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Methoxyperylene Bisimides and Perylene Lactame Imides: Novel, Red Fluorescent Dyes

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Abstract: The synthesis of methoxyperylene bisimides and perylene lactame imides with aliphatic *N*-substituents is described. Both classes of dyes exhibit fluorescence in the bathochromic region of visible light so that red light is obtained. The lightfastness of the dyes is very high, thus, there is special interest for diverse applications.

Keywords: dyes/pigments · fluorescence spectroscopy · nucleophilic displacement · perylenes

Introduction

Perylene dyes, perylene-3,4:9,10-tetracarboxylic bisimides (**1**) are remarkable for their extraordinarily high lightfastness.[1,2] Readily soluble derivatives were obtained by the attachment of *tert*-butylphenyl substituents[3] or long-chain *sec*-alkyl groups ("swallow-tail substituents")[4,5] at the nitrogen atoms of **1**. These dyes exhibit very strong fluorescence.

The substitution of the core of the perylene dyes is of special interest because the introduction of donor groups, such as ether groups in the positions 1, 6, 7 and 12,[6] should cause bathochromic shifts. Such shifts were documented for four aliphatic and aromatic ether groups,[7–9] respectively. However, the accumulation of substituents in these positions causes a strong deformation of the aromatic core by steric interactions.[10] We wanted to test if one single donor group, although causing less steric strain, could nevertheless produce a sufficiently strong bathochromic shift. For example, one could halogenate the core of **1** and then exchange the halogen group with an ether function, as was described for the tetraether derivatives. However, the halogenation gives mixtures of halogenation products that are difficult to separate. The exchange reaction with the rough halogenation product is not a solution to this problem, because the separation of the resulting reaction mixtures proved to be similarly difficult. The tracked synthesis of the hitherto unknown monoalkoxy derivatives of **1** would enable appreciable progress to be made.

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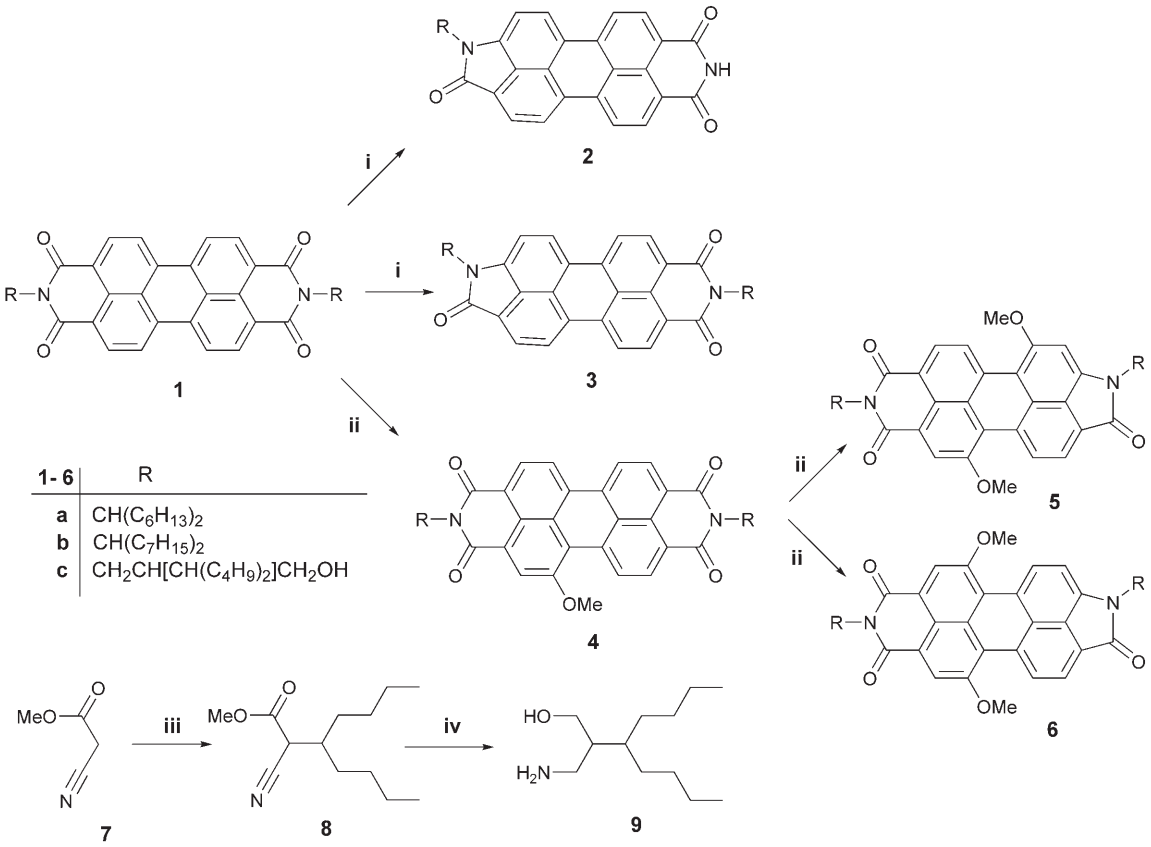
Results and Discussion

