Novel Fluorescent Dyes by the Extension of the Core of Perylenetetracarboxylic Bisimides

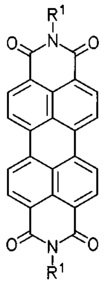
Heinz Langhals[a] and Susanne Kirner**[a]**

Dedicated to Prof. Dr. C. Rüchardt on the occasion of his 70th birthday

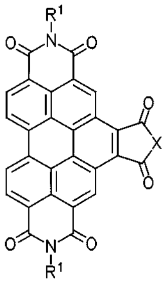
Keywords: Fluorescent dyes / Perylenes / Heterocycles / NIR dyes

Core-extended perylenetetracarboxylic bisimides were prepared by Diels–Alder reaction followed by reduction, or by nitration followed by cyclisation. Highly fluorescent dyes were obtained with absorption regions from the visible to the NIR. Applications for solar energy harvesting, and quantum counters were suggested.

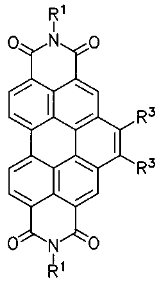
Perylene dyes such as perylene-3,4:9,10-tetracarboxylic bisimides **1**, exhibit unusually good properties such as high photostabilities and high fluorescence quantum yields.[1] The introduction of solubilizing groups such as *tert*-butylaryl[2] groups or long-chain *sec*-alkyl groups ("swallow-tail" substituents[3]) render the dyes soluble in organic solvents. The extension of the aromatic core of perylene is a modern topic in chemistry; see for example ref.[4] The reaction of perylene itself to form benzperylenedicarboximides[5] as well as the anellation of perylene-3,4-dicarboximide with heterocycles has been studied in preceding papers.[6] However, such extensions of **1** are unknown.



1



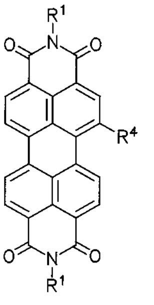
2: X = O
3: X = NR^2



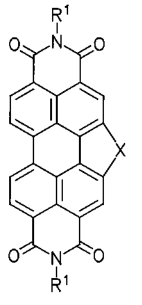
4: R^3 = CO$_2$C$_2$H$_5$
5: R^3 = H

1, 2, 4, 5, 6, 7, 8, 9, 10, 11, 13, 14, 15, 16	R^1
a	CH(C$_6$H$_{13}$)$_2$
b	CH(C$_4$H$_9$)$_2$
c	2,5-di-*t*-C$_4$H$_9$C$_6$H$_3$

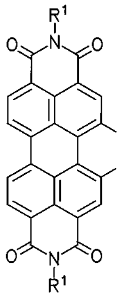
3	R^1	R^2
a	CH(C$_6$H$_{13}$)$_2$	*Cyclo*-C$_6$H$_{11}$
b	CH(C$_6$H$_{13}$)$_2$	2,5-di-*t*-C$_4$H$_9$C$_6$H$_3$



6: R^4 = NO$_2$
7: R^4 = PO(OC$_2$H$_5$)$_2$
8: R^4 = Br
9: R^4 = NH$_2$
10: R^4 = N(CH$_3$)$_2$



11: X = S
12: X = NR^5



13

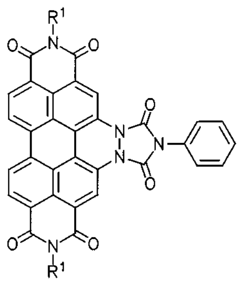
12	R^1	R^5
a	CH(C$_6$H$_{13}$)$_2$	H
b	CH(C$_4$H$_9$)$_2$	H
c	CH(C$_6$H$_{13}$)$_2$	CH$_3$
d	CH(C$_4$H$_9$)$_2$	CH$_3$
e	CH(C$_6$H$_{13}$)$_2$	CH$_2$C$_6$H$_5$
f	CH(C$_4$H$_9$)$_2$	CH$_2$C$_6$H$_5$
g	CH(C$_6$H$_{13}$)$_2$	CH$_2$CO$_2$C$_2$H$_5$
h	CH(C$_6$H$_{13}$)$_2$	COCH$_3$
i	CH(C$_4$H$_9$)$_2$	COCH$_3$
j	CH(C$_6$H$_{13}$)$_2$	COC$_6$H$_5$

The Diels−Alder reaction of perylene with maleic anhydride proceeds easily[1,7,8] so that a complete conversion is obtained within 10 min at 190−200°C. The bisimide **1** is less electron-rich than perylene and therefore less reactive and gives insignificant yields in this reaction. However, a prolongation of the reaction time to 4 d, and a simultaneous aromatization with chloranil led to a yield of some 70% of the benzperylenebisimide anhydrides **2**. This reac-

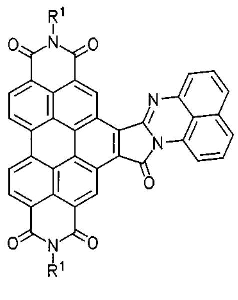
---

[a] Institut für Organische Chemie der Universität München,
Butenandtstraße 5-13 (Haus F), D-81377 München, Germany
Fax: (internat.) + 49-(0)89/2180-7640
E-mail: Langhals@lrz.uni-muenchen.de

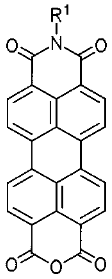
1434−193X/00/0102−365 $ 17.50+.50/0



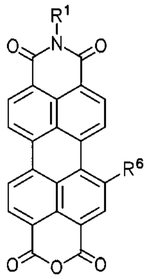
14



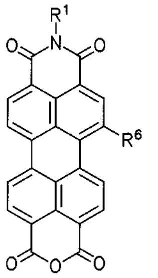
15



16



17



18

17, 18	R^1	R^6
a	$CH(C_6H_{13})_2$	NO_2
b	$CH(C_6H_{13})_2$	NH_2
c	$CH(C_6H_{13})_2$	$N(CH_3)_2$

tion is not affected by the addition of Lewis acids such as $AlCl_3$. In contrast to perylene *peri*-anhydrides, the anhydride **2** is sensitive to moisture and slowly forms the free acid, but can be regenerated by heating. Compound **2** may be further condensed with primary amines to form the trisimides **3** or with *peri*-diaminonaphthalene to give **15**. A combination of dicyclohexyl carbodiimide and trifluoroacetic acid gives a novel reagent which favours the condensation appreciably. Each component alone supports the reaction, however their combination is appreciably more effective. The anhydride **2**, after ring opening with ethanol or the free acid, can easily be transformed to the diethyl ester (**4**) with ethyl iodide and DBU. No ester could be obtained with ethanol and catalytic amounts of mineral acid. The anhydride **2** or the free acid can be transformed to the benzperylene bisimide **5** with the reaction of copper powder in refluxing quinoline in analogy to ref.[9] A decarboxylation with copper(I) oxide gave varying yields.

The Diels−Alder reaction of **1** proceeds even more easily with the strong dienophile *N*-phenyltriazolinedione[10−13] and forms directly the rearomatized **14** in low yield (5%). An addition of chloranil as an oxidant improves the synthesis of **14** appreciably (25% yield) and the reaction is over within 24 h.

The unknown 1-nitroperylenebisimides (**6**) are key intermediates for the preparation of heterocyclic anellated dyes. Literature procedures[14][15] for the nitration of perylene derivatives have not been tested for the preparation of **6** because the regiospecific mononitration of **1** was required and proceeded with N_2O_4 in CH_2Cl_2 according to ref.[16] A catalytic amount of methanesulfonic acid further increases the yield of **6** to 90%. An excess of nitration reagent is recommended, since small amounts of dinitration products are more easily removed than any remaining starting material (**1**). The low reactivity of the perylene bisimides towards electrophiles is also demonstrated by the attempted bromination of **1**, where no reaction could be observed with bromine, even at 100°C. A large excess of bromine (150 mol/mol of **1**) and the addition of potassium carbonate[17] (14 mol/mol of **1**) was required to prepare **8** (86%).

Compound **6** was reduced to amine **9** by iron powder and hydrochloric acid in either ethanol or THF. The reduction with formic acid[18] or triethyl ammonium formate[19] and palladium on carbon is an alternative. However, catalyst poisoning must be excluded. The amine **9** may be alkylated to **10** with formic acid or formaldehyde (Leuckart−Wallach reaction or Eschweiler−Clarke reaction, respectively). However, better results were obtained by a reaction with methyl iodide, KOH powder, and benzyl triethyl ammonium chloride.

The analogous nitration of the anhydride imide **16**[20] gave an analytically pure mixture of the two isomers **17a** and **18a**. Their low solubility and similar chromatographic properties makes their separation difficult. The mixture was therefore directly reduced to a mixture of the amines **17b** and **18b**, which exhibit very low and also very similar chromatographic migrations. This mixture of the amines was then directly converted into the dimethylamino derivatives **17c** and **18c**, which could be separated by column chromatography.

The reaction of the nitro compound **6** with a phosphorous ester yields a mixture of **7** and **12**, which can be easily separated by column chromatography. Compound **7** is of interest as a label for transphosphorylation reactions. **12a** and **12b** are of general interest as monofunctionalized fluorescent labels for electrophiles because the pyrrole nitrogen atom can be easily deprotonated with DBU and forms a strong nucleophile. Examples of alkylations (methyl iodide and benzyl bromide) and acylations (acetyl chloride and benzoyl chloride) of **12a** and **12b** are therefore given. The reaction of **12a** with bromoacetic acid ethyl ester is of special interest for an umpolung of the reagent because labelling can proceed with nucleophiles via the carboxyl ester group.

The reaction of the nitro compound **6** with sulfur in DMF forms a mixture of the two sulfur-containing heterocycles, **11** and **13** which can be separated by column chromatography (45% and 40% isolated yield, respectively). Two other derivatives of **11** have been prepared by another route,[21][22] the heterocycle **13** is new. The solvent *N*-methylpyrrolidone increases the reaction rate appreciably and favours the formation of **11**. An increase of the reaction temperature, for example in refluxing DMF, also favours the formation of **11** (71%), so that no **13** could be detected.

