

Perylene Dyes with High Resistance to Alkali

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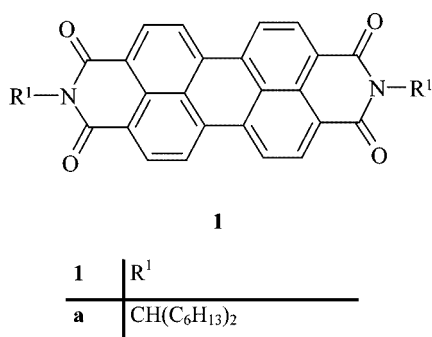
The attachment of a γ -hydroxy alkyl group to a nitrogen atom of perylene-3,4:9,10-tetracarboxylic bisimides results in a persistency to alkaline hydrolysis, even to alkali alcoholates. The solubility of these dyes can be controlled by substituents in the β -position of the alkyl groups so that either highly

stable pigments or dyes for homogeneous solutions with high fluorescence quantum yields are obtained.

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Introduction

Perylene dyes, perylene-3,4:9,10-tetracarboxylic bisimides^[1] such as **1** are well-known for their high thermal (550 °C),^[2] chemical and photochemical persistency. Treatment with concentrated sulphuric acid requires 220 °C for a chemical degradation;^[3] other acids are even less effective.^[1,4] On the other hand, the persistency of the dyes to bases is not so pronounced.^[5,6] Molten KOH and concentrated bleach^[7] do not affect the dyes, however, alcoholic alkali causes solvolysis^[8] of the imide group and a ring-contraction reaction,^[9] respectively. In some cases a partial degradation was found for the application of **1** as vat dyes.^[5] A protection of the dyes against even a severe attack of alkali would be an appreciable improvement.



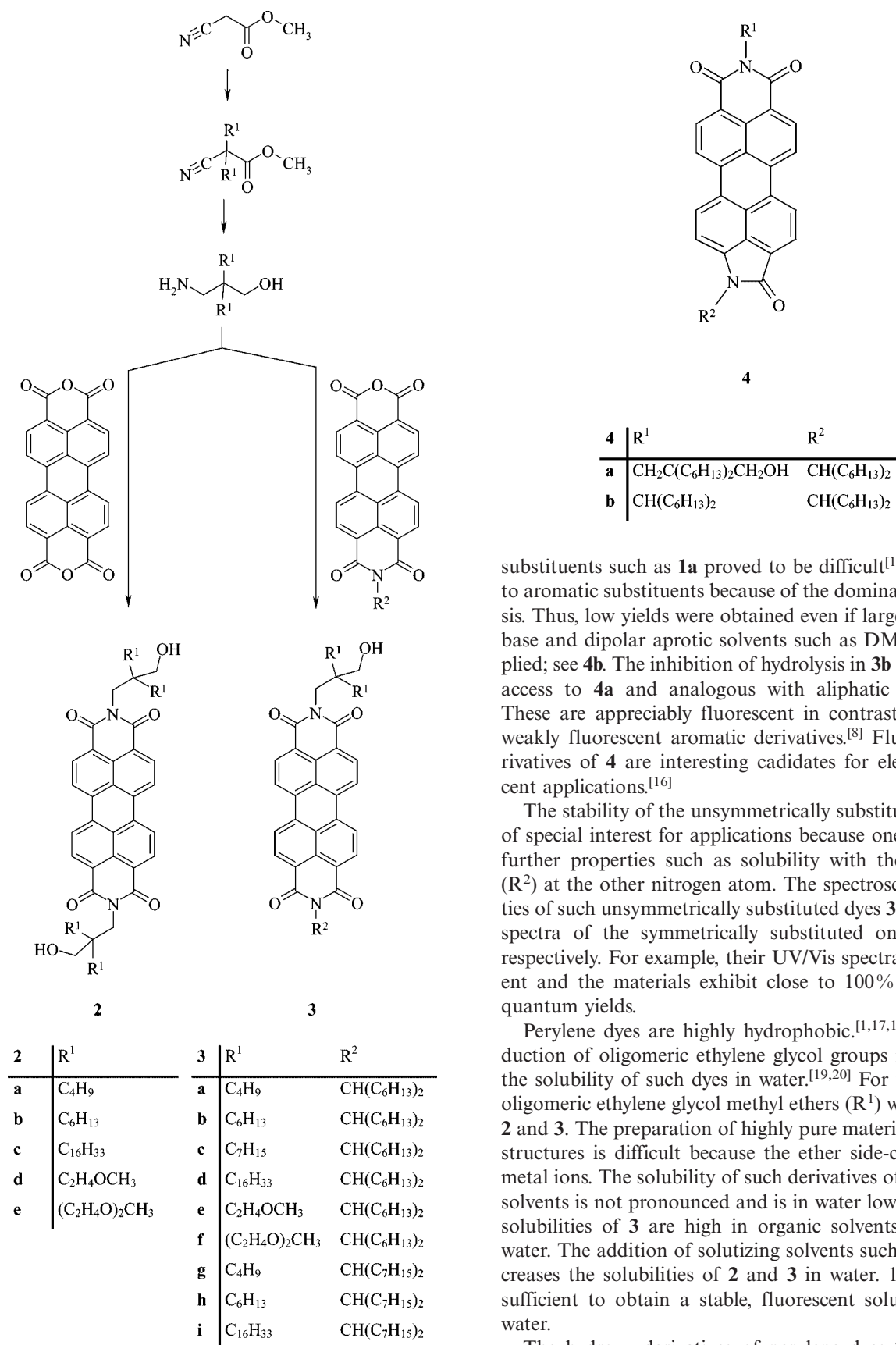
Results and Discussion

The persistency of perylene dyes to alkali can be very much increased by the attachment of γ -hydroxyalkyl groups with a further substitution with geminal alkyl groups at the β -position with respect to the nitrogen atoms of **1**. These dyes cannot be degraded even not by attack of alcoholic

alkali (see Exp. Section). Completely new fields of application are opened for this novel type of perylene dye. The solubility of such dyes with γ -hydroxyalkyl substituents can be controlled by the introduction of long-chain alkyl groups into the β -position of these substituents. The synthesis of the starting materials for such dyes is straight-forward and is suitable, even for bulk quantities: ethyl cyanoacetate is alkylated with *n*-alkyl halogenides and the reaction product reduced by the application of complex hydrides such as lithium aluminium hydride to the hydroxy amines (see Scheme 1). The latter are condensed with perylene-3,4:9,10-tetracarboxylic bisanhydride to give the bisimides **2**. The derivatives of the dyes with short side-chains such as methyl groups exhibit low solubilities, and may be applied as pigments. The solubility increases with the length of the side chains so that soluble dyes like **2b** or **2c** can be prepared. The spectra of the dyes **2** are congruent with the spectra of other alkylated perylene dyes and also fluorescence quantum yields close to 100%^[10] were observed.

The effect of the hydroxy alkyl group on the stability of the bisimides was studied with unsymmetrically substituted perylene bisimides. To this end, perylene dyes were prepared with long-chain secondary alkyl groups “swallow-tail” at the nitrogen atoms such as the 1-hexylheptyl substituent (**1a**)^[11] in order to render the material soluble.^[12] These were transformed to the anhydride carboximides^[8] by partial solvolysis and further condensed with the γ -hydroxy amines mentioned above (see Scheme 1). Surprisingly, these dyes are comparably stable concerning alkaline solvolysis as the symmetrically substituted dyes with two γ -hydroxyalkyl substituents; see the reaction of **3f**. Obviously, the γ -hydroxyalkyl substituent at one nitrogen atom of **3** acts as a general protecting group against hydrolytic attack by alkali. Also with the lower homologue **3b** and prolonged reaction times not even traces of products of hydrolysis could be detected. The inhibition of hydrolysis favours a slow ring-contraction^[13,14] leading to the lactam imide **4a**. This is remarkable because such ring contractions of **1** with aliphatic

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Scheme 1. Synthesis of the perylene bisimides **2** and **3**.

substituents such as **1a** proved to be difficult^[15] in contrast to aromatic substituents because of the dominating hydrolysis. Thus, low yields were obtained even if large amounts of base and dipolar aprotic solvents such as DMSO were applied; see **4b**. The inhibition of hydrolysis in **3b** offers a good access to **4a** and analogous with aliphatic substituents. These are appreciably fluorescent in contrast to the only weakly fluorescent aromatic derivatives.^[8] Fluorescent derivatives of **4** are interesting candidates for electroluminescent applications.^[16]

The stability of the unsymmetrically substituted dyes **3** is of special interest for applications because one can control further properties such as solubility with the substituent (R^2) at the other nitrogen atom. The spectroscopic properties of such unsymmetrically substituted dyes **3** resemble the spectra of the symmetrically substituted ones **2** and **1**, respectively. For example, their UV/Vis spectra are congruent and the materials exhibit close to 100% fluorescence quantum yields.

Perylene dyes are highly hydrophobic.^[1,17,18] The introduction of oligomeric ethylene glycol groups may increase the solubility of such dyes in water.^[19,20] For this purpose, oligomeric ethylene glycol methyl ethers (R^1) were linked to **2** and **3**. The preparation of highly pure materials with such structures is difficult because the ether side-chains collect metal ions. The solubility of such derivatives of **2** in organic solvents is not pronounced and is in water low, whereas the solubilities of **3** are high in organic solvents and low in water. The addition of solutizing solvents such as DMF increases the solubilities of **2** and **3** in water. 10% DMF is sufficient to obtain a stable, fluorescent solution of **3** in water.

The hydroxy derivatives of perylene dyes **2**, and **3** are also of interest for fluorescence labelling because the hydroxy group can be easily transformed to fluorescent esters and ethers, respectively. This is demonstrated by the esterifi-

cation of **3h** and **3i**, respectively, with methacroyl chloride. These are starting materials for macromolecular dyes.

Experimental Section

Alkylation of Methyl Cyanoacetate. General Procedure:^[21,22] A freshly prepared solution of sodium methoxide (46 g, 2.00 mol sodium in 1000 mL of anhydrous methanol) was added dropwise with gentle warming and the exclusion of moisture within 1 h to a mixture of cyanoacetic acid methylester (99 g, 1.00 mol) and 2.00 mol of the corresponding alkyl bromide and then refluxed for 6 h. Methanol was evaporated in weak vacuo and ice water was added until the solution of salts. The organic phase was separated and the aqueous one extracted two times with diethyl ether (2 × 200 mL). The combined organic phases were dried with sodium sulfate, evaporated and distilled from over a 30 cm Vigreux column.