We attempted to incorporate a methoxy group into **1** by the direct nucleophilic attack on its core. However, the basic reaction conditions necessary for this cause the hydrolysis of **1** to dominate. We applied the dipolar aprotic solvent dimethyl sulfoxide (DMSO) to increase the nucleophilicity of the methoxylate for competing with the hydrolysis (Scheme 1). Dyes **1** with aromatic substituents R undergo efficiently a ring contraction under these conditions, initiated by a nucleophilic attack on a carbonyl group of **1**. However, this novel ring transformation proceeds only slowly if the substituents R are aliphatic,[11] presumably because of the stronger electron-releasing properties of these groups. Therefore, the attack of the methoxide anion on the perylene core offers an alternative route. Finally, the product-forming step is expected to be the release of a hydride ion; this is favoured by the presence of methanol as a weak acid under the strongly alkaline conditions. This selected combination of reagents favour the formation of **4a** up to 8%. We introduced β-hydroxy groups into the side chain of **1** to suppress hydrolysis.[11] To this end, we alkylated cyano acetic acid (**7**) with 5-bromononane; this single alkylation proceeds easily and the double alkylation proved to be difficult. The alkylated cyano ester **8** was reduced to the amino alcohol **9**, then condensed with perylene tetracarboxylic bisanhydride to **1c** and finally allowed to react to **4c**; thus, the yield of methoxy derivative could be increased to about 24%.



Scheme 1. Synthesis of the perylene dyes **2** and **3**. i) KOH/MeOH; ii) KOH/MeOH/DMSO; iii) $BrCH(C_4H_9)_2/K_2CO_3$; iv) $LiAlH_4$.

The suppression of hydrolysis by the substituents of **1c** has a further consequence: the use of KOH in *tert*-butyl alcohol with additional methanol as the standard mixture for hydrolysing perylene imides **1c** causes not only a ring contraction of one carboxylic imide to a lactam unit, but also the loss of the alkyl group at the remaining carboxylic imide structure to form **2**, and a difficult-to-separate mixture of **5** and **6** as products of the substitution of the core. The formation of **2** proceeds presumably by a nucleophilic displacement reaction because the carboxylic imide anion is an acceptable leaving group, the attached carbon atom is primary and the neighboured carbon atom is only tertiary. Dye **2** is of special interest because there is no synthetic procedure for such dyes and because the imide nitrogen atom can be readily deprotonated and applied as a nucleophile for labelling or linkage to other chromophores (compare reference [12]).

The UV-visible absorption and fluorescence spectra of **1c** correspond to the spectra of other perylene bisimides with aliphatic substituents R, and the spectra of **3c** correspond to those of other lactame imides with aliphatic substituents.[11]

The UV-visible spectra of the methoxy derivatives **4** are remarkable because of the bathochromic shift induced by the methoxy group; about 30 nm for **4c** relative to **1c** (Figure 1). The bright-red fluorescence of **4c** is comparable with the fluorescence of the perylene bisimide tetraether derivatives and exhibits a fluorescence quantum yield of 86%. This bathochromic shift facilitates the use of **4c** not only in the operation region of the widely used laser dye Rhodamine 6G, but also for many applications that require a red fluorescent material, such as the fluorescent planar concentrator.[13] The photostability of **4c** is very high; no bleaching process could be detected by using solar radiation (many dyes direct solar radiation of a diluted solution in chloroform), and the rate of photobleaching is more than 50 times

