluorescence spectra.

Keywords: NIR-dyes; Diels–Alder reactions; Fluorescence spectroscopy; Perylenes

1. Introduction

Near infrared (NIR) dyes are gaining increasing interest because of the new technologies of communication, and the novel methods and applications in analysis and medicine [1]. Highly photostable materials are required for such applications.

2. Results and discussion

The perylene-3,4:9,10-tetracarboxylic bisimides, e.g. **1** ($R^1{-}R^4 = H$) and **2,** represent an extraordinarily photostable chromophore [2], however, the light absorption of this chromophoric system generally lies in the visible region. A shift of the absorption of **1a** into the NIR region would be an appreciable advance, and such a shift could be attained most efficiently by suitable substitution of the core of **1a**. The influence of core substituents can be estimated by quantum chemical calculations and even HMO calculations can predict such effects on the absorption of the π-system essentially correctly.

A pronounced bathochromic shift is expected if donor groups are attached to the positions 1,6,7 and 12 of **1,** the effect of donor or acceptor groups being very much smaller at the other positions. An increasing bathochromic shift is predicted if an increasing number of amino groups is attached to these positions (see Fig. 1 and Table 1).

Experimental results, especially with phenoxy- [3], and amino-derivatives [4,5,6] provide basic verification of this influence of substituents. One can ask if it is possible to increase the bathochromic shift further by the incorporation of the

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☆ This paper is an addendum to the memorial edition of the journal, and is dedicated to the memory of Professor Masaru Matsuoka.

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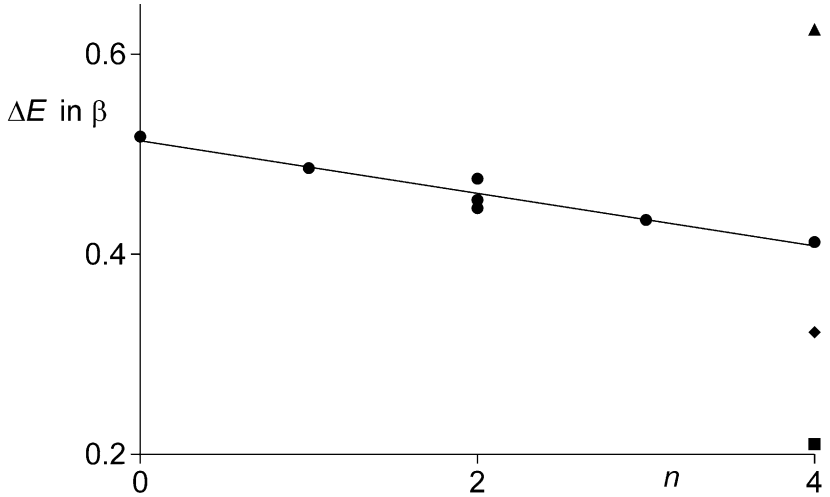
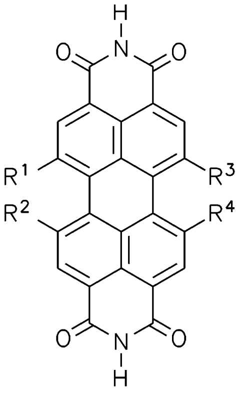


Fig. 1. Calculated HOMO–LUMO energy difference (Δ*E*, HMO-model) for perylene bisimides **1** with *n* amino groups in the positions 1,6,7 and 12 (●) and regression line. For *n* = 2: from top to bottom: 1,6- (**1c**), 1,12- (**1e**), 1,7-diamino derivative (**1d**). Comparison with the energies of the *bis*-hydrazino derivative **1l** (■), the *bis*-pyrrolo derivative **1j** (▲) and the mixed hydrazine pyrrolo derivative **1k** (◆).

