The Synthesis of Perylenebisimide Monocarboxylic Acids

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The synthesis and properties of perylene-bisimides **4** with one carboxylic acid anchor group are described. The properties of **4** are strongly influenced by the spacer between the carboxylic acid group and the imide moeity. Dyes with aliphatic (**4d**−**4g**) and aromatic (**4a**−**4c**) spacers have been prepared.

Perylene dyes, perylene-3,4:9,10-tetracarboxylic bisimides **2**, exhibit unusually valuable properties like high fluorescence quantum yields and thermal, chemical and photochemical persistency; for a review see ref.[1]. Their substitution with one carboxylic group would render them of special interest for example because of the solubilizing effect in water, the formation of micelles and of fluorescent labelling in biochemistry and medicine. However, there are no synthetic procedures for such dyes, especially if they are needed in a highly pure state. Their preparation with standard procedures proved to be very difficult; they behave like a "sponge" both for cations and neutral impurities. This is caused by their properties as anionic detergents.

The nitrogen atoms of **2** are good positions for functionalizing substituents because there are nodes in HOMO and LUMO[2]. So the UV/Vis spectra are only slightly affected by these substituents. For the preparation of **4** perylene-3,4:9,10-tetracarboxylic bisanhydride (**1**) was condensed with primary amines to **2**. Long-chain secondary alkyl groups R ("swallow-tail" substituents[3]) guarantee good solubilities in organic solvents for all derivatives. **2** was partially saponificated to **3**[4] and then condensed with aminoacids ($H_2N-X-CO_2H$) to **4**. This step proved to be difficult under usual rough reaction conditions because of problems with the removal of by-products. However, surprisingly good results have been obtained with mild reaction conditions for the condensation in molten imidazole; a bath temperature of max. 130°C and a reaction time of 1 h for aliphatic and 2 h for aromatic aminocarboxylic acids thus suppressed the formation of by-products. Zinc acetate which acts as a catalyst may be either added according to the standard procedure or may be omitted if **4** must be free of any trace of heavy metal. The work-up of the reaction mixture needs to be adapted to the special properties of **4** concerning the strong detergent properties and tendency to form micelles in alkaline solution. Best results were obtained by keeping a strongly acid medium for any step of work-up which suppresses the surface active properties. The commonly applied extraction of the rough reaction mixture with alcohol should be omitted for the carboxylic acids **4** because this may cause an acid catalyzed partial esterification of **4**, and these esters are difficult to remove again. On the other hand, standard chromatography is a very useful method to prepare analytically pure dyes on a preparative scale. Perylene-3,4-dicarboxylic anhydride can be monofunctionalized in the same way as **3** which is verified by the preparation of **5**. All acids **4** exhibit a low solubility in pure water and the solubility remains low even in alkaline solution (1/1000 N KOH) so that only weakly coloured solutions were formed. Higher solubilities with deeply coloured solutions were obtained by the addition of solutizing organic solvents like ethanol to the aqueous phases.

The solubilities of **4** in organic solvents such as chloroform or toluene are controlled both by the "swallow-tail" substituent R and the spacer X. The dyes **4** exhibit sufficiently high solubilities for R = 1-hexylheptyl and a further extension of the chain length is of minor influence. On the other hand, the chain-length of the spacer X is of major influence: dye **4d** with a C-1 spacer exhibits only a rather low solubility ($1.2 \cdot 10^{-4}$ mol·l^{-1} in $CHCl_3$ at 20°C after three weeks equilibration) which is appreciably increased with increasing chain-length from **4e** ($1.7 \cdot 10^{-4}$ mol·l^{-1}) to **4f** ($1.4 \cdot 10^{-3}$ mol·l^{-1}) so that **4g** with a C-10 spacer is a very soluble dye (more than 10^{-2} mol·l^{-1}). The aromatic carboxylic acids **4a** and **4b** with the carboxylic acid function in *m*- and *p*-position are medium soluble ($5.3 \cdot 10^{-4}$ mol·l^{-1} for **4a** and $3.9 \cdot 10^{-4}$ mol·l^{-1} for **4b**). The equilibrium solubility of **4c** is $2.9 \cdot 10^{-4}$ mol·l^{-1} which is below the solubility of **4a** and **4b**. However, the rate of dissolution of the *o*-derivative **4c** is appreciably higher. A reason for this may be the dimerization of carboxylic acids by hydrogen bonds[5] which can proceed for **4a** and **4b**, but is supposed to be sterically hindered for the *o*-derivative **4c**. An evidence of this is either the high TLC R_f value of **4c** compared with **4a** and **4b** or characteristic deviations in the ^{1}H NMR chemical shifts of **4c** or a characteristic IR absorption at