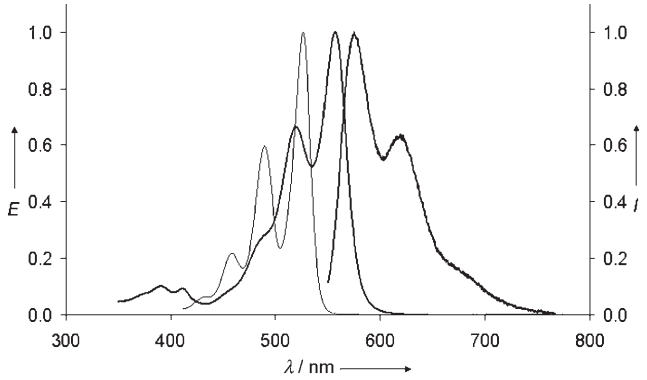


Figure 1. UV/Vis absorption spectrum (*E*) of compound **1a** (thin line) and UV/Vis absorption (thick line left) and fluorescence spectra (*I*, thick line right)of compound **4c** in chloroform.

lower than that of Rhodamine B (see Supporting Information).

Experimental Section

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 (3a) and 2,9-bis-(1-hexylheptyl)-5-methoxyanthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (4a): 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, 0.503 mmol) was heated with a mixture of potassium hydroxide (85%, 700 mg, 12.5 mmol), DMSO (4 mL) and methanol (6 mL) at 100 °C for 5 h to give a deep green mixture. This was quenched with distilled water to yield a red and bluish-black precipitate that was neutralised with 2 N HCl (colour change to red and violet), collected by vacuum filtration, washed with distilled water, treated twice with boiling aqueous K_2CO_3 (200 mL, 10%) and purified by column separation (silica gel, chloroform) to obtain the starting material as the first fraction, followed closely by a mixture of **3a** and **4a**. The latter was separated by column separation (silica gel, chloroform/acetone 5:1).

First fraction: Yield 30 mg (8%) fine, violet powder of **4a**. R_f = 0.64 (silica gel, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83 (t, 12H; $2CH_3$), 1.24–1.39 (m, 32H; $16CH_2$), 1.83–1.92 (m, 4H; $2CH_2$), 2.17–2.31 (m, 4H; $2CH_2$), 4.34 (s, 3H; O–CH_3), 5.19 (m, 2H; 2CH), 8.47 (brs, 1H; perylene), 8.55 (d, 2H; perylene), 8.58 (d, 1H; perylene), ≈8.56 (brs, 1H; perylene), 8.64 (brs, 2H; perylene), 9.48 ppm (d, 1H; perylene); ^{13}C NMR ($CDCl_3$): δ = 164.1, 165.2, 158.3, 134.5, 134.3, 134.0, five signals between 133 and 130 ppm, 129.2, 128.6, 128.4, 127.0, 124.5, 123.4, 122.8, 122.4, 121.9, 120.8, 118.0, 117.4, 56.9, 54.6, 32.4, 31.8, 29.2, 27.0, 22.6, 14.1 ppm; IR (KBr): $\tilde{\nu}$ = 3443 (m), 2980 (m), 2925 (s), 2859 (m), 1695 (s), 1680 (s), 1670 (s), 1660 (s), 1615 (m), 1590 (s), 1575 (m), 1556 (m), 1520 (s), 1498 (w), 1489 (w), 1469 (m), 1450 (s), 1428 (m), 1405 (s), 1490 (s), 1485 (s), 1349 (s), 1330 (s), 1266 (m), 1250 (m), 1240 (m), 1145 (m), 1110 (w), 930 (w), 902 (m), 865 (m), 850 (m), 811 (m), 795 (w), 751 (m), 712 (w), 695 (w), 640 (m) cm^{-1}; UV/Vis($CHCl_3$): λ_{max} = 372, 387, 408, 485, 515, 552 nm; fluorescence ($CHCl_3$): λ_{max} = 575, 604 nm; MS (70 eV): *m*/*z* (%): 784 (100) [M^+], 767 (14) [M^+-17], 713 (1), 699 (4) [$M^+-C_6H_{13}$], 615 (2) [699–C_6H1_3], 602 (45) [$M^+-C_{13}H_{26}$], 585 (9) [602–17], 517 (1) [602–C_6H1_3], 420 (78) [$M^+-2C_{13}H_{26}$], 406 (20), 405 (16) [420–CH_3], 403 (5), 378 (2), 362 (9), 360 (5), 334 (5); HRMS (70 eV): *m*/*z* calcd for $C_{51}H_{64}N_2O_5$: 784.4815; found: 784.4765.

