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Synthesis of Readily Soluble Tetraazaviolanthrone and -isoviolanthrone Fluorescent Dyes

Heinz Langhals and Haleh Bastani-Oskoui

München, Institut für Organische Chemie der Universität

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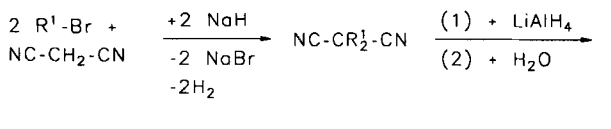
Abstract. Readily soluble, photostable and highly red fluorescent dyes (**3**–**5**) have been obtained from a condensation of perylenetetracarboxylic bisanhydride with primary aliphatic 1,3-diamines containing two geminal long-chain alkyl groups. Analogous red fluorescing dyes have been prepared by the condensation of a corresponding perylene anhydride imide.

Photostable, red fluorescing dyes are of interest because of their colour [1–4], their fluorescence [4–7] and their applications in electronics [4]. In a preceeding paper [8] we have described the tetraazaviolanthrone and -iso-violanthrone dyes (**3a** and **4a**, $R^1 = CH_3$) which exhibit UV/VIS absorptions at long wavelengths and a red fluorescence. However, the solubility of these dyes is so low that even their investigation was difficult and a separation of the isomers **3a** and **4a** was not possible. On the other hand, long-chain secondary alkyl groups („swallow-tail" groups) have been reported [9] to increase appreciably the solubility of such dyes. It is therefore of interest to replace the geminal methyl groups of **3a** by geminal long-chain alkyl groups.

Results and Discussion

The starting materials for the preparation of dyes **3** were 1,3-diaminopropanes (**1**) with two alkyl groups in position 2.



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Scheme 1

These diamines have been prepared according to scheme 1 from malodinitrile by twofold alkylation [10], reduction [11] and then condensat with perylene-3,4:9,10-tetracarboxylic bisanhydride (**2**), or perylene anhydrides imides **6**, respectively, which have been prepared by partial saponification of **7** [12]. The condensation was carried out in ethylene glycol [13] without further additives at 130 ... 160 °C which gave better results for **3**–**5**, than the standard procedure [14] with zinc acetate in imidazole or quinoline, because fewer by-products were formed. These as well as traces of the solvent which dissolves in methanol can be more easily removed. The condensation of diamines with the anhydride in the non-activating solvent ethylene glycol is presumably favored by the facts that the diamines are aliphatic and the ring closure proceeds to a stable six-membered ring.

The condensation of the diamines with the anhydride lead to a *cis- trans*-mixture of dyes, the tetraazavioanthrone (**3**) and -isoviolanthrone (**4**) derivatives, which could not be separated on a larger preparative scale. However, small amounts of the pure isomers have been separated by means of preparative T. L. C.. The isomer with lower R_f value is attributed to the *cis*-isomer **3** because of its dipole moment, whereas the *trans*-isomer **4** has point symmetry and is therefore not dipolar. The UV/VIS-spectra of **3** and **4** as shown in Fig. 1 are very similar.

The long-wavelength absorption of **3b** at λ_{max}/nm = 548 is only 3 nm bathochromically shifted as compared