Table 1
Calculated energies (HMO) of substituted perylene bisimides (**1**)

Nr.	Substituents				E_{HOMO} in β	E_{LUMO} in β	Δ*E* in β
	R^1	R^2	R^3	R^4			
1a	H	H	H	H	0.5176	0.0000	0.5176
1b	NH_2	H	H	H	0.4682	−0.0178	0.4860
1c	NH_2	H	NH_2	H	0.4394	−0.0361	0.4755
1d	NH_2	H	H	NH_2	0.4217	−0.0335	0.4542
1e	NH_2	NH_2	H	H	0.4140	−0.0321	0.4461
1f	NH_2	NH_2	NH_2	H	0.3859	−0.0483	0.4342
1g	NH_2	NH_2	NH_2	NH_2	0.3508	−0.0613	0.4121
1h	–NH–		H	H	0.5176	−0.0578	0.5754
1i	–NH–NH–		H	H	0.2457	−0.0218	0.2675
1j	–NH–		–NH–		0.5176	−0.1068	0.6244
1k	–NH–NH–		–NH–		0.2457	−0.0764	0.3221
1l	–NH–NH–		–NH–NH–		0.1678	−0.0424	0.2102

amino groups into ring structures. However, a hypsochromic shift is predicted if the donor groups are included in five membered rings (e.g. **1h**, **1j**), and the donor activity is weakened by such double use. This corresponds to the experimental results observed with a condensed pyrrole ring at the positions 1 and 12 [4]. On the other hand, pronounced bathochromic shifts are expected if the neighbouring donor groups are joined to form six-membered rings, and this can be explained by the α-effect, which amplifies the electron donor effect. Moreover, incorporation of the donor functions into six-membered rings prevents a deformation of the perylene system by steric interactions in the bay-positions (S_3-element of structure [7]).



1

Such target compounds might be synthesized by a fourfold halogenation of the perylene core and a subsequent reaction with *N*-nucleophiles and ring closure. Such a halogenation procedure is known [8], but mixtures of products are obtained that are difficult to separate, principally because of incomplete halogenation. Consequently, we have tried to introduce the four donor groups regioselectively and completely by Diels–Alder reactions in order to avoid separation problems.

The bisimides **2** were used as the starting materials for cycloaddition rather than the insoluble pigment **1a** because their long-chain secondary alkyl groups (“swallow-tail” substituents [9]) render them soluble. The four carbonyl groups of **2** lower the electron density of the perylene structure so that no more than one cycloaddition is observed under standard reaction conditions if electron deficient dienophiles are employed (compare also ref. [10]). Acceptable yields are obtained only if a rearomatising reagent is simultaneously applied [6] (Clar-reaction). However, if the highly reactive dienophile 4-phenyl-1,2,4-triazoline-3,5-dione is applied in a large excess (10 mole per mole of **2,** or more) and chloranil is used as reagent for aromatisation, **4** can be obtained in 20% yield, together with 49% of **3**. 4-Phenyl-1,2,4-triazoline-3,5-dione has to be added in one step because of its low stability; higher yields are obtained from larger batches. The twofold Diels–Alder reaction is so difficult that the slightly less reactive azodicarbxylic ester is useless under these reaction conditions. On the other hand, the reaction products **3** and **4** can be separated by column chromatography without problems so that the Diels–Alder reactions are suitable for preparative scale work.

The structures of **3c** and **4c** have been calculated by the AM1 method [11,12] (Fig. 2). Planarity was found for the perylene unit including the dihydropyridazine rings of **3** and **4**; the five-membered rings condensed thereon are distorted by about 45° out of plane. This can be interpreted as a