1434−193X/98/0505−0847 $ 17.50+.50/0

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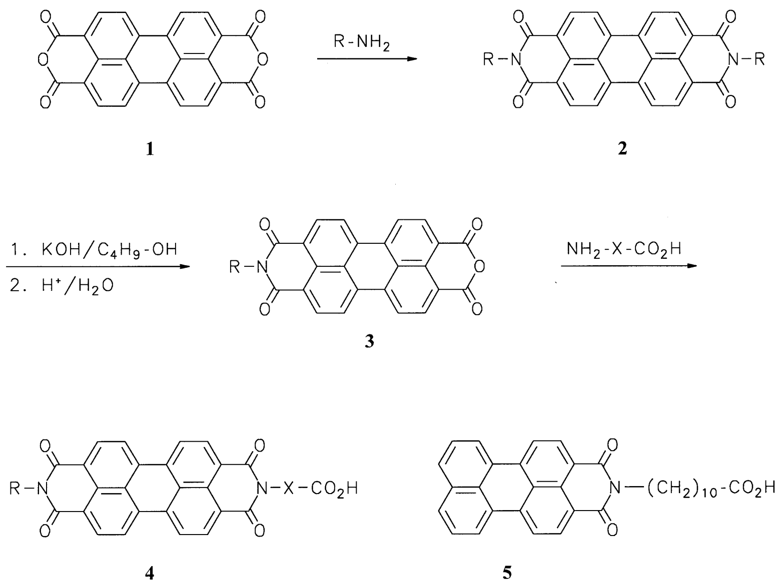
Scheme 1



2, 3	R	**4**	R	X
a	CH(C_6H_{13})$_2$	**a**	CH(C_6H_{13})$_2$	1,4-C_6H_4
b	CH(C_9H_{19})$_2$	**b**	CH(C_9H_{19})$_2$	1,3-C_6H_4
		c	CH(C_9H_{19})$_2$	1,2-C_6H_4
		d	CH(C_6H_{13})$_2$	CH_2
		e	CH(C_6H_{13})$_2$	$(CH_2)_3$
		f	CH(C_6H_{13})$_2$	$(CH_2)_5$
		g	CH(C_6H_{13})$_2$	$(CH_2)_{10}$

1715 cm^{-1} for **4c** which is typical for non associated carboxylic groups.

The UV/Vis spectra of **4** in chloroform are nearly identical to those for **2** and a strong fluorescence (see experimental part for fluorescence quantum yields) in non aqueous solution is observed such as in chloroform, toluene or ethanol which is decreased by the addition of larger amounts of water and becomes very low in pure water. This is certainly caused by the formation of aggregates (compare also ref.[6]). The dyes **4** can be easily adsorbed to surfaces because of their carboxylic groups and remain highly fluorescent in this state; the investigation of such adsorbates will be reported elsewhere. Some derivatives such as **4a** exhibit also a strong fluorescence in the solid-state which is of interest for technical applications.

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Experimental Section

Compound **4a**: *N*-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic 3,4-anhydride 9,10-imide (**3a**, 400 mg, 0.70 mmol), 4-aminobenzoic acid (290 mg, 2.10 mmol), zinc acetate dihydrate (100 mg, 0.46 mmol) and imidazole (4 g) were heated for 2 h (bath temp. 130°C). Chloroform was added (200 ml) and the organic phase was twice extracted with aqueous hydrochloric acid. The aqueous phases were discarded. The organic phase was chromatographically filtered with chloroform/acetic acid (10 + 1) over alumina (4 x 20 cm) and further purified by column separation. For this procedure, the dye was dispersed in acetic ester and added to the chromatographic column as well as the solid particles and eluted with acetic ester until nearly colourless. Then the dye is collected with chloroform/acetic acid (10 + 1) which was evaporated. The residue was dissolved in a minimal amount of chloroform, filtered through a glass filter (D4), abundant distilled water was added and the chloroform was completely removed in vacuo. The solid was collected by vacuum filtration (D4 glass filter) and dried at 100°C with repeated pulverization in an agate mortar (because of the occlusion of water) until the solid became a fine, dry powder. This was further dried for 24 h in medium vacuum at 80°C to give 290 mg (60%) of **4a**, m.p. > 350°C. − R_f (silica gel, $CHCl_3$/ethanol (10 + 1)) = 0.48. − R_f (silica gel, $CHCl_3$/acetic acid (10 + 1)) = 0.71. − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1} (m), 2926 (m), 2856 (m), 1709 (s sh), 1702 (s sh), 1698 (s), 1658 (s br.), 1618 (w), 1594 (s), 1579 (m), 1509 (w), 1460 (w), 1434 (w), 1405 (m), 1343 (s), 1254 (m), 1199 (w), 1176 (m), 1122 (w), 1108 (w), 1020 (w), 968 (w), 852 (m), 811 (s), 801 (w), 796 (w), 767 (m), 745 (m). − ^{1}H NMR ([D$_6$]DMSO/90°C): δ = 0.82 (t, 6 H, 2 CH_3), 1.29 (m$_c$, 16 H, 8 CH_2), 1.88 (m$_c$, 2 H, 2 α-CH_2), 2.16 (m$_c$, 2 H, 2 α-CH_2), 5.02 (m$_c$, 1 H, NCH), (^3J = 8.7 Hz, ^4J = 2.2 Hz, 2 H, aryl-H), (^3J = 8.6 Hz, ^4J = 2.2 Hz, 2 H, aryl-H), 8.19 (d, ^3J = 7.8 Hz, 2 H, perylene), 8.27 (d, ^3J = 7.8 Hz, 2 H, perylene), 8.29 (s br., 4 H, perylene). − ^{13}C NMR ([D$_6$]DMSO/90°C): δ = 13.28, 21.54, 26.12, 28.13, 30.73, 31.64, 53.57, 122.20, 122.47, 123.29, 123.40, 124.77, 124.94, 127.93, 128.99, 129.34, 130.18, 130.92, 133.00, 133.49, 139.13, 162.08, 162.84, 166.40. − UV ($CHCl_3$): λ_{max} (ε) = 527 nm (91000), 490 (54700), 460 (19800) (The sample was allowed to stand for 24 h for equilibration.). − Fluorescence ($CHCl_3$): λ_{max} = 534 nm, 575.

