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Tangentially Coupled π Systems and their Through-Space Interaction – Trichromophoric Perylene Dyes

Heinz Langhals, and Josef Gold

München, Institut für Organische Chemie der Universität

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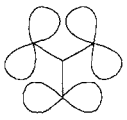
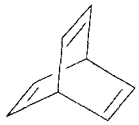
Abstract. Three perylene tetracarboxylic bisimide chromophores have been attached to a benzene ring in *m*-position (**3**). In this way steric and through-bond interactions of the chromophores are minimized and their through-space-interactions can be studied for which an unusually high bathochromic shift has been found. This indicates a destabilization. No exciton coupling has been observed in the trichromophoric dyes.

The tangential coupling of π systems **1**, known as „longicyclics", has been under discussion for a long time[1]. The effect has been experimentally studied with barrelene [2] (**2**) as a probe. A stabilizing interaction of the π system of **2** has been taken into account [3] as well as a destabilizing [1].



1



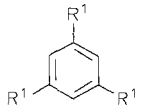
2

Experimental data [4, 5] have not helped to clarify the problem concerning the π interaction of **2**, but indicate only the strain of the system. There was also no explanation for the strongly negative heat of hydrogenation of the first double bond on the basis of force field calculations [6] and thus a destabilizing effect by π interaction was supposed.

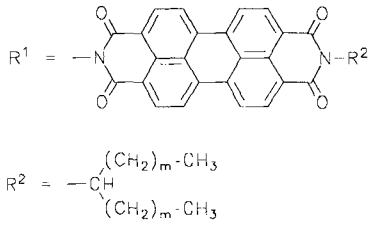
A tangential interaction of aryl units has been discussed in the same way as the interaction of olefins[7]. A final experimental proof of the effect is also lacking in this case because of difficulties in separation of interactions through space and through bond.

Concept

A chromophore is a sensitive probe for π interactions which cause characteristic shifts in the UV spectra. These can be easily determined with precision even when they are small. Furthermore, if fluorescent chromophores are used, information may be obtained about fast dynamic processes. Thus a tangential coupling of chromophores would be a good model for the investigation of this type of π interaction.