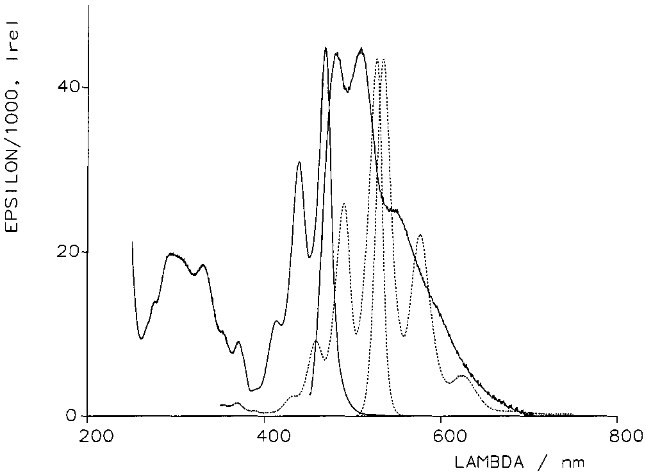


Figure 1. UV/Vis absorption and fluorescence spectra of **2a** (color coordinates x = 0.3767, y = 0.4315, Y = 96.49, 2°, normlight C at $T_{\min}$ = 0.1) in chloroform compared to **1a** [R^1 = $CH(C_6H_{13})_2$, half of the molar absorptivity of **1a**] (···)

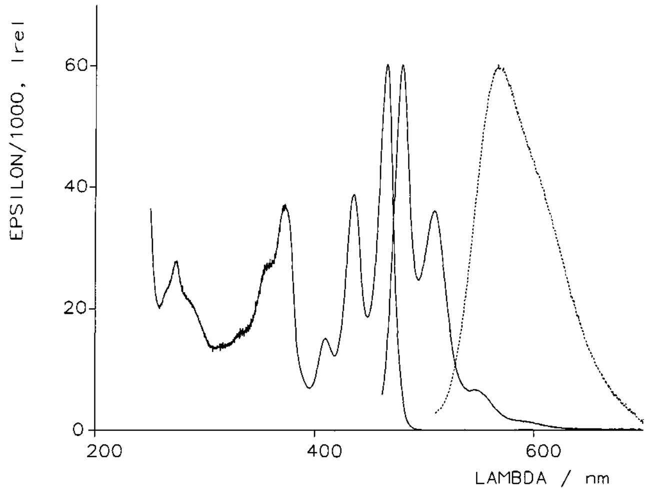


Figure 2. UV/Vis absorption and fluorescence spectra of **3a** (color coordinates x = 0.3637, y = 0.4156, Y = 97.40, 2°, normlight C at $T_{\min}$ = 0.1) in chloroform; (···): solid-state fluorescence

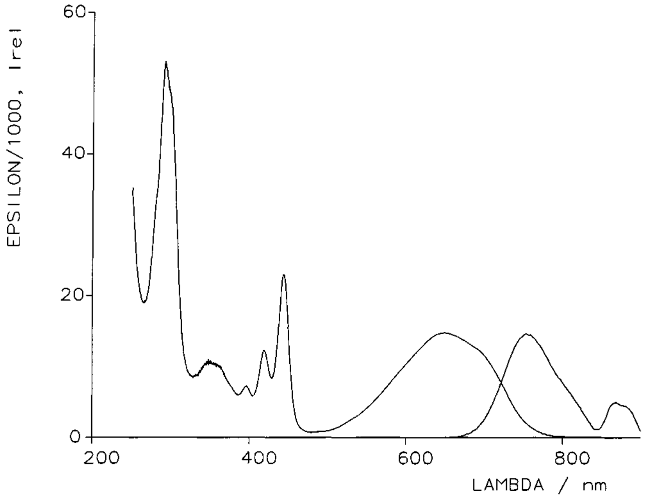


Figure 3. UV/Vis absorption and fluorescence spectra of **14a** (color coordinates x = 0.2489, y = 0.3507, Y = 59.04, 2°, normlight C at $T_{\min}$ = 0.1) in chloroform

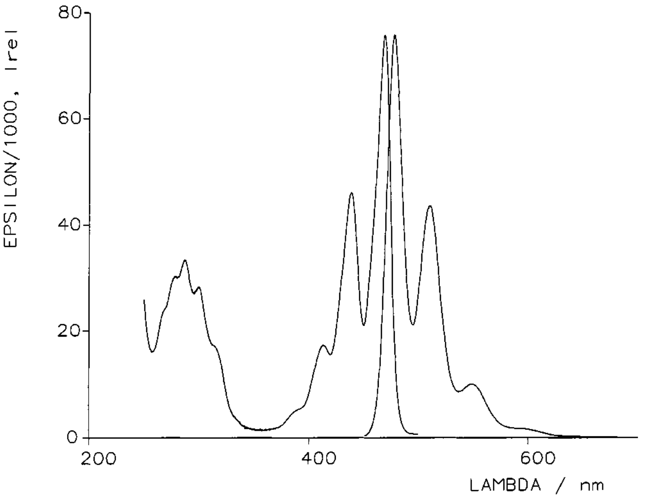


Figure 4. UV/Vis absorption and fluorescence spectra of **5a** (color coordinates x = 0.3658, y = 0.4150, Y = 97.29, 2°, normlight C at $T_{\min}$ = 0.1) in chloroform

The structured UV/Vis absorption of the benzperylenebisimide **5** (468 nm) is hypsochromically shifted by about 60 nm compared to **1**; see Figure 4. Compound **5** is highly fluorescent (77% quantum yield of **5a** in chloroform[23]); see Figure 4. The electron-withdrawing ester group in **4** affects these spectra only slightly (466 nm) and the fluorescent quantum yield is similarly high (85% quantum yield of **4a** in chloroform). The ester groups are expected to act mainly inductive electron-withdrawing because steric interactions should place their π system orthogonal to the chromophore. The anhydride group in **2** may additionally act as mesomerically electron-withdrawing because of the planarity in **2**, but this is also of little influence to the spectra: absorption at 468 nm, fluorescence quantum yield 74%; see Figure 1.

Even the condensation of **2** with primary amines to form **3** does not notably alter the spectra: absorption at 465 nm, fluorescence quantum yield 45% for **3a** or **3b**; see Figure 2. An intense solid-state fluorescence was observed both for **3a** and **3b,** as well as additional absorptions in the near UV (372 nm). The latter are even more pronounced for **15**, which has a further extended π system; see Figure 7. There is also a weaker absorption for **15** at long wavelengths in the visible region (500−650 nm). Compound **15** exhibits no fluorescence. All dyes are highly lightfast; they can be irradiated for weeks with direct solar radiation in solution without detectable decomposition.

Whereas the effect of the electron-withdrawing substituents of **2** and **4** on the UV/Vis spectra is only negligible, strong electron donors such as the nitrogen atoms in **14**

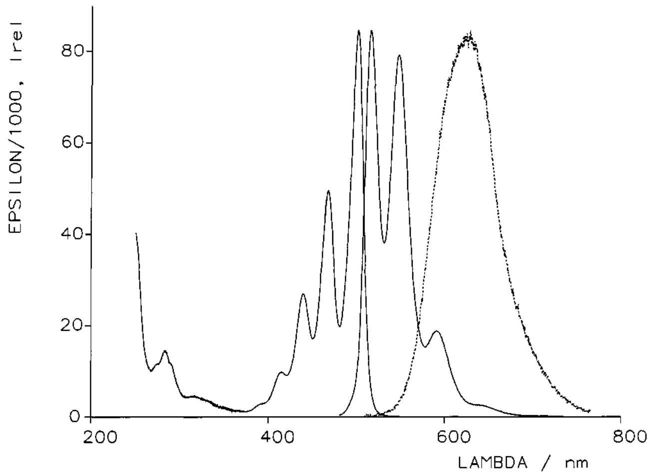


Figure 5. UV/Vis absorption and fluorescence spectra of **11a** (color coordinates $x = 0.3711$, $y = 0.3808$, $Y = 90.66$, 2°, normlight C at $T_{\min} = 0.1$) in chloroform; (···): solid-state fluorescence

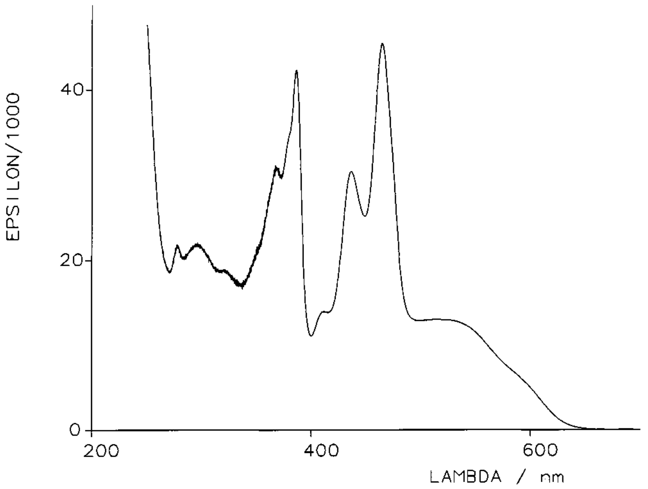


Figure 7. UV/Vis absorption and fluorescence spectra of **15a** (color coordinates $x = 0.4091$, $y = 0.3951$, $Y = 64.71$, 2°, normlight C at $T_{\min} = 0.1$) in chloroform

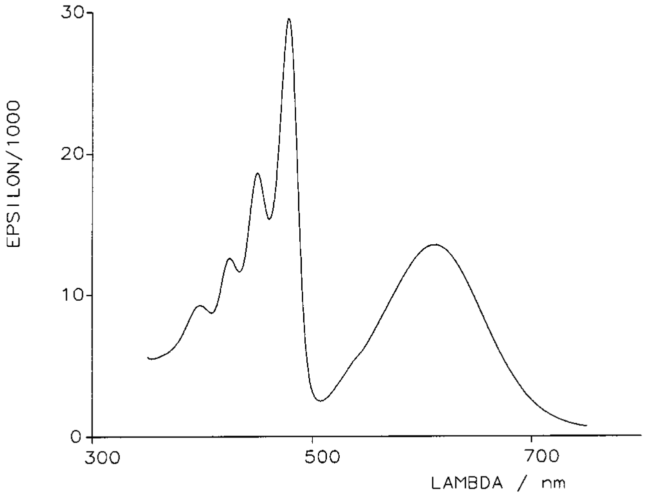


Figure 6. UV/Vis absorption spectrum of **13a** (color coordinates $x = 0.3091$, $y = 0.4071$, $Y = 53.01$, 2°, normlight C at $T_{\min} = 0.1$) in chloroform

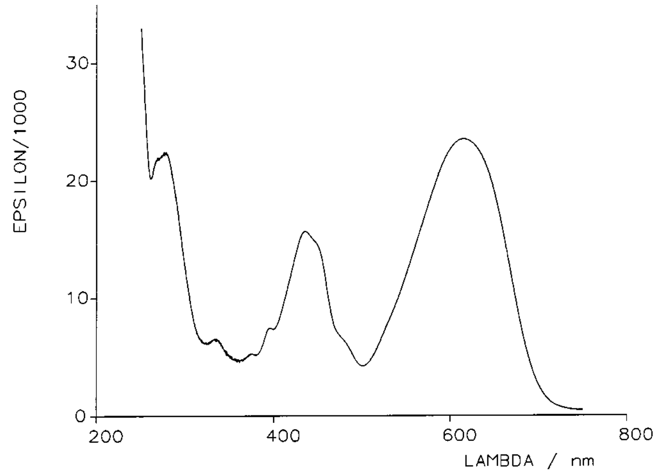


Figure 8. UV/Vis absorption spectrum of **10a** (color coordinates $x = 0.2142$, $y = 0.3240$, $Y = 29.78$, 2°, normlight C at $T_{\min} = 0.1$) in chloroform

cause a pronounced bathochromic absorption at 600 nm; see Figure 3. This broad and only slightly structured band reaches even the NIR. Interestingly, there is a strong fluorescence of **14** far into the NIR which is of interest for the modern information technology.