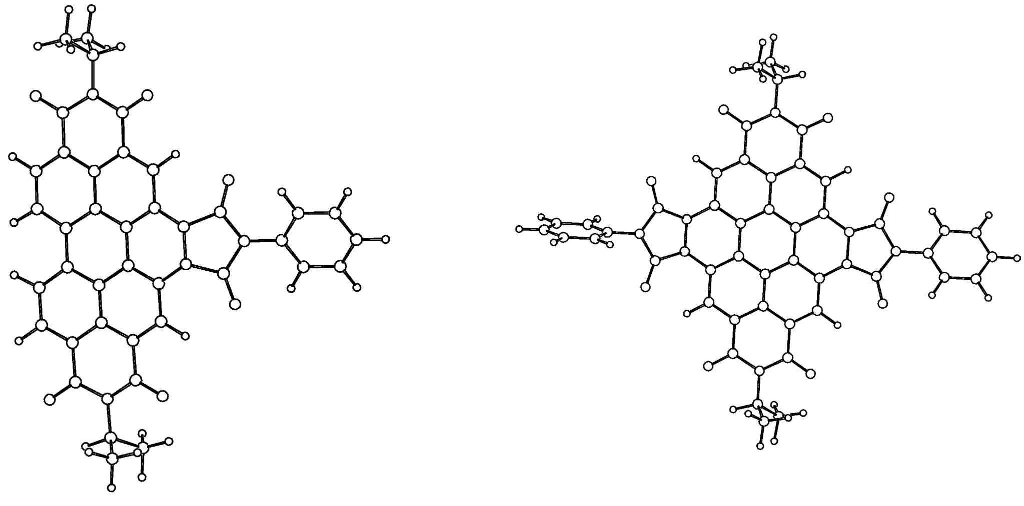
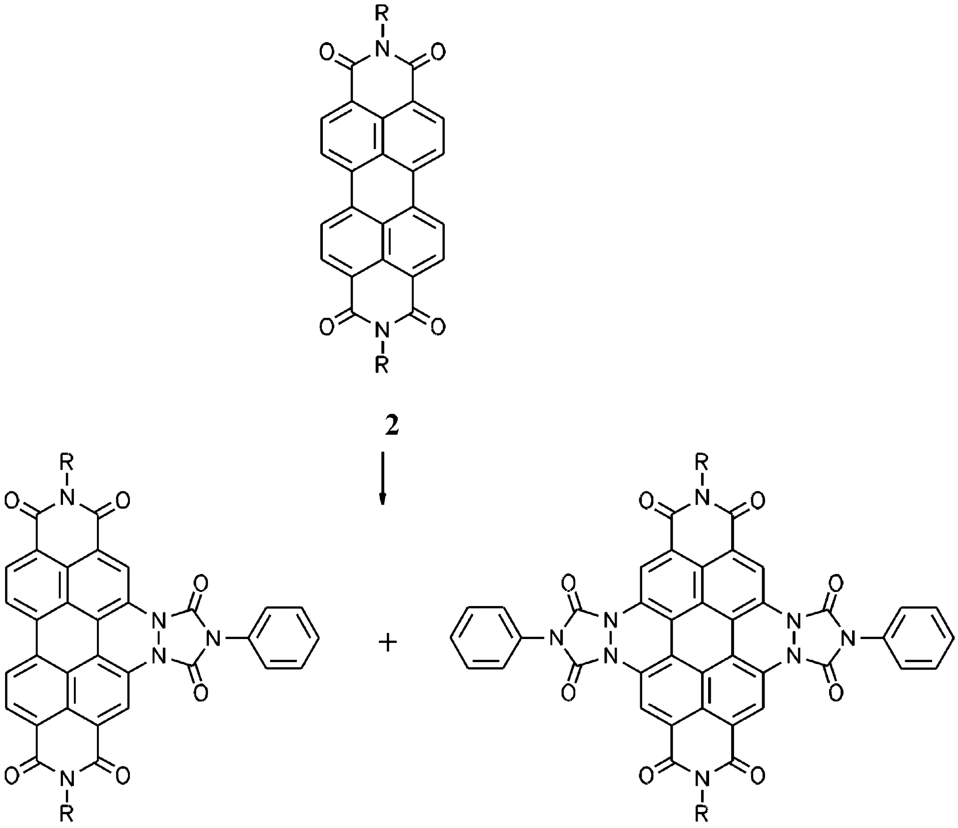


Fig. 2. Calculated structures of **3c** and **4c**.