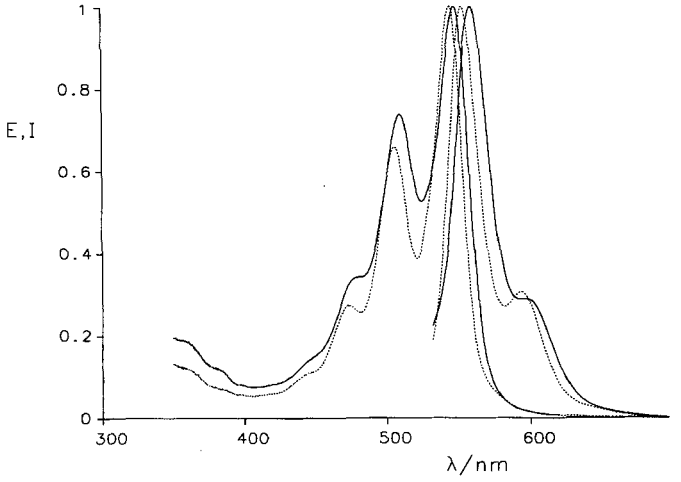
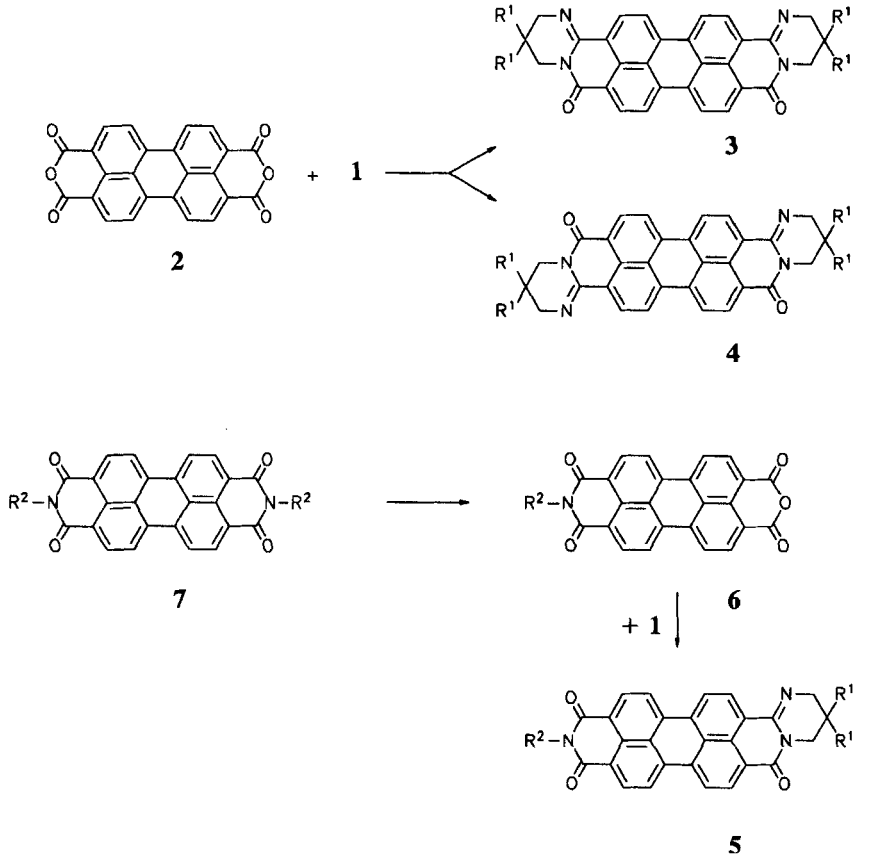


Fig. 1 UV/VIS absorption and fluorescence spectra of **3b** (—) (colour coordinates: x = 0.3737, y = 0.2637, z = 0.3626 at T_{max} = 0.1, normlight C at 2°) and **4b** (···) (colour coordinates: x = 0.3649, y = 0.2690, z = 0.3661 at T_{max} = 0.1) in chloroform. Fluorescence spectra normalized to the maximum of absorption

to **4b**. The differences in their fluorescence maxima are slightly larger ($\Delta\lambda$ = 6 nm).Both isomers are highly fluorescent and the relative fluorescence quantum yield of **4b** versus **3b** is 96%. As expected, the chain lengths of the geminal alkyl groups have only a negligible influence on the UV/VIS spectra. However, the solubility of these dyes strongly increases and their tendency to form aggregates decreases with increasing alkylchains. Therefore, for most applications a separation of the isomers **3** and **4** is not necessary, especially for fluorescence applications because of the similarity of their spectra. The UV/VIS spectrum of an 1:1 mixture of **3c** and **4c** is shown in Fig. 2, which exhibits a bathochromic shift of $\Delta\lambda$ = 19 nm as compared to **7b**, so that a pinky red fluorescence is obtained. The vibrational fine structure of the UV/VIS spectrum of **7** is conserved for **3** and **4** (see Figs. 1 and 2).

On the other hand, the problem of the separation of *cis/trans*-isomers is avoided with dyes **5** with only one imino and one imide structure. However, a bifluorophor-



3, 4	R^1
a	CH_3
b	n-C_6H_{13}
c	n-C_8H_{17}

6, 7	R^2
a	CH_3
b	n-C_6H_{13}
c	n-C_8H_{17}

5	R^1	R^2
a	CH_3	$CH(n\text{-}C_6H_{13})_2$
b	n-C_6H_{13}	$CH(n\text{-}C_6H_{13})_2$
c	n-C_8H_{17}	$CH(n\text{-}C_6H_{13})_2$
d	CH_3	CH_3