Second fraction: Yield 25 mg (6%) violet powder of **3a**. R_f = 0.43 (silica gel, $CHCl_3$); R_f = 0.96 (silica gel, $CHCl_3$/acetone 10:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.82 (t, 12H; $4CH_3$), 1.19–1.29 (m, 32H; $16CH_2$), 1.78–1.86 (m, 4H; $2CH_2$), 2.10–2.15 (m, 2H; CH_2), 2.20–2.25 (m, 2H; CH_2), 4.51 (brm, 1H; CH), 5.17 (m, 1H; CH), 7.14 (d, J(H,H) = 7.8 Hz, 1H; perylene), 8.14 (d, J(H,H) = 7.6 Hz, 1H; perylene), 8.23 (d, J(H,H) = 7.9 Hz, 1H; perylene), 8.33 (d, J(H,H) = 8.1 Hz, 1H; perylene), 8.47 (d, J(H,H) = 8.1 Hz, 1H; perylene), 8.48 (d, J(H,H) = 7.8 Hz, 1H; perylene), 8.57 ppm (brdd, 2H; perylene); ^{13}C NMR ($CDCl_3$): 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 ($2CH_2$), 32.4 ($2CH_2$), 31.8 ($2CH_2$), 31.6 ($2CH_2$), 29.2 ($2CH_2$), 29.0 ($2CH_2$), 27.0 ($2CH_2$), 26.6 ($2CH_2$), 22.6 ($2CH_2$), 22.5 ($2CH_2$), 14.0 ($2CH_3$), 13.99 ppm ($2CH_3$); 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}; UV/Vis($CHCl_3$): λ_{max} = 578 (sh), 543, 482 (sh), 444, 411, 396, 362 nm; fluorescence ($CHCl_3$): λ_{max} = 621 nm; MS (70 eV): *m*/*z* (%): 726 (100) [M^+], 709 (8) [M^+-17], 641 (9) [$M^+-C_6H_{13}$], 544 (23) [$M^+-C_{13}H_{26}$], 527 (3) [544–OH], 459 (15) [544–C_6H_{13}], 389 (3), 375 (14), 362 (21) [544–$C_{13}H_{26}$], 345 (3) [362–17], 317 (3) [345–CO].

1,8-Bis(1-heptyloctyl)-1*H*-indolo[5′,4′,3′:10,5,6]anthra[2,1,9-*def*]isoquinoline-2,7,9(8*H*)-trione (3b) and 2,9-bis-(1-heptyloctyl)-5-methoxyanthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (4b): 2,9-Bis-(1-heptyloctyl)anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (**1b**, 390 mg, 0.450 mmol) was allowed to react analogously to **3a**. Yield 5 mg (1%) violet powder of **4b**. R_f = 0.92 (silica gel, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81 (t, 12H; $4CH_3$), 1.19–1.52 (m, 20H; $10CH_2$), 1.85 (m, 4H; $2CH_2$), 2.23 (m, 4H; $2CH_2$), 4.34 (s, 3H; O–CH_3), 5.17 (m, 2H; 2CH), 8.50 (m, 2H; perylene), 8.64 (d, J(H,H) = 7.6 Hz, 2H; perylene), 8.68 (d, J(H,H) = 8.0 Hz, 2H; perylene), 9.56 ppm (d, J(H,H) = 8.4 Hz, 1H; perylene); MS (70 eV): *m*/*z* (%): 840 (71) [M^+], 823 (12) [M^+-OH], 755 (1), 741 (3) [$M^+-C_7H_{15}$], 644 (6) [$M^+-2C_7H_{14}$], 630 (45) [$M^+-C_{15}H_{30}$], 613 (9) [630–17], 450 (3), 434 (11), 420 (100) [$M^+-2C_{15}H_{30}$], 407 (11), 406 (30), 405 (20), 403 (6), 362 (10), 360 (6); UV/Vis($CHCl_3$): λ_{max} = 371, 388, 408, 485, 516, 553 nm; fluorescence ($CHCl_3$): λ_{max} = 574, 606 nm.