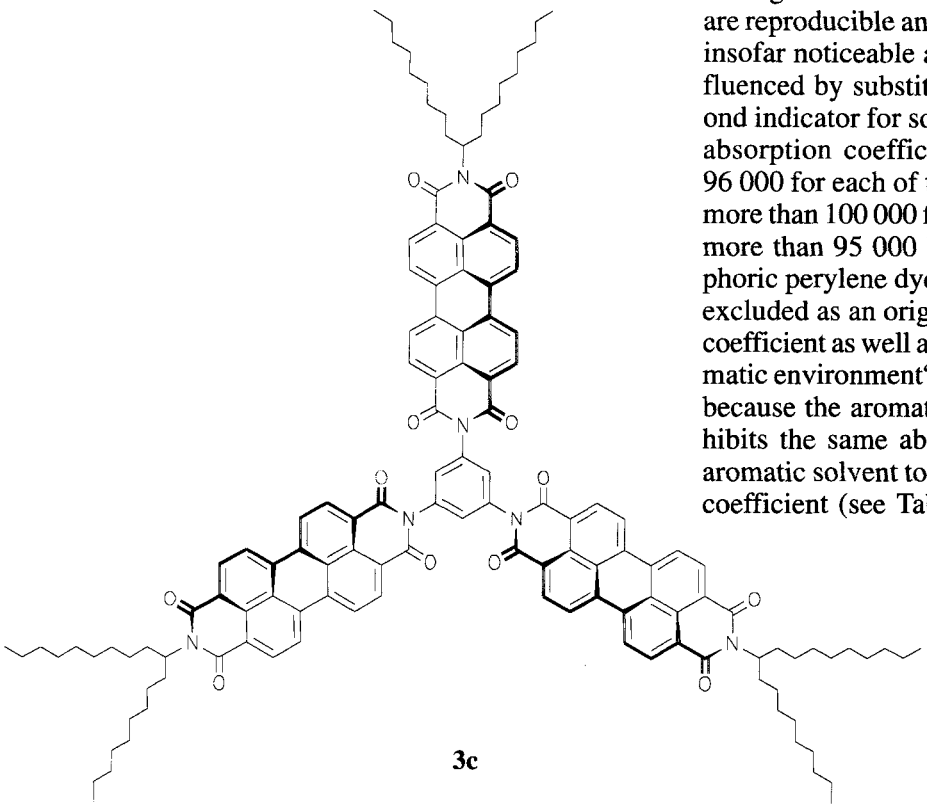


3	m
a	5
b	6
c	8



The choice of chromophores and their attachment to a base structure should guarantee that the main π interactions proceed through space. We used benzene as a rigid base structure and placed the chromophores orthogonally into the positions 1, 3 and 5 (R^1 in partial structure **3**) to minimize steric interactions and conjugation. As chromophores in these positions we attached perylene-3,4:9,10-tetracarboxylic bisimide units (perylene dye) via the nitrogen atoms (R^1), because there are nodes in the HOMO and LUMO at these atoms and nodes or small atomic coefficients in the HOMO-1 and LUMO+1 [8]. This causes an efficient decoupling of the chromophore from any other π system, and even interactions via the σ skeleton are minimized in this way. Further advantages of the chromophore R^1 are high fluorescence quantum yields and chemical and photochemical inertness (for a review see ref. [9]).

However, such a simple trichromophoric perylene dye would have a very low solubility in organic solvents, which makes its preparation and spectroscopic investigation very difficult. We overcompensated the low solubility by the introduction of the solubility increasing long-chain secondary alkyl groups R^2 („swallow tail" substituents [10]) which were attached to the second nitrogen atom of R^1.



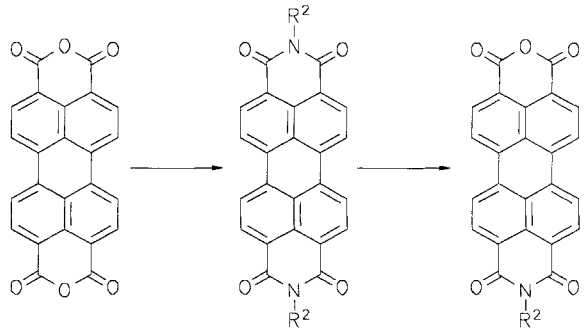
3c

The solubility of the dyes remains still rather low for R^2 with as many as 13 carbon atoms (**3a**) [11], but a further increase of chain length to 15 (**3b**), 17 and 19 (**3c**) carbon atoms is expected to guarantee a sufficient solubility. Dye **3c** is therefore the most interesting derivative for spectroscopic investigations.

Results and Discussion

The starting material for the preparation of trichromophoric perylene dyes was the technical bisanhydride **4** which was condensed with 8-aminopentadecane and its higher homologoue 10-aminoundecane, respectively [12], to the symmetrical perylene dyes **5** and then partially saponificated with KOH in *tert*-butylalcohol [13]. The monoanhydride monoimide **6** thus obtained may be condensed with triaminobenzene. However only monochromophoric and dichromophoric dyes have been obtained with this procedure. The trichromophoric dyes **3** could be prepared by condensing the more reactive [11] trisformamide of triaminobenzene with **6**.

The trichromophoric dyes **3b** and **3c** are red powders which are highly fluorescent in solution. Their solubilities in organic solvents increase with chain length as expected and their UV/VIS spectra resemble the spectra of the monochromophoric dyes **5** exept for small but significant bathochromic shifts, see table 1. These are reproducible and outside experimental error and are insofar noticeable as the spectra of **5** are only little influenced by substituents and solvation[14,15]. A second indicator for some unusual interaction is the molar absorption coefficient of **3a** and **3b** which exceeds 96 000 for each of the three chromophores and reaches more than 100 000 for **3c** (in chloroform), whereas never more than 95 000 have been found for monochromophoric perylene dyes [9]. A change in lineshape can be excluded as an origin of this increase of the absorption coefficient as well as some possible influence of an „aromatic environment" within the dye on the chromophore because the aromatic substituted dye **5d** (Table 1) exhibits the same absorption coefficient as **5a**, and the aromatic solvent toluene even decreases the absorption coefficient (see Table 1). The increase of the absorp-



4 **5** **6**

5, 6	R^2
a	1-Hexylheptyl
b	1-Heptyloctyl
c	1-Nonyldecyl
d	2,5-Di-*tert*-butylphenyl

Table 1 Absorption and fluorescence spectra of perylene derivatives in chloroform.