The UV/Vis absorption spectrum of the nitro compound **6** is nearly identical with the spectrum of **1**, but **6** does not exhibit fluorescence. The low influence of electron acceptor substituents on the spectra of **1** corresponds to the influence of substituents in **5**. On the other hand, the reduction of **6** to **9** switches the substituent from an electron acceptor to an electron donor and causes a pronounced bathochromic shift (571 nm in chloroform). Compound **9** is positively solvatochromic both in absorption (ethanol: 600 nm, cyclohexane: 556 nm) and fluorescence (ethanol: 761 nm, cyclohexane: 633 nm). A positive solvatochromism is also obtained for the dimethylamino derivative **10** in absorption (DMF: 624 nm, ethanol: 613 nm, chloroform: 614 nm, cyclohexane: 580 nm) and strong fluorescence (DMF: 768 nm, ethanol: 764 nm, chloroform: 725 nm, cyclohexane: 670 nm). Obviously, the inductive effect of the methyl groups in **10** causes an additional bathochromic shift; see Figure 8. The dye **10** is not only of interest because of the strong NIR fluorescence, but there is an appreciable light absorption from the UV throughout the visible region so that the molar coefficient of extinction never drops below 4200 $L \cdot mol^{-1} \cdot cm^{-1}$. Such fluorescent dyes are of interest for quantum counter applications, which integrate light quanta of any wavelengths in the visible to fluorescent light in the NIR. On the other hand, the broad absorption throughout the visible region makes this dye also of interest for light harvesting systems. Unfortunately, **10** has no anchor group for such applications. More suitable therefore are the structurally related perylene derivatives, **17c** and **18c**, which exhibit similar UV/Vis spectra; see Figure 9. Their anhydride rings may serve as anchor groups for cations such as Ti^{4+} with an oxygen affinity, for example with

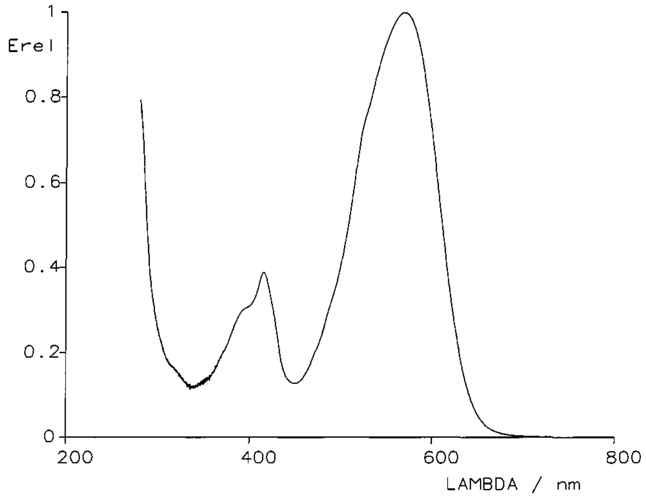


Figure 9. UV/Vis absorption spectrum of a mixture of **17c** and **18c** (color coordinates $x = 0.2761$, $y = 0.1731$, $Y = 23.54$, 2°, normlight C at $T_{\min} = 0.1$) in chloroform

ring opening to the dicarboxylate. Indeed, dye **17c** can be used as a sensitizer in the Gräzel[24][25] TiO_2 electrovoltaic solar cell, and attains an overall conversion of 0.5% from solar radiation to electrical energy.[26] Interestingly, the structurally similar dye **18c** is completely inactive in this cell. Further details of this work will be reported elsewhere.

The UV/Vis spectra of **12a** are similar to the spectra of **1** and only slightly bathochromically shifted. A further substitution of the nitrogen atom causes slightly bathochromic shifts for alkylation (R^5 = alkyl) and slightly hypsochromic shifts for acylation (R^5 = acyl). The fluorescence quantum yields of **12** are between 62 and 99% so that **12** can be taken as a light-stable fluorescent-labelling reagent because of its simple monofunctionaliszation.

The UV/Vis spectra of the thiopheno derivative **11** exhibit a hypsochromic shift of 12 nm compared to **1**, and the structure of the spectra are similar; see Figure 5. The fluorescence quantum yield is 71% in solution and there is an intense solid-state fluorescence; see Figure 5. The more sulfur-rich **13** exhibits a similar absorption as **11**, but there is an additional broad structureless band at 611 nm, so that a brilliant green solution of the dye is obtained; see Figure 6. Dye **13** does not exhibit fluorescence and is appreciably less stable than all the other prepared dyes. The lack of fluorescence and the broadness of the absorption may be taken as an indicator that the bathochromic absorption of **13** is a result of a charge-transfer-transition. Bathochromically shifted absorptions have previously been observed with 1,2-dithiin, and were discussed in terms of $\pi-\pi^*$ transitions,[27][28] or interactions with vacant 3d orbitals.[29]

Experimental Section

N_2O_4 Solution: N_2O_4 gas was prepared by strong heating of $Pb(NO_3)_2$, and was introduced into dichloromethane until saturation was obtained. For the determination of the concentration of N_2O_4, 10.0 mL of the solution was shaken with 10 mL of 30% hydrogen peroxide until the light brown color disappeared. The organic phase was removed and the oxidation product, nitric acid, was determined by titration with NaOH, using phenolphthalein as the indicator.

Nitration of 1. − General Procedure: The calculated amount of N_2O_4 in dichloromethane was added to a solution of the perylene-3,4;9,10-bis(dicarboximide), dissolved in a minimal amount of dichloromethane (1 mol of N_2O_4 per mol of **1**). A few drops of methanesulfonic acid were added and the red solution was stirred at room temperature until nearly all of the fluorescent starting material was converted (controlled by DC; 5−12 h). The solvent was removed in vacuo and the residue purified by column separation (silica gel, toluene). The dinitrated, nonfluorescent reaction product eluted first, followed by the nonfluorescent mononitration product, and the highly fluorescent starting material. Generally, the dinitrated product can be more easily separated than the starting bis(imide) from the mononitration product, so the application of an excess of the reagent for nitration and a complete reaction is recommended. However, for imide anhydrides **16** the starting material can be more easily removed from **17a** and **18a** than dinitration products, so a molar ratio of 1:0.8−0.9 for **16**/N_2O_4 is recommended. The nitration of **1** proceeds slowly if not catalyzed. Only 60% of **6a** was obtained after 72 h reaction time, whereas more than 90% of **6a** was isolated after 5 h reaction time with the addition of methanesulfonic acid.

***N,N′*-Bis(1-butylpentyl)-1-nitroperylene-3,4:9,10-bis(dicarboximide) (6b):** *N,N′*-Bis(1-butylpentyl)perylene-3,4:9,10-bis(dicarboximide) (**1b**, 2.00 g, 3.12 mmol) was dissolved to give a nearly saturated solution in dichloromethane. An N_2O_4 solution in dichloromethane (37 mL, 0.085 M, 3.15 mmol) and methanesulfonic acid (0.02 mL, 30 mg, 0.30 mmol) were added, and the solution was stirred at room temperature for 5−6 h. The solvent and the remaining N_2O_4 were removed by distillation, and the residue was taken up in toluene and purified by column separation (silica gel, toluene). Yield 2.1 g (98%) of **6b** as a dark red powder, m.p. 304 °C. − R_f (silica gel, toluene) = 0.31. − R_f (silica gel, toluene/acetone, 10:1) = 0.77. − IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1} (m), 2930 (m), 2861 (m), 1702 (s), 1662 (s), 1596 (s), 1581 (w), 1537 (s), 1467 (w), 1455 (w), 1427 (w), 1406 (m), 1350 (m), 1338 (s), 1254 (m), 1183 (w), 1170 (w), 855 (w), 812 (m), 717 (m). − UV/Vis ($CHCl_3$): λ_{max} (ε) = 489 nm (30740), 523 (46060). − ^1H NMR ($CDCl_3$): δ = 0.83 (t, 12 H, CH_3), 1.20−1.34 (m, 16 H, CH_2), 1.86 (m_C, 4 H, $CH-CH_2$), 2.21 (m_C, 4 H, $CH-CH_2$), 5.15 (m_C, 2 H, N−CH), 8.23 (d, J = 8.1 Hz, 1 H, perylene), 8.50 (d, J = 8.2 Hz, perylene), 8.67−8.79 (m, 5 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.01, 22.58, 29.08, 31.94, 32.04, 54.92, 55.20, 124.02, 124.48, 126.70, 127.54, 127.94, 129.13, 129.39, 129.51, 132.95, 135.50, 147.72. − MS (70 eV): *m/z* (%): 689 (11), 688 (47), 687 (100) [M^+], 670 (10), 630 (6), 564 (7), 563 (31), 562 (77), 561 (80) [$M^+ - C_9H_{18}$], 546 (5), 544 (7), 516 (7), 448 (5), 438 (8), 437 (32), 436 (61), 435 (87) [$M^+ - 2 \times C_9H_{18}$], 418 (5), 406 (7), 405 (8), 402 (11), 392 (6), 391 (26), 390 (68), 389 (10) [$M^+ - 2 \times C_9H_{18} - NO_2$], 373 (5), 372 (11), 364 (10), 362 (13), 345 (8), 344 (20). − $C_{42}H_{45}N_3O_6$ (687.8): calcd. C 73.34, H 6.59, N 6.11; found C 73.44, H 6.67, N 6.22.

***N,N′*-Bis(1-hexylheptyl)-1-nitroperylene-3,4:9,10-bis(dicarboximide) (6a):** *N,N′*-Bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**1a**, 2.07 g, 2.75 mmol), a 0.198 M N_2O_4 solution (14.0 mL, 2.77 mmol N_2O_4), and methanesulfonic acid (0.05 mL, 74 mg, 0.77 mmol) were stirred at room temperature for 7 h. The solvent was removed by vacuum distillation and the residue purified by column separation (silica gel, toluene). Yield 2.04 g (93%) of **6a** as a dark red powder, m.p. 121 °C. − R_f (silica gel, chloroform): 0.84.