2-Cyano-3-butyl-1-methylheptanoate (8): Anhydrous K_2CO_3 (6.9 g, 50 mmol) was added to a mixture of methyl cyanoactate (**7**, 3.96 g, 39.6 mmol) and 5-bromononane (10.5 g, 50.6 mmol) in dry DMF (20 mL) and heated with stirring under argon for 12 h, diluted with distilled water and extracted with ether (3 × 50 mL). The combined ether phases were washed with water (3 × 30 mL), dried ($MgSO_4$), filtrated and evaporated (10.3 g of a viscous oil) and purified by flash chromatography (silica gel, isohexane) to remove unconverted 5-bromononane. The reaction product was eluted after the addition of 10% ethyl acetate. Yield 3.19 g (86% with respect to converted starting material) colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (m, 6H; $2CH_3$), 1.40 (m, 12H; $6CH_2$), 2.10 (m, 1H; CH), 3.62 (d, J(H,H) = 4.15 Hz, 1H; CH) 3.82 ppm (s, 3H; CO_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.89, 13.93, 22.58, 22.67, 28.86, 29.03, 31.36, 31.52, 39.41, 41.87, 53.27, 115.53, 166.98 ppm; IR (KBr): $\tilde{\nu}$ = 2933 (s), 2958 (s), 2862 (s), 2249 (w), 1749 (s), 1467 (m), 1459 (m), 1437 (m), 1380 (w), 1256 (s), 1209 (s), 1018 (m), 732 (w) cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 226 (68) [M^++H], 227 (8) [M^++H+1], 196 (2) [M^++H–C_2H_6], 168 (12), 143 (4), 140 (22), 136 (12), 108 (4), 100 (100) [M^++H–C_9H_{18}], 85 (8), 71 (10), 41 (13); elemental analysis calcd (%) for $C_{13}H_{23}NO_2$ (225.3): C 69.29, H 10.29, N 6.22; found: C 69.37, H 10.38, N 6.37.

2-Aminomethyl-3-butyl-1-heptanol (9): 2-Cyano-3-butyl-1-methylheptanoate (**8**, 3.60 g, 16.0 mmol) in *tert*-butyl methyl ether (50 mL) was added under argon to a stirred suspension of $LiAlH_4$ (3.56 g, 93.6 mmol) in anhydrous *tert*-butyl methyl ether (50 mL) over 1 h (ice bath), allowed to react at room temperature for 1 h, refluxed for 5 h, allowed to stand for 16 h, quenched by the addition of 10% NaOH and extracted with *tert*-butyl methyl ether. The combined organic phases were washed with distilled water (3 × 50 mL), dried ($MgSO_4$), filtrated, evaporated (3.31 g viscous oil) and purified by vacuum distillation. Yield 2.35 g (73%) colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, J(H,H) = 6.6 Hz, 6H; $2CH_3$), 1.26 (m, 12H; $6CH_2$), 1.70 (m, 1H; CH), 2.70 (2H; CH_2) 3.75 ppm (2H; CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.11 (6C; $2CH_3$), 38.62 (1C; CH), 43.65 (1C; CH), 23.05 (2C; $2CH_2$), 30.04 (2C; $2CH_2$), 30.73 (1C; CH_2), 30.91 (1C; CH_2), 45.37 (1C; CH_2–NH_2), 67.06 ppm (1C; CH_2–OH); IR (KBr): $\tilde{\nu}$ = 3293 (br), 2956 (s), 2928 (s), 2860 (s), 1574 (m), 1467 (s), 1378 (m), 1327 (w), 1152 (m), 1035 (s), 828 (w), 729 (w) cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 202 (13) [M+H]$^+$, 172 (11), 168 (10), 144 (12), 126 (32), 112 (30), 98 (35), 84 (28), 75 (70), 70 (73), 69 (48), 58 (16), 57 (50), 56 (52), 55 (100), 46 (19); elemental analysis calcd (%) for $C_{12}H_{27}NO$ (201.4): C 71.58, H 13.52, N 6.96; found: C 72.16, H 13.60, N 6.57.