2

3

4

2 – 4	R
a	$CH(C_6H_{13})_2$
b	$CH(C_8H_{17})_2$
c	$CH(CH_3)_2$

consequence of the α-effect because deviation of the hybridisation of the nitrogen atoms from sp^2 to sp^3 diminishes the repulsion of the lone pairs. The phenyl groups at the nitrogen atoms are turned out of plane by about 40° as might be expected.

The known compound **3** absorbs at long wavelengths because of the two donor groups, and consequently it is green in solutions ($\lambda_{max.} = 650$ nm in chloroform) [6]. The additional two donor groups in **4** cause a further pronounced bathochromic shift so that the band reaches the NIR region, with $\lambda_{max.} = 778$ nm (bluish green, lightfast solutions; see Fig. 3). This absorption at long wavelengths is remarkable because the electron donor functions are weakened by the carbonyl groups. Even larger bathochromic shifts are to be expected if there were no weakening by these groups.

Compounds **3** and **4** exhibit strong fluorescence: the emission of **3a** is at $\lambda_{max} = 775$ and is thus shifted into the NIR. The emission of **4a** is strongly further shifted into the NIR, with a fluorescence maximum at at 873 nm, and fluorescence emission can even be recorded beyond 1100 nm. Complete Gaussian analyses were successful for the absorption and fluorescence spectra of **3a** and **4b** [13] (for *R*-values see Table 2): see Fig. 4. The

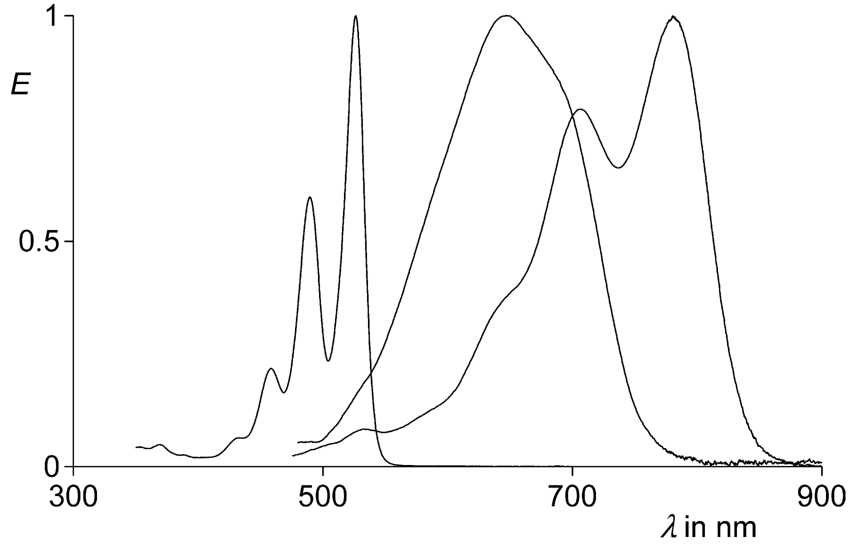


Fig. 3. Normalized UV/Vis/NIR absorption spectra in chloroform solution; from left to right: **2a**, **3a** and **4b**.

Table 2
Gaussian analysis of UV/Vis spectra in chloroform (330–757 nm)