− Fluorescence quantum yield (6.83·10^{-7} mol·l^{-1} in CHCl$_3$, reference **2a** with Φ = 100%) = 86%. − Solid-state fluorescence: λ_{max} = 641 nm. − MS (70 eV); *m/z* (%): 693 (6), 692 (13) [M$^+$], 675 (3) [M$^+$ − OH], 512 (21), 511 (66), 510 (100) [M$^+$ − C$_{13}$H$_{26}$], 509 (13), 466 (5) [510 − CO$_2$], 465 (6) [510 − CO$_2$H], 373 (4), 87 (5), 85 (34), 83 (54), 81 (5), 55 (10), 47 (10). − C$_{44}$H$_{40}$N$_2$O$_6$ (692.8): calcd. C 76.28, H 5.82, N 4.04; found C 76.52, H 5.60, N 4.06.

Compound **4b**: *N*-(1-nonyldecyl)perylene-3,4:9,10-tetracarboxylic 3,4-anhydride 9,10-imide **3b** (300 mg, 0.47 mmol), 3-aminobenzoic acid (190 mg, 1.39 mmol) and imidazole (4 g) were allowed to react and purified analogously to **4a**, but without addition of zinc acetate to give 160 mg (45%) of **4b**, m.p. > 350°C. − R_f (silica gel, CHCl$_3$/ethanol (10 + 1)) = 0.50. − R_f (silica gel, CHCl$_3$/acetic acid (10 + 1)) = 0.75. − IR (KBr): $\tilde{\nu}$ = 2952 cm^{-1} (m), 2925 (s), 2854 (m), 1710 (s sh), 1699 (s), 1661 (s br.), 1594 (s), 1579 (m), 1506 (w), 1449 (m br.), 1435 (m), 1405 (m), 1365 (m sh), 1355 (m sh), 1343 (s), 1303 (w), 1255 (m), 1198 (m), 1177 (m), 1149 (w), 1126 (w), 965 (w), 855 (w), 811 (s), 799 (w), 746 (m), 651 (m), 638 (w). − ^{1}H NMR (CDCl$_3$/[D$_6$]DMSO (1 + 1)): δ = 0.82 (m$_c$, 6 H, 2 CH$_3$), 1.25 (m$_c$, 28 H, 14 CH$_2$), 1.86 (m$_c$, 2 H, 2 α-CH$_2$), 2.22 (m$_c$, 2 H, 2 α-CH$_2$), 5.11 (m$_c$, 1 H, NCH), 7.66 (m$_c$, 2 H, aryl-H), 8.02 (t, 1 H, aryl-H), 8.13 (m$_c$, 1 H, aryl-H), 8.51 (d, ^3J = 8.1 Hz, 4 H, perylene), 8.55 (d, ^3J = 8.1 Hz, 4 H, perylene). − ^{13}C NMR (CDCl$_3$/[D$_6$]DMSO (1 + 1)): δ = 13.75, 22.09, 26.45, 28.70, 28.95, 28.98, 31.31, 31.77, 53.81, 122.49, 123.15, 123.36, 125.46, 125.69, 128.57, 128.76, 128.88, 129.26, 129.96, 130.88, 132.10, 132.98, 133.52, 134.31, 135.31, 162.70, 166.75. − UV (CHCl$_3$): λ_{max} (ε) = 527 nm (84200), 490 (50500), 459 (18300). − Fluorescence (CHCl$_3$): λ_{max} = 533 nm, 574. − Fluorescence quantum yield (7.71·10^{-7} mol·l^{-1} in CHCl$_3$, reference **2a** with Φ = 100%) = 86%. − MS (70 eV); *m/z* (%): 777 (10), 776 (18), [M$^+$], 759 (4) [M$^+$ − OH], 513 (4), 512 (21), 511 (66), 510 (100) [M$^+$ − C$_{19}$H$_{38}$], 509 (10), 493 (5) [510 − OH], 466 (5) [510 − CO$_2$], 465 (8) [510 − CO$_2$H], 421 (3), 395 (1), 373 (3), 55 (3). − C$_{50}$H$_{52}$N$_2$O$_6$ (777.0): calcd. C 77.29, H 6.74, N 3.60; found C 77.47, H 6.90, N 3.61.