	Absorption		Fluorescence
No.	λ_{max} (nm)	ε (l mol^{-1} cm^{-1})	λ_{max} (nm)
5a	525.9	95 700	532.7
5a	(526.7	67 100) [a]	
5d [b]	526.9	95 000	533.2
3a	530.0	299 000	538
3b	530.3	294 000	535.3
3c	530.4	308 000	534.7
7c	529.2	189 700	534
8b	527.6		531

[a]) in toluene [b]) R_2 = 2,5-di-*tert*-butylphenyl

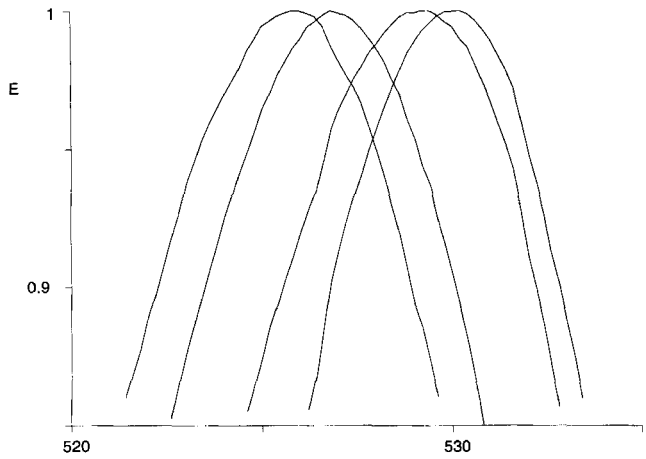
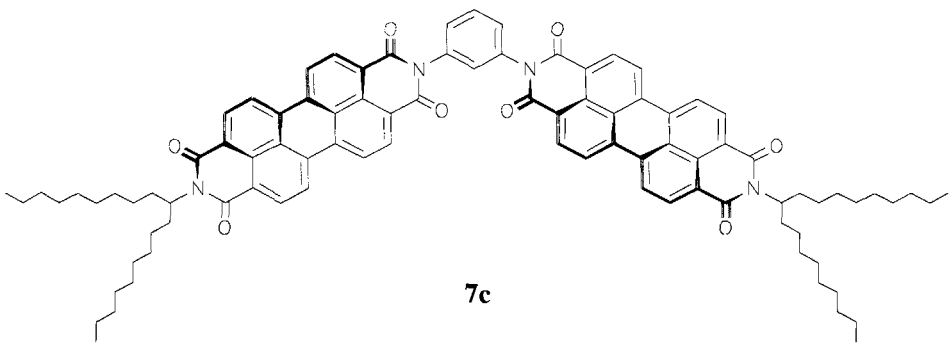


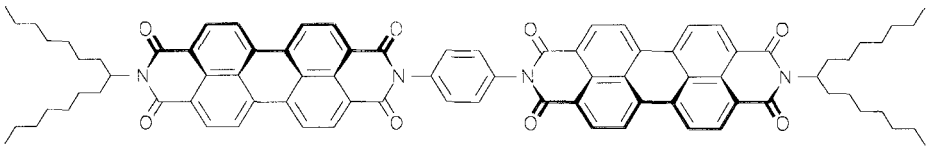
Fig. 1 Absorption maxima of perylene dyes in chloroform. From left to right **5a**, **5d**, **7c** and **3c**

tion coefficient is a good indicator for the extension of the chromophore in space and finds its correspondence for example in the spectra of alkinylated benzenes [16, 17].

The bichromophoric dyes **7c** and **8b** were prepared for the comparison: an attachement of two chromophores to the benzene ring in *p*-position gives no significant bathochromic shift (**8b**) in the absorption (see table 1 and Fig. 1). Two chromophores in *m*-position (**7c**) result in an intermediate bathochromic shift, and the largest shift is obtained with three chromophores in *m*-position.