Dye	**4b** abs.	**3a**-1 abs.	**3a**-2 abs.	**3a** flu.	**4b** flu.	**2a** abs.
$\lambda_{max}(1)$[a]	785.2	705.6	477.1	774.5	836.6	526.3
$2\sigma^2(1)$[b]	0.305	0.376	2.798	0.596	0.366	0.123
$E_{max}(1)$[c]	0.924	0.273	0.070	0.951	0.956	0.985
$\lambda_{max}(2)$[a]	751.9	669.0	442.9	848.6	899.1	512.5
$2\sigma^2(2)$[b]	0.159	1.424	0.187	0.440	0.187	0.085
$E_{max}(2)$[c]	0.154	0.59	1.179	0.236	0.340	0.251
$\lambda_{max}(3)$[a]	707.8	635.7	432.8	890.2	944.1	489.4
$2\sigma^2(3)$[b]	0.619	1.216	1.007	0.694	0.223	0.268
$E_{max}(3)$[c]	0.721	0.449	0.400	0.501	0.601	0.586
$\lambda_{max}(4)$[a]	645.5	591.4	417.5	1049.2	985.3	458.7
$2\sigma^2(4)$[b]	0.537	1.303	0.209	5.122	0.576	0.526
$E_{max}(4)$[c]	0.202	0.351	0.499	0.058	0.171	0.213
$\lambda_{max}(5)$[a]	622.3	550.2	393.9			436.0
$2\sigma^2(5)$[b]	4.356	2.789	1.408			0.127
$E_{max}(5)$[c]	0.145	0.17	0.454			0.022
$\lambda_{max}(6)$[a]	530.4	520	367.7			428.4
$2\sigma2(6)$[b]	0.311	0.311	0.288			0.252
$\varepsilon_{max}(6)$[c]	0.029	0.013	0.060			0.044
$\lambda_{max}(7)$[a]	493.1					412.2
$2\sigma^2(7)$[b]	4.987					0.777
$E_{max}(7)$[c]	0.043					0.019
R[d]	0.020	0.004	0.020	0.038	0.047	0.017

[a] Calculated wavelength in nm.

[b] Line-width in 10^6 cm^{-2} (kK^2).

[c] Calculated absorptivity in L mol^{-1}·cm^{-1}.

[d] Residual; $R = \sqrt{\int\left[\varepsilon(\lambda)_{\text{calcd.}} - \varepsilon(\lambda)_{\text{exp}}\right]^2 \mathrm{d}\lambda \Big/ \int\left[\varepsilon(\lambda)_{\text{exp}}\right]^2 \mathrm{d}\lambda}$ 385 … 500 nm and 500 … 700 nm for the absorption of **3a** and 750 … 900 nm for **4b**. 700 … 1200 nm for the fluorescence.

UV/Vis spectrum of **3a** consists of two structured partial spectra. These are assigned to the S_o–S_1 and the S_o–S_2-transitions, respectively. The spectrum of the S_o–S_1-transition exhibits comparable broad vibrational bands, but not the typical vibrational structure of perylene bisimides; the latter is found for the S_o–S_2-transition. On the other hand, the fine-structure of the fluorescence spectrum is typical for perylene bisimides. In contrast to this, the more bathochromically absorbing **4a** exhibits only one absorption band in the visible and the NIR and this shows the structure typical for perylene bisimides. The fluorescence band of **4a** is a mirror image of the absorption band.

3. Experimental section

UV/Vis/NIR-absorption spectra were measured on an OMEGA 20 (Bruins instruments). Fluorescence spectra were measured on a FluoroLog 2 with a detector R5108 (of Jobin Yvon GmbH); the spectrometer was optimized for its sensitivity up to 1700 nm. Fluorescence spectra are not corrected, so that there are uncertainties in fluorescence intensities. However, the positions of bands could be located with precision (cf. the chain rule of differentiation).