Compound **4c**: *N*-(1-nonyldecyl)perylene-3,4:9,10-tetracarboxylic 3,4-anhydride 9,10-imide (**3b**, 300 mg, 0.47 mmol), 2-aminobenzoic acid (200 mg, 1.46 mmol), zinc acetate dihydrate (80 mg, 0.36 mmol) and imidazole (4 g) were allowed to react and purified analogously to **4a** and purified by column separation over alumina with chloroform. The acid was strongly adsorbed to alumina and two by-products were eluted. As soon as the eluting solvent became nearly colourless 10 vol.% of acetic acid was added to obtain the main product. The further purification proceeded as described for **4a** to give 150 mg (42%) of **4c**, m.p. 328−330°C (dec.). − R_f (silica gel, CHCl$_3$/ethanol (10 + 1)) = 0.30. − R_f (silica gel, CHCl$_3$/acetic acid (10 + 1)) = 0.65. − R_f (alumina, CHCl$_3$/acetic acid (10 + 1)) = 0.49. − IR (KBr): $\tilde{\nu}$ = 2950 cm^{-1} (m), 2926 (s), 2854 (m), 1715 (s), 1699 (s), 1660 (s br.), 1594 (s), 1579 (m), 1505 (w), 1490 (w), 1456 (m), 1435 (m), 1405 (s), 1370 (m sh), 1351 (s sh), 1345 (s), 1300 (w), 1256 (m), 1202 (w), 1178 (w), 1140 (w), 1125 (w), 1075 (w), 960 (w), 851 (m), 810 (s), 794 (w), 747 (m), 648 (w), 635 w. − ^{1}H NMR (CDCl$_3$): δ = 0.84 (m$_c$, 6 H, 2 CH$_3$), 1.28 (m$_c$, 28 H, 14 CH$_2$), 1.92 (m$_c$, 2 H, 2 α-CH$_2$), 2.20 (m$_c$, 2 H, 2 α-CH$_2$), 5.11 (m$_c$, 1 H, NCH), 7.40 (d, ^3J = 7.5 Hz, 1 H, aryl-H), 7.49 (m$_c$, 5 H, 4 H perylene + 1 aryl-H), 7.75 (td, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 1 H, aryl-H), 8.04 (d, ^3J = 7.7 Hz, 2 H, perylene), 8.10 (s br., 2 H, perylene), 8.26 (dd, ^3J = 7.9 Hz, ^4J = 1.3 Hz, 1 H, aryl-H). − ^{13}C NMR (CDCl$_3$): δ = 14.10, 22.65, 27.07, 29.28, 29.59, 31.86, 54.85, 122.18, 122.39, 122.53, 124.88, 125.42, 127.30, 128.18, 128.86, 129.28, 130.55, 131.13, 132.41, 132.73, 133.70, 133.92, 135.93, 163.62, 166.13. − UV (CHCl$_3$): λ_{max} (ε) = 526 nm (82000), 490 (49800), 458 (18500). − Fluorescence (CHCl$_3$): λ_{max} = 534 nm, 574. − Fluorescence quantum yield (7.58·10^{-7} mol·l^{-1} in CHCl$_3$, reference **2a** with Φ = 100%) = 88%.. − MS (70 eV); *m/z* (%): 778 (6), 777 (25), 776 (47) [M$^+$], 760 (4), 759 (7) [M$^+$ − OH], 522 (5), 513 (6), 512 (30), 511 (90), 510 (100) [M$^+$ − C$_{19}$H$_{38}$], 493 (4) [510 − OH], 467 (10), 466 (34) [510 − CO$_2$], 465 (60) [510 − CO$_2$H], 419 (4), 57 (5), 55 (7). − C$_{50}$H$_{52}$N$_2$O$_6$ (777.0): calcd. C 77.29, H 6.74, N 3.60; found C 77.14, H 7.09, N 3.80.