− R_f (silica gel, toluene): 0.63. − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1} (m), 2927 (m), 2856 (m), 1702 (s), 1660 (s), 1596 (s), 1581 (w), 1537 (m), 1467 (w), 1426 (w), 1406 (m), 1349 (m), 1338 (s), 1251 (m), 1178 (w), 1112 (w), 855 (w), 812 (m), 746 (m). − ^{1}H NMR (CDCl$_3$): δ = 0.81 (t, 12 H, C*H*$_3$), 1.16−1.31 (m, 32 H, C*H*$_2$), 1.83 (m$_C$, 4 H, CH−C*H*$_2$), 2.20 (m$_C$, 4 H, CH−C*H*$_2$), 5.14 (m$_C$, 2 H, N−C*H*), 8.25 (d, *J* = 8 Hz, 1 H, perylene), 8.57 (d, *J* = 8 Hz, 1 H, perylene), 8.63−8.79 (m, 5 H, perylene). − ^{13}C NMR (CDCl$_3$): δ = 14.02, 22.57, 26.88, 29.16, 31.73, 32.26, 32.35, 39.24, 55.01, 55.29, 124.02, 124.48, 126.51, 126.69, 127.57, 127.95, 129.15, 129.40, 129.52, 132.97, 135.52, 147.75. − UV/Vis (CHCl$_3$): λ_{max} (ε) = 490 nm (30820), 523 (46100). − MS (70 eV): *m*/*z* (%): 801 (18), 800 (62), 799 (100) [M$^+$], 783 (7), 782 (13), 714 (6), 620 (14), 619 (56), 618 (98), 617 (87) [M$^+$ − C$_{13}$H$_{26}$], 601 (5), 600 (7), 448 (6), 438 (16), 437 (59), 436 (71), 435 (93) [M$^+$ − 2 × C$_{13}$H$_{26}$], 418 (6),416 (5), 407 (8), 406 (10), 405 (11), 404 (6), 403 (5), 402 (8), 392 (14), 391 (36), 390 (76), 389 (10) [M$^+$ − 2 × C$_{13}$H$_{26}$ − NO$_2$], 372 (8), 364 (9), 362 (11), 345 (6), 344 (14). − C$_{50}$H$_{61}$N$_3$O$_6$ (800.1): calcd. C 75.06, H 7.69, N 5.25; found C 75.24, H 7.68, N 5.12.

***N*,*N*′-Bis(2,5-di-*tert*-butylphenyl)-1-nitroperylene-3,4:9,10-bis-(dicarboximide) (6c):** Compound **1c** (800 mg, 1.04 mmol) was dissolved in dichloromethane to give a nearly saturated solution. A 0.05 M N$_2$O$_4$ solution (21.0 mL, 1.05 mmol N$_2$O$_4$) and methanesulfonic acid (0.05 mL, 74 mg, 0.77 mmol) were added. The mixture was stirred at room temperature for 4 h, the solvent and unchanged N$_2$O$_4$ were removed by distillation and the residue was taken up in chloroform and purified by column separation (silica gel, chloroform). Yield 800 mg (94%) of **6c** as a dark red crystal powder, m.p. > 300 °C. − R_f (silica gel/chloroform): 0.45. − IR (KBr): $\tilde{\nu}$ = 3077 cm^{-1} (m), 2963 (m), 2869 (w), 1712 (s), 1675 (s), 1596 (s), 1539 (m), 1503 (w), 1466 (w), 1423 (m), 1402 (m), 1343 (s), 1252 (m), 1201 (s), 1003 (w),977 (w), 822 (m), 812 (m), 750 (m), 728 (w). − ^{1}H NMR (CDCl$_3$): δ = 1.289 and 1.295 (s each, 18 H), 1.313 and 1.316 (s each, 18 H), 6.990 (s, 2 H, phenyl), 7.467 and 7.483 (dd each, $^3J_{CH}$ = 8.5 and 8.3 Hz, $^4J_{CH}$ = 2.3 Hz, 2 H, phenyl), 7.596 and 7.607 (d each, $^3J_{CH}$ = 8.5 Hz, 2 H, phenyl), 8.317 and 8.324 (d each, *J* = 8.1 Hz, 1 H, perylene), 8.672 and 8.699 (s each, 1 H, perylene), 8.751−8.885 (m, perylene). − ^{13}C NMR (CDCl$_3$): δ = 31.18, 31.76, 34.25, 34.28, 35.55, 35.58, 123.39, 124.17, 124.30, 124.49, 124.77, 125.18, 126.54, 126.71, 126.76, 127.20, 127.22, 127.46, 127.56, 127.87, 127.89, 128.22, 128.89, 129.00, 129.34, 129.38, 129.72, 129.75, 129.86, 129.89, 131.63, 131.89, 132.21, 132.22, 133.36, 133.41, 133.44, 135.96, 143.75, 143.79, 147.81, 150.25, 150.27, 150.40, 150.42, 162.85, 163.69, 163.77, 164.09. − UV/Vis (CHCl$_3$): λ_{max} ($E_{rel.}$) = 369 nm (0.08), 457 (0.20), 490 (0.65), 524 (1.0). − MS (70 eV): *m*/*z* (%): 757 (5), 756 (18), 755 (55), 754 (100) [M$^+$ − C$_4$H$_9$], 714 (7), 710 (7), 709 (16), 708 (10) [M$^+$ − C$_4$H$_9$−NO$_2$], 699 (7). − C$_{48}$H$_{40}$N$_3$O$_6$ (754.86): calcd. 754.2917; found 754.2949 (MS). − C$_{52}$H$_{49}$N$_3$O$_6$ (812.0): calcd. C 76.92, H 6.08, N 5.18; found C 74.69, H 5.98, N 5.02.

Nitration of *N*-(1-Hexylheptyl)perylene-3,4:9,10-tetracarboxylic 3,4-Anhydride 9,10-Imide (16a): Compound **16a** (100 mg, 0.175 mmol) was dissolved in dichloromethane (50 mL). A 0.030 M solution of N$_2$O$_4$ in dichloromethane (5.50 mL, 0.165 mmol N$_2$O$_4$) and methanesulfonic acid (0.05 mL, 74 mg, 0.77 mmol) were added. The mixture was stirred at room temperature for 4 h, the solvent removed by distillation, and the residue purified by column separation (silica gel, chloroform/7% acetic acid or dichloromethane/2% acetic acid). Yield 83 mg (77%) of a mixture of **17a** and **18a** as a dark red powder, m.p. 189−191 °C. − R_f (silica gel, dichloromethane/2% acetic acid): 0.73. − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1} (w), 2927 (m), 2857 (w), 1778 (s), 1739 (m), 1705 (m), 1662 (s), 1598 (s), 1538 (m), 1456 (w), 1405 (w), 1354 (w), 1322 (s), 1248 (m), 1161 (w), 1059 (w), 1034 (w), 857 (w), 810 (m), 740 (w). − ^{1}H NMR (CDCl$_3$): δ = 0.80 (t, *J* = 6.4 Hz, 6 H, C*H*$_3$), 1.20−1.30 (m, 16 H, C*H*$_2$), 1.84 (m$_C$, 2 H, CH−C*H*$_2$), 2.13−2.26 (m, 2 H, CH−C*H*$_2$), 5.13 (tt, $^3J_1$ = 5.6 Hz, $^3J_2$ = 9.2 Hz, 1 H, N−C*H*), 8.22 and 8.25 (d each, *J* = 8.3 Hz, 1 H, perylene), 8.58 (d, *J* = 8.1 Hz, 1 H, perylene), 8.68−8.80 (m, 5 H, perylene). − ^{13}C NMR (CDCl$_3$): δ = 14.0, 22.5, 26.9, 29.1, 31.7, 32.2, 32.3, 55.1, 55.4, 118.6, 119.5, 119.8, 120.6, 124.1, 124.6, 125.0, 125.4, 126.5, 126.8, 127.6, 127.9, 128.2, 128.6, 128.8, 128.9, 129.0, 129.4, 130.8, 131.1, 131.2, 131.5, 132.1, 133.2, 133.5, 134.5, 134.7, 134.9, 137.4, 147.3, 148.1, 158.3, 158.8, 159.1, 159.4, 167.7. − UV/Vis (CHCl$_3$): λ_{max} (ε) = 359 nm (6410), 452 (9100), 489 (25750), 519 (38050). − MS (70 eV): *m*/*z* (%): 620 (9), 619 (41), 618 (100) [M$^+$], 439 (21), 438 (93), 437 (79), 436 (88) [M$^+$ − C$_{13}$H$_{26}$], 407 (7), 406 (10) [M$^+$ − C$_{13}$H$_{26}$ − NO], 392 (15), 391 (36) [M$^+$ − C$_{13}$H$_{26}$ − NO$_2$ + H], 365 (5), 364 (5) [M$^+$ − C$_{13}$H$_{26}$ − C$_2$O$_3$], 363 (5), 318 (5) [M$^+$ − C$_{13}$H$_{26}$ − C$_2$O$_3$ − NO$_2$]. − C$_{37}$H$_{34}$N$_2$O$_7$ (618.7): calcd. C 71.83, H 5.54, N 4.53; found C 71.69, H 5.82, N 4.31.