Scheme 2

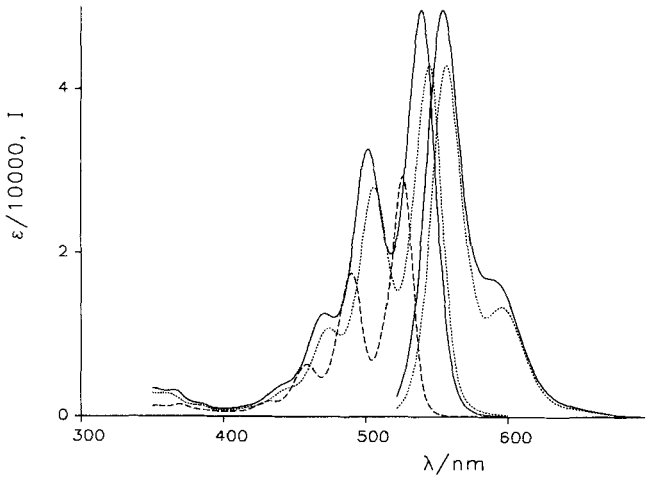
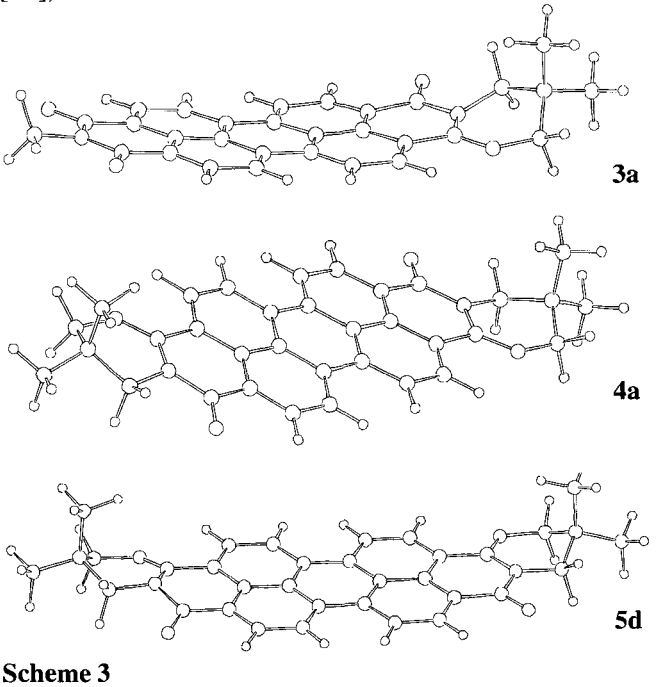


Fig. 2 UV/VIS absorption and fluorescence spectra of **3c** and **4c** as a mixture(···) (colour coordinates: x = 0.3616, y = 0.2669, z = 0.3715 at T_{max} = 0.1, normlight C at 2°), **5c** (—) (colour coordinates: x = 0.3678, y = 0.2764, z = 0.3558 at T_{max} = 0.1) and **7c** (1/3 e) (---) in chloroform. Fluorescence spectra normalized to the maximum of absorption

ic by-product is obtained the yield of which can be increased by application of an excess of **6** (see experimental part). Surprisingly, the bathochromic shift of the long-wavelength absorption maxima of **5** versus **7** with $\Delta\lambda$ = 16 nm reaches nearly the shift of **3/4**. Therefore, the small perturbation of the chromophore of **7** by exchange of only one carbonyl group by an imino group is obviously sufficient for a large bathochromic shift and a further perturbation is of minor influence only. The dyes **5** are also highly pink fluorescent (compare [15]).



Scheme 3

Tab. 1 AM1 calculations of **3a**, **3a** and **5d**

	3a	**4a**	**5d**
H_f [a, b])	68.70	67.71	25.46
Dipole [c])	2.374	0.243	3.443
E_{HOMO} [a])	−192.3	−192.4	−198.63
E_{LUMO} [a])	−48.34	−48.29	−53.52
H_f-S_1 [a, b, d])	143.42	142.58	100.65
Dipole-S_1 [c, d])	0.276	3.73	

[a]) In kcal/mol. [b]) Heat of formation. [c]) Dipole moment in Debye. [d]) Excited state.

The conformation of the six-membered rings of **3**–**5** with geminal alkyl groups is determined by two different influences: the tendency to planarize caused by the unsaturated part of the ring and the tendency of puckering caused by the geminal alkyl groups. For the investigation of this problem, the geometry of **3a**, **4a** and **5d** was optimized by MM2 force-field calculations and refined by AM1 quantum-mechanical calculations [16, 17] resulting in nearly planar rings for **3a** and **4a**, except for the carbon atoms with geminal alkyl groups. Therefore, a half-chair conformation is obtained for **3a** and **4a**, whereas for **5d** the bond to the imide nitrogen atom is found to be bent out of plane by about 25° with a more twist-like conformation (see scheme 3). These conformational differences are expected to have only a minor influence on the UV/VIS spectra of the dyes because very small atomic coefficients have been calculated for the imide nitrogen atoms in the HOMO and LUMO: the central nodal line through the two nitrogen atoms of **7** [14, 18] is nearly conserved in the perturbed structures **3**–**5**. One must thus conclude that the bathochromic shift of **3**–**5** as compared to **7** is essentially caused by the perturbation of the highly symmetric π-system of **7**.