Compound **4d**: *N*-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic 3,4-anhydride 9,10-imide (**3a**, 110 mg, 0.19 mmol) and glycine (180 mg, 2.40 mmol) were allowed to react and purified analogously to **4b** (1 h, 120°C). The chloroform phase (500 ml) of the rough reaction mixture was extracted with conc. HCl (100 ml), 2N aqueous HCl and distilled water. The chloroform phase was concentrated to 30 ml in vacuo and purified by column separation firstly over alumina (chloroform/acetic acid 10 + 1) and secondly two times over silica gel (chloroform/acetic acid 10 + 1) to give 70 mg (58%) of **4d**, m.p. 348−350°C. − R_f (silica gel, CHCl$_3$/ethanol (10 + 1)) = 0.10. − R_f (silica gel, CHCl$_3$/acetic acid (10 + 1)) = 0.63. − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1} (m), 2929 (m), 2857 (m), 1735 (w br.), 1700 (s), 1660 (s), 1616 (w), 1595 (s), 1579 (m), 1507 (w), 1457 (w), 1437 (m), 1404 (m), 1378 (w), 1346 (s br.), 1304 (w), 1253 (m), 1195 (w), 1173 (m), 1129 (w), 993 (w), 855 (w), 810 (s), 749 (m), 623 (w). − ^{1}H NMR (CDCl$_3$/[D$_6$]DMSO)): δ = 0.73 (t, 6 H, 2 CH$_3$), 1.28 (m$_c$, 16 H, 8 CH$_2$), 1.77 (m$_c$, 2 H, 2 α-CH$_2$), 2.14 (m$_c$, 2 H, 2 α-CH$_2$), 4.79 (s, 2 H, CH$_2$), 5.06 (m$_c$, 1 H, NCH), 8.55 (m$_c$, 8 H, perylene). − UV (CHCl$_3$): λ_{max} (ε) = 526 nm (79000), 490 (47300), 458 (16900). − Fluorescence (CHCl$_3$): λ_{max} = 537 nm, 575, 620. − Fluorescence quantum yield (7.05·10^{-7} mol·l^{-1} in CHCl$_3$, reference **2a** with Φ = 100%) = 82%. − MS (70 eV); *m/z* (%): 631 (12), 630 (27) [M$^+$], 613 (6) [M$^+$ − OH], 461 (6), 450 (23), 449 (74), 448 (100) [M$^+$ − C$_6$H$_{13}$], 431 (6) [M$^+$ − C$_6$H$_{13}$ − OH], 406 85), 405 (23), 404 (59) [448 − CO$_2$], 403 (7) [448 − CO$_2$H], 390 (1), 376 (6), 373 (3), 359 (7), 347 (6), 345 (3), 55 (6). − C$_{39}$H$_{38}$N$_2$O$_6$ (630.7): calcd C 74.27, H 6.07, N 4.44; found C 74.21, H 6.18, N 4.49.

Compound **4e**: *N*-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic 3,4-anhydride 9,10-imide (**3a**, 290 mg, 0.51 mmol), 4-aminobutyric acid (80 mg, 0.78 mmol) and imdazole (4 g) were allowed to react and purified analogously to **4b** (2 h, 140°C). The reaction product was purified by three column separations (alumina, chloroform/acetic acid (10 + 1) and twice silica gel, chloroform/acetic acid (10 + 1)) (230 mg, 70%). A further purification was obtained by an extractive[7] recrystallization from chloroform. The final chloroform phase was layered with pentane and allowed to stand for several days in a closed vessel. The solid was collected by vacuum filtration and further dried as is described for **4a** to give 180 mg (56%) of **4e**, m.p. 307−308°C. − R_f (silica gel, CHCl$_3$/ethanol (10 + 1)) = 0.35. − R_f (silica gel, CHCl$_3$/acetic acid (10 + 1)) = 0.65. − IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1} (m), 2926 (m), 2856 (m), 1730 (w br.), 1696 (s), 1658 (s), 1616 (w), 1595 (s), 1579 (m), 1506 (w), 1457 (w), 1442 (m), 1405 (m), 1342 (s br.), 1252 (m br.), 1177 (w), 1166 (w), 1128 (w), 902 (w), 855 (w), 810 (s), 746 (s). − ^{1}H NMR (CDCl$_3$/[D$_6$]DMSO, 50°C): δ = 0.84 (t, 6 H, 2 CH$_3$), 1.28 (m$_c$, 16 H, 8 CH$_2$), 1.87 (m$_c$, 2 H, 2 α-CH$_2$), 2.00 (q, ^3J = 7.3 Hz, 2 H, CH$_2$), 2.22 (m$_c$, 2 H, 2 α-CH$_2$), 2.36 (t, ^3J = 7.4 Hz, 2 H, CH_2COOH), 4.14 (t, ^3J = 7.0 Hz, 2 H, NCH$_2$), 5.11 (m$_c$, 1 H, NCH), 8.36 (d, ^3J = 8.1 Hz, 2 H, perylene), 8.46 (d, ^3J = 7.9 Hz, 2 H, perylene), 8.50 (d, ^3J = 8.0 Hz, 2 H, perylene), 8.55 (d, ^3J = 8.0 Hz, 2 H, perylene). − ^{13}C NMR (CDCl$_3$/[D$_6$]DMSO, 50°C): δ = 13.54, 21.89, 23.02, 26.29, 28.50, 31.07, 31.40, 31.77, 39.17, 53.68, 122.22, 123.09, 123.16, 125.32, 128.27, 128.52, 130.42, 133.50, 133.69, 162.42, 173.66. − UV (CHCl$_3$): λ_{max} (ε) = 526 nm (81100), 490 (49100), 458 (17900). − Fluorescence (CHCl$_3$): λ_{max} =