Reaction of *N*,*N*′-Bis(1-hexylheptyl)-1-nitroperylene-3,4:9,10-bis(dicarboximide) (6a) with Triethyl Phosphite: Compound **6a** (150 mg, 0.188 mmol) was dissolved in triethyl phosphite (5 mL, 4.84 g, 29.1 mmol) and heated under argon at 130 °C for 5 h (until no non fluorescent starting material, **6a,** could be detected by TLC), precipitated by adding in 1 N HCl (150 mL), and stirred at room temperature for 16 h to hydrolyse the triethyl phosphite. The precipitate was collected by vacuum filtration (dark red precipitate), dried and purified by column separation (alumina, chloroform). − **First Fraction:** yield 43 mg (26%) of **7a**, m.p. 61−63 °C. − R_f (Al$_2$O$_3$, chloroform): 0.82. − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1} (s), 2928 (s), 2857 (m), 1698 (s), 1659 (s), 1592 (s), 1578 (w), 1456 (m), 1446 (m), 1404 (m − s), 1340 (s), 1250 (m − s), 1176 (w), 1110 (w), 1045 (m, P−O−Et), 1020 (m, P−O−Et), 978 (m, br., P−O−Et), 814 (m), 749 (m). − ^{1}H NMR (CDCl$_3$): δ = 0.78 and 0.79 (t each, *J* = 6.4 Hz, 12 H, C*H*$_3$), 1.15−1.38 (m, 38 H, 16 × C*H*$_2$ + 2 × O−CH$_2$−C*H*$_3$), 1.82 (m$_C$, 4 H, CH−C*H*$_2$), 2.20 (m$_C$, 4 H, CH−C*H*$_2$), 4.21 (m$_C$, 4 H, O−C*H*$_2$−CH$_3$), 5.15 (tt, $^3J_1$ = 9.3 Hz, $^3J_2$ = 5.7 Hz, 2 H, N−C*H*), 8.61−8.78 (m, 5 H, perylene), 9.14 (br. d, *J* = 13.81 Hz, 1 H, perylene), 9.27 (d, *J* = 8.1 Hz, 1 H, perylene). − ^{13}C NMR (CDCl$_3$): δ = 13.96, 16.24 (d, $^3J_{PC}$ = 6.2 Hz, *C*H$_3$), 22.50, 26.84, 29.12, 31.68, 32.28, 32.32, 54.72, 54.82, 63.41 (d, $^2J_{CP}$ = 6.5 Hz), 123.52, 125.20, 126.44, 127.47, 127.67, 127.69, 128.43, 129.95 (d, J_{PC} = 2.4 Hz), 132.87, 133.19, 135.13, 140.95 (d, $^1J_{CP}$ = 9.4 Hz), 163.33, 164.64. − ^{31}P NMR (CDCl$_3$): δ = 18.21. − UV/Vis (CHCl$_3$): λ_{max} ($E_{rel.}$) = 375 nm (0.03), 434 (0.06), 463 (0.26), 493 (0.69), 529 (1.0). − Fluorescence (chloroform): λ_{max} ($I_{rel.}$) = 548 nm (1.0), 590 (0.66), 643 (0.18). − Fluorescence quantum yield (1.03 × 10^{-6} mol/L in CHCl$_3$, reference *N*,*N*′-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**1a**) with Φ = 100%, $\lambda_{excit.}$ = 490 nm) = 91%. − MS (70 eV): *m*/*z* (%): 892 (18), 891 (60), 890 (100) [M$^+$], 874 (6), 873 (10) [M$^+$ − OH], 755 (14), 754 (25) [M$^+$ − PO(OEt)$_2$ + H], 710 (10), 709 (27), 708 (36) [M$^+$ − C$_{13}$H$_{26}$], 573 (14), 572 (15) [M$^+$ − C$_{13}$H$_{26}$ − PO(OEt)$_2$ + H], 528 (6), 527 (19), 526 (38) [M$^+$ − 2 × C$_{13}$H$_{26}$], 471 (17), 470 (9), 469 (9) [M$^+$ − 2 × C$_{13}$H$_{26}$ − C$_4$H$_9$], 453 (14), 452 (7), 435 (7), 392 (10), 391 (30), 390 (44) [M$^+$ − 2 × C$_{13}$H$_{26}$ − PO(OEt)$_2$ + H]. − C$_{54}$H$_{71}$N$_2$O$_7$P (891.1): calcd. C 72.78, H 8.03, N 3.14; found C 71.93, H 8.40, N 3.10. − **Second Fraction:** Yield 91.0 mg (63%) of **12a**, m.p. 204−205 °C. − R_f (Al$_2$O$_3$, chloroform): 0.42. − IR (nujol): $\tilde{\nu}$ = 2955 cm^{-1} (s), 2927 (s), 2854 (s), 1693 (s), 1656 (s), 1607 (m), 1561 (m), 1460 (s), 1411 (w), 1377 (m), 1339 (w), 1287 (m), 1256 (w), 1207 (w), 1191 (w), 1164 (w), 1141 (w), 1117 (w), 845 (w), 804 (m), 743 (m), 725 (w). − ^{1}H NMR (CDCl$_3$): δ = 0.79 (t, 12 H, C*H*$_3$), 1.21−1.40 (m, 32 H, C*H*$_2$), 1.93 (m$_C$, 4 H, CH−CH_2), 2.32 (m$_C$, 4 H, CH−CH_2), 5.32 (m$_C$, 2 H, N−C*H*), 8.80 (d, *J* = 7.0 Hz, 1 H, perylene), 8.85 (d, *J* = 7.2 Hz, 1 H, perylene), 8.92 (d, *J* = 7.9 Hz, 2 H, perylene), 8.99 (s, 1 H, perylene), 9.04 (s, 1 H, perylene), 10.66 (s, 1 H, N*H*). − ^{13}C NMR (CDCl$_3$): δ = 14.10, 22.73, 29.35, 33.12, 54.04, 54.88, 119.87, 120.14, 120.63,121.75, 123.70, 124.56, 124.69, 127.24, 127.68, 128.38, 128.83, 130.93, 132.84, 133.75, 165.20, 165.64, 166.52. − UV/Vis (CHCl$_3$): λ_{max} (ε) = 457 nm (19300), 490 (43490), 524 (80280). − Fluorescence (chloroform): 539 nm, 575. − MS (70 eV): *m/z* (%): 768 (15), 767 (27) [M$^+$], 751 (5), 750 (10), 587 (8), 586 (24), 585 (29) [M$^+$ − $C_{13}H_{26}$], 568 (7), 416 (8), 405 (13), 404 (51), 403 (97) [M$^+$ − 2 × $C_{13}H_{26}$], 386 (14), 358 (7). − $C_{50}H_{61}N_3O_4$ (768.0): calcd. C 78.19, H 8.01, N 5.47; found C 77.98, H 8.16, N 5.51.

Reaction of *N,N′*-Bis(1-butylpentyl)-1-nitroperylene-3,4:9,10-bis(dicarboximide) (6b) with Triethyl Phosphite: Compound **6b** (300 mg, 0.437 mmol) in triethyl phosphite (10.0 mL, 9.69 g, 58.3 mmol) was heated under argon at 130°C for 3 h (until no non-fluorescent starting material **6b** could be detected by TLC), precipitated by pouring in 1 N HCl (100 mL), and stirred at room temperature for 16 h to hydrolyse the triethyl phosphite. The dark red precipitate was collected by vacuum filtration, dried and purified by column separation (alumina activity II, chloroform/1% ethanol). − **First Fraction:** Yield 109 mg (32%) of *N,N′*-bis(1-butylpentyl)perylene-3,4:9,10-bis(dicarboximide)-1-diethylphosphonate (**7b**), m.p. 122−124°C. − R_f (Al$_2$O$_3$, chloroform): 0.62. − IR (KBr): ṽ = 2957 cm^{-1} (m), 2929 (m), 2862 (w), 1699 (s), 1660 (s), 1592 (m), 1446 (w, br.), 1404 (m), 1340 (m), 1253 (m), 1106 (w), 1044 (m, P−O−Et), 1020 (m, P−O−Et), 970. (w br., P−O−Et), 814 (m), 750 (w). − ^{1}H NMR (CDCl$_3$): δ = 0.85 and 0.86 (each t, *J* = 6.9 Hz, 12 H, CH_3), 1.15−1.38 (m, 22 H, 8·CH_2 + 2·O−CH$_2$−CH_3), 1.83−1.94 (m, 4 H, CH−CH_2), 2.21−2.33 (m, 4 H, CH−CH_2), 4.24 (m$_C$, 4 H, O−CH_2−CH$_3$), 5.20 (m$_C$, 2 H, N−C*H*) 8.65−8.83 (m, 5 H, perylene), 9.18 (br. d, $^3J_{PH}$ = 14.02 Hz, 1 H, perylene), 9.31 (d, *J* = 8.1 Hz, 1 H, perylene). − ^{13}C NMR (CDCl$_3$): δ = 14.06, 16.32 (d, $^3J_{PC}$ = 5.6 Hz, *C*H$_3$), 22.63, 29.13, 32.05, 32.09, 54.73, 54.84, 63.50 (d, $^2J_{PC}$ = 6.5 Hz), 123.61, 125.22, 126.50, 127.53, 127.72, 128.49, 130.03 (d, *J* = 2.6 Hz), 132.94, 133.26, 135.21, 141.03 (d, $^1J_{PC}$ = 8.8 Hz). − ^{31}P NMR (CDCl$_3$): δ = 18.22. − UV/Vis (CHCl$_3$): λ_{max} (ε) = 349 nm (3950), 433 (4980), 464 (16040), 493 (38360), 529 (54680). − Fluorescence (chloroform): λ_{max} ($I_{rel.}$) = 551 nm (1.0), 589 (0.82), 642 (0.18). − MS (70 eV): *m/z* (%): 780 (14), 779 (51), 778 (100) [M$^+$], 762 (9), 761 (17) [M$^+$ − OH], 749 (5) [M$^+$ − C_2H_5], 721 (6) [M$^+$ − C_4H_9], 654 (10), 653 (32), 652 (54) [M$^+$ − C_9H_{18}], 635 (9), 623 (5) [M$^+$ − C_9H_{18} − C_2H_5], 528 (8), 527 (28), 526 (66) [M$^+$ − 2 × C_9H_{18}], 499 (8), 498 (11) [M$^+$ − 2 × C_9H_{18} − C_2H_4], 472 (8), 471 (30), 470 (17), 469 (17) [M$^+$ − 2 × C_9H_{18} − C_4H_9], 454 (9), 453 (28), 452 (13), 407 (6), 391 (5), 390 (6). − $C_{46}H_{55}N_2O_7P$: calcd. 778.3747, found 778.3738 (MS). − $C_{46}H_{55}N_2O_7P$ (778.9): calcd. C 70.93, H 7.12, N 3.60; found C 70.07, H 7.22, N 3.57. − **Second Fraction:** Yield 160 mg (56%) of **12b**, m.p. > 300°C. − R_f (Al$_2$O$_3$ neutral, chloroform): 0.24. − IR (KBr): ṽ = 2957 cm^{-1} (m), 2928 (m), 2860 (m), 1693 (s), 1656 (s), 1606 (m), 1560 (m), 1538 (w), 1457 (m), 1437 (m), 1411 (m), 1379 (m), 1336 (m), 1286 (s), 1258 (m), 1207 (w), 1193 (w), 1137 (w), 1114 (w), 845 (w), 805 (m), 744 (m). − ^{1}H NMR (CDCl$_3$): δ = 0.82 (t, 12 H, CH_3), 1.23−1.40 (m, 16 H, CH_2), 1.93 (m$_C$, 4 H, CH−CH_2), 2.33 (m$_C$, 4 H, CH−CH_2), 5.33 (m$_C$, 2 H, N−C*H*), 8.72 (m$_C$, 4 H, perylene), 8.97 (br. s, 1 H, perylene), 9.00 (br. s, 1 H, perylene), 10.30 (s, 1 H, N*H*). − ^{13}C NMR (CDCl$_3$): δ = 14.03, 22.59, 27.09, 29.30, 31.79, 32.25, 54.92, 119.78, 120.41, 122.02, 122.45, 123.98, 124.90, 127.87, 128.61, 133.11, 133.72. − UV/Vis (CHCl$_3$): λ_{max} (ε) = 457 nm (18330), 489 (41140), 523 (75450). − Fluorescence (chloroform): λ_{max} = 541 nm, 575. − Fluorescence quantum yield (1.03 × 10^{-6} mol/L in CHCl$_3$, reference *N,N′*-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**1a**) with Φ = 100%, $\lambda_{excit.}$ = 490 nm) = 84%. − MS (70 eV): *m/z* (%): 656 (12), 655 (27) [M$^+$], 638 (9), 531 (5), 530 (19), 529 (29) [M$^+$ − C_9H_{18}], 512 (8), 416 (9), 405 (12), 404 (49), 403 (100) [M$^+$ − 2 × C_9H_{18}], 387 (6), 386 (17), 359 (7), 358 (12). − $C_{42}H_{45}N_3O_4$ (655.8): calcd. C 76.92, H 6.92, N 6.41; found C 76.95, H 6.98, N 6.30.