3.1. *3a and 4a*

4-Phenyl-1,2,4-triazolin-3,5-dione (30.0 mmol, 5.25 g) was added to a solution of **2a** (3.00 mmol, 2.26 g) and *p*-chloranil (3.00 mmol, 732 mg) in dry toluene (100 ml, dried over molecular sieve 4 Å), and the mixture was refluxed for 10 h. The reaction mixture was then cooled to room temperature, filtered (glass filter D 4), and the residue was washed with a little toluene. The combined filtrates and washings were evaporated to dryness and the almost black solid was air-dried (90 °C, 24 h), and then purified by column separation (silica gel, chloroform). The green **3a** was obtained as the fraction before the less soluble bluish green **4a**; 10% acetone was added for the elution of the latter. Both dyes were obtained by concentration and precipitation with methanol. 1st fraction **3a**: yield 1.36 g (48.9%) **3a** as a green powder, m.p. > 300 °C. R_f (silica gel, chloroform): 0.25. 2nd fraction **4a**: yield 657 mg (19.9%) **4a** as a blue powder, m.p. > 300 °C. R_f (silica gel, chloroform): 0.09. IR (KBr): $\tilde{\nu}=3150$ cm^{-1} (w), 2955 (m), 2926 (m), 2856 (m), 1775 (m), 1731(s), 1705 (m), 1662 (s), 1604 (w), 1574 (w), 1500 (m), 1459 (w), 1432 (m), 1401 (m), 1368 (s), 1302 (s), 1233 (w), 1175 (w), 1075 (w), 984 (w), 925 (w), 808 (w), 754 (m), 730 (m), 688 (w), 643 (m), 546 (w), 505 (w). ^{1}H NMR ($C_2D_2Cl_4$): $\delta=0.83$ (t, 12 H, CH_3), 1.20–1.35 (m, 32 H, CH_2), 1.80 (m, 4 H, CH–CH_2), 2.12 (m, 4 H, CH–CH_2), 5.03 (tt, 2 H, CH(CH$_2$)$_2$), 7.48 (t, 2 H, $^3J=7.2$ Hz, phenyl), 7.55 (t, 4 H, $^3J=7.2$ Hz, phenyl), 7.60 (d, 4 H, $^3J=7.2$ Hz, phenyl), 9.06 (s, br, 4H, perylene). ^{13}C NMR ($C_2D_2Cl_4$): δ =14.1, 22.5, 26.7, 29.0, 29.6, 31.6, 32.0, 55.2, 69.0, 116.7, 118.2, 118.9, 123.4, 123.8, 125.1 125.4, 125.8, 127.1, 128.8, 129.2, 129.4, 129.5, 129.8, 130.8, 131.7, 133.1, 143.4, 149.4, 161.2. UV/VIS ($CHCl_3$): λ_{max} (ε) = 310 nm (91,740), 644 (6530), 705 (13,240), 778 (15,890). Fluorescence (**4b**) ($CHCl_3$): λ_{max} (I_{rel}) = 837 (1.0), 938 (0.84). MS (70 eV): *m*/*z* (%): 1100 (22) [M$^+$], 918 (14) [M$^+$–$C_{13}H_{27}$], 736 (6) [M$^+$–2·$C_{13}H_{27}$], 589 (4) [M$^+$–2·$C_{13}H_{27}$–C_6H_5NCO–CO], 530 (9), 265 (8), 182 (27), 119 (21), 111 (12), 97 (36), 84 (27), 83 (56), 82 (10), 81 (7), 71 (17), 70 (61), 69 (100), 67 (18), 57 (40). $C_{66}H_{68}N_8O_8$ (1101.3): calcd. C 71.98, H 6.22, N 10.17; found C 71.79, H 6.34, N 10.09.

3.2. *3b and 4b*

A solution of **2b** (1.117 mmol, 1.030 g) and *p*-chloranil (1.117 mmol, 273 mg) in dry toluene (30 ml) was allowed to react analogously to **3a** and **4a** with 4-phenyl-1,2,4-triazolin-3,5-dione (11.17 mmol, 1.955 g). Yield 477 mg (38.1%) of **3b** as a green resin, m.p. > 300 °C. R_f (silica gel, chloroform): 0.56. IR (KBr): $\tilde{\nu}=3108$ cm^{-1} (w), 2955 (m), 2925 (s), 2853 (m), 1774 (m), 1727 (s), 1703 (s), 1663 (s), 1600 (m), 1577 (m), 1502 (m), 1458 (w), 1422 (m), 1393 (s), 1378 (m), 1338 (m), 1299 (m), 1243 (w), 1179 (w), 1169 (w), 928 (w), 851 (w), 809 (m), 750 (m), 742 (m), 729 (w), 687 (w), 645 (w), 538 (w), 504 (w). ^{1}H NMR ($CDCl_3$): $\delta=0.84$ (t, 12 H, CH_3), 1.20–1.35 (m, 56 H, CH_2), 1.85 (m, 4 H, CH–CH_2), 2.18 (m, 4 H, CH–CH_2), 5.10 (tt, 2 H, CH(CH$_2$)$_2$), 7.51 (t, 1 H, $^3J=7.2$ Hz, phenyl),