Methyl 2-Butyl-2-cyanohehexanoate: 1-Butyl bromide (43.0 mL, 400 mmol) and methyl cyanoacetate (15.6 mL, 200 mmol) were allowed to react according to the general procedure. Yield 25.5 g (61%), colourless liquid, b.p. 113 °C/0.01 Torr, $n_D^{20} = 1.4360$. IR (film): $\tilde{\nu} = 2985$ s, 2950 s, 2880 s, 2240 w, 1750 s, 1645 w, 1465 m, 1380 w, 1235 s, 1180 m, 1145 m, 725 w cm^{-1} . ^1H NMR (80 MHz/ CCl_4): $\delta = 0.9$ (m, 6 H, 2 CH_3), 1.3 (m, 8 H, 4 CH_2), 1.8 (m, 4 H, 2 CH_2), 3.8 (s, 3 H, CO_2CH_3) ppm. $\text{C}_{12}\text{H}_{21}\text{NO}_2$ (211.1): calcd. C 68.27, H 9.94, N 6.63; found C 68.61, H 10.15, N 6.77.

Methyl 2-Cyano-2-hexyloctanoate: 1-Hexyl bromide (57.0 mL, 400 mmol) and methyl cyanoacetate (15.6 mL, 200 mmol) were allowed to react according to the general procedure. Yield 37.1 g (69%), colourless liquid, b.p. 115 °C/0.06 Torr, $n_D^{20} = 1.4358$. IR (film/KBr): $\tilde{\nu} = 3441$, 2955 m, 2919 s, 2365 w, 2851 s, 1743 s, 1653 w, 1472 s, 1458 m, 1437 w, 1261 m, 1244 m, 1231 m, 719 m cm^{-1} . ^1H NMR (80 MHz/ CCl_4): $\delta = 0.9$ (m, 6 H, 2 CH_3), 1.3 (m, 16 H, 8 CH_2), 1.8 (m, 4 H, 2 CH_2), 3.7 (s, 3 H, CO_2CH_3) ppm.

Methyl 2-Cyano-2-heptylnonanoate: 1-Heptyl bromide (62.8 mL, 400 mmol) and methyl cyanoacetate (15.6 mL, 200 mmol) were allowed to react according to the general procedure. Yield 41.1 g (72%), colourless liquid, b.p. 146 °C/0.03 Torr. IR (film/KBr): $\tilde{\nu} = 3475$ (w), 2956 (s), 2929 (s), 2858 (s), 2243 (m), 1748 (s), 1460 (s), 1379 (m), 1340 (w), 1239 (s), 1180 (m), 1139 (m), 1078 (w), 993 (w), 945 (w), 889 (w), 827 (w), 796 (w), 724 (m) cm^{-1} . ^1H NMR (80 MHz/ CCl_4): $\delta = 3.81$ (s, 3 H, CH_3), 1.81 (m, 2 H, CH_2), 1.55 (m, 4 H, 2 CH_2), 1.20 (m, 18 H, 9 CH_2), 0.80 (t, $J = 6.7$ Hz, 6 H, 2 CH_3) ppm.

Methyl 2-Cyano-2-hexadecyloctadecanoate: 1-Hexadecyl bromide (123 mL, 400 mmol) and methyl cyanoacetate (15.6 mL, 200 mmol) were allowed to react according to the general procedure. Yield 56 g (53%), colourless powder (from diethyl ether and methanol), m.p. 62 °C. IR (KBr): $\tilde{\nu} = 3447$ m, 2945 s, 2917 s, 2850 s, 2365 w, 2245 w, 1745 s, 1472 s, 1457 m, 1437 m, 1263 w, 1246 m, 1231 w, 718 m cm^{-1} . ^1H NMR (80 MHz/ CCl_4): $\delta = 0.9$ (m, 6 H, 2 CH_3), 1.2 (m, 56 H, 28 CH_2), 1.7 (m, 4 H), 3.6 (s, 3 H, CO_2CH_3) ppm. $\text{C}_{36}\text{H}_{69}\text{NO}_2$ (547.3): calcd. C 78.99, H 12.60, N 2.55; found C 78.74, H 12.54, N 2.37.

Preparation of Hydroxyamines by the Reduction of Cyanoacetic Esters. General Procedure:^[23–25] 94 mmol of the corresponding methyl cyanoacetate in anhydrous *tert*-butyl methyl ether (100 mL) was added dropwise within 1 h under argon atmosphere with strong stirring and cooling (less than 10 °C reaction temperature) to lithium aluminium hydride (8.7 g, 0.23 mol) in *tert*-butyl methyl ether (250 mL), refluxed for 1 h, stirred at room temperature for 16 h and quenched by cautious addition of 10% NaOH.^[22] The organic

phase was filtered and the residue extracted three times by refluxing with ether. **2-Aminomethyl-2-butylhexan-1-ol:** Methyl 2-butyl-2-cyanohehexanoate (20.66 g, 97.77 mmol) was allowed to react according to the general procedure. Yield 13.53 g (69%), colourless liquid, b.p. 98 °C/0.01 Torr, $n_D^{20} = 1.4652$. IR (film): $\tilde{\nu} = 3390$ m br, 2980 s, 2920 s, 2880 s, 1600 w br, 1475 m, 1380 m, 1055 s, 740 m cm^{-1} . ^1H NMR (80 MHz/ CCl_4): $\delta = 0.8$ (m, 6 H, 2 CH_3), 1.2 (m, 12 H, 6 CH_2), 2.6 (s, 2 H, 1 CH_2), 3.4 (s, 2 H, 1 CH_2) ppm. $\text{C}_{11}\text{H}_{25}\text{NO}$ (187.1): calcd. C 70.61, H 13.36, N 4.48; found C 70.51, H 13.35, N 4.47.

2-Aminomethyl-2-hexyloctan-1-ol: Methyl 2-cyano-2-hexyloctanoate (37.1 g, 139 mmol) was allowed to react according to the general procedure. Yield 14 g (41%), viscous, colourless liquid, b.p. 115 °C/0.03 Torr, $n_D^{20} = 1.4644$. IR (film): $\tilde{\nu} = 3885$ m br, 3300 m, 2959 m, 2925 s, 2873 s, 1615 w, 1470 m, 1457 w, 1381 w, 1140 w, 1064 m, 812 m, 785 w, 725 m cm^{-1} . ^1H NMR (80 MHz/ CCl_4): $\delta = 0.75$ (m, 6 H, 2 CH_3), 1.15 (m, 20 H, 10 CH_2), 2.60 (s br, 2 H, 1 CH_2), 3.40 (s, 2 H, 1 CH_2) ppm. $\text{C}_{15}\text{H}_{33}\text{NO}$ (243.2): calcd. C 74.09, H 13.57, N 5.77; found C 74.55, H 13.44, N 6.29.

2-Aminomethyl-2-heptylnonan-1-ol: Methyl 2-cyano-2-hexyloctanoate (41.1 g, 154 mmol) and lithium aluminium hydride (13.4 g, 309 mmol) were allowed to react according to the general procedure. Yield 34 g (86%), viscous, colourless liquid, b.p. 162 °C/0.02 mbar IR (film): $\tilde{\nu} = 3360$ (s, br.), 3303 (s), 2954 (s), 2926 (s), 2856 (s), 1581 (m), 1574 (m), 1464 (s), 1455 (s), 1378 (m), 1336 (m), 1053 (m), 956 (w), 819 (w), 765 (w), 723 (m) cm^{-1} . ^1H NMR (CDCl_3): $\delta = 3.41$ (s, 2 H, CH_2), 2.62 (s, 2 H, CH_2), 1.15 (m, 24 H, 12 CH_2), 0.79 (t, $J = 6.7$ Hz, 6 H, 2 CH_3) ppm. ^{13}C NMR (CDCl_3): $\delta = 70.4$ ($\text{CH}_2\text{-OH}$), 49.7 ($\text{CH}_2\text{-NH}_2$), 40.2 (quat. C), 32.2, 32.1, 30.9, 29.6, 23.2, 23.0, 22.7 (12 CH_2), 14.4 (2 CH_3) ppm.

2-Aminomethyl-2-hexadecyloctadecan-1-ol: Methyl 2-cyano-2-hexadecyloctadecanoate (28.30 g, 51.70 mmol) was allowed to react according to the general procedure. Yield 25.1 g (92%), colourless solid, m.p. 48 °C from methanol. IR (film): $\tilde{\nu} = 3445$ m br, 2920 s, 2953 s, 2850 s, 1617 w, 1475 m, 1465 m, 1383 m, 1350 w, 1130 m, 1074 m, 1015 w, 950 w, 812 w cm^{-1} . ^1H NMR (400 MHz/ CDCl_3): $\delta = 0.88$ (m, 6 H, 2 CH_3), 1.26 (m, 60 H, 30 CH_2), 2.77 (s, 2 H, 1 CH_2), 3.56 (s, 2 H, 1 CH_2) ppm. $\text{C}_{35}\text{H}_{73}\text{NO}$ (523.3): calcd. C 80.32, H 13.94, N 2.67; found C 80.36, H 13.99, N 2.66.

2-Aminomethyl-4-methoxy-2-(2-methoxyethyl)butan-1-ol: Methyl 2-cyano-4-methoxy-2-(2-methoxyethyl)butanoate (10.67 g, 49.60 mmol) and lithium aluminium hydride (5.70 g, 150 mmol) were allowed to react according to the general procedure. Yield 5.5 g (58%), colourless liquid, b.p. 120 °C/0.07 Torr. IR (film): $\tilde{\nu} = 3400$ m br, 2925 s, 2885 s, 1645 m br, 1565 m, 1455 s, 1380 m, 1360 m, 1250 m, 1200 s, 1110 s, 1030 m, 850 m cm^{-1} . ^1H NMR (80 MHz/ CCl_4): $\delta = 1.5$ (m, 4 H, 2 CH_2), 2.5 (s, 2 H, 1 CH_2), 2.6 (s, 2 H, NH_2), 3.2 (s, 6 H, 2 OCH_3), 3.4 (m, 6 H, 3 CH_2) ppm. $\text{C}_9\text{H}_{21}\text{NO}_3$ (191.1): calcd. C 56.57, H 10.99, N 7.32, found C 56.82, H 10.92, N 7.30.