7c



8b

The unusually large bathochromic shift of **3** compared with **5a**, **7c** and **8b** is certainly not a simple consequence of an „aromatic environment" of the chromophore because neither the aromatic solvent toluene (see Table 1) can induce such a shift in **5a** nor aromatic substituents as in **5d** which should induce a shift for **3a** between those of **5a** and **5d**.

One could furthermore expect exciton coupling [18–20] in **3**. This would induce a splitting of the absorption band into a more hypsochromic and a more bathochromic part. The angle of 120° between the chromophores would make the absorption at longer wavelength the more intense [18]. An exciton effect can be of only minor importance in **3** because neither a line splitting is observed nor even a line broadening which might be a consequence of a small splitting. No exciton coupling is also found in the bichromophoric dye **8b** with two chromophores at an angle of 180° which favors usually the bathochromic part of exciton couplings. The lack of exciton coupling found experimentally still needs further investigation.

Conclusions

The unusually large bathochromic shift and the amplified absorption coefficient of **3** indicate a through-space interaction of the linked chromophores according to **1**. Other origins for the shift like internal solvation or exciton coupling are less probable although they cannot be completely excluded. The bathochromic shift of **3** proves a decrease of the HOMO-LUMO-gap and because no special effect is expected for LUMO in the perylene chromophore the decrease indicates some elevation of the HOMO and therefore a small destabilization. The spectroscopic investigations of **3** may therefore support a destabilization by interactions according to **1**.

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Experimental

IR-spectra: IFS 45, Bruker. – UV/VIS-spectra: OMEGA 20, Bruins Instruments. – Fluorescence spectra: FS 3000, Perkin Elmer. – NMR-Spectra: VXR 400S, Varian. – Mass spectra: SN 1B, Varian MAT.

N,N'-1,3-Diaminobenzene-bis-formamide

m-Phenylenediamine (4.00 g, 36.9 mmol) are refluxed with conc. formic acid (10 ml) for 4 h according to a general procedure of ref. [21]. Ether (30 ml) is added to the cold solution with stirring, and the product is collected by vacuum filtration with a D4 glass filter after crystallisation is complete. Yield 3.55 g (59%) of a gray powder). The solid is recrystallized from ethanol and dried in vacuo for 8h at 60 °C. Yield 2.49 g (41%) colourless crystals, *m.p.* 155–156 °C ([22] 155 °C). IR (KBr): ν = 3260 cm^{-1} m (NH), 3210 m (NH), 3145 m, 3080 m (CH), 3050 m (CH), 2900 m (CH), 1690 s (C=O), 1655 s (NH), 1615 s (C=C), 1552 s (C=C), 1475 m (CH), 1455 s (CH), 1405 m, 1295 m, 1245 m, 1175 m, 900 m, 795 m, 695 m. – MS (70eV), *m/z* (%): 164 (100) [M^+], 163 (1) [$M^+ - H$], 162 (2) [$M^+ - H_2$], 136 (15) [$M^+ - CO$], 134 (4) [$M^+ - H_2 - CO$], 108 (33) [$M^+ - 2\ CO$], 107 (5) [$M^+ - 2\ CO - H$], 91 (4) [$M^+ - 2\ CO - NH_3$], 81 (26), 80 (26), 65 (4), 53 (5), 52 (4).

$C_8H_8N_2O_2$	calcd.:	C 58.53	H 4.91	N 17.07
(164.2)	found:	C 58.56	H 5.00	N 16.86

2-(1-Heptyloctyl)-9-(3,5-bis(2-(1-heptyloctyl)-anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetrone-9-yl)-phenyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetrone (**3b**)