2,9-Bis-(3-butyl-2-hydroxymethylheptyl)anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (1c): Perylene-3,4:9,10-tetracarboxylic-3,4:9,10-bisanhydride (2.10 g, 5.36 mmol), 2-aminomethyl-3-butyl-1-heptanol (**6**, 2.42 g, 12.1 mmol) and imidazole (20 g) were heated under argon with stirring to 140 °C for 5 h, allowed to cool, treated while still warm (≈90 °C) with 2 N HCl (100 mL), allowed to stand for 1 h at room temperature, collected by vacuum filtration, washed with distilled water, dried in air (80 °C, 16 h) and purified by column separation (silica gel, chloroform/5% methanol). Yield 3.50 g (86%) red powder of **1c**. M.p. 266–268 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, J(H,H) = 6.8 Hz, 12H; $4CH_3$), 1.38–1.58 (m, 24H; $12CH_2$), 1.68 (m, 2H; 2CH), 2.01 (m, 2H; 2CH), 3.54 (ABq, J(H,H) = 3.6 Hz, 2H; CH_2), 3.71 (ABq, J(H,H) = 4.4 Hz, 2H; CH_2), 4.24 (ABq, J(H,H) = 4 Hz, 2H; CH_2), 4.36 (m, 2H; CH_2), 8.58 (d, J(H,H) = 8 Hz, 4H; perylene), 8.67 ppm (d, J(H,H) = 8 Hz,

4H; perylene); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.18 (4C; 4CH_3), 23.15 (4C; 4CH_2), 29.57 (2C; CH_2), 29.67 (2C; 2CH_2), 30.54 (2C; 2CH_2), 30.63 (2C; CH_2), 38.71 (1C; CH), 40.75 (1C; CH_2), 42.04 (1C; CH), 61.39 (1C; CH_2), 123.15 (4C; 4CH perylene), 131.72 (4C; 4CH perylene), 126.35 (2C; 2C perylene), 129.34 (2C; 2C perylene), 134.71 (4C; 4C perylene), 164.15 ppm (4C; 4CO perylene); IR (KBr): $\tilde{\nu}$ = 3447 (br), 2956 (s), 2928 (s), 2860 (m), 1695 (s), 1652 (s), 1595 (s), 1579 (m), 1508 (w), 1443 (m), 1404 (m), 1342 (s), 1153 (m), 1170 (w), 1017 (w), 975 (w), 854 (w), 811 (s), 747 (m) cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 529 (86320), 492 (51880), 461 nm (18860 L mol^{-1} cm^{-1}); fluorescence quantum yield ($CHCl_3$, reference **1a** with Φ = 100%) = 1.0%; MS (70 eV, EI): *m*/*z* (%): 760 (21), 759 (15), 758 (13) $[M]^+$, 587 (22), 576 (27), 575 (62), 557 (13), 431 (19), 417 (19), 416 (19), 405 (43), 404 (65), 403 (39), 393 (23), 392 (72), 391 (100), 390 (27), 376 (21), 375 (19), 373 (21), 347 (13), 346 (18), 345 (13), 321 (17); elemental analysis calcd (%) for $C_{48}H_{58}N_2O_6$ (759.0): C 75.96, H 7.70, N 3.69; found: C 75.99, H 8.00, N 3.63.

1,8-Bis-(3-butyl-2-hydroxymethylheptyl)-1*H*-indolo[5′,4′,3′:10,5,6]anthra[2,1,9-*def*]isoquinoline-2,7,9(8*H*)-trione (3c) and 1-(3-butyl-2-hydroxymethyl-heptyl)-4,11-dimethoxy-1*H*-indolo[5′,4′,3′:10,5,6]anthra[2,1,9-*def*]isoquinoline-2,7,9(8*H*)-trione (2c): A mixture of 2,9-bis-(3-butyl-2-hydroxymethylheptyl)anthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (**1c**, 100 mg, 0.130 mmol) and KOH powder (85%, 400 mg, 6.07 mmol) in methanol (30 mL) was refluxed for 1.5 h, evaporated (50 °C), dispersed in *tert*-butyl alcohol (50 mL), refluxed with stirring (5 h, bath at 100 °C), poured into distilled water (300 mL), acidified with 2N HCl (20 mL), diluted with distilled water (200 mL), heated to 100 °C for 10 min, cooled to room temperature, collected by vacuum filtration, dried in air (120 °C, 2 h, 88 mg) and purified by column separation (silica gel, 2% MeOH/$CHCl_3$).