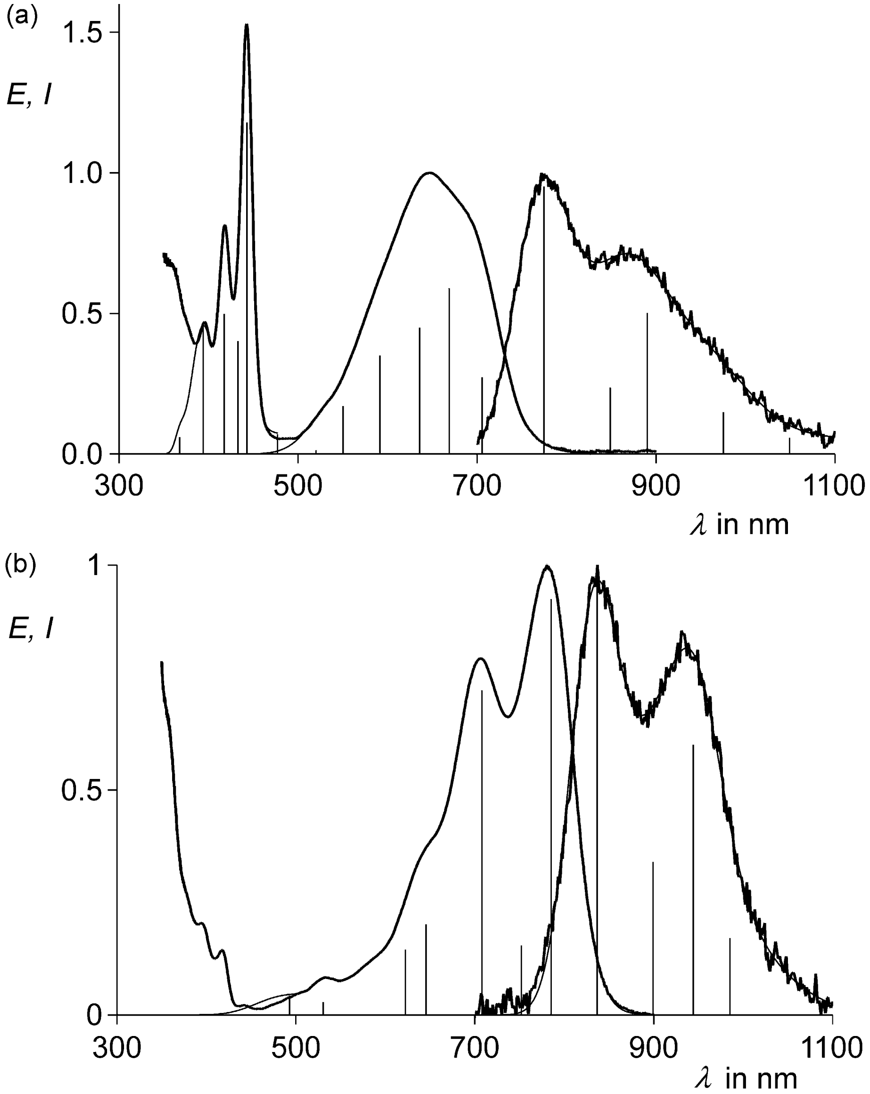


Fig. 4. UV/Vis/NIR absorption spectra (thick line left) and fluorescence spectra (thick line right) of **3a** and **4b** in chloroform. Thin lines: simulated spectra on the basis of Gaussian analysis. Bars: calculated line positions and intensities of the vibration bands.