2-Aminomethyl-4-(2-methoxyethoxy)-2-[2-(2-methoxyethoxy)ethyl]butan-1-ol: Methyl 2-cyano-4-(2-methoxyethoxy)-2-[2-(2-methoxyethoxy)ethyl]butanoate (14.45 g, 47.67 mmol) and LiAlH_4 (5.70 g, 150 mmol) was allowed to react according to the general procedure. Yield 5.8 g (41%), colourless liquid, b.p. 110 °C/0.07 Torr. IR (film): $\tilde{\nu} = 3395$ m br, 2920 s, 2880 s, 1640 m br, 1570 m, 1455 s, 1385 m, 1365 m, 1300 w, 1245 w, 1200 s, 1115 m, 1035 m, 980 w, 900 w, 850 m cm^{-1} . ^1H NMR (80 MHz/ CCl_4): $\delta = 0.9$ (s, 2 H, NH_2), 1.5 (m, 4 H, 2 CH_2), 2.5 (s, 2 H, 1 CH_2), 3.25 (s, 6 H, 2 OCH_3), 3.5 (m, 14 H, 7 CH_2) ppm. $\text{C}_{13}\text{H}_{29}\text{NO}_5$ (278.1): calcd. C 55.94, H 10.39, N 5.01; found C 55.45, H 10.67, N 4.81.

Alkylation of Cyanoacetic Acid by Means of Sodium Hydride.^[22]

General Procedure: Methyl cyanoacetate (8.9 g, 90 mmol) was added under argon atmosphere dropwise with stirring to a suspension of sodium hydride (4.36 g, 180 mmol) in DMSO (80 mL), gently warmed for 15 min, allowed to react with dropwise added of the corresponding chloro glycol (180 mmol) with stirring, stirred at 90 °C for further 2 h (brownish mixture), decanted from the excess of sodium hydride, poured into ice water (500 mL), extracted with diethyl ether (3 × 100 mL), dried with magnesium sulfate, evaporated and distilled in medium vacuum.

Methyl 2-Cyano-4-methoxy-2-(2-methoxyethyl)butanoate: Methyl cyanoacetate (8.90 g, 90.0 mmol) and 2-chloro-1-methoxyethane (17.0 g, 180 mmol) were allowed to react with sodium hydride according to the general procedure. Yield 10.7 g (54%), b.p. 78 °C/0.04 Torr. IR (film): $\tilde{\nu}$ = 2920 s, 2860 s, 2835 w, 2240 m, 1749 s, 1475 w, 1390 m, 1330 m, 1300 w, 1240 s, 1200 s, 1160 m, 1120 s, 1040 w, 985 w, 895 m, 825 m cm⁻¹. ¹H NMR (80 MHz/CCl₄): δ = 2.1 (m_c, 4 H, 2 CH₂), 3.2 (s, 6 H, 2 OCH₃), 3.45 (m_c, 4 H, 2 CH₂), 3.6 (s, 3 H, CO₂CH₃) ppm. C₁₀H₁₇NO₄ (215.1): calcd. C 55.84, H 7.90, N 6.50; found C 55.84, H 7.94, N 6.70.

Methyl 2-Cyano-4-(2-methoxyethoxy)-2-[2-(2-methoxyethoxy)ethyl]butanoate: methyl cyanoacetate (24.1 g, 243 mmol) and 1-chlorodiethylene glycol methyl ether (67.3 g, 486 mmol) were allowed to react with sodium hydride according to the general procedure. Yield 14.5 g (20%), b.p. 120 °C/0.01 Torr. IR (film): $\tilde{\nu}$ = 2960 m, 2940 m, 2200 w, 1750 s, 1450 m, 1400 w, 1398 m, 1280 m, 1240 m, 1180 w, 1020 w, 940 w, 850 w cm⁻¹. ¹H NMR (80 MHz/CCl₄): δ = 2.15 (m_c, 4 H, 2 CH₂), 3.2 (s, 6 H, OCH₃), 3.45 (m_c, 12 H, 6 CH₂), 3.6 (s, 3 H, CO₂CH₃) ppm. C₁₄H₂₅NO₆ (303.1): calcd. C 55.47, H 8.24, N 4.61; found C 55.79, H 8.55, N 4.40.

Synthesis of Symmetrically Substituted Perylene Dyes. General Procedure: Ethylene glycol (50 mL), perylene-3,4,9,10-tetracarboxylic bisanhydride (1.0 g, 2.55 mmol) and the corresponding amine (10 mmol) were stirred under argon atmosphere at 160 °C for 2 h, cooled to room temperature and diluted with methanol (20 mL). The precipitated dye was collected by vacuum filtration (D4 glass filter) treated with boiling aqueous potassium carbonate (10%, light green fluorescence), collected by vacuum filtration, washed with distilled water and dried in air (130 °C, 8 h).

2,9-Bis[2-butyl-2-(hydroxymethyl)hexyl]anthra[2,1,9-def;6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (2a): Perylene-3,4,9,10-tetracarboxylic bisanhydride (3.52 g, 6.14 mmol), 2-aminomethyl-2-butylhexan-1-ol (4.30 g, 23.0 mmol) and ethylene glycol (50 mL) were allowed to react according to the general procedure and purified by an extractive recrystallization^[26] from toluene (the dye is only sparingly soluble in chloroform and is firmly adsorbed to silica gel so that a chromatographic purification becomes difficult). Yield 3.74 g (83%), red powder with a metallic lustre, m.p. > 300 °C. IR (KBr): $\tilde{\nu}$ = 3480 m, 2985 m, 2970 m, 1700 s, 1650 s, 1600 s, 1580 w, 1455 m, 1410 m, 1375 m, 1345 m, 1255 w, 1035 w, 815 w, 755 w cm⁻¹. C₄₆H₅₄N₂O₆ (730.4): calcd. C 75.63, H 7.39, N 3.83; found C 75.31, H 7.38, N 4.02.

2,9-Bis[2-hexyl-2-(hydroxymethyl)octyl]anthra[2,1,9-def;6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (2b): Perylene-3,4,9,10-tetracarboxylic bisanhydride (1.48 g, 3.77 mmol), 2-aminomethyl-2-hexyloctan-1-ol (5.48 g, 22.5 mmol) in ethylene glycol (50 mL) were allowed to react according to the general procedure and two times purified by column separation (silica gel, CHCl₃/acetic acid, 10:1 and CHCl₃). The product was precipitated with methanol/chloroform (2:1), collected by vacuum filtration, dried in air and extractively recrystallized^[26] from distilled toluene. Yield 2.58 g (80%), dark red powder with a strong copper-like metallic lustre, m.p. >

300 °C. *R_f* (silica gel, CHCl₃/acetic acid, 10:1) = 0.72. IR (KBr): $\tilde{\nu}$ = 3490 m, 2980 m, 2940 m, 2880 m, 1700 s, 1650 s, 1600 s, 1580 m, 1450 m, 1420 m, 1365 m, 1350 s, 1265 m, 1190 m, 1145 w, 1060 m, 850 w, 820 m, 805 w cm⁻¹. ¹H NMR (400 MHz/CDCl₃): δ = 0.85 (t, 12 H, 4 CH₃), 1.30 (m_c, 40 H, 20 CH₂), 3.22 (s, 4 H, 2 CH₂-OH), 4.21 (s, 4 H, 2 CH₂), 8.70 (m_c, 8 H, aromatic) ppm. ¹³C NMR (400 MHz/CDCl₃): δ = 14.12 (CH₃), 22.73 (CH₂), 22.95 (CH₂), 30.31 (CH₂), 32 (CH₂), 43.11 (N-CH₂), 123.09, 123.35, 132.05, 134.84, 164.85 ppm. UV/Vis (CHCl₃): $\lambda_{\max}$ (ϵ) = 528 (89340), 492 (53250), 460 (19520) nm. Fluorescence (CHCl₃): $\lambda_{\max}$ = 530, 570 nm. MS (70 eV), *m/z* (%): 846 (3) [*M*⁺], 843 (54), 842 (89) [*M*⁺ - 2 H], 812 (100) [*M*⁺ - 3 H - CH₃O], 782 (25), 617 (25), 619 (3) [*M*⁺ - C₁₅H₃₁O], 600 (13), 587 (19), 392 (24), 391 (53), 390 (58), 373 (16), 345 (10), 69 (18). C₅₄H₇₀N₂O₆ (846.5): calcd. C 76.92, H 8.37, N 3.32; found C 76.82, H 8.80, N 3.36.

2,9-Bis[2-hexadecyl-2-(hydroxymethyl)octadecyl]anthra[2,1,9-def;6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (2c): Perylene-3,4,9,10-tetracarboxylic bisanhydride (1.00 g, 2.55 mmol), 2-aminomethyl-2-hexadecyloctadecan-1-ol (13.30 g, 25.41 mmol) in ethylene glycol (50 mL) were allowed to react according to the general procedure and two times purified by column separation (silica gel, CHCl₃/acetic acid, 10:1 and CHCl₃). The product was precipitated with methanol/chloroform,(2:1) collected by vacuum filtration, dried in air and extractively recrystallized^[26] from distilled toluene. Yield 3.00 g (83%), red powder, m.p. 259 °C. *R_f* (silica gel/CHCl₃) = 0.22. IR (KBr): $\tilde{\nu}$ = 2940 s, 2880 m, 1700 s, 1649 s, 1615 m, 1590 m, 1475 m, 1450 m, 1410 m, 1370 m, 1349 s, 1265 m, 1035 m, 820 m, 760 m cm⁻¹. ¹H NMR (400 MHz/CDCl₃): δ = 0.80 (m_c, 12 H, 4 CH₃), 1.25 (m_c, 120 H, 60 CH₂), 3.20 (s, 4 H, 2 CH₂-OH), 4.21 (s, 4 H, 2 CH₂), 8.70 (m_c, 8 H, aromatic) ppm. UV/Vis (CHCl₃): $\lambda_{\max}$ (ϵ) = 528 (84452), 490 (52713), 460 (19520) nm. Fluorescence (CHCl₃): $\lambda_{\max}$ = 532, 578 nm. MS (70 eV), *m/z* (%): 1403 (14) [*M*⁺], 1373 (11) [*M*⁺ - CH₃O], 910 (3) [*M*⁺ - C₃₄H₆₉O], 897 (29), 896 (5), 893 (10), 892 (15), 880 (10), 418 (12), 417 (38) [*M*⁺ - 2 C₃₄H₆₉O], 405 (30), 404 (94), 403 (92), 390 (10), 389 (55), 372 (10), 125 (11), 111 (28), 97 (58), 96 (10), 83 (66). C₉₄H₁₅₀N₂O₆ (1402.9) calcd. C 80.47, H 10.69, N 1.99; found C 80.63, H 10.70, N 2.04.