N-(1-Heptyloctyl)perylene-3,4:9,10-tetracarboxylic-3,4-anhydride-9,10-imide (**6b**, 1.50 g, 2.49 mmol), N,*N'*,*N''*-1,3,5-triaminobenzene-tris-formamide [11] (172 mg, 0.83 mmol) and imidazole (6 g, 88 mmol) are heated under argon at 185 °C for 5 h. The cold reaction mixture is dispersed in ethanol (500 ml). Conc. HCl (50 ml) is added to the mixture which is then stirred for at least 2 h at room temperature. The resulting solid is collected by vacuum filtration through a D4 glass filter. It is washed with distilled water (about 200 ml) until the washings are neutral and dried at 120 °C for 2 h in an drying oven (1.42 g, 91%). It is further purified by column separation with (40 × 4cm, Al_2O_3, chloroform/butanol 20:1) with which some by-products are removed as yellow forerun. The more reddish main fraction is purified by a second column separation (silica gel, chloroform/acetic acid 10:1) which removes 4% of a pink coloured by-product (a further purification is brought about by additional column separations with silica gel, chloroform/ethanol 10:1). A solution of the purified dye in chloroform is filtered through a D5 glass filter. The solvent is removed in vacuo, the residue washed with distilled water and dried in medium vacuum for 14 h at 115 °C. Yield 500 mg (32%), *m.p.* 280 °C (dec.). – R_f (silica gel, chloroform/ethanol 10:1) = 0.58. – IR (KBr): ν = 3085 cm^{-1} w (CH), 2955 w (CH), 2926 m (CH), 2855 s (CH), 1713 w (C=O), 1698 m (C=O), 1677 w, 1660 m, 1634 w, 1618 w, 1594 s (C=C), 1579 m (C=C), 1510 m (C=C), 1461 w (CH), 1457 w (CH), 1431 m (CH), 1405 s, 1339 s br., 1252 s, 1195 w, 1174 s, 1140 w, 1125 m, 995 m, 970 m, 855 s, 811 s, 795 m, 746 s, 725 w (CH), 665 m, 648 s. – UV ($CHCl_3$): λ_{max} (lg ε) = 437 nm (4.130), 460 (4.684), 492 (5.172), 530 (5.469). – UV (toluene): λ_{max} (lg ε) = 435 nm (4.141), 466 (4.621), 496 (4.993), 531 (5.120), 552 sh(4.789). – UV (THF): λ_{max} (lg ε) = 430 nm (4.140), 457 (4.661), 488 (5.124), 525 (5.388). – Fluorescence ($CHCl_3$): λ_{max} = 535 nm, 575. - Fluorescence (toluene): λ_{max} = 536 nm, 576. – Fluorescence (THF): λ_{max} = 529 nm, 569. – ^{1}H-NMR ($CDCl_3$): δ = 0.81 (t, 18 H, 6 CH_3), 1.24 (m, 60 H, 30 CH_2), 1.81 (m, 6 H, 3 α-CH_2), 2.15 (m, 6 H, 3 α-CH_2), 5.18 (m, 3 H, 3 CH), 8.61 (m, 27 H, aryl; line broadening by association). – MS (FAB, m-NBA), *m/z* (%) = 1896 (0.14) [M^+ + Na], 1873 (0.02) [M^+], 1686 (0.05) [$M^+ + Na - C_{15}H_{30}$], 1265 (0.04), 1245 (0.04), 1243 (0.08), 896 (0.03), 854 (0.04), 853 (0.07), 541 (0.15), 516 (0.25), 423 (0.14), 391 (0.4), 373 (0.49), 270 (100), 140 (6), 55 (8).

$C_{123}H_{120}N_6O_{12}$	calcd.:	C 78.82	H 6.45	N 4.48
(1874.3)	found:	C 79.10	H 6.74	N 4.72.