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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.

9,9-Dicyanoheptadecane

Sodium hydride (4.36 g, 180 mmol) was dispergiert in anhydrous DMSO (20 ml) under argon. Molten malodinitrile (5.94 g, 90.0 mmol) was added dropwise to the mixture and, after stirring for 15 min at room temperature, 1-bromo-*n*-octane (34.8 g, 180 mmol) was added within 1 h with ice cooling. Toluene (150 ml) was added to the viscous mixture which was stirred until the evolution of hydrogen ceased (1 h). The mix-

ture was then refluxed for 4 h, allowed to cool, poured into ice water (1.5 l) and extracted with diethyl ether. The ether phase was dried ($MgSO_4$) and distilled to give 12.1 g (46%) of 9,9-dicyanoheptadecane, *b.p.* 145 °C/0.01 torr. – IR (neat): ν/cm^{-1} = 3450 (m), 2945 (m), 2235 (s), 1650 (m), 1460 (s), 1380 (s), 1330 (s), 1300 (m), 1255 (m), 1200 (m), 1120 (m), 1080 (m), 1020 (m), 895 (m), 730 (s). – ^{1}H NMR (80 MHz/CCl_4): δ/ppm = 0.9 (m_c, 6 H), 1.5 (m_c, 28 H).

$C_{19}H_{34}N_2$	calcd.:	C 78.63	H 11.71	N 9.64
(290.2)	found:	C 78.22	H 11.66	N 9.59.

1-Amino-2-aminomethyl-2-hexyloctane (**1b**)

A solution of 7,7-dicyano-*n*-tridecane [19] (22 g, 94 mmol) in *tert*-butyl methyl ether (100 ml) was added dropwise with vigorous stirring under argon to a mixture of lithium aluminiumhydride (8.7 g, 0.23 mol) in *tert*-butyl methyl ether (250 ml) at 10 °C within 1 h and then refluxed for another hour. The reaction was quenched by the addition of 10% aqueous NaOH [10]. The ether phase was collected and the solid was refluxed three times with diethyl ether (50 ml each). The combined organic phases were dried ($MgSO_4$), the solvent was evaporated and the residue distilled *in vacuo* to give 9.8 g (45%) ([19] 49%) of 1-amino-2-aminomethyl-2-hexylheptane; *b.p.* 129 °C/0.06 Torr (138–142 °C/0.07 Torr [2]). – IR (neat): ν/cm^{-1} = 3360 (w), 3300 (w), 2960 (m), 2925 (s), 2855 (s), 1600 (w, br), 1465 (s), 1380 (m), 1325 (w), 1075 (w), 820 (m), 735 (m). – ^{1}H NMR (400 MHz/$CDCl_3$): δ/ppm= 0.80 (*t*, 6 H, $2CH_3$), 0.92 (s, 4 H, $2NH_2$), 1.08 (s, 8 H, $4CH_2$), 1.23 (m, 12 H, $6CH_2$), 2.43 (s, 4 H, $2C\underline{H}_2$–NH_2).

$C_{15}H_{34}N_2$	calcd.:	C 74.39	H 14.04	N 11.56
(242.2)	found:	C 74.62	H 13.92	N 10.93.

1-Amino-2-aminomethyl-2-octyldecane (**1c**)

8,8-Dicyano-*n*-heptadecane (11.09 g, 38.21 mmol) and lithium aluminiumhydride (4.5 g, 0.11 mol) were allowed to react and worked-up as is described for 1-amino-2-aminomethyl-2-hexylheptane to give 5.4 g (51%) of 1-amino-2-aminomethyl-2-octylnonane; *b.p.* 148 °C/0.07 Torr. – IR (neat): ν/cm^{-1} = 3890 (m), 3800 (m), 2980 (m), 2950 (s), 2875 (s), 1600 (m, br.), 1465 (s), 1380 (m), 1315 (m), 1110 (w), 1075 (w), 815 (m), 725 (m). – ^{1}H NMR (400 MHz/$CDCl_3$): δ/ppm= 0.77 (*t*, 6 H, $2CH_3$), 0.90 (s, 4 H, $2NH_2$), 1.06 (s, 24 H, $12CH_2$), 1.17 (s, 4 H, $2CH_2$), 2.41 (s, 4 H, $2CH_2$).