Methylation of **12b.** − **Method A:** Compound **12b** (100 mg, 0.153 mmol) was dissolved in ethanol (10 mL), deprotonated with 85% KOH powder (17.0 mg, 0.258 mmol, dark violet solution). Iodomethane (0.500 mL, 1.14 g, 8.0 mmol) was added, the mixture stirred at room temperature for 16 h, the ethanol was removed by distillation, the residue taken up in chloroform, washed repeatedly with water, dried (MgSO$_4$), concentrated by vacuum distillation and purified by column separation (silica, chloroform). Yield 93 mg (91%) of **12d** as a cherry-red powder. − **Method B:** *N,N′′*-bis(1-butylpentyl)pyrrolo[2,3,4,5-*hik*]perylene-3,4:8,9-bis(dicarboximide) (**12b**, 100 mg, 0.153 mmol) was dissolved in ethanol (10 mL), deprotonated with 85% KOH powder (17.0 mg, 0.258 mmol, violet solution), concentrated by vacuum distillation and taken up in *N*-methylpyrrolidone. Iodomethane (0.100 mL, 0.230 g, 1.60 mmol) was added. The mixture was stirred at room temperature for 12 h and poured in water. Ethanol was added until the *N*-methylpyrrolidone dissolved and the solution was stirred at room temperature for 16 h to age the precipitate which was further purified as was described for Method A. − Yield 93 mg (91%) of **12d** as a cherry-red powder, m.p. > 300°C. − R_f (silica gel, chloroform): 0.61. − R_f (Al$_2$O$_3$, chloroform): 0.77. − IR (KBr): ṽ = 2956 cm^{-1} (m), 2929 (m), 2860 (m), 1695 (s), 1653 (s), 1604 (m), 1558 (w), 1457 (w), 1444 (w), 1423 (m), 1392 (w), 1380 (w), 1350 (m), 1312 (s), 1258 (m), 1222 (w), 1175 (w), 1135 (w), 1130 (w), 1115 (w), 1110 (w), 900 (w), 845 (w), 804 (m), 741 (m). − ^{1}H NMR (CDCl$_3$): δ = 0.84 (t, *J* = 6.9 Hz, 12 H, CH_3), 1.24−1.42 (m, 16 H, CH_2), 1.88−1.96 (m, 4 H, CH−CH_2), 2.28−2.38 (m, 4 H, CH−CH_2), 4.50 (s, 3 H, N−CH_3), 5.32 [m, 2 H, C*H*-(CH$_2$)$_2$], 8.82 (s, 2 H, perylene), 8.93 (d, *J* = 8.1 Hz, 2 H, perylene), 8.97 (s, 2 H, perylene). − ^{13}C NMR (CDCl$_3$): δ = 14.1, 22.7, 29.3, 32.4, 35.5 [N−*C*H$_3$], 54.8, 119.7, 122.0, 124.0, 124.8, 132.9, 135.5. − UV/Vis (CHCl$_3$): λ_{max} (ε) = 410 nm (1890), 435 (7080), 465 (18730), 494 (40320), 530 (78790). − Fluorescence (chloroform): λ_{max} ($I_{rel.}$) = 540 nm (1.0), 578 (0.68), 621 (0.11). − Fluorescence quantum yield (9.60 × 10^{-7} mol/l in CHCl$_3$, reference *N,N′*-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**1a**) with Φ = 100%, $\lambda_{excit.}$ = 490 nm) = 56%. − MS (70 eV): *m/z* (%): 670 (19), 669 (41) [M$^+$], 653 (7), 652 (13) [M$^+$ − OH], 545 (5), 544 (18), 543 (29) [M$^+$ − C_9H_{18}], 527 (5), 526 (10) [M$^+$ − C_9H_{18} − OH], 430 (9), 419 (11), 418 (51), 417 (100) [M$^+$ − 2 × C_9H_{18}], 401 (5), 400 (16) [M$^+$ − 2 × C_9H_{18} −OH], 373 (8), 372 (15). − $C_{43}H_{47}N_3O_4$ (669.9): calcd. C 77.10, H 7.07, N 6.27; found C 76.74, H 7.38, N 6.08.

Benzylation of *N,N′*-Bis(1-hexylheptyl)pyrrolo[2,3,4,5-*hik*]perylene-3,4:8,9-bis(dicarboximide) (12a). − Method A: Compound **12a** (100 mg, 0.130 mmol) was dissolved in ethanol (10 mL) and deprotonated with 85% KOH powder (11.0 mg, 0.167 mmol). Benzyl bromide (222 mg, 1.30 mmol) was added and the mixture stirred at room temperature for 12 h, concentrated and purified by column separation (silica gel, petroleum ether/chloroform, 5:1 and then with chloroform). Yield 83.0 mg (74%) of **12e** as a red powder. − **Method B:** Compound **12a** (100 mg, 0.130 mmol) was dissolved in THF (10 mL) and deprotonated with DBU (30.0 mg, 0.197 mmol). Benzyl bromide (222 mg, 1.30 mmol) was added and the mixture was stirred at room temperature until the starting material could not be detected by TLC, concentrated, and purified as was described for Method A. Yield 97 mg (87%) of **12e**, m.p. 134−135 °C. − R_f (silica gel, chloroform): 0.62. − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1} (m), 2927 (s), 2856 (m), 1693 (s), 1655 (s), 1604 (m), 1559 (m), 1455 (w), 1444 (w), 1424 (m), 1401 (w), 1380 (w), 1351 (m), 1303 (s), 1258 (w), 1205 (w), 1167 (w), 1114 (w), 1028 (w), 848 (w), 806 (m), 743 (m), 705 (w). − ^{1}H NMR ($CDCl_3$): δ = 0.79 (t, *J* = 7 Hz, 12 H, C*H*$_3$), 1.23−1.68 (m, 32 H, C*H*$_2$), 1.89−1.96 (m, 4 H, CH−C*H*$_2$), 2.29−2.33 (m, 4 H, CH−C*H*$_2$), 5.26−5.36 [m, 2 H, C*H*(CH$_2$)$_2$], 5.94 (s, 2 H, C*H*$_2$−phenyl), 7.28−7.30 (m, 5 H, phenyl), 8.75−8.89 (m, 6 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.0, 22.6, 27.1, 29.3, 31.8, 32.6, 50.3 (*C*H$_2$−phenyl), 54.9, 118.4, 119.1, 119.6, 121.6, 122.3, 123.0, 123.8, 124.7, 127.0, 127.6, 128.3, 128.6, 129.3, 132.6, 134.8, 136.1, 164.0, 165.0, 166.2. − UV/Vis ($CHCl_3$): λ_{max} (ε) = 406 nm (4840), 435 (10770), 463 (23660), 493 (46140), 528 (86280). − Fluorescence (chloroform): λ_{max} ($I_{rel.}$) = 537 nm (1.0), 577 (0.45), 623 (0.10). − Fluorescence quantum yield (8.66 × 10^{-7} mol/L in $CHCl_3$, reference *N*,*N*′-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**1a**) with Φ = 100%, $\lambda_{excit.}$ = 490 nm) = 62%. − MS (70 eV): *m/z* (%): 859 (20), 858 (59), 857 (97) [M$^+$], 841 (16), 840 (28) [M$^+$ − OH], 772 (5) [M$^+$ − C_6H_{12}], 768 (7), 767 (15) [M$^+$ − C_7H_7], 677 (14), 676 (39) [M$^+$ − C_9H_{18}], 659 (9), 658 (15) [M$^+$ − C_6H_{12} − OH], 586 (9), 585 (10) [M$^+$ − C_7H_7], 507 (5), 506 (10), 495 (22), 494 (69), 493 (100) [M$^+$ − 2 × C_9H_{18}], 476 (10), 416 (5), 404 (16), 403 (29) [M$^+$ − 2 × C_9H_{18} − C_7H_7], 386 (5). − $C_{57}H_{67}N_3O_4$ (858.2): calcd. C 78.78, H 7.87, N 4.90; found C 78.89, H 7.68, N 4.88.