2,9-Bis[2-(hydroxymethyl)-4-methoxy-2-(2-methoxyethyl)butyl]anthra[2,1,9-def;6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (2d): Perylene-3,4,9,10-tetracarboxylic bisanhydride (0.18 g, 0.46 mmol), 2-aminomethyl-4-methoxy-2-(2-methoxyethyl)butan-1-ol (0.87 g, 0.46 mol) in ethylene glycol (50 mL) were allowed to react according to the general procedure and two times purified by column separation (silica gel, CHCl₃/acetic acid, 10:1 and CHCl₃). The product was precipitated with methanol/chloroform,(2:1) collected by vacuum filtration, dried in air and extractively recrystallized^[26] from distilled toluene. Yield 190 mg (56%), red powder, m.p. > 300 °C. *R_f* (Al₂O₃, CHCl₃/acetic acid, 10:1) = 0.58. IR (KBr): $\tilde{\nu}$ = 3475 m, 2935 s, 2875 m, 1695 s, 1648 s, 1599 s, 1575 m, 1505 w, 1489 m, 1400 s, 1348 s, 1255 m, 1180 w, 1125 s, 1050 w, 1020 w, 975 w, 875 w, 820 m, 750 m cm⁻¹. ¹H NMR (400 MHz/CDCl₃): δ = 1.72 (m_c, 8 H, 4 CH₂), 3.20 (s, 4 H, 2 CH₂OH), 3.36 (m, 12 H, 4 O-CH₃), 3.58 (m_c, 8 H, 4 O-CH₂), 4.29 (s, 4 H, 2 N-CH₂), 8.57 (m_c, 8 H, aromatic) ppm. ¹³C NMR (CDCl₃): δ = 27.01 (CH₂), 33.20 (CR₄), 49.45 (OCH₃), 58.71 (N-CH₂), 68.84 (CH₂-OH and CH₂-O), 123.08, 123.34, 126.30, 131.96, 134.70, 164.71. UV/Vis (CHCl₃): $\lambda_{\max}$ (ϵ) = 528 nm (73381), 489 (44671), 460 (16350) ppm. Fluorescence (CHCl₃): $\lambda_{\max}$ = 534, 577 nm. MS (70 eV), *m/z* (%): 738 (27) [*M*⁺], 706 (64) [*M*⁺ - CH₃OH], 674 (24), 631 (15), 565 (14) [*M*⁺ - C₉H₁₇O₃], 533 (13), 457 (14), 419 (11), 406 (17), 405 (53), 404 (100), 392 (29), 390 (60), 376 (15), 373 (36), 123 (11), 109 (31), 82 (19). C₄₂H₄₆N₂O₁₀ (738.3): calcd. C 68.31, H 6.23, N 3.79; found C 68.88, H 5.91, N 3.71.

2,9-Bis-{2-(hydroxymethyl)-4-(2-methoxyethoxy)-2-[2-(2-methoxyethoxy)ethyl]butyl}anthra[2,1,9-def;6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (2e): perylene-3,4,9,10-tetracarboxylic bisanhydride (180 mg, 0.46 mmol) and 2-aminomethyl-4-(2-methoxyethoxy)-2-[2-(2-methoxyethoxy)ethyl]butan-1-ol (1.28 g, 460 mmol) in ethylene glycol (50 mL) were allowed to react according to the general procedure and purified by column separation (alumina, CHCl₃/acetic acid, 10:1), dissolved in a small amount of chloroform, precipitated with *n*-pentane and dried in air (130 °C). Yield 100 mg (24%), m.p. > 300 °C. *R_f* (Al₂O₃, CHCl₃/acetic acid, 10:1) = 0.66. IR (KBr): $\tilde{\nu}$ = 3455 m, 2935 m, 2925 m, 1696 s, 1665 s, 1599 m, 1575 w, 1445 w, 1405 m, 1345 m, 1300 m, 1260 w, 1120 m, 850 w, 810 m, 750 m cm⁻¹. ¹H NMR (400 MHz/CDCl₃): δ = 1.85 (m_c, 8 H, 4 CH₂), 2.20 (m_c, 2 H, 2OH), 3.20 (s, 4 H, 2 CH₂-OH), 3.39 (s, 12 H, 4 O-CH₃), 3.65 (m_c, 24 H, 12 CH₂), 4.23 (m_c, 4 H, 2 CH₂), 8.6 (m_c, 8 H, aromatic) ppm. ¹³C NMR (400 MHz/CDCl₃): δ = 29.73 (CH₂), 38.03 (C), 59.06 (N-CH₂), 69.42 (CH₂-OH), 70.13, 71.94 [CH₂-O-CH₂], 122.99, 123.22, 131.67, 134.62, 163.96 (C=O) ppm. UV/Vis (CHCl₃): $\lambda_{\max}$ (ϵ) = 527 (74160), 490 (42130), 457 (17970) nm. Fluorescence (CHCl₃): $\lambda_{\max}$ = 534, 574 nm. MS (70 eV), *m/z* (%): 653 (21) [*M*⁺ - C₁₃H₂₅O₅], 634 (23), 558 (16), 534 (18), 475 (27), 458 (10), 404 (17), 391 (36), 373 (28), 345 (24), 275 (10), 142 (10). C₅₀H₆₂N₂O₁₄ (914.2) calcd. C 65.67, H 6.78, N 3.06; found C 66.44, H 5.95, N 3.35.

9-(1-Heptyloctyl)-2-(2-hydroxyethyl)anthra[2,1,9-def;6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone: 9-(1-Heptyloctyl)-1*H*-2-benzopyrano[6',5',4':10,5,6]anthra[2,1,9-def]isoquinoline-1,3,8,10(9*H*)-tetrone^[8] (1.20 g, 1.99 mmol) and 2-ethanolamine (2.00 g, 32.8 mmol) in ethylene glycol (50 mL) were allowed to react according to the general procedure, suspended in methanol (50 mL), collected by vacuum filtration (D4 glass filter), dried in air (130 °C, 8 h), purified by column separation over a short column (neutral alumina, 40 cm, CHCl₃ for removing the starting material and acetic acid), dried in air (120 °C, 8 h, red powder), further purified by column separation (silica gel, CHCl₃/acetic acid, 10:1), extractively recrystallized^[26] from distilled toluene and dried in medium vacuum. Yield 620 mg (51%), red powder, m.p. >300 °C. *R_f* (silica gel, CHCl₃/acetic acid, 10:1) = 0.16. IR (KBr): $\tilde{\nu}$ = 3550 br. m, 3000 s, 2920 s, 1698 s, 1665 s, 1648 s, 1600 s, 1590 s, 1470 w, 1440 m, 1402 s, 1350 s, 1255 m, 1180 m, 1120 w, 1040 w, 850 m, 815 s, 740 s cm⁻¹. ¹H NMR (400 MHz/CDCl₃): δ = 0.82 (m, 12 H, 4 CH₃), 1.25 (m_c, 20 H, 10 CH₂), 1.90 (m_c, 2 H, 1 α -CH₂), 2.25 (m_c, 2 H, 1 α -CH₂), 3.20 (d, 2 H, CH₂-OH), 4.20 (s, 2 H, 1 CH₂), 5.20 (m_c, 1 H, 1 CH), 8.64 (m_c, 8 H, aromatic) ppm. ¹³C NMR (CDCl₃): δ = 14.06 (2 CH₃), 22.62, 27.00, 29.23, 29.52, 31.81, 32.38, 42.96 (1 N-CH₂), 54.86 (1 N-CH), 61.76 (1 CH₂-OH), 122.99, 131.74, 134.23, 135.09, 164.29 (4 C=O) ppm. UV/Vis (CHCl₃): $\lambda_{\max}$ (ϵ) = 528 (82280), 490 (54370), 460 (18630) nm. Fluorescence (CHCl₃): $\lambda_{\max}$ = 535, 575 nm. MS (70 eV), *m/z* (%): 645 (25), 644 (55) [*M*⁺ + 1], 627 (10) [*M*⁺ - OH], 435 (61) [*M*⁺ - C₁₅H₃₀], 434 (56), 391 (100) [*M*⁺ - C₁₅H₃₀ - C₂H₄O], 390 (43), 373 (12), 345 (11). C₄₁H₄₄N₂O₅ (642.7): calcd. C 76.61, H 6.84, N 4.35, found C 76.28, H 6.93, N 4.47.

2-[2-Butyl-2-(hydroxymethyl)hexyl]-9-(1-hexylheptyl)anthra[2,1,9-def;6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (3a): 9-(1-Hexylheptyl)-1*H*-2-benzopyrano[6',5',4':10,5,6]anthra[2,1,9-def]isoquinoline-1,3,8,10(9*H*)-tetrone^[8] (760 mg, 1.33 mmol) and 2-aminomethyl-2-butylhexan-1-ol (790 mg, 3.96 mmol) in ethylene glycol (50 mL) were allowed to react according to the general procedure, purified two times by column separation (silica gel, CHCl₃/acetic acid, 10:1), evaporated and extractively^[26] recrystallized from toluene. Yield 720 mg (74%) red powder. *R_f* (silica gel, CHCl₃) = 0.1. *R_f* (silica gel, CHCl₃/acetic acid, 10:1) = 0.56. IR (KBr): $\tilde{\nu}$ = 3458

m, 2980 s, 2870 s, 1700 s, 1660 s, 1600 s, 1590 m, 1450 m, 1410 s, 1350 s, 1260 s, 1180 m, 860 m, 815 s, 750 s cm⁻¹. ¹H NMR (400 MHz/CDCl₃): δ = 0.81 (t, 6 H, 2 CH₃), 0.91 (t, 6 H, 2 CH₃), 1.27 (m_c, 32 H, 16 CH₂), 1.85 (m_c, 2 H, 1 α -CH₂), 2.22 (m, 2 H, 1 α -CH₂), 3.20 (s, 2 H, CH₂OH), 4.18 (s, 2 H, CH₂), 5.18 (m_c, 1 H, CH), 8.56 (m_c, 8 H, aromatic) ppm. ¹³C NMR (400 MHz/CDCl₃): δ = 14.05 (2 CH₃), 14.13 (2 CH₃), 22.61, 23.67, 25.17, 26.99, 29.24, 31.69, 31.79, 32.40, 43.0 (quat. C), 43.65 [N-CH₂], 54.89 (N-CH), 65.69 [CH₂-OH], 122.71, 122.94, 123.23, 126.26, 129.26, 129.49, 131.05, 131.87, 134.02, 134.95, 164.80 (4 C=O, perylene) ppm. UV/Vis (CHCl₃): $\lambda_{\max}$ (ϵ) = 528 (81650), 490 (51130), 458 (19160) nm. Fluorescence (CHCl₃): $\lambda_{\max}$ = 535, 575 nm. MS (70 eV), *m/z* (%): 743 (50), 742 (100) [*M*⁺], 713 (26), 712 (51) [*M*⁺ - CH₂O], 573 (23), 572 (10) [*M*⁺ - C₁₁H₂₂O], 561 (10) [*M*⁺ - C₁₃H₂₆], 530 (8), 404 (78), 391 (62), 390 (78), 373 (19), 345 (13). C₄₈H₅₈N₂O₅ (742.4) calcd. C 77.64, H 7.81, N 3.77; found C 77.04, H 7.75, N 3.87.