$C_{19}H_{42}N_2$	calcd.:	C 76.52	H 14.08	N 9.38
(298.2)	found:	C 76.43	H 13.99	N 8.98.

2,3,4,4a,10a,11,12,13-Octahydro-3,3,12,12-tetra-n-hexyl-1,4a,10a,14-tetraazaviolanthrone/1,2,3,9a,10,11,12,18a-Octahydro-2,2,11,11-tetrahexyl-4,9a,13,18a-tetraazaisoviolanthrone (**3b/4b**)

Perylene-3,4:9,10-tetracarboxylic bisanhydride (**2**, 1.50 g, 3.75 mmol) and 1-amino-2-aminomethyl-2-*n*-hexyloctane (**1b**, 2.72 g, 11.3 mmol) in ethylene glycol (50 ml) were stirred for 3 h under argon at 160 °C, cooled, then methanol (50 ml) was added and the black violet solid was collected by vacuum filtration, washed with water and methanol, dried for 8 h at 100 °C in the air, treated with hot 10% aqueous K_2CO_3 solution until the washings were only weakly fluorescent and purified by column separation with chloroform/triethylamine (10:1) and silica gel. A red fluorescent fore-run was discarded and the pink fluorescent main fraction was further purified by column separation with chloroform/acetic acid (5:1) and silica gel, by column separation with chloroform/acetone (5:1) and silica gel, and by cosis precipitation from a hot concentrated solution in chloroform with methanol. The product was finally dried with KOH *in vacuo* at 80 °C to give 1.31 g (43%) of a black violet powder of a mixture of **3b/4b**; *m.p.* 239 °C, R_f (chloroform/triethylamine (10:1); silica gel): 0.56, R_f (chloroform/acetic acid (5:1); silica gel): 0.33. – IR (KBr): ν/cm^{-1} = 2915 (s), 2850 (m), 1660 (s, br.), 1610 (s), 1584 (m), 1565 (w), 1460 (m, br.), 1355 (s), 1340 (w), 1265 (m), 1170 (w), 845 (m), 800 (m), 750 (m). – UV ($CHCl_3$): λ_{max}/nm (lg ε) = 545 (49492), 507 (28869), 474 (8105), 444 (1136). – Fluorescence ($CHCl_3$) λ_{max}/nm = 562, 593. – ^{1}H NMR (400 MHz/$CDCl_3$): δ/ppm = 0.87 (m, 12H, $4CH_3$), 1.28 (m, 32H, $16CH_2$), 1.80 (m, 8H, $4CH_2$), 3.61 (s, 4H, $2CH_2$), 3.85 (s, 4H, $2CH_2$), 8.30 (m_c, 8H, perylene). – ^{13}C NMR ($CDCl_3$): δ/ppm = 14.07, 22.65, 22.95, 23.57, 23.81, 29.82, 30.04, 31.66, 31.75, 31.83, 32.50, 33.93, 40.59, 48.12 (N–CH_2), 55.14 (C=N–$\underline{C}H_2$), 119.99, 121.63, 121.92, 122.27, 122.84, 123.22, 126.25, 126.66, 128.38, 128.82, 128.86, 129.09, 133.98, 146.08 (C=N), 161.29 (C=O), 162.49 (C=O), 164.32 (C=O). – Ms (70 eV); *m/z* (%): 804 (15) [M^+], 719 (100) [M^+–C_6H_{13}], 705 (15), 649 (15), 635 (40) [M^+–$C_{12}H_{26}$], 551 (5), 524 (5), 467 (7) [M^+–$2C_{12}H_{26}$], 439 (5), 413 (5), 357 [467–$2C_3H_4N$], 317 (9), 275 (11).

$C_{54}H_{68}N_4O_2$	calcd.:	C 80.61	H 8.45	N 6.96
(804.5)	found:	C 80.43	H 8.29	N 6.98.

A sample of **3b/4b** was separated by preparative T. L. C. with chloroform/ethanol (10:1) and silica gel. **3b** was obtained as the fraction with the lower R_f-value. – UV ($CHCl_3$): λ_{max}/nm (E_{rel}) = 547.9 (1.00), 509.5 (0.744), 479.5 (0.357). – Fluorescence ($CHCl_3$): λ_{max}/nm = 559.2. – **4b** was obtained as the fraction with the higher R_f-value. – UV ($CHCl_3$): λ_{max}/nm (E_{rel}) = 544.8 nm (1.00), 505.8 (0.662), 473.5 (0.280). – Fluorescence ($CHCl_3$): λ_{max}/nm = 553.