***N*,*N*′′-Bis(1-butylpentyl)-*N*′-benzylpyrrolo[2,3,4,5-*hik*]perylene-3,4:8,9-bis(dicarboximide) (12f):** *N*,*N*′′-Bis(1-butylpentyl)pyrrolo[2,3,4,5-*hik*]perylene-3,4:8,9-bis(dicarboximide) (**12b**, 40 mg, 0.06 mmol) was dissolved in THF, deprotonated with DBU (19 mg, 0.13 mmol), alkylated with benzyl bromide (25 mg, 0.15 mmol) analogous to Method B for **12a** (2 h), and poured into 2 N HCl (50 mL). The excess benzyl bromide was dissolved by the addition of acetone. The product was collected by vacuum filtration, dried and purified by column separation (silica gel activity IV/chloroform). Yield 35 mg (77%) of **12f** as a bright red powder, m.p. 212−213 °C. − R_f (silica gel, chloroform): 0.42. − IR (KBr): $\tilde{\nu}$ = 2956 cm^{-1} (m), 2928 (m), 2861 (m), 1693 (s), 1654 (s), 1604 (m), 1560 (m), 1456 (w), 1444 (w), 1425 (m), 1402 (w), 1380 (w), 1351 (w), 1305 (s, br.), 1259 (w), 1174 (w), 806 (m), 743 (m), 703 (w). − ^{1}H NMR ($CDCl_3$): δ = 0.84 (t, *J* = 7.0 Hz, 12 H, C*H*$_3$), 1.21−1.42 (m, 16 H, C*H*$_2$), 1.87−1.98 (m, 4 H, CH−C*H*$_2$), 2.28−2.36 (m, 4 H, CH−C*H*$_2$), 5.30 (tt, $^3J_1$ = 9.1 Hz, $^3J_2$ = 5.9 Hz, 2 H, N−C*H*), 5.99 (s, 2 H, N−C*H*$_2$−phenyl), 7.31−7.36 (m, 5 H, phenyl), 8.80−8.90 (m, 6 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 22.7, 29.3, 32.3, 50.4 (*C*H$_2$−phenyl), 54.8, 118.5, 119.3, 119.8, 121.6, 121.9, 122.3, 123.1, 124.0, 124.8, 127.1, 127.7, 128.4, 128.6, 129.3, 132.8, 135.0, 136.2, 164.1, 165.2, 166.3. − UV/Vis ($CHCl_3$): λ_{max} (ε) = 434 nm (9320), 465 (22820), 493 (45250), 529 (85900). − Fluorescence (chloroform): λ_{max} ($I_{rel.}$) = 543 nm (1.0), 580 (0.50), 624 (0.05). − MS (70 eV): *m/z* (%): 747 (15), 746 (55), 745 (100) [M$^+$], 729 (9), 728 (16) [M$^+$ − OH], 621 (8), 620 (25), 619 (32) [M$^+$ − C_9H_{18}], 603 (65), 602 (11), 506 (9), 495 (15), 494 (57), 493 (94) [M$^+$ − 2 × C_9H_{18}], 476 (6), 92 (5), 91 (77) [C_7H_7]. − $C_{49}H_{51}N_3O_4$ (746.0): calcd. C 78.90, H 6.89, N 5.63; found C 78.51, H 6.86, N 5.61.

***N*′-(Ethoxycarbonylmethyl)-*N*,*N*′′-bis(1-hexylheptyl)pyrrolo[2,3,4,5-*hik*]perylene-3,4:8,9-bis(dicarboximide) (12g):** Compound **12a** (105 mg, 0.137 mmol) was dissolved in tetrahydrofuran (15 mL), deprotonated with DBU (31.0 mg, 0.204 mmol), alkylated with bromoacetic acid ethyl ester (46.0 mg, 0.277 mmol, color changes from blue-violet to red within a few minutes), immediately acidified with 2 N HCl as soon as no starting material could be detected by TLC. The excess bromoacetic ester was dissolved with the addition of acetone. The red precipitate was collected by vacuum filtration, dried and purified by column separation (silica gel, chloroform). Yield 95 mg (81%) of **12g** as a bright red powder, m.p. 110−111 °C. − R_f (silica gel, chloroform): 0.56. − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1} (s), 2926 (s), 2856 (s), 1749 (m), 1694 (s), 1654 (s), 1605 (s), 1560 (m), 1480 (w), 1459 (m), 1446 (w), 1425 (s), 1403 (w), 1377 (w), 1350 (w), 1316 (s, br), 1295 (m), 1257 (w), 1204 (m, br, sh. w), 1168 (m), 1115 (w), 1035 (w, sh.), 900 (w), 850 (w), 805 (s), 742 (m). − ^{1}H NMR ($CDCl_3$): δ = 0.80 (t, *J* = 6.7 Hz, 12 H, C*H*$_3$), 1.21−1.37 (m, 35 H, C*H*$_2$ + C*H*$_3$), 1.87−1.93 (m, 4 H, CH−C*H*$_2$), 2.28−2.36 (m, 4 H, CH−C*H*$_2$), 4.31 (q, *J* = 7.2 Hz, 2 H, O−C*H*$_2$−CH$_3$), 5.30 (m$_C$, 2 H, N−C*H*), 5.53 (s, 2 H, N−C*H*$_2$−CO$_2$Et), 8.80−8.91 (m, 6 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.0, 14.2, 22.6, 27.0, 29.3, 31.8, 32.6, 47.3, 54.9, 62.6, 118.1, 118.9, 120.1, 121.8, 122.0, 122.5, 123.2, 124.1, 125.0, 127.9, 128.7, 133.0, 135.4, 164.1, 165.1, 166.3, 167.4. − UV/Vis ($CHCl_3$): λ_{max} (ε) = 405 nm (3240), 431 (9250), 460 (23340), 490 (46420), 525 (89690). − Fluorescence (chloroform): λ_{max} = 535 nm, 570. − MS (70 eV): *m/z* (%): 855 (18), 854 (53), 853 (89) [M$^+$], 837 (10), 836 (16) [M$^+$ − OH], 768 (6) [M$^+$ − C_6H_{13}], 673 (14), 672 (37), 671 (30) [M$^+$ − $C_{13}H_{26}$], 655 (5), 654 (10) [M$^+$ − $C_{13}H_{26}$ − OH], 587 (5) [[M$^+$ − $C_{13}H_{26}$ − C_6H_{13}], 503 (5), 502 (11) [M$^+$ − $C_{13}H_{27}$ − 2 × C_6H_{13}], 491 (18), 490 (59), 489 (100) [M$^+$ − 2 × $C_{13}H_{26}$], 462 (9), 444 (8), 417 (12), 416 (35) [M$^+$ − CO$_2$Et], 373 (5). − $C_{54}H_{67}N_3O_6$ (854.1): calcd. C 75.94, H 7.96, N 4.92; found C 75.77, H 7.96, N 4.83.

***N*′-Acetyl-*N*,*N*′′-bis(1-hexylheptyl)pyrrolo[2,3,4,5-*hik*]perylene-3,4:8,9-bis(dicarboximide) (12h):** Compound **12a** (56 mg, 0.07 mmol) was dissolved in THF, deprotonated with DBU (17 mg, 0.11 mmol), acylated with acetyl chloride (12 mg, 0.15 mmol) (color changes from bluish-violet to red), poured into water (50 mL), and allowed to stand for 16 h. The product was collected by vacuum filtration, dried, and purified by column separation (chloroform/silica gel). Yield 43 mg (73%) of **12h** as a bright red powder, m.p. > 300 °C. − R_f (silica gel, chloroform): 0.62. − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1} (s), 2926 (s), 2854 (s), 1726 (w, CH$_3$−C=O), 1700 (s), 1675 (w), 1658 (s, br), 1608 (m), 1600 (w), 1563 (m), 1550 (w), 1523 (w), 1457 (w), 1419 (m), 1399 (w), 1376 (m), 1366 (m), 1347 (m), 1312 (s), 1305 (s, sh), 1256 (m), 1206 (w), 1184 (w), 1169 (w), 1094 (w), 1026 (w), 925 (w), 902 (w), 849 (m), 806 (s), 740 (s), 617 (w). − ^{1}H NMR ($CDCl_3$): δ = 0.81 (t, *J* = 7 Hz, 12 H, C*H*$_3$), 1.20−1.37 (m, 32 H, C*H*$_2$), 1.95 (m$_C$, 4 H, CH−C*H*$_2$), 2.30 (m$_C$, 4 H, CH−C*H*$_2$), 3.11 (s, 3 H, C*H*$_3$−CO), 5.27 [m$_C$, 2 H, C*H*−(CH$_2$)$_2$], 8.61 (d, *J* = 7.9 Hz, 2 H, perylene), 8.71 (br. d, 2 H, perylene), 9.10 (s, 2 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.0, 22.6, 25.9 (*C*H$_3$−CO), 27.1, 29.3, 31.8, 32.6, 55.1, 121.3, 122.0, 122.2, 123.0, 123.3, 124.1, 124.2, 125.8, 129.6, 130.2, 133.2, 133.3, 143.2, 163.3, 164.3, 165.4, 169.6 (CH$_3$−*C*=O). − UV/Vis ($CHCl_3$): λ_{max} (ε) = 408 nm (7460), 432 (17740), 452 (15730), 482 (46350), 517 (86180). − Fluorescence (chloroform): λ_{max} = 526 nm, 562. − Fluorescence quantum yield (8.09 × 10^{-7} mol/L in $CHCl_3$, reference *N*,*N*′-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**1a**) with Φ = 100%, $\lambda_{excit.}$ = 484 nm) = 99%. − MS (70 eV): *m/z* (%): 811 (14), 810 (47), 809 (79) [M$^+$], 793 (8), 792 (13) [M$^+$ − OH], 769 (8), 768 (30), 767 (54) [M$^+$ − CH$_2$=C=O], 751 (5), 750 (9), 724 (5), 629 (15), 628 (40), 627 (49) [M$^+$ − $C_{13}H_{26}$], 610 (6), 587 (7), 586 (24), 585 (30) [M$^+$ − $C_{13}H_{26}$ − CH$_2$=C=O], 568 (5), 447 (10), 446 (29), 445 (47) [M$^+$ − 2 × $C_{13}H_{26}$], 416 (8), 405 (15), 404 (62), 403 (100) [M$^+$ − 2 × $C_{13}H_{26}$−CH$_2$=C=O], 387 (5), 386 (13), 358 (5). − $C_{52}H_{63}N_3O_5$ (810.1): calcd. C 77.10, H 7.84, N 5.19; found C 76.99, H 7.72, N 5.14.

N'-Acetyl-N,N''-bis(1-butylpentyl)pyrrolo[2,3,4,5-*hik*]perylene-3,4:8,9-bis(dicarboximide) (12i): Compound **12b** (48.0 mg, 0.0730 mmol) was dissolved in THF, deprotonated with DBU (22.0 mg, 0.145 mmol), acylated with acetyl chloride (10.0 mg, 0.128 mmol), analogously to **12h**, precipitated with water, collected by vacuum filtration, dried, and purified by column separation (silica gel, dichloromethane). Yield 35 mg (69%) of **12i** as a bright-red powder, m.p. > 300°C. − R_f (silica gel, chloroform): 0.23. − IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1} (m), 2929 (m), 2861 (w), 1724 (w, $CH_3-C=O$), 1698 (s), 1656 (s), 1608 (m), 1565 (w), 1420 (m), 1397 (w), 1376 (w), 1348 (w), 1313 (s), 1258 (m), 1209 (w), 1188 (w), 1114 (w), 1030 (w), 849 (w), 808 (m), 742 (m), 618 (w), 579 (w). − ^{1}H NMR ($CDCl_3$): δ = 0.87 (t, J = 7.0 Hz, 12 H, CH_3), 1.27−1.45 (m, 16 H, CH_2), 1.90−2.01 (m, 4 H, $CH-CH_2$), 2.25−2.37 (m, 4 H, $CH-CH_2$), 3.09 (s, 3 H, CH_3-CON), 5.27 (m_C, 2 H, N−C*H*), 8.59 (d, J = 7.8 Hz, 2 H, perylene), 8.69 (br. d, 2 H, perylene), 9.08 (s, 2 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 22.7, 25.8, 29.3, 32.2, 55.0, 121.1, 121.9, 122.2, 122.8, 123.2, 124.1, 125.7, 129.5, 130.2, 133.0, 133.2, 163.3, 164.3, 165.4, 169.6 ($CH_3-C=O$). − UV/Vis ($CHCl_3$): λ_{max} (ε) = 278 nm (23260), 409 (8690), 432 (19170), 452 (16930), 483 (47680), 517 (86920). − Fluorescence (chloroform): λ_{max} ($I_{rel.}$) = 531 nm (1.0), 567 (0.74), 612 (0.15). − MS (70 eV): *m/z* (%): 699 (12), 698 (47), 697 (100) [M$^+$], 681 (6), 680 (15) [$M^+ - OH$], 655 (6) [$M^+ - CH_2=C=O$], 640 (6), 573 (12), 572 (38), 571 (53) [$M^+ - C_9H_{18}$], 554 (8), 447 (9), 446 (33), 445 (57) [$M^+ - 2 \times C_9H_{18}$], 416 (8), 405 (11), 404 (19), 403 (65) [$M^+ - 2 \times C_9H_{18} - CH_2=C=O$], 387 (5), 386 (15), 359 (5), 358 (8). − $C_{44}H_{47}N_3O_5$ (697.9): calcd. C 75.73, H 6.79, N 6.02; found C 75.66, H 6.79, N 5.99.