537 nm, 575. − Fluorescence quantum yield ($5.72 \cdot 10^{-7}$ mol·l^{-1} in $CHCl_3$, reference **2a** with Φ = 100%) = 92%. − MS (70 eV); *m/z* (%): 659 (9), 658 (28) [M^+], 641 (5) [$M^+ - OH$], 489 (9), 477 (29), 476 (100) [$M^+ - C_{13}H_{26}$], 458 (9), 417 (6), 416 (6), 414 (8), 405 (6), 404 (19), 403 (10), 392 (9), 391 (40), 390 (94) [$476 - C_4H_6O_2$], 373 (19), 346 (14), 345 (23), 83 (11), 69 (27), 55 (50). − $C_{41}H_{42}N_2O_6$ (658.8): calcd. C 74.75, H 6.43, N 4.25; found C 74.61, H 6.38, N 4.25.

Compound **4f**: *N*-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic 3,4-anhydride 9,10-imide (**3a**, 400 mg, 0.70 mmol), 6-aminocapronic acid (130 mg, 1.00 mmol) and imidazole (5 g) were allowed to react and purified as is described for **4b** (2 h, 130°C). The chloroform phase (200 ml) was extracted with a little conc. HCl and then with 200 ml of 2 N aqueous HCl and washed with distilled water. A further purification proceeded by column separation over alumina with chloroform/acetic acid (9 + 1) and over silica gel with chloroform/acetic acid (10 + 1); an inhomogeneous orange red forerun was separated and discarded. The further purification proceeded as described for **4a** to give 280 mg (58%) of **4f**, m.p. 246−248°C. − R_f (silica gel, $CHCl_3$/acetic acid (10 + 1)) = 0.66. − R_f (silica gel, $CHCl_3$/ethanol (10 + 1)) = 0.60. − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1} (m), 2928 (m), 2857 (m), 1730 (w sh), 1696 (s br.), 1658 (s), 1616 (w), 1595 (s), 1579 (m), 1506 (w), 1457 (w), 1439 (m), 1405 (s), 1385 (w), 1355 (m), 1342 (s), 1253 (m), 1217 (w), 1176 (w), 1126 (w), 905 (w), 855 (w), 810 (s), 747 (m), 668 (w). − ^1H NMR ($CDCl_3$): δ = 0.81 (t, 6 H, 2 CH_3), 1.28 (m_c, 16 H, 8 CH_2), 1.49 (m_c, 2 H, CH_2), 1.76 (m_c, 4 H, 2 CH_2), 1.88 (m_c, 2 H, 2 α-CH_2), 2.23 (m_c, 2 H, 2 α-CH_2), 2.39 (t, ^3J = 7.6 Hz, 2 H, CH_2COOH), 4.17 (t, ^3J = 7.6 Hz, 2 H, NCH_2), 5.16 (m_c, 1 H, NCH), 8.44 (d, ^3J = 8.3 Hz, 2 H, perylene), 8.47 (d, ^3J = 8.0 Hz, 2 H, perylene), 8.54 (d, ^3J = 7.8 Hz, 2 H, perylene), 8.58 (s br., 2 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.01, 22.56, 24.36, 26.51, 26.94, 27.66, 29.20, 31.74, 32.37, 33.51, 40.30, 54.83, 122.83, 122.97, 123.05, 126.19, 126.29, 129.23, 129.43, 131.26, 134.14, 134.54, 163.23, 177.66. − UV ($CHCl_3$): λ_{max} (ε) = 526 nm (80800), 489 (48400), 458 (17700). − Fluorescence ($CHCl_3$): λ_{max} = 535 nm, 574. − Fluorescence quantum yield ($8.01 \cdot 10^{-7}$ mol·l^{-1} in $CHCl_3$, reference **2a** with Φ = 100%) = 94%. − MS (70 eV); *m/z* (%): 688 (9), 687 (34), 686 (73) [M^+], 669 (11) [$M^+ - OH$], 517 (5), 507 (5), 506 (26), 505 (81), 504 (100) [$M^+ - C_{13}H_{26}$], 487 (9), 405 (8), 404 (23), 402 (9), 391 (31), 390 (58) [$504 - C_6H_{10}O_2$], 372 (10), 345 (10), 55 (5). − $C_{43}H_{46}N_2O_6$ (686.9): calcd. C 75.19, H 6.75, N 4.08; found C 75.28, H 6.94, N 4.08.