2,3,4,4a,10a,11,12,13-Octahydro-3,3,12,12-tetra-n-octyl-1,4a,10a,14-tetraazaviolanthrone/1,2,3,9a,10,11,12,18a-Octahydro-2,2,11,11-tetrahexyl-4,9a,13,18a-tetraazaisoviolanthrone (**3c/4c**)

Perylene-3,4:9,10-tetracarboxylic bisanhydride (**2**, 1.00 g, 2.55 mmol) and 1-amino-2-aminomethyl-2-*n*-octyldecane (**1c**, 3.05 g, 10.22 mmol) in ethylene glycol (50 ml) were allowed to react as described for **3b/4b**. The crude product was refluxed for 15 min with 10% aqueous K_2CO_3 to remove the unreacted bisanhydride. It was purified by column separation with chloroform/triethylamine (10:1) and silica gel, adsorbed with chloroform/acetic acid to silica gel, fluorescent by-products were eluted with this solvent, and **3c/4c** was obtained by an increase of the amount of acetic acid. This main fraction was further purified by column separation with chloroform/1-butanol (40:1) and silica gel with which a red fluorescent fore-run could be completely separated. Finally, the product was precipitated from a hot concentrated solution in chloroform by addition of methanol and was dried over KOH *in vacuo* at 40 °C to give 1.10 g (47%) of a mixture of **3c/4c** as a black violet powder; *m.p.* 215 °C, R_f (chloroform/acetic

acid (5:1), silica gel): 0.21, R_f (chloroform/1-butanol (40:1), silica gel): 0.30. – IR (KBr): ν/cm^{-1} = 2820 (s), 2740 (m), 1660 (s, br.), 1615 (s), 1590 (m), 1570 (s), 1460 (w), 1360 (s), 1265 (m), 840 (m), 810 (m), 750 (m). – UV ($CHCl_3$): λ_{max}/nm (lg ε) = 545 (4.695), 506 (4.454), 474 (3.928). – Fluorescence ($CHCl_3$): λ_{max}/nm = 562, 600. – ^{1}H NMR (400 MHz/$CDCl_3$): δ/ppm = 0.85 (m, 12 H, $4CH_3$), 1.25 (m, 40 H, 20 CH_2), 1.85 (m, 8H, $4CH_2$), 3.63 (s. 4H, $2CH_2$), 3.86 (mc, 4H, $2CH_2$), 8.3 (m, 8H, aryl-H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 14.05, 22.62, 22.91, 29.24, 29.44, 30.28, 31.84, 32.41, 33.81, 48.11 (N–CH_2), 54.73 (C=N–$\underline{C}H_2$), 122.30, 122.53, 126.18, 128.76, 129.35, 132.54, 146.12 (C=N), 160.77 (C=O), 161.22 (C=O), 162.41 (C=O), 164.26 (C=O). – Ms (70 eV); *m/z* (%): 916 (16) [M^+], 805 (25), 804 (72), 803 (100) [M^+–C_8H_{17}], 789 (4), 705 (14), 691 (32) [M^+–$C_{16}H_{35}$], 552 (6), 453 (5), 439 (5), 357 (4).

$C_{62}H_{84}NO_2$	calcd.:	C 81.23	H 9.16	N 6.10
(916.6)	found:	C 80.93	H 9.25	N 6.10.

A sample of **3c/4c** was separated by preparative T. L. C. with chloroform/ethanol (10:1) and silica gel. **3c** was obtained as the fraction with the lower R_f-value. – UV ($CHCl_3$): λ_{max}/nm (E_{rel}) = 546.5 (1.00), 510.2 (0.649). – Fluorescence ($CHCl_3$): λ_{max}/nm = 557.5. – **4c** was obtained as the fraction with the higher R_f-value. – UV ($CHCl_3$): λ_{max}/nm (E_{rel}) = 544.6 (1.00), 506.0 (0.625), 473.9 (0.267). – Fluorescence ($CHCl_3$): λ_{max}/nm = 553.2 nm.