2-(1-Hexylheptyl)-9-[2-hexyl-2-(hydroxymethyl)octyl]anthra[2,1,9-def;6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (3b): 9-(1-hexylheptyl)-1*H*-2-benzopyrano[6',5',4':10,5,6]anthra[2,1,9-def]isoquinoline-1,3,8,10(9*H*)-tetrone^[8] (1.48 g, 2.58 mmol) and 2-aminomethyl-2-hexyloctan-1-ol (1.21 g, 5.00 mmol) in ethylene glycol (50 mL) were allowed to react according to the general procedure, purified by column separation (silica gel, CHCl₃/acetic acid, 10:1 and silica gel, CHCl₃), evaporated and extractively^[26] recrystallized from toluene. Yield 939 mg (47%), m.p. >300 °C. *R_f* (silica gel, CHCl₃) = 0.16. *R_f* (silica gel, CHCl₃/acetic acid, 10:1) = 0.83. IR (KBr): $\tilde{\nu}$ = 2954 m br, 2927 m, 2856 m, 1697 s, 1658 s, 1600 m, 1580 w, 1506 w, 1458 w, 1440 m, 1405 m, 1350 s, 1287 w, 1249 m, 1171 w, 1135 w, 1110 w, 1060 w, 855 w, 810 m, 745 m cm⁻¹. ¹H NMR (400 MHz/CDCl₃): δ = 0.83 (t, 6 H, 2 CH₃), 0.90 (t, 6 H, 2 CH₃), 1.30 (m_c, 36 H, 18 CH₂), 1.95 (m_c, 2 H, 1 α -CH₂), 2.22 (m_c, 2 H, 1 α -CH₂), 3.21 (s, 2 H, CH₂-OH), 4.20 (s, 2 H, CH₂), 5.18 (m_c, 1 H, 1 CH), 8.63 (m_c, 8 H, aromatic) ppm. ¹³C NMR (CDCl₃): δ = 14.06 (2 CH₃), 14.13 (2 CH₃), 22.63, 22.77, 23.27, 29.27, 30.36, 31.82, 31.91, 32.06, 32.44, 43.14 (quat. C), 43.70 [N-CH₂], 54.90 (N-CH), 65.75 [CH₂-OH], 122.86, 123.05, 123.34, 126.45, 126.50, 129.44, 129.62, 132.05, 135.17, 164.93 ppm. UV/Vis (CHCl₃): $\lambda_{\max}$ (ϵ) = 527 (89447), 489 (51798), 458 (19190) nm. Fluorescence (CHCl₃): $\lambda_{\max}$ (*I_{rel}*) = 532.1 (1.00), 572.0 (0.43), 620.2 (0.05) nm. MS (70 eV), *m/z* (%): 800 (17), 799 (60), 798 (100) [*M*⁺], 784 (3), 783 (5), 782 (10), 770 (10), 769 (33), 768 (56) [*M*⁺ - CH₂O], 617 (7) [*M*⁺ - C₁₃H₂₆], 616 (3), 586 (17), 585 (7) 574 (13), 573 (30), 572 (19) [*M*⁺ - C₁₅H₃₀O], 406 (10), 404 (79), 391 (73), 390 (99), 373 (18), 345 (10), 197 (17), 196 (12). C₅₂H₆₆N₂O₅ (798.5): calcd. C 78.21, H 8.26, N 3.50; found C 77.86, H 8.27, N 3.54.

2-[2-Heptyl-2-(hydroxymethyl)nonyl]-9-(1-hexylheptyl)anthra[2,1,9-def;6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (3c): 9-(1-Hexylheptyl)-1*H*-2-benzopyrano[6',5',4':10,5,6]anthra[2,1,9-def]isoquinoline-1,3,8,10(9*H*)-tetrone^[8] (500 mg, 0.87 mmol) and 2-aminomethyl-2-heptylnonan-1-ol (780 mg, 2.6 mmol) in ethylene glycol (25 mL) were allowed to react according to the general procedure (160 °C, 4 h), purified by column separation (silica gel, CHCl₃/ethanol, 10:1). Yield 520 mg (70%). IR (KBr): $\tilde{\nu}$ = 3452 (s), 2957 (s), 2933 (s), 2871 (m), 1702 (s), 1656 (s), 1595 (s), 1579 (m), 1467 (w), 1442 (m), 1404 (s), 1370 (m), 1338 (s), 1253 (m), 1218 (w), 1182 (w), 1117 (w), 1047 (w), 1028 (w), 869 (w), 811 (m), 796 (w), 750 (w) cm⁻¹. MS (70 eV), *m/z* (%): 827 (54) [*M*⁺ + 1], 826 (92) [*M*⁺], 796 (51) [*M*⁺ - CH₂O], 573 (24) [*M*⁺ + 1 - C₁₇H₃₄O], 572 (13) [*M*⁺ - C₁₇H₃₄O], 404 (60) [*M*⁺ - C₁₃H₂₆ - C₁₆H₃₂O], 390 (52) [*M*⁺ - C₁₃H₂₆ - C₁₇H₃₄], 353 (100), 337 (11), 229 (30).

2-[2-Hexadecyl-2-(hydroxymethyl)octadecyl]-9-(1-hexylheptyl)-anthra[2,1,9-def;6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (3d):

9-(1-Hexylheptyl)-1*H*-2-benzopyrano[6',5',4':10,5,6]anthra[2,1,9-*def*]isoquinoline-1,3,8,10(9*H*)-tetrone^[8] (1.45 g, 2.53 mmol) and 2-aminomethyl-2-hexadecyloctadecan-1-ol (5.23 g, 10 mmol) in ethylene glycol (50 mL) were allowed to react according to the general procedure. The reaction product forms an oily layer after cooling becoming solid below 4 °C. This material was collected, washed with distilled water and methanol and dried in air at 90 °C for 8 h, purified twice by column separation (silica gel, CHCl₃) and recrystallized from methanol/chloroform, 2:1. Yield 1.93 mg (71%), red powder, m.p. 176 °C. *R*_f (silica gel, CHCl₃) = 0.41. IR (KBr): $\tilde{\nu}$ = 2924 m, 2854 m, 1700 s, 1675 m, 1553 m, 1598 m, 1616 w, 1595 m, 1577 m, 1515 w, 1465 w, 1457 m, 1429 m, 1339 m, 1254 m, 1176 m, 1107 m, 809 s, 746 m cm⁻¹. ¹H NMR (400 MHz/CDCl₃): δ = 0.81 (t, 6 H, 2 CH₃), 0.83 (t, 6 H, 2 CH₃), 1.22 (m_c, 76 H, 38 CH₂), 1.83 (m_c, 2 H, 1 α -CH₂), 2.22 (m_c, 2 H, 1 α -CH₂), 3.20 (s, 2 H, CH₂-OH), 4.19 (s, 2 H, CH₂), 5.18 (m_c, 1 H, 1 CH), 8.68 (m_c, 8 H, aromatic) ppm. ¹³C NMR (CDCl₃): δ = 14.06 (2 CH₃), 14.13 (2 CH₃), 22.64, 22.74, 23.03, 27.01, 29.28, 29.43, 29.69, 29.73, 29.79, 29.80, 30.70, 31.83, 31.99, 32.06, 32.44, 43.14 (quat. C), 43.70 [N-CH₂], 54.90 (N-CH), 122.86, 123.86, 123.03, 123.31, 126.46, 126.48, 129.43, 129.69, 132.03, 134.21, 135.14, 164.90 ppm. UV/Vis (CHCl₃): $\lambda_{\max}$ (ϵ) = 528 (85140), 490 (52740), 459 (19470) nm. Fluorescence (CHCl₃): $\lambda_{\max}$ = 534, 578 nm. MS (70 eV), *m/z* (%): 1079 (25), 1078 (65) [*M*⁺], 1077 (10), 1050 (15), 897 (7) [*M*⁺ - C₁₃H₂₆], 896 (3), 586 (15), 573 (15), 572 (9) [*M*⁺ - C₃₅H₇₀O], 404 (95), 391 (100), 390 (93), 373 (10), 111 (10). C₇₂H₁₀₆N₂O₅ (1078.7): calcd. C 80.16, H 9.82, N 2.59; found C 79.87, H 9.76, N 2.54.

2-(1-Hexylheptyl)-9-[2-(hydroxymethyl)-4-methoxy-2-(2-methoxyethyl)butyl]anthra[2,1,9-*def*;6,5,10-*d'e'**f'*]diisoquinoline-1,3,8,10-tetraone (3e):** 9-(1-Hexylheptyl)-1*H*-2-benzopyrano[6',5',4':10,5,6]anthra[2,1,9-*def*]isoquinoline-1,3,8,10(9*H*)-tetrone^[8] (560 mg, 0.98 mmol) and 2-aminomethyl-4-methoxy-2-(2-methoxyethyl)butan-1-ol (1.88 g, 9.83 mmol) in ethylene glycol (50 mL) were allowed to react according to the general procedure (readily soluble material), purified by column separation (neutral alumina, CHCl₃) and precipitated with methanol/chloroform, 2:1. Yield 430 mg (54%), bright light red powder, m.p. >300 °C. *R*_f (Al₂O₃, CHCl₃) = 0.35. IR (KBr): $\tilde{\nu}$ = 3450 m, 2920 m, 1698 s, 1655 s, 1598 s, 1575 w, 1435 w, 1400 m, 1340 m, 1250 m, 1110 m, 810 m, 750 m cm⁻¹. ¹H NMR (400 MHz/CDCl₃): δ = 0.81 (t, 6 H, 2 CH₃), 1.30 (m_c, 16 H, 8 CH₂), 1.67 (br. s, 4 H, 2 CH₂), 1.83 (m_c, 2 H, 1 α -CH₂), 2.22 (m_c, 2 H, 1 α -CH₂), 3.32 (s, 6 H, 2 O-CH₃), 3.38 (t, 2 H, CH₂-OH), 3.58 (m, 4 H, 2 OCH₂), 4.29 (s, 2 H, 1 N-CH₂), 5.18 (m_c, 1 H, 1 CH), 8.67 (m_c, 8 H, aromatic) ppm. ¹³C NMR (CDCl₃): δ = 14.03 (CH₃), 22.59, 26.96 (CH₂), 29.23, 31.78, 32.42, 33.19 (C), 54.86 (N-CH), 58.68 (N-CH₂), 68.85 (CH₂OH), 123.05, 123.36, 132.02, 135.19, 164.88 (C=O) ppm. UV/Vis (CHCl₃): $\lambda_{\max}$ (ϵ) = 528 (62470), 490 (38280), 458 (14810) nm. Fluorescence (CHCl₃): $\lambda_{\max}$ = 540, 578 nm. MS (70 eV), *m/z* (%): 746 (25) [*M*⁺], 716 (27), 715 (35), 714 (70) [*M*⁺ - CH₃OH], 697 (8), 586 (8), 574 (14), 573 (20) [*M*⁺ - C₉H₁₇O₃], 404 (66), 390 (100), 373 (27), 345 (17). C₄₆H₅₄N₂O₇ (746.4): calcd. C 74.01, H 7.23, N 3.75; found C 73.80, H 7.23, N 4.00.