7.59 (t, 2 H, $^3J=7.2$ Hz, phenyl), 7.67 (d, 2 H, $^3J=7.2$ Hz, phenyl), 8.22 (d, 2 H, $^3J=7.5$ Hz, perylene), 8.39 (d, 2 H, $^3J=7.5$ Hz, perylene), 9.30 (s, 2 H, perylene). ^{13}C NMR ($CDCl_3$): $\delta=14.1$, 22.7, 27.0, 29.3, 29.6, 31.9, 32.3, 55.1, 117.3, 123.7, 125.2, 126.6, 129.2, 129.5, 130.1, 132.7, 133.7, 143.5. UV/VIS ($CHCl_3$): λ_{max} (ε) 291 nm (54,060), 348 (11,590), 358 (11,060), 396 (7700), 418 (12,750), 443 (23,580), 648 (15,120), 692 (12,690) sh. MS (70 eV): m/z (%): 1097 (32), 1069 (80) [M^+], 1095 (100), 831 (11), 830 (20) [$M^+–C_{19}H_{39}$], 829 (12), 564 (12), 563 (24) [$M^+–2\cdot C_{19}H_{39}$], 562 (17), 418 (6), 417 (21) [$M^+–2\cdot C_{19}H_{39}–C_6H_5NCO–CO$], 416 (24). $C_{70}H_{89}N_5O_6$ (1096.5): calcd. C 76.68, H 8.18, N 6.39; found C 76.66, H 8.07, N 6.39. Yield 317 mg (21.9%) of **4b** as a blue powder, m.p. > 300 °C. R_f (silica gel, chloroform): 0.19. IR (KBr): $\tilde{\nu}=3110$ cm^{-1} (w), 2955 (m), 2925 (m), 2854 (m), 1776 (m), 1731(s), 1704 (m), 1662 (s), 1605 (w), 1574 (w), 1500 (m), 1459 (w), 1432 (m), 1401 (m), 1368 (s), 1302 (s), 1228 (w), 1173 (w), 1075 (w), 1030 (w), 989 (w), 925 (w), 808 (w), 751 (m), 730 (m), 687 (w), 644 (m), 546 (w), 504 (w). ^{1}H NMR ($CDCl_3$): $\delta = 0.85$ (t, 12 H, CH_3), 1.23–1.30 (m, 56 H, CH_2), 1.84 (m, 4 H, CH–CH_2), 2.12 (m, 4 H, CH-CH_2), 5.01 (tt, 2 H, $CH(CH_2)_2$), 7.55 (t, 2 H, $^3J = 7.2$ Hz, phenyl), 7.62 (t, 4 H, $^3J = 7.2$ Hz, phenyl), 7.66 (d, 4 H, $^3J = 7.2$ Hz, phenyl), 8.92 (d, br, 4 H, perylene). ^{13}C NMR ($CDCl_3$): $\delta = 14.3$, 23.1, 27.4, 29.8, 30.0, 30.5, 32.3, 32.5, 55.8, 117.0, 123.8, 124.4, 126.4 126.8, 129.8, 129.9, 130.4, 133.7, 143.8. UV/VIS ($CHCl_3$): λ_{max} (ε) = 310 nm (91,980), 645 (6430), 705 (13,210), 778 (16,180). Fluorescence ($CHCl_3$): λ_{max} = 837 nm, 938. – MS (70 eV): m/z (%): 1271 (12), 1270 (39) [M^+], 1269 (77), 1268 (100), 1005 (11), 1004 (26), 1003 (78), 1002 (92) [$M^+ – C_{19}H_{39}$], 738 (27), 737 (51) [$M^+ – 2 \cdot C_{19}H_{39}$], 736 (49), 590 (28), 589 (31) [$M^+ – 2 \cdot C_{19}H_{39} – C_6H_5NCO – CO$], 443 (19), 442 (38), 268 (37). $C_{78}H_{92}N_8O_8$ (1269.7): calcd. C 73.79, H 7.30, N 8.83%; found C 73.63, H 7.08, N 8.83%.

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