2-(1-Nonyldecyl)-9-(3,5-bis(2-(1-nonyldecyl)-anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetrone-9-yl)-phenyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetrone (**3c**)

N-(1-Nonyldecyl)-3,4:9,10-perylenetetracarboxylic-3,4-anhydride-9,10-imide (**6c**, 1.50 g, 2.28 mmol), *N*,*N'*,N''-1,3,5-triaminobenzene-tris-formamide [11] (158 mg, 0.76 mmol) and imidazole (6 g, 88 mmol) are allowed to react and the mixture is worked up as described in the preparation of **3b**. (Yield 1.50 g (97%). The product is purified by column separation with silca gel and chloroform/ethanol 10:1 and a second separation with chloroform/acetic acid 10:1 (a further purification is brought about by additional column separations with chloroform/ethanol 10:1). Yield 500 mg (32%), *m.p.* 330 °C (dec.). – R_f (silica gel, $CHCl_3$/ethanol 10:1) = 0.82. – R_f (silica gel, $CHCl_3$/acetic acid 10:1) = 0.66. – IR (KBr): ν = 3095 cm^{-1} w (CH), 2924 s (CH), 2854 m, 1713 m (C=O), 1698 s (C=O), 1678 m, 1660 s, 1594 s (C=C), 1579 m (C=C), 1506 w (C=C), 1458 w (CH), 1431 w (CH), 1405 m, 1339 s, 1253 m, 1195 w, 1174 w, 1137 w, 1122 w, 992 w, 965 w, 855

w, 811 m, 795 w, 746 m, 722 w, 647 m. – UV ($CHCl_3$): λ_{max} (lg ε) = 435 nm (4.206), 460 (4.726), 492 (5.198), 530 (5.488). – UV (toluene): λ_{max} (lg ε) = 433 nm (4.117), 467 (4.646), 496 (5.012), 532 (5.114), 553 sh (4.801). – UV (THF): λ_{max} (lg ε) = 430 nm (4.198), 457 (4.702), 488 (5.160), 525 (5.432). – Fluorescence ($CHCl_3$): λ_{max} = 535 nm, 575. – Fluorescence (toluene): λ_{max} = 536 nm, 576. – Fluorescence (THF): λ_{max} = 529 nm, 569. – ^{1}H-NMR ($CDCl_3$): δ = 0.75 (t, 18 H, 6 CH_3), 1.14 (m, 84 H, 42 CH_2), 1.81 (m, 6 H, 3 α-CH_2), 2.16 (m, 6 H, 3 α-CH_2), 5.10 (m, 3 H, 3 CH), 8.58 (m, 27 H, aryl; line broadening by association). – ^{13}C-NMR ($CDCl_3$): δ = 14.08, 22.65, 26.96, 27.20, 29.29, 29.54, 29.70, 31.86, 33.29, 54.84, the signals at 120–135 and 160–165 are not resolved. – MS (FAB, m-NBA): *m/z* (%) = 2065 (0.5) [M^+ + Na], 2042 (0.2) [M^+],1799 (0.2) [M^+ + Na – $C_{19}H_{38}$], 1292 (0.2), 1266 (0.5), 1246 (0.8), 1244 (1.6), 1229 (0.3), 1200 (0.2), 853 (1.2), 506 (1.2), 480 (1.4), 461 (2.3), 424 (2.3), 415 (2.7), 391 (6.3), 373 (9.0), 346 (6.8), 307 (25), 289 (17), 154 (100).

$C_{135}H_{144}N_6O_{12}$	calcd.:	C 79.38	H 7.11	N 4.11
(2042.7)	found:	C 79.09	H 7.04	N 4.06.

2-(1-Nonyldecyl)-9-(3-(2-(1-nonyldecyl)-anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetrone-9-yl)-phenyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetrone (**7c**)