12-(1-Hexylheptyl)-3,3-dihexyl-pyrimidino[2,1a]anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-6,11,13(2H,3H,4H,12H)-trione (**5b**)

6b (1.00 g, 1.74 mmol) and 1-amino-2-aminomethyl-2-*n*-hexyloctane (1b, 840 mg, 3.5 mmol) in ethylene glycol (50 ml) were allowed to react and worked up as described for **3b/4b**. The dye was purified by column separation with chloroform/triethylamine (10:1) and silica gel. The solvent with the pink fluorescent fraction was thoroughly removed by vacuum distillation. The residue was purified by column separation with chloroform/acetic acid (10:1) and silica gel in order to remove a red fluorescent fore-run. A by a second column separation with chloroform/acetone (5:1) and silica gel and a precipitation from a concentrated solution in chloroform with methanol and desiccation in medium vacuo with solid KOH at 40 °C gave 730 mg (54%) of **5b**; *m.p.* 135 °C, R_f (chloroform/silica gel): 0.33, R_f (chloroform/triethyl amine (10:1); silica gel): 0.80, R_f ($CHCl_3$/acetic acid (10:1), silica gel): 0.70. – IR (KBr): ν/cm^{-1} = 2955 (m), 2925 (m), 2857 (m), 1699 (s), 1658 (s), 1623 (s, br), 1598 (s), 1576 (w), 1504 (vw), 1460 (w), 1435 (w), 1405 (m), 1350 (s, br), 1270 (m), 1250 (w), 1215 (vw), 1175 (w), 1128 (w), 1107 (w), 850 (w), 810 (m), 750 (m), 720 (w). – UV ($CHCl_3$): λ_{max}/nm (lg ε) = 542 (4.674), 502 (4.536), 470 (4.221). – Fluorescence ($CHCl_3$): λ_{max}/nm = 560, 593. – ^{1}H NMR (400 MHz/$CDCl_3$): δ/ppm = 0.84 (m, 12H, $4CH_3$), 1.28 (m 36 H, $18CH_2$), 1.88 (m, 2H, 1α-CH_2), 2.26 (m, 2H, 1α-CH_2), 3.61 (s, 2H, CH_2), 3.85 (s, 2H, CH_2), 5.19 (mc, H, CH), 8.52 (mc, 8H, aryl-H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 14.05, 22.61, 26.95, 29.25, 31.73, 32.14, 48.14 (N–CH_2), 54.70 (N–CH), 55.40 (C=N–$\underline{C}H_2$), 121.78, 122.10, 122.95, 123.24, 126.26, 127.52, 128.84, 129.05, 129.34, 129.71, 131.09, 131.84, 132.28, 133.50, 134.71, 142.10 (C=N), 161.41, 163.23, 164.14. – MS (70 eV); *m/z* (%): 780 (12), 779 (23) [M^+], 680 (8), 695 (100) [M^+–C_6H_{12}], 624 (12), 610 (27) (M^+–$2C_6H_{12}$), 512 (22), 428 (12) [M^+–$2C_6H_{12}$ –$C_{13}H_{26}$], 373 (14) [428–C_3H_4N].

$C_{52}H_{65}N_3O_3$	calcd.:	C 80.11	H 8.33	N 5.38
(779.5)	found:	C 79.90	H 8.24	N 5.41.

Bis-(N-(1-hexylheptyl)-perylene-3,4:9,10-tetracarboxylic-bisimide)-N'-yl-methyl)-tridecan (**8**)

6b (2.00 g, 3.53 mmol) and 1-amino-2-aminomethyl-2-*n*-hexyloctane (**1b**, 426 mg, 1.76 mmol) in ethylene glycol (50 ml) were allowed to react and worked up as described for **3b/4b**. The reaction mixture mainly consists of three products with R_f (chloroform/acetic acid (10:1); silica gel) = 0.0 (brown, non fluorescent), R_f = 0.33 (violet, pink fluorescent) and R_f = 0.43 (red, intensely red fluorescent). The dye was purified once by column separation with chloroform/triethylamine (10:1) and silica gel to remove the brown product and then repeatedly with chloroform/acetic acid (10:1) and silica gel to remove the red product to give 70 mg (3%) of bis-(*N*-(1-hexylheptyl)-perylene-3,4:9,10-tetracarboxylic-bisimide)-*N'*-yl-methyl)-tridecan; R_f (chloroform/silica gel): 0.43, R_f (chloroform/triethylamine (10:1); silica gel): 0.80. – IR (KBr): ν/cm^{-1} = 2960 (m), 2925 (s), 2880 (m), 1700 (s), 1660 (s), 1599 (s), 1580 (w), 1540 (m), 1520 (w), 1505 (w), 1470 (w), 1455 (m), 1435 (w), 1405 (m), 1340 (s), 1255 (m), 1170 (m), 1110 (m), 850 (w), 810 (m), 750 (m). – UV ($CHCl_3$): λ_{max}/nm (lg ε) = 528 (5.247), 490 (5.060), 458 (4.640). – Fluorescence ($CHCl_3$): λ_{max}/nm = 535, 575. – ^{1}H NMR (400 MHz/$CDCl_3$): δ/ppm= 0.82 (m, 18H, $6CH_3$), 1.23 (m, 52H, $26CH_2$), 1.83 (mc, 4H, 2α-CH_2), 2.21 (mc, 4H, 2α-CH_2), 4.45 (s, 4H, $2CH_2$), 5.18 (mc, 2H, 2CH), 8.59 (2 mc, 16H, aryl-H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 14.04, 22.59, 26.95, 29.24, 31.77, 31.78, 32.40, 54.79 (1-hexylheptyl-CH), 122.97, 123.24, 123.38, 126.35 131.48, 134.51, 164.44. – Ms (70 eV); *m/z* (%): 1353 (40) [M^+], 1352 (38), 768 (37), 767 (67), 598 (10), 586 (18), 585 (35), 573 (69), 495 (10), 404 (10), 391 (100), 373 (25), 345 (10), 182 (19).