First fraction: Yield 14 mg (15%) reddish-violet powder of **3c**. MS (70 eV, EI): *m*/*z* (%): 730 (100) $[M]^+$.

Second fraction: Yield 15 mg (21%) dark violet powder of **2c**. IR (KBr): $\tilde{\nu}$ = 3442 (br), 2954 (w), 2925 (m), 2856 (w), 1692 (s), 1644 (s), 1583 (s), 1492 (s), 1462 (w), 1441 (w), 1390 (s), 1352 (w), 1319 (w), 1243 (m), 1164 (w), 843 (w), 806 (m), 740 (m) cm^{-1}; MS (70 eV): *m*/*z* (%): 546 (30) $[M]^+$; elemental analysis calcd (%) for $C_{35}H_{34}N_2O_4$ (546.7): C 76.90, H 6.27, N 5.12; found: C 75.33, H 6.77, N 4.74.

2,9-Bis-(3-butyl-2-hydroxymethylheptyl)-5-methoxyanthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (4c), 1,8-bis-(3-butyl-2-hydroxymethyl-heptyl)-4,11-dimethoxy-1*H*-indolo[5′,4′,3′:10,5,6]anthra[2,1,9-*def*]isoquinoline-2,7,9(8*H*)-trione (5c) and 1,8-bis-(3-butyl-2-hydroxymethyl-heptyl)-5,11-dimethoxy-1*H*-indolo[5′,4′,3′:10,5,6]anthra[2,1,9-*def*]isoquinoline-2,7,9(8*H*)-trione (6c): A mixture of *N*,*N*′-bis-(2-hydroxymethyl-3-butylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**1c**, 400 mg, 0.520 mmol) and KOH powder (85%, 1.72 g, 26.0 mmol) in DMSO/MeOH (80:40, 120 mL) was refluxed at 110 °C for 3 h, cooled to RT, poured into 2N HCl (100 mL), stirred for 2 h, collected by vacuum filtration, dried in air (120 °C, 2 h; 265 mg of a dark violet powder) and purified by column separation (silica gel, 2% MeOH/$CHCl_3$).

First fraction: Approximately 100 mg (24%) reddish-violet powder of 2,9-bis-(3-butyl-2-hydroxymethyl-heptyl)-5-methoxyanthra[2,1,9-def;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (**4c**). M.p. >250 °C; R_f = 0.31 (silica gel, $CHCl_3$/ethanol 20:1); ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.84–0.88 (m, 12H; 4CH_3), 1.25–1.69 (m, 28H; 12CH_2, 4CH), 2.04 (s, 2H; CH_2), 2.95 (br s, 2H; 2OH), 3.57 (m, 2H; N–CH_2), 3.73 (m, 2H; N–CH_2), 4.13–4.40 (m, 7H; 2OCH_2R, $ROCH_3$), 8.13–8.48 (m, 6H; aromatic CH), 9.17–9.28 ppm (m, 1H; aromatic CH); ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 14.2, 23.0, 23.2, 29.7, 30.5, 30.7, 38.7, 40.7, 40.9, 42.0, 56.8 ($ROCH_3$), 61.8, 117.3, 121.2, 121.6, 122.2, 122.3, 123.2, 123.4, 123.7, 126.2, 128.5, 128.7, 130.3, 131.8, 134.0, 158.0, 163.6, 164.0, 164.1 ppm; IR (KBr): $\tilde{\nu}$ = 3468.0 (w, br), 2956.5 (s), 2924.6 (vs), 2854.6 (s), 1737.8 (m), 1693.1 (m), 1649.9 (m), 1593.6 (m), 1462.8 (m), 1404.2 (w), 1378.0 (w), 1335.0 (w), 1268.1 (w), 1120.0 (w), 1072.0 (w), 808.0 (w), 746.0 (w) cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 391 (0.10), 411 (0.09), 489 (sh) (0.27), 520 (0.66), 558 nm (1.00); fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 575 (1.00), 620 nm (0.61); fluorescence quantum yield ($CHCl_3$, λ_{exc} = 483 nm, $E_{483\,nm}$ = 0.0138 cm^{-1}, reference: 2,9-bis-(1-hexylheptyl)anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (**1a**) with Φ = 1.00) = 0.86; MS (70 eV, DEI$^+$): *m*/*z* (%): 788 (100) $[M^+]$, 770 (17) $[M^+-17]$, 760 (14) $[M^+-CO]$, 758 (13) $[M^+-OCH_3]$, 727 (10) $[M^+-2CH_2OH]$, 605 (79) $[M^+-C_{12}H_{25}O]$, 587 (16) $[M^+-C_{12}H_{25}O-OH]$, 575 (8) $[M^+-C_{12}H_{25}O-OCH_3]$, 420 (56) $[M^+-2C_{12}H_{25}O]$, 390 (9) $[M^+-2C_{12}H_{25}O-OCH_3]$: HMRS: *m*/*z* calcd for ($C_{49}H_{60}N_2O_7$): 788.4401; found: 788.4452.