Compound **4g**: *N*-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic 3,4-anhydride 9,10-imide (**3a**, 300 mg, 0.52 mmol), 11-aminoundecanoic acid (160 mg, 0.79 mmol) and imidazole (4 g) were allowed to react (1 h, 130°C) and purified as described for **4b** with one column separation with chloroform/acetic acid (10 + 1) over alumina and a second column separation with chloroform/acetic acid (10 + 1) over silica gel; coloured by-products were thus eluted and the solvent was changed to chloroform/ethanol (4 + 1) for the elution of the main product to give 210 mg (53%) of **4g**, m.p. 168−170°C. − R_f (silica gel, $CHCl_3$/ethanol (10 + 1)) = 0.61. − R_f (silica gel, $CHCl_3$/acetic acid (10 + 1)) = 0.66. − IR (KBr): $\tilde{\nu}$ = 2953 cm^{-1} (m), 2926 (s), 2855 (m), 1728 (m sh), 1697 (s), 1658 (s), 1615 (w), 1595 (s), 1579 (m), 1508 (w), 1458 (m), 1439 (m), 1405 (s), 1389 (w), 1355 (m sh), 1342 (s), 1254 (m), 1217 (w), 1176 (m), 1126 (w), 1108 (w), 1092 (w), 853 (m), 810 (s), 796 (w), 746 (m), 655 (w). − ^1H NMR ($CDCl_3$): δ = 0.81 (t, 6 H, 2 CH_3), 1.29 (m_c, 28 H, 8 CH_2 + 6 CH_2 carboxylic acid), 1.61 (m_c, 2 H, CH_2), 1.69 (m_c, 2 H, CH_2), 1.89 (m_c, 2 H, 2 α-CH_2), 2.24 (m_c, 2 H, 2 α-CH_2), 2.33 (t, ^3J = 7.5 Hz, 2 H, CH_2), 4.08 (t, ^3J = 7.5 Hz, 2 H CH_2), 5.15 (m_c, 1 H, NCH), 8.20 (d, ^3J = 8.2 Hz, 2 H, perylene), 8.29 (d, ^3J = 8.3 Hz, 2 H, perylene), 8.34 (d, ^3J = 8.1 Hz, 2 H, perylene), 8.50 (s br., 2 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.04, 22.60, 24.67, 26.99, 27.09, 28.02, 28.98, 29.13, 29.25, 29.28, 29.39, 31.77, 32.38, 33.94, 40.60, 54.87, 122.62, 122.71, 122.89, 123.21 br., 123.91 br., 125.86, 128.88, 129.26, 130.87, 131.49 br., 133.81, 134.06, 162 93, 163 .26 br., 164.32 br., 179.20. − UV ($CHCl_3$): λ_{max} (ε) = 526 nm (82100), 490 (49400), 458 (18000). − Fluorescence ($CHCl_3$): λ_{max} = 537 nm, 575. − Fluorescence quantum yield ($6.87 \cdot 10^{-7}$ mol·l^{-1} in $CHCl_3$, reference **2a** with Φ = 100%) = 92%. − MS (70 eV); *m/z* (%): 758 (15), 757 (53), 756 (100) [M^+], 740 (8), 739 (15), 576 (9), 575 (36), 574 (79) [$M+ - C_{13}H_{26}$], 558 (4), 557 (11), 405 (6), 404 (19), 403 (13), 392 (12), 391 (39), 390 (36) [$574 - C_{11}H_{20}O_2$], 373 (8), 345 (5). − $C_{48}H_{56}N_2O_6$ (757.0): calcd. C 76.16, H 7.46, N 3.70; found C 76.10, H 7.45, N 3.70.

Compound **5**: Perylene-3,4-dicarboxylic anhydride[8][9] (120 mg, 0.37 mmol), 11-aminoundecylic acid (110 mg, 0.55 mmol) and imidazole (3 g) were allowed to react (1 h, 120°C) and purified as described for **4b** to give 110 mg (59%) **5**, m.p. 186−187°C. − R_f (silica gel, $CHCl_3$/acetic acid (10 + 1)) = 0.66. − R_f (silica gel, $CHCl_3$/ethanol (10 + 1)) = 0.60. − R_f (alumina, $CHCl_3$/acetic acid (10 + 1)) = 0.46. − IR (KBr): $\tilde{\nu}$ = 3200 cm^{-1} (w br.), 3050 (w), 2927 (s), 2854 (m), 1733 (m), 1700 (m sh), 1691 (s), 1651 (s), 1618 (w), 1592 (s), 1571 (m), 1500 (w), 1435 (w), 1422 (w), 1410 (w), 1383 (m), 1374 (m), 1356 (s), 1293 (m), 1246 (m), 1091 (w), 838 (w), 810 (s), 754 (m). − ^1H NMR ($CDCl_3$/[D_6]DMSO/50°C): δ = 1.36 (m_c, 12 H, 6 CH_2), 1.56 (m_c, 2 H, CH_2), 1.70 (m_c, 2 H, CH_2), 2.20 (t, ^3J = 7.4 Hz, 2 H, CH_2CO_2H), 4.05 (t, ^3J = 7.5 Hz, 2 H, NCH_2), 7.49 (t, ^3J = 7.7 Hz, 2 H, perylene), 7.79 (d, ^3J = 8.0 Hz, 2 H, perylene), 8.15 (d, ^3J = 8.0 Hz, 2 H, perylene), 8.22 (d, ^3J = 7.5 Hz, 2 H, perylene), 8.23 (d, ^3J = 8.1 Hz, 2 H, perylene). − ^{13}C NMR ($CDCl_3$/[D_6]DMSO/50°C): δ = 24.39, 26.55, 27.46, 28.51, 28.61, 28.67, 28.75, 28.81, 33.65, 39.54, 119.75, 120.08, 123.32, 125.73, 126.50, 126.88, 128.21, 128.73, 130.25, 130.43, 133.51, 136.09, 162.73, 174.43. − UV ($CHCl_3$): λ_{max} (ε) = 506 nm (29900), 484 (30800). − Fluorescence ($CHCl_3$): λ_{max} = 541 nm, 574. − Fluorescence quantum yield (6.87 $1.051 \cdot 10^{-6}$ mol·l^{-1} in $CHCl_3$, reference **2a** with Φ = 100%) = 88%. − MS (70 eV); *m/z* (%): 507 (6), 506 (35), 505 (100) [M^+], 489 (4), 488 (13), 461 (7) [$M^+ - CO_2$], 336 (5), 335 (22) [$M^+ - C_{10}H_{18}O_2$], 334 (11) 323 (5), 322 (29), 321 (69) [$M^+ - C_{11}H_{20}O_2$], 304 (6), 277 (8), 276 (7), 251 (4), 250 (7), 223 (6). − $C_{33}H_{31}NO_4$ (505.6): calcd. C 78.39, H 6.18, N 2.77; found C 78.20, H 6.07, N 2.81.