2-(1-Hexylheptyl)-9-[2-(hydroxymethyl)-4-(2-methoxyethoxy)-2-[2-(2-methoxyethoxy)ethyl]butyl]anthra[2,1,9-*def*;6,5,10-*d'e'**f'*]diisoquinoline-1,3,8,10-tetraone (3f):** 9-(1-Hexylheptyl)-1*H*-2-benzopyrano[6',5',4':10,5,6]anthra[2,1,9-*def*]isoquinoline-1,3,8,10(9*H*)-tetrone^[8] (250 mg, 0.44 mmol) and 2-aminomethyl-4-(2-methoxyethoxy)-2-[2-(2-methoxyethoxy)ethyl]butan-1-ol (610 mg, 2.18 mmol) in ethylene glycol (25 mL) were allowed to react according to the general procedure (140 °C, 2 h), purified by column separation (neutral alumina, CHCl₃, red fluorescent main fraction after a yellow forerun) and extractively recrystallized^[26] from toluene.

Yield 150 mg (41%), bright light red powder, m.p. >300 °C. *R*_f (Al₂O₃/CHCl₃) = 0.30. IR (KBr): $\tilde{\nu}$ = 3450 m, 2925 m, 1699 s, 1659 s, 1599 s, 1575 w, 1435 w, 1400 m, 1340 m, 1255 m, 1110 m, 815 m, 755 m cm⁻¹. ¹H NMR (400 MHz/CDCl₃): δ = 0.81 (t, 6 H, 2 CH₃), 1.26 (m_c, 16 H, 8 CH₂), 1.60 (s, br. 4 H, 2 CH₂), 1.83 (m_c, 2 H, 1 α -CH₂), 2.22 (m_c, 2 H, 1 α -CH₂), 3.37 (s, 6 H, 2 OCH₃), 3.54 (m_c, 2 H, CH₂-OH), 3.65 (m_c, 4 H, 2 CH₂), 4.21 (m_c, 2 H, 1 CH₂), 5.18 (m_c, 1 H, 1 CH), 8.66 (m_c, 8 H, aromatic) ppm. ¹³C NMR (CDCl₃): δ = 14.04, 22.59, 26.95 (CH₂), 29.22, 31.77, 32.40, 54.84 (N-CH), 58.06 (N-CH₂), 69.40 (CH₂-OH), 70.12 (CH₂-O), 71.92 (CH₂-O), 75.91 (CH₂-O), 123.05, 123.37, 131.89, 135.20, 164.19 (C=O) ppm. UV/Vis (CHCl₃): $\lambda_{\max}$ (ϵ) = 528 (61880), 490 (37960), 458 (14220) nm. Fluorescence (CHCl₃): $\lambda_{\max}$ = 540, 577 nm. MS (70 eV), *m/z* (%): 834 (0.25) [*M*⁺], 804 (0.62) [*M*⁺ - CH₂O], 732 (9), 657 (35), 656 (65), 573 (59) [*M*⁺ - C₁₃H₂₅O₅], 551 (15), 475 (14), 457 (11), 429 (11), 404 (33), 391 (100), 362 (11), 345 (22), 83 (48). C₅₀H₆₂N₂O₉ (834.4): calcd. C 71.96, H 7.43, N 3.35; found C 72.43, H 6.97, N 3.59.

2-[2-Butyl-2-(hydroxymethyl)hexyl]-9-(1-Heptyloctyl)anthra[2,1,9-*def*;6,5,10-*d'e'**f'*]diisoquinoline-1,3,8,10-tetraone (3g):** 9-(1-Heptyloctyl)-1*H*-2-benzopyrano[6',5',4':10,5,6]anthra[2,1,9-*def*]isoquinoline-1,3,8,10(9*H*)-tetrone^[8] (540 mg, 0.89 mmol) and 2-aminomethyl-2-butylhexan-1-ol (1.70 g, 9.08 mmol) in ethylene glycol (50 mL) were allowed to react according to the general procedure, purified two times by column separation (silica gel, CHCl₃, a red fluorescent forerun was separated and discarded), evaporated and extractively^[26] recrystallized from cyclohexane. Yield 532 mg (77%), m.p. 275 °C. *R*_f (silica gel, CHCl₃) = 0.72. IR (KBr): $\tilde{\nu}$ = 3500 br. m, 2860 s, 2680 s, 1698 s, 1665 s, 1648 s, 1600 s, 1590 m, 1505 w, 1470 w, 1440 m, 1402 s, 1350 s, 1255 m, 1180 m, 1120 w, 1040 w, 850 m, 815 s, 740 s cm⁻¹. ¹H NMR (400 MHz/CDCl₃): δ = 0.82 (t, 6 H, 2 CH₃), 0.91 (t, 6 H, 2 CH₃), 1.30 (m_c, 32 H, 16 CH₂), 1.90 (m_c, 2 H, 1 α -CH₂), 2.25 (m_c, 2 H, 1 α -CH₂), 3.18 (d, *J* = 4 Hz, 2 H, CH₂-OH), 3.94 (t, *J* = 7 Hz, 1 H, OH), 4.12 (s, 2 H, 1 CH₂), 5.18 (m_c, 1 H, 1 CH), 8.49 (m_c, 8 H, aromatic) ppm. ¹³C NMR (CDCl₃): δ = 14.09 (2 CH₃), 14.15 (2 CH₃), 22.67, 23.71, 25.20, 27.13, 29.31, 29.60, 29.75, 31.69, 31.88, 32.43, 43.01 (quat. C), 43.71 (1 CH₂-N), 54.94 (1 N-CH), 65.69 (1 CH₂-OH), 122.58, 122.75, 123.04, 123.56, 124.26, 123.97, 125.99, 129.04, 129.06, 129.37, 130.80, 131.61, 133.71, 134.60, 134.62, 163.26, 164.36, 164.58, 164.60 (4 C=O) ppm. UV/Vis (CHCl₃): $\lambda_{\max}$ (ϵ) = 528 (86730), 490 (55110), 460 (19630) nm. Fluorescence (CHCl₃): $\lambda_{\max}$ = 532, 575 nm. MS (70 eV), *m/z* (%): 771 (64), 770 (100) [*M*⁺], 754 (17), 741 (32), 740 (71) [*M*⁺ - CH₂O], 680 (10), 679 (24), 614 (14), 601 (31), 600 (15) [*M*⁺ - C₁₁H₂₂O], 560 (12) [*M*⁺ - C₁₅H₃₀], 530 (10), 406 (13), 405 (39), 404 (98), 392 (27), 391 (74), 390 (91), 373 (16). C₅₀H₆₂N₂O₅ (770.5): calcd. C 77.94, H 8.04, N 3.63; found C 77.83, H 7.94, N 3.44.

9-(1-Heptyloctyl)-2-[2-hexyl-2-(hydroxymethyl)octyl]anthra[2,1,9-*def*;6,5,10-*d'e'**f'*]diisoquinoline-1,3,8,10-tetraone (3h):** 9-(1-Heptyloctyl)-1*H*-2-benzopyrano[6',5',4':10,5,6]anthra[2,1,9-*def*]isoquinoline-1,3,8,10(9*H*)-tetrone^[8] (1.40 g, 2.32 mmol) and 2-aminomethyl-2-hexyloctan-1-ol (1.80 g, 7.38 mmol) in ethylene glycol (50 mL) were allowed to react according to the general^[26] from cyclohexane and dried in medium vacuum. Yield 1.13 g (58%), red powder, m.p. 161 °C. *R*_f (silica gel, CHCl₃) = 0.48. IR (KBr): $\tilde{\nu}$ = 3500 br. m, 2860 s, 2680 s, 1700 s, 1665 s, 1650 s, 1600 s, 1590 m, 1510 w, 1470 w, 1440 m, 1400 s, 1350 s, 1255 m, 1180 m, 1120 w, 1040 w, 850 m, 820 s, 750 s cm⁻¹. ¹H NMR (400 MHz/CDCl₃): δ = 0.82 (t, 6 H, 2 CH₃), 0.89 (t, 6 H, 2 CH₃), 1.30 (m_c, 40 H, 20 CH₂), 1.88 (m_c, 2 H, 1 α -CH₂), 2.23 (m_c, 2 H, 1 α -CH₂), 3.20 (d, *J* = 4 Hz, 2 H, CH₂-OH), 4.06 (t, *J* = 7 Hz, 1 H, 1 OH), 4.19 (s, 2 H, 1 CH₂), 5.19 (m_c, 1 H, 1 CH), 8.49 (m_c, 8 H, aromatic) ppm.

^{13}C NMR (CDCl_3): δ = 14.06 (2 CH_3), 14.12 (2 CH_3), 22.62, 22.73, 22.96, 27.01, 29.23, 29.52, 30.32, 31.81, 31.86, 32.01, 32.39, 43.10 (1 quat. C), 43.65 (1 $\text{CH}_2\text{-N}$), 54.86 (1 N-CH), 65.71 (1 $\text{CH}_2\text{-OH}$), 122.79, 123.01, 123.03, 126.37, 126.42, 129.37, 129.56, 131.99, 134.17, 135.09, 164.88 (4 C=O) ppm. UV/Vis (CHCl_3): λ_{max} (ϵ) = 528 (91560), 490 (55210), 460 (20430), 431 (81150) nm. Fluorescence (CHCl_3): λ_{max} = 536, 579 nm. MS (70 eV), m/z (%): 826 (100) [M^+], 796 (42) [$M^+ - \text{CH}_2\text{O}$], 601 (15) [$M^+ - \text{C}_{15}\text{H}_{30}\text{O}$], 404 (41), 403 (10), 392 (167), 391 (43), 390 (37). $\text{C}_{54}\text{H}_{70}\text{N}_2\text{O}_5$ (826.5): calcd. C 78.46, H 8.46, N 3.38; found C 78.59, H 8.41, N 3.51.