N-(1-Nonadecyl)-3,4:9,10-perylenetetracarboxylic-3,4-anhydride-9,10-imide (**6c**, 1.64 g, 2.50 mmol), *N,N'*-1,3-diaminobenzenebisformamide [22] (205 mg, 1.25 mmol) and imidazole (6 g, 88 mmol) are allowed to react and the mixture is worked up as described in the preparation of **3b**. Yield 1.70 g (98 %). The product is purified by column separation with silica gel and chloroform/acetic acid 10:1. Yield 300 mg (17%), *m.p.* >350 °C. – R_f (silica gel, $CHCl_3$/acetic acid 10:1) = 0.73. – R_f (silica gel, $CHCl_3$/ethanol 10:1) = 0.45. IR (KBr): ν = 3090 cm^{-1} w (CH), 2930 s (CH), 2860 m (CH), 1703 s (C=O), 1665 s (C=O), 1600 s (C=C), 1593 m (C=C), 1510 w (C=C), 1493 w, 1470 w (CH), 1438 w (CH), 1410 m (CH), 1347 s, 1260 m, 1205 w, 1184 m, 1124 w, 971 w, 862 w, 818 m, 780 w, 754 m. – UV ($CHCl_3$): λ_{max} (lg ε) = 432 nm (4.026), 459 (4.574), 491 (5.027), 529 (5.278). – Fluorescence ($CHCl_3$): λ_{max} = 534 nm, 574. – Solid-state fluorescence λ_{max} = 620 nm. – ^{1}H-NMR ($CDCl_3$): δ = 0.81 (t, 12 H, 4 CH_3), 1.19 –1.29 (m, 56 H, 28 CH_2), 1.84 (m, 4 H, 2 α-CH_2), 2.22 (m, 4H, 2 α-CH_2), 5.15 (m, 2 H, 2 CH), 7.43 (s, 1H, subst. phenyl), 7.53 (d, 2 H, phenyl), 7.77 (t, 1 H, phenyl), 8.45–8.70 (m, 16 H, perylene). – MS (FAB, m-NBA), *m/z* (%): 1388 (5) [M^+], 1122 (1) [M^+ – $C_{19}H_{38}$], 856 (9), 855 (12), 657 (5), 466 (5), 465 (6), 449 (4), 415 (4), 408 (4), 407 (4), 404 (5), 403 (5), 391 (36), 373 (13), 289 (11), 154 (100).

$C_{92}H_{98}N_4O_8$	calcd.:	C 79.62	H 7.12	N 4.04
(1387.8)	found:	C 78.52	H 6.10	N 4.13.

2-(1-Heptyloctyl)-9-(4-(2-(1-heptyloctyl)-anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetrone-9-yl)-phenyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetrone (**8b**)

N-(1-Heptyloctyl)perylene-3,4:9,10-tetracarboxylic-3,4-anhydride-9,10-imide (**6b**, 931 mg, 1.55 mmol), *N,N'*-1,4-diaminobenzene-bis-formamide (127 mg, 0.77 mmol) [1] and imidazole (4 g, 59 mmol) are allowed to react, and the mixture is worked up as described in the preparation of **3b**. Yield 900 mg (91%). It is further purified by column separation (80 × 4 cm, silica gel, chloroform/acetic acid 10:1) and by a second column separation (silica gel, toluene/ethanol 10:1) which removes a pink coloured by-product. Yield 500 mg (51%); *m.p.* 275 °C. – IR (KBr): ν = 3080 cm^{-1} w (CH), 2930 s (CH), 2850 m (CH), 1704 s (C=O), 1665 s (C=O), 1600 s (C=C), 1585 m (C=C), 1520 w (C=C), 1510 w (C=C), 1460 w (CH), 1410 m (CH), 1350 s, 1325 m, 1275 w, 1250 w, 1185 w, 1025 w, 860 w, 815 w, 750 w. – UV ($CHCl_3$): λ_{max} = 430 nm, 460, 491, 527. – Fluorescence ($CHCl_3$): λ_{max} = 531 nm, 571. – MS (FAB, m-NBA), *m/z* (%): 1276 (0.04) [M^+ + H], 1275 (0.02) [M^+], 1200 [0.1], 974 (0.1), 855 (0.3), 826 (0.3), 720 (6), 601 (21), 391 (100), 375 (14), 321 (16), 275 (8), 154 (6), 133 (10).

$C_{84}H_{82}N_4O_8 \cdot H_2O$	calcd.:	C 77.99	H 6.54	N 4.33
(1293.6)	found:	C 77.80	H 6.69	N 4.12

The product is dehydrated in medium vacuum at 110 °C within 12 h:

$C_{84}H_{82}N_4O_8$	calcd.:	C 79.09	H 6.48	N 4.39
(1275.6)	found:	C 77.93	H 6.62	N 4.12.

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Address for correspondence:
Prof. Dr. H. Langhals
Ludwig Maximilians Universität München
Institut für Organische Chemie
Karlstraße 23
D-80333 München, Germany