N-(1-Hexylheptyl)-N'-(6-hexanoxycarbonyl)perylene-3,4:9,10-bis(dicarboximide): Compound **4f** 137 (150 mg, 0.22 mmol), glycerol (22 mg, 0.24 mmol), toluenesulfonic acid monohydrate (100 mg) and chloroform/5% ethanol (20 ml) were refluxed (4 h). The solvent was slowly distilled off and the residue purified by column separation with chloroform/ethanol (10 + 1) over silica gel and over alumina. Methanol was added to the pure main fraction which was then filtered through a D4 glass filter and evaporated and dried at 80°C in vacuo to give 52 mg (33%), m.p. 192−193°C. − R_f (silica gel, $CHCl_3$/ethanol (10 + 1)) = 0.83. − R_f (alumina/$CHCl_3$) = 0.70. − IR (KBr): $\tilde{\nu}$ = 2956 cm^{-1} (m), 2928 (m), 2858 (m), 1724 (m), 1697 (s), 1658 (s), 1596 (s), 1578 (m), 1508 (w), 1458 (w), 1438 (m), 1404 (m), 1343 (s), 1253 (m), 1178 (m), 1126 (w), 1109 (w), 1084 (w), 1032 (w), 853 (w), 810 (m), 796 (w), 747 (m). − ^1H NMR ($CDCl_3$): δ = 0.81 (t, 6 H, 2 CH_3), 1.28 (m_c, 16 H, 8 CH_2), 1.23 (t, ^3J = 7.1 Hz, 3 H, CH_3), 1.47 (m_c, 2 H, CH_2), 1.74 (m_c, 4 H, 2 CH_2), 1.88 (m_c, 2 H, 2 α-CH_2), 2.23 (m_c, 2 H, 2 α-CH_2), 2.32 (t, ^3J = 7.3 Hz, 2 H, CH_2CO_2R), 4.11 (q, ^3J = 7.1 Hz, 2 H, $CO_2CH_2CH_3$), 4.17 (t, ^3J = 7.5 Hz, 2 H, NCH_2), 5.16 (m_c, 1 H, NCH), 8.53 (d, ^3J = 8.1 Hz, 2 H, perylene), 8.56 (d, ^3J = 8.1

Hz, 2 H, perylene), 8.62 (d, ^3J = 7.9 Hz, 4 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.02, 14.23, 22.57, 24.67, 26.64, 26.93, 27.75, 29.21, 29.67, 31.74, 32.37, 34.21, 40.36, 54.81, 60.19, 122.86, 122.99, 123.08, 123.30 br., 124.02 br., 126.22, 126.33, 129.25, 129.46, 131.03 br., 131.25, 131.68 br., 134.20, 134.55, 163.22, 164.52 br., 173.58. − UV ($CHCl_3$): λ_{max} (ε) = 526 nm (81350), 489 (48800), 458 (18000). − Fluorescence ($CHCl_3$): λ_{max} = 535 nm, 574, 618 br. − Solid-state fluorescence: λ_{max} = 528 nm, 570, 625. − MS (70 eV); *m*/*z* (%): 716 (13), 715 (49), 714 (100) [M^+], 698 (4), 697 (9), 617 (4), 669 (8), 534 (17), 533 (55), 532 (72) [$M^+ - C_{13}H_{26}$], 515 (5), 445 (5), 405 (6), 404 (17), 403 (9), 392 (6), 391 (25), 390 (39), 373 (7), 345 (4). − $C_{45}H_{50}N_2O_6$ (714.9): calcd. C 75.60, H 7.05, N 3.92; found C 75.35, H 6.99, N 3.94.

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