Second fraction: Yield ≈30 mg (7%) bluish-violet powder of a mixture of 1,8-bis-(3-butyl-2-hydroxymethylheptyl)-4,11-dimethoxy-1*H*-indolo[5′,4′,3′:10,5,6]anthra[2,1,9-*def*]isoquinoline-2,7,9(8*H*)-trione (**5c**) and 1,8-bis-(3-butyl-2-hydroxymethylheptyl)-5,11-dimethoxy-1*H*-indolo[5′,4′,3′:10,5,6]anthra[2,1,9-*def*]isoquinoline-2,7,9(8*H*)-trione (**6c**). M.p. >250 °C; R_f = 0.21 (silica gel, $CHCl_3$/ethanol 20:1); ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.80–0.90 (m, 12H; 4CH_3), 1.19–1.64 (m, 28H; 4CH, 12CH_2), 1.88–2.02 (m, 2H; CH_2), 3.42–3.68 (m, 4H; 2CH_2), 3.83–4.39 (m, 7H; 2CH_2, OCH_3), 6.87–6.92 (m, 1H; aromatic CH), 8.26–8.63 (m, 5H; aromatic CH), 8.96–9.06 ppm (m, 1H; aromatic CH); 2D-NMR (dQCOSY, 400 MHz, $CDCl_3$, 24 °C): two sets of signals in the aromatic region and several sets of signals in the aliphatic region because of stereo isomers were obtained; ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 14.1, 23.1, 29.5, 29.6, 29.7, 29.8, 30.0, 30.1, 30.2, 30.6, 30.7, 38.3, 38.7, 40.0, 42.1, 42.5, 56.0 (OCH_3), 56.8 (OCH_3), 61.2 ppm; IR (KBr): $\tilde{\nu}$ = 3435.9 (vs, br), 2955.6 (s), 2924.8 (vs), 2855.1 (m), 1685.7 (m), 1637.1 (m), 1583.7 (m), 1501.3 (w), 1463.5 (m), 1390.5 (m), 1344.1 (w), 1240.0 (w), 1166.5 (w), 1068.0 (w), 802.5 (w), 740.6 (w) cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 373 (0.28), 389 (0.40), 408 (0.52), 574 nm (1.00); fluorescence ($CHCl_3$): not detectable; MS (70 eV, DEI$^+$): *m*/*z* (%): 760 (100) $[M^+]$, 730 (7) $[M^+-OCH_3]$, 577 (48) $[M^+-C_{12}H_{25}O]$, 435 (3) $[M^+-OCH_3-C_9H_{19}-C_{12}H_{25}NO]$, 419 (9) $[M^+-C_{12}H_{25}O-OCH_3-C_9H_{19}]$, 391 (15) $[M^+-C_{12}H_{25}O-OCH_3-C_9H_{19}-CO]$, 346 (3) $[M^+-C_{12}H_{25}O-OCH_3-C_9H_{19}-C_3H_7NO]$; HMRS: *m*/*z* calcd for ($C_{49}H_{60}N_2O_7$): 790.4557; found: 790.4650.

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