12-(1-Hexylheptyl)-3,3-dioctylpyrimidino[2,1a]anthra-[2,1,9-def:6,5,10-d'e'f']diisoquinolin-6,11,13(2H,3H,4H,12H)-trione (**5c**)

6b (500 mg, 0.876 mmol), 1-amino-2-aminomethyl-2-*n*-octylnonane (**1c**, 527 mg, 1.76 mmol) in ethylene glycol (50 ml) were allowed to react as described for **3b/4b**. The reaction product was precipitated by addition of ethanol and acetic acid to the crude reaction mixture and was collected by vacuum filtration, washed with water, dried at 100 °C for 8 hrs. in the air and purified by column separation with chloroform/silica gel. A red fluorescent by-product (see above) was eluted with chloroform and the dark violet main product which was non-fluorescent in concentrated solution (in diluted solution brightly pink fluorescent) was eluted with chloroform/acetic acid (10:1) and further purified by a separation with a short column (chloroform/silica gel) to give 420 mg (57%) of **5c**; *m.p.* 113 °C, R_f (chloroform/silica gel): 0.48, R_f (chloroform/acetic acid (10:1); silica gel): 0.80. – IR (KBr): ν/cm^{-1} = 2980 (m), 1960 (s), 2860 (s), 1700 (s), 1660 (s, br), 1625 (m), 1600 (s), 1580 (w), 1540 (w), 1470 (s), 1440 (m), 1410 (s), 1350 (s), 1275 (m), 1250 (m), 1190 (s), 1115 (m),

850 (m), 815 (s), 750 (s), 720 (m). – UV ($CHCl_3$): λ_{max}/nm (lg ε) = 542 (4.632), 502 (4.495), 470 (4.078). – Fluorescence ($CHCl_3$): λ_{max}/nm = 560, 592. – ^{1}H NMR (400 MHz/$CDCl_3$): δ/ppm = 0.84 (m, 12 H, $4CH_3$), 1.25 (m, 36H, $18CH_2$), 1.9 (m, 2H, 1α-CH_2), 2.25 (m, 2H, 1α-CH_2), 3.61 (s, 2H, CH_2), 3.85 (s, 2H, CH_2), 5,19 (m, H, CH), 8.41 (m, 8H, aryl-H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 14.09, 22.67, 22.97, 23.87, 27.10, 29.27, 29.30, 29.47, 30.16, 30.37, 31.82, 31.87, 32.47, 32.56, 33.88, 48.10 (N–CH_2), 54.76 (N–CH), 55.16 (C=N–CH_2-), 121.43, 121.68, 122.03, 122.82, 123.08, 126.25, 128.79, 129.56, 131.38, 132.45, 133.48, 134.70, 145.31 (C=N), 161.08 (C=O), 161.35 (C=O), 163.60 (C=O), 164.59 (C=O). – Ms (70 eV); *m/z* (%): 835 (18) [M^+], 722 (100) [$M^+ - C_8H_{17}$], 624 (13), 611 (11), 610 (25) $M^+ - 2C_8H_{17}$), 540 (21), 541 (10), 540 (16), 442 (10), 428 (7) [$M^+ - 2C_8H_{17} - C_{13}H_{26}$], 414 (6), 402 (6), 373 (9) [428– C_3H_4N].

$C_{56}H_{73}N_3O_3$	calcd.:	C 80.49	H 8.73	N 5.02
(835.5)	found:	C 80.57	H 8.99	N 4.83.

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Address for correspondence:
Prof. Dr. H. Langhals
Institut für Organische Chemie der Universität München
Karlstraße 23
D-80333 München
Telefax: +49-(0)-89-5902-483
E-mail: Langhals@lrz.uni-muenchen.de