9-(1-Heptyloctyl)-2-[2-hexadecyl-2-(hydroxymethyl)octadecyl]-anthra[2,1,9-def;6,5,10-d'-e'f']diisoquinoline-1,3,8,10-tetraone (3i): 9-(1-Heptyloctyl)-1*H*-2-benzopyrano[6',5',4':10,5,6]anthra[2,1,9-def]isoquinoline-1,3,8,10(9*H*)-trione^[8] (1.00 g, 1.66 mmol) and 2-aminomethyl-2-hexadecyloctadecan-1-ol (5.21 g, 9.96 mmol) in ethylene glycol (50 mL) were allowed to react according to the general procedure, purified by column separation (silica gel, CHCl_3 for the separation of a red fluorescent forerun and then with CHCl_3 /acetic acid, 10:1) and dried in medium vacuum. Yield 1.23 g (67%), m.p. 132 °C. R_f (silica gel, CHCl_3) = 0.42. IR (KBr): $\tilde{\nu}$ = 2920 s, 2850 m, 1700 s, 1650 s, 1595 m, 1470 w, 1400 w, 1145 m, 1250 w, 810 m, 750 m cm^{-1} . ^1H NMR (400 MHz/ CDCl_3): δ = 0.85 (t, 6 H, 2 CH_3), 0.91 (t, 6 H, 2 CH_3), 1.30 (m_c , 80 H, 40 CH_2), 1.92 (m_c , 2 H, 1 $\alpha\text{-CH}_2$), 2.29 (m_c , 2 H, 1 $\alpha\text{-CH}_2$), 3.22 (d, J = 4 Hz, 2 H, $\text{CH}_2\text{-OH}$), 4.15 (t, J = 7 Hz, 1 H, 1 OH), 4.22 (s, 2 H, 1 CH_2), 5.21 (m_c , 1 H, 1 CH), 8.59 (m_c , 8 H, aromatic) ppm. ^{13}C NMR (CDCl_3): δ = 14.07 (2 CH_3), 14.12 (2 CH_3), 22.64, 22.71, 23.002, 27.07, 29.27, 29.39, 29.55, 29.69, 29.75, 30.67, 31.84, 31.95, 32.04, 32.40, 43.09 (1 quat. C), 43.65 (1 N-CH_2), 54.86 (1 N-CH), 65.71 (1 $\text{CH}_2\text{-OH}$), 122.67, 122.87, 123.14, 126.16, 131.77, 134.81, 164.71 (4 C=O) ppm. UV/Vis (CHCl_3): λ_{max} (ϵ) = 528 (85700), 493 (54710), 460 (18520) nm. Fluorescence (CHCl_3): λ_{max} = 530, 570 nm. MS (70 eV), m/z (%): 1107 (33), 1106 (41) [M^+], 1077 (21), 1076 (28) [$M^+ - \text{CH}_2\text{O}$], 866 (5), 614 (10), 602 (18), 600 (38) [$M^+ - \text{C}_{35}\text{H}_{70}\text{O}$], 405 (41), 404 (76), 391 (100), 373 (19). $\text{C}_{74}\text{H}_{110}\text{N}_2\text{O}_5$ (1106.7): calcd. C 80.30, H 9.93, N 2.53; found C 80.89, H 10.07, N 2.74.

2-Hexyl-2-{9-(1-heptyloctyl)-1,3,8,10-tetraoxo-3,8,9,10-tetrahydro-1*H*-anthra[2,1,9-def;6,5,10-d'-e'f']diisoquinolin-2-ylmethyl}octyl Methacrylate: A solution of 2-(1-heptyloctyl)-9-[2-hexyl-2-(hydroxymethyl)octyl]anthra[2,1,9-def;6,5,10-d'-e'f']diisoquinoline-1,3,8,10-tetraone (3 h, 900 mg, 1.06 mmol) and pyridine (9 mL) in anhydrous toluene (10 mL) was added dropwise with stirring at room temperature within 1 h to a solution of methacryloyl chloride (7.5 mL, 72 mmol) in anhydrous toluene. The mixture was stirred for 16 h, hydrolyzed with ice water (200 mL) and acidified with concd. hydrochloric acid. The red organic phase was separated, washed two times with distilled water, evaporated in vacuo, dried at 100 °C in air and purified by column separation (40 cm of silica gel, CHCl_3). A forerun was discarded and the firmly adsorbed product eluted with a mixture of CHCl_3 /acetic acid, 10:1. A chromatography with neutral alumina and chloroform is an alternative where the product is obtained as the first fraction. Analytical purity of the dye is obtained by a second chromatography with silica gel and chloroform, evaporation and drying in medium vacuum at 40 °C. Yield 460 mg (48%) red powder, m.p. 193 °C. R_f (silica gel/ CHCl_3) = 0.43. R_f (Al_2O_3 / CHCl_3) = 0.91. IR (KBr): $\tilde{\nu}$ = 3450 m, 2930 m, 2880 m, 1700 s, 1670 s, 1600 s, 1450 m, 1410 m, 1350 s, 1260 m, 1180 m, 860 m, 820 s, 755 m cm^{-1} . ^1H NMR (400 MHz/ CDCl_3): δ = 0.83 (t, 6 H, 2 CH_3), 0.87 (t, 6 H, 2 CH_3), 1.22 (m_c , 40 H, 20 CH_2), 1.56 (s, 3 H, 1 CH_3), 1.67 (s, 3 H, 1 CH_3), 1.89 (m_c , 2 H, 1 $\alpha\text{-CH}_2$), 2.24 (m_c , 2 H, 1 $\alpha\text{-CH}_2$), 4.20 (s, 2 H, 1 CH_2), 4.34 (s, 2 H, 1 CH_2), 5.16 (s, 1 H, olefinic), 5.20 (m_c , 1 H, 1

CH), 5.78 (s, 1 H, olefinic), 8.58 (m_c , 8 H, aromatic) ppm. ^{13}C NMR (CDCl_3): δ = 14.06, 14.08, 18.06, 22.62, 22.66, 23.12, 27.02, 29.25, 29.54, 30.28, 31.79, 31.82, 32.40, 33.84, 41.74, 54.83 (N-CH), 69.13 ($\text{CH}_2\text{-O-COR}$), 122.96, 123.06, 123.30, 124.66 ($\text{CH}_2=\text{CR}_2$), 126.33, 126.41, 129.24, 129.60, 131.54, 134.38, 134.59, 136.36 ($\text{CH}_2=\text{CR}_2$), 164.14 (C=O , imide), 167.06 (CO_2) ppm. UV/Vis (CHCl_3): λ_{max} (ϵ) = 526 (79900), 489 (48550), 458 (17690), 433 (5190) nm. Fluorescence (CHCl_3): λ_{max} = 535, 577 nm. MS (70 eV): m/z (%): 895 (65), 894 (100) [M^+], 877 (3), 827 (2), 826 (2), 825 (3), 810 (3), 809 (6) [$M^+ - \text{C}_4\text{H}_5\text{O}_2$], 808 (6), 796 (3), 795 (3), 724 (2), 686 (5), 685 (13), 684 (8) [$M^+ - \text{C}_{15}\text{H}_{30}$], 614 (15), 613 (28), 602 (8), 601 (22) [$M^+ - \text{C}_{19}\text{H}_{34}\text{O}_2$], 600 (5), 406 (3), 405 (19), 404 (43), 393 (3), 392 (14), 391 (42), 390 (30), 373 (14), 345 (10), 391 (42), 69 (23). $\text{C}_{58}\text{H}_{74}\text{N}_2\text{O}_6$ (894.5): calcd. C 77.87, H 8.27, N 3.13; found C 77.62, H 8.53, N 3.09.

2-[9-(1-Heptyloctyl)-1,3,8,10-tetraoxo-3,8,9,10-tetrahydro-1*H*-anthra[2,1,9-def;6,5,10-d'-e'f']diisoquinolin-2-ylmethyl]-2-hexadecyloctadecyl Methacrylate: A solution of 2-(1-heptyloctyl)-9-[2-hexadecyl-2-(hydroxymethyl)octadecyl]anthra[2,1,9-def;6,5,10-d'-e'f']diisoquinoline-1,3,8,10-tetraone (3i, 1.09 g, 98.4 mmol) and pyridine (6 mL) in anhydrous toluene (10 mL) is added dropwise with stirring at room temperature within 1 h to a solution of methacryloyl chloride (5.0 mL, 47.8 mmol) in anhydrous toluene (10 mL), stirred at 90 °C for 1 h, cooled to room temperature and poured into a mixture of distilled water (100 mL) and concentrated hydrochloric acid (10 mL). The red organic phase was separated, washed with water two times, evaporated in vacuo, dried in air (100 °C, 8 h) dissolved in a small amount of chloroform, purified by column separation (neutral alumina, CHCl_3) to separate a small amount of a second fraction, purified by column separation (silica gel, CHCl_3) to separate a forerun close to the main fraction, filtered through a D5 glass filter, evaporated in vacuo and dried in medium vacuum (40 °C, 8 h). Yield 740 mg (64%) red powder, m.p. 139 °C. R_f (silica gel, CHCl_3) = 0.28. R_f (Al_2O_3 , CHCl_3) = 0.60. IR (KBr): $\tilde{\nu}$ = 3450 m, 2920 m, 2850 m, 1700 s, 1660 s, 1600 s, 1470 w, 1405 m, 1340 s, 1255 w, 1185 m, 810 m, 750 m cm^{-1} . ^1H NMR (400 MHz/ CDCl_3): δ = 0.83 (t, 6 H, 2 CH_3), 0.89 (t, 6 H, 2 CH_3), 1.24 (m_c , 60 H, 30 CH_2), 1.57 (s, 3 H, CH_3), 1.69 (s, 3 H, CH_3), 1.88 (m_c , 2 H, 1 $\alpha\text{-CH}_2$), 2.25 (m_c , 2 H, 1 $\alpha\text{-CH}_2$), 4.10 (s, 2 H, 1 CH_2), 4.37 (s, 2 H, 1 CH_2), 5.17 (s, 1 H, olefinic), 5.20 (m_c , 1 H, 1 CH), 5.80 (s, 1 H, olefinic), 8.64 (m_c , 8 H, aromatic) ppm. ^{13}C NMR (CDCl_3): δ = 14.05 (2 CH_3), 14.12 (2 CH_3), 18.08 (1 CH_3), 22.62, 22.70, 23.16, 26.99, 29.23, 29.38, 29.52, 29.58, 29.66, 29.68, 29.69, 29.73, 30.60, 31.81, 31.95, 32.40, 33.86, 41.73, 54.81 (N-CH), 69.16 ($\text{CH}_2\text{-O-COR}$), 123.02, 123.11, 123.36, 124.68 ($\text{CH}_2=\text{CR}_2$), 126.34, 126.50, 129.33, 129.64, 131.64, 134.49, 134.71, 136.37 ($\text{CH}_2=\text{CR}_2$), 164.22 (C=O , imide), 167.08 (CO_2) ppm. UV/Vis (CHCl_3): λ_{max} (ϵ) = 527 (79900), 487 (49650), 457 (18190), 432 (5230) nm. Fluorescence (CHCl_3): λ_{max} = 533, 578 nm. MS (70 eV): m/z (%): 1175 (32), 1174 (38) [M^+], 1090 (11), 1089 (16) [$M^+ - \text{C}_4\text{H}_5\text{O}_2$], 964 (3) [$M^+ - \text{C}_{15}\text{H}_{30}$], 614 (11), 613 (14), 602 (19), 601 (49) [$M^+ - \text{C}_{39}\text{H}_{74}\text{O}_2$], 600 (13), 405 (27), 404 (54), 391 (100), 390 (60), 373 (18), 125 (13), 109 (14), 97 (14), 57 (73).

1-(1-Hexylheptyl)-8-[2-hexyl-2-(hydroxymethyl)octyl]-1*H*-indolo-[5',4',3':10,5,6]anthra[2,1,9-def]isoquinoline-2,7,9(8*H*)-trione (4a): 2-(1-Hexylheptyl)-9-[2-hexyl-2-(hydroxymethyl)octyl]anthra[2,1,9-def;6,5,10-d'-e'f']diisoquinoline-1,3,8,10-tetraone (3b, 1.50 g, 1.88 mmol) was refluxed with *tert*-butyl alcohol for 15 min, treated with finely pulverized KOH (630 mg, 85%, 11.3 mmol) and further refluxed for 30 min. The mixture was further refluxed until only little starting material could be detected by TLC (silica gel, CHCl_3 /acetone, 30:1; the starting material exhibits a slightly higher R_f value than the reaction product). The reaction was quenched by the ad-

dition of a mixture of acetic acid and 2 N HCl (150 mL 1:1) and the precipitate collected by vacuum filtration, dried in air (120 °C), purified by column separation (silica gel, CHCl₃/acetone, 30:1, 200 × 4 cm), slowly precipitated from the solution in chloroform with methanol, collected by vacuum filtration and dried in air (120 °C). Yield 980 mg (68%) blackish violet powder, m.p. >250 °C. *R_f* (silica gel, CHCl₃/acetone, 30:1) = 0.39. IR (KBr): $\tilde{\nu}$ = 3069 w, 2954 m, 2927 s, 2856 m, 1692 s, 1655 s, 1625 m, 1584 s, 1493 s, 1462 m, 1398 m, 1352 s, 1319 w, 1288 w, 1245 w, 1214 w, 1188 w, 1167 w, 1105 w, 1034 w, 951 w, 864 w, 806 m, 740 m, 597 w, 521 w cm⁻¹. ¹H NMR (400 MHz/CDCl₃): δ = 0.82 (t, 6 H, 2 CH₃), 0.85 (t, 6 H, 2 CH₃), 1.23–1.32 (m, 36 H, 18 CH₂), 1.96 (m, 2 H, α -CH₂), 2.20 (m, 2 H, α -CH₂), 3.24 (d, 2 H, 2 CH₂-OH), 3.92 (s, 2 H, 1 CH₂), 4.25 (t, 1 H, OH), 5.19 (m, 1 H, CH), 7.58 (d, 1 H, perylene), 8.20 (d, 1 H, perylene), 8.27 (d, 1 H, perylene), 8.34 (d, 1 H, perylene), 8.39 (d, 2 H, perylene), 8.44–8.52 (br. m, 2 H, perylene) ppm. ¹³C NMR (CDCl₃): δ = 14.1, 22.6, 27.0, 29.2, 30.2, 31.8, 31.9, 32.0, 32.5, 43.2, 46.1, 54.7, 65.3, 107.9, 120.6, 122.5, 123.9, 124.5, 125.8, 126.2, 126.5, 130.2, 134.5, 135.5, 141.9, 170.0 ppm. UV/Vis (CHCl₃): $\lambda_{\max}$ (ϵ) = 411.8 (8334), 532.9 (27880) nm. Fluorescence (CHCl₃): $\lambda_{\max}$ (*I_{rel}*) = 535.4 (0.38), 618.0 (1.00) nm. Fluorescence quantum yield (CHCl₃, *c* = 7.27 × 10⁻⁷ mol·L⁻¹, *d* = 1 cm, λ_{excit} = 488 nm, reference: 2,9-bis(1-hexylheptyl)anthra[2,1,9-*def*;6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-tetraone (**1a**)^[10] with Φ = 1.00): 0.28. MS (70 eV), *m/z* (%): 770 (100) [*M*⁺], 752 (22) [*M*⁺ – OH + H], 740 (7), 589 (6) [*M*⁺ – C₁₃H₂₆], 557 (31) [*M*⁺ – C₁₅H₃₂], 375 (20), 362 (9), 347 (6), 55 (4). C₅₁H₆₆O₄N₂ (771.1): calcd. C 79.44, H 8.62, N 3.63; found C 79.44, H 8.50, N 3.59.

1,8-Bis(1-hexylheptyl)-1*H*-indolo[5',4',3':10,5,6]anthra[2,1,9-*def*]isoquinoline-2,7,9(8*H*)-trione (4b**):**^[15] 2,9-Bis(1-hexylheptyl)-anthra[2,1,9-*def*;6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-tetraone (**1a**, 380 mg, 0.50 mmol), 85% KOH (700 mg, 12.5 mmol), dimethyl sulphoxide (4 mL) and methanol (6 mL) were heated (bath 100 °C) for 5 h, cooled, treated with distilled water (100 mL), neutralized with 2 N HCl, collected by vacuum filtration, extracted two times with 10% K₂CO₃ (200 mL each), washed with hot distilled water and purified by column separation (silica gel/CHCl₃). The third fraction was further purified by two column separations (silica gel, CHCl₃ and silica gel, CHCl₃/acetone, 5:1). Yield: 25 mg (6%), violet powder. *R_f* (silica gel, CHCl₃) = 0.43. *R_f* (silica gel, CHCl₃/acetone, 10:3) = 0.96. IR (KBr): $\tilde{\nu}$ = 3440 m, 2960 s, 2934 s, 2862 s, 1719 s, 1700 s, 1665 s, 1605 s, 1626 m, 1590 s, 1560 w, 1542 w, 1521 w, 1511 w, 1497 m, 1470 m, 1460 m, 1405 m, 1358 s, 1342 m, 1290 w, 1270 w, 1252 w, 1225 w, 1070 w, 826 w, 815 w, 749 w cm⁻¹. ¹H NMR (400 MHz/CDCl₃): δ = 0.82 (t, 12 H, 4 CH₃), 1.19–1.29 (m, 32 H, 16 CH₂), 1.78–1.86 (m, 4 H, 2 CH₂), 2.10–2.15 (m, 2 H, CH₂), 2.20–2.25 (m, 2 H, CH₂), 4.51 (m, br., 1 H, CH), 5.17 (m, 1 H, CH), 7.14 (d, *J* = 7.8 Hz, 1 H, perylene), 8.14 (d, *J* = 7.6 Hz, 1 H, perylene), 8.23 (d, *J* = 7.9 Hz, 1 H, perylene), 8.33 (d, *J* = 8.1 Hz, 1 H, perylene), 8.47 (d, *J* = 8.1 Hz, 1 H, perylene), 8.48 (d, *J* = 7.8 Hz, 1 H, perylene), 8.57 (dd, br., 2 H, perylene) ppm. ¹³C NMR (CDCl₃): δ = 168.3, 135.8, 134.8, 133.8, 130.2, 126.4, 126.3, 126.0, 125.6, 124.8, 124.5, 123.8, 123.7, 122.0, 120.1, 108.2, 55.2 (CH), 55.15 (CH), 33.4 (2 CH₂), 32.4 (2 CH₂), 31.8 (2 CH₂), 31.6 (2 CH₂) 29.2 (2 CH₂), 29.0 (2 CH₂), 27.0 (2 CH₂), 26.6 (2 CH₂), 22.6 (2 CH₂), 22.5 (2 CH₂), 14.0 (2 CH₃), 13.99 (2 CH₃) ppm. UV/Vis (CHCl₃): $\lambda_{\max}$ = 578 sh, 543, 482 sh, 444, 411, 396, 362 nm. Fluorescence (CHCl₃): $\lambda_{\max}$ = 621 nm. MS (70 eV), *m/z* (%): 726 (100) [*M*⁺], 709 (8), 641 (9) [*M*⁺ – C₆H₁₃], 544 (23) [*M*⁺ – C₁₃H₂₆], 527 (3), 459 (15) [544 – C₆H₁₃], 389 (3), 375 (14), 362 (21) [544 – C₁₃H₂₆], 345 (3), 317 (3) [345 – CO].

Test for the Alkaline Saponification of 2,9-Bis[2-hexyl-2-(hydroxymethyl)octyl]anthra[2,1,9-*def*;6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-

tetraone (2b): 2,9-Bis[2-hexyl-2-(hydroxymethyl)octyl]anthra[2,1,9-*def*;6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-tetraone (**2b**) (500 mg, 0.59 mmol) in *tert*-butyl alcohol (20 mL) were heated until reflux. KOH powder (190 mg, 2.1 mmol, 85%) was added and the mixture was kept refluxing. The reaction was followed by means of TLC. No reaction could be detected after one hour, neither a degradation of the starting material nor the formation of the potassium salts of an anhydride imide^[8] or the perylenetetracarboxylic bisanhydride nor the perylene-lactam^[9]. In contrast to this, hydrolysable perylene bisimides such as **1a** with R¹ = 1-hexylheptyl are appreciably saponified under these conditions within a short time.

Test for the Alkaline Saponification of 2-[2-Heptyl-2-(hydroxymethyl)nonyl-9-(1-hexylheptyl)]anthra[2,1,9-*def*;6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-tetraone (3c): 2-[2-(hydroxymethyl)-2-heptyl-nonyl]-9-(1-hexylheptyl)anthra[2,1,9-*def*;6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10-tetraone (**3c**) (470 mg, 0.57 mmol) in *tert*-butyl alcohol (20 mL) was heated until reflux. KOH powder (720 mg, 11 mmol, 85%) was added and the mixture was kept refluxing for 16 h. The reaction was quenched by the addition of a mixture of acetic acid (20 mL) and 2 N HCl (20 mL) and the precipitate collected by vacuum filtration. 430 mg (92%) of **3c** was recovered. TLC *R_f* values and spectroscopic data were identical with an authentic sample from synthesis.

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