Attempted Acylation of N,N''-Bis(1-butylpentyl)pyrrolo[2,3,4,5-*hik*]perylene-3,4:8,9-bis(dicarboximide) (12b) without Addition of a Base: Compound **12b** (48.0 mg, 0.0730 mmol) was dissolved in toluene. Acetyl chloride (30.0 mg, 0.385 mmol) was added and the mixture was stirred at room temperature for 24 h. No formation of **12i** could be detected by TLC.

N'-Benzoyl-N,N''-bis(1-hexylheptyl)pyrrolo[2,3,4,5-*hik*]perylene-3,4:8,9-bis(dicarboximide) (12j): Compound **12a** (80.0 mg, 0.104 mmol) was dissolved in THF, deprotonated with DBU (25.0 mg, 0.164 mmol), acylated with benzoyl chloride (44.0 mg, 0.314 mmol, colour changes from blue-violet to dark red within a few minutes) and poured into water (50 mL). Acetone (10 mL) was added and the mixture was allowed to stand for 16 h. The precipitate was collected by vacuum filtration, dried and purified by column separation (silica gel, chloroform), analogously to **12h**. Yield 84.0 mg (92%) of **12i** as a bright-red powder, m.p. 181−183°C. − R_f (silica gel, chloroform): 0.51. − IR (KBr): $\tilde{\nu}$ = 2956 cm^{-1} (s), 2928 (s), 2856 (s), 1697 (s), 1658 (s), 1609 (m), 1565 (m), 1465 (w), 1457 (w), 1440 (w), 1421 (m), 1394 (w), 1349 (m), 1313 (s, br.), 1257 (m, br.), 1205 (w), 1169 (w), 808 (m), 743 (m). − ^{1}H NMR ($CDCl_3$): δ = 0.80 (t, J = 6.8 Hz, 12 H, CH_3), 1.21−1.33 (m, 32 H, CH_2), 1.86−1.92 (m, 4 H, $CH-CH_2$), 2.22−2.30 (m, 4 H, $CH-CH_2$), 5.21−5.28 [m, 2 H, $N-CH(CH_2)_2$], 7.71 (t, J = 7.6 Hz, 2 H, phenyl), 7.87 (t, J = 7.5 Hz, 1 H, phenyl), 7.92 (d, J = 6.9 Hz, 2 H, phenyl), 8.61−8.76 (m, 6 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.0, 22.6, 27.0, 29.3, 31.8, 32.5, 55.0, 121.6, 122.4, 122.8, 123.0, 123.5, 123.8, 124.3, 126.0, 129.3, 129.4, 130.3, 133.4, 133.5, 133.9, 134.6, 163.6, 164.2, 164.6, 165.4, 169.1 (phenyl−*C*=O). − UV/Vis ($CHCl_3$): λ_{max} (ε) = 407 nm (7050), 431 (17430), 450 (14760), 480 (43820), 514 (80820). − Fluorescence (chloroform): λ_{max} = 523 nm, 560. − Fluorescence quantum yield (8.40 × 10^{-7} mol/L in $CHCl_3$, reference *N,N'*-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**1a**) with Φ = 100%, $\lambda_{excit.}$ = 484 nm) = 98%. − MS (70 eV): *m/z* (%): 873 (20), 872 (62), 871 (100) [M$^+$], 855 (8), 854 (14) [$M^+ - OH$], 691 (13), 690 (40), 689 (41) [$M^+ - C_{13}H_{26}$], 672 (7) [$M^+ - C_{13}H_{26} - OH$], 509 (10), 508 (32), 507 (42) [$M^+ - 2 \times C_{13}H_{26}$], 418 (6), 404 (6), 106 (5), 105 (76) [C_6H_6-CO]. − $C_{57}H_{65}N_3O_5$ (872.2): calcd. C 78.50, H 7.51, N 4.82; found C 78.53, H 7.66, N 4.63.

1-Bromo-*N,N'*-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (8a): Compound **1a** (200 mg, 0.265 mmol) was dissolved in chlorobenzene. Bromine (1.00 mL, 3.14 g, 39.3 mmol) and anhydrous potash (520 mg, 3.77 mmol) were added. The mixture was stirred (24 h, 60°C), concentrated and purified by column separation (silica gel, chloroform). Yield 190 mg (86%) of **8a** as a dark red powder, m.p. 136−138°C. − R_f (silica gel, chloroform): 0.79. − IR (KBr): $\tilde{\nu}$ = 2956 cm^{-1} (m), 2926 (s), 2856 (m), 1702 (s), 1660 (s), 1593 (s), 1458 (w), 1400 (m), 1387 (w), 1334 (s), 1245 (m), 1178 (w), 1108 (w), 848 (w), 810 (m), 745 (m). − ^{1}H NMR ($CDCl_3$): δ = 0.80 (t, J = 6.6 Hz, 12 H, CH_3), 1.21−1.35 (m, 32 H, CH_2), 1.84 (m_C, 4 H, $CH-CH_2$), 2.22 (m_C, 4 H, $CH-CH_2$), 5.09−5.22 (m, 2 H, N−C*H*), 8.59 (d, J = 8.1 Hz, 2 H, perylene), 8.66 (m_C, 3 H, perylene), 8.90 (s, 1 H, perylene), 9.76 (d, J = 8.3 Hz, 1 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.0, 22.6, 26.9, 29.2, 31.7, 32.3, 32.4, 54.8, 55.0, 120.9, 123.0, 123.7, 127.1, 128.1, 128.8, 129.0, 130.8, 131.4, 133.5, 133.9, 163.3, 164.4. − UV/Vis ($CHCl_3$): λ_{max} (ε) = 381 nm (3970), 430 (4170), 458 (15420), 488 (41500), 524 (64700). − Fluorescence (chloroform): λ_{max} ($I_{rel.}$) = 540 nm (1.0), 582 (0.61), 634 (0.13). − Fluorescence quantum yield (1.00 × 10^{-6} mol/L in $CHCl_3$, reference *N,N'*-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**1a**) with Φ = 100%, $\lambda_{excit.}$ = 488 nm) = 93%. − MS (70 eV): *m/z* (%): 834 (67), 832 (60) [M$^+$], 754 (100) [$M^+ - Br$], 653 (22), 652 (31), 651 (26), 650 (21) [$M^+ - C_{13}H_{26}$], 574 (12), 573 (29), 572 (31) [$M^+ - C_{13}H_{26} - Br$], 471 (32), 470 (47), 469 (29), 468 (36) [$M^+ - 2 \times C_{13}H_{26}$], 392 (18), 391 (51), 390 (73) [$M^+ - 2 \times C_{13}H_{26} - Br$]. − $C_{50}H_{61}BrN_2O_4$ (834.0): calcd. C 72.01, H 7.37, N 3.36, Br 9.58; found C 71.89, H 7.26, N 3.26, Br 9.52.

Attempted Bromination of *N,N'*-Bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (1a) without Catalysis: Compound **1a** (200 mg, 0.265 mmol) and bromine (1.00 mL, 3.14 g, 39.3 mmol) were heated under reflux in chlorobenzene for 12 h. No formation of 1-bromo-*N,N'*-bis(1-hexylheptyl)perylene-3,4;9,10-bis(dicarboximide) (**8a**) could be detected by TLC.

1-Amino-*N,N'*-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (9a) by Reduction with Iron and Hydrochloric Acid (A): Compound **6a** (100 mg, 0.125 mmol) and iron (50.0 mg, 0.893 mmol) were dispersed in ethanol (or *n*-butyl alcohol or THF). Concd. HCl (0.5 mL) was added. The mixture was heated under reflux (10−30 min) until no **6a** could be detected (TLC) and the product was precipitated with water. The solid was collected by vacuum filtration, dried, and purified by column separation (silica gel, chloroform and alumina, chloroform). Yield 78.0 mg (81%) of **9a** as a dark-blue powder (physical data see B below).

1-Amino-*N,N'*-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (9a) by Reduction with Triethylammonium Formate and Palladium/Carbon (B): Compound **6a** (20.0 mg, 0.025 mmol) was dissolved in THF. Triethylamine (0.200 mL, 145 mg, 1.44 mmol) and palladium/carbon (5 mg, 5%) were added. The mixture was heated under reflux (30 min, to remove any catalyst poison). Formic acid (0.040 mL, 48.8 mg, 1.06 mmol) and additional palladium/carbon (5 mg, 5%) was added. The mixture was heated under reflux (15−30 min) until no starting material could be detected by TLC. The purification was carried out analogously to A. − Yield 14.0 mg (73%) of **9a** as a dark blue powder, m.p. 93−95°C. − R_f (silica gel, chloroform): 0.34. − R_f (Al_2O_3, chloroform): 0.54.

− IR (KBr): ṽ = 3349 cm^{-1} (m, N−H), 3245 (w, N−H), 2955 (m), 2926 (s), 2856 (m), 1693 (s), 1651 (s, br.), 1615 (s), 1602 (s), 1590 (s), 1573 (s), 1565 (m), 1512 (w), 1465 (m), 1428 (s), 1397 (w), 1373 (m), 1339 (s), 1312 (m), 1269 (m, C−N), 1253 (m), 1180 (w), 1125 (w), 845 (w), 809 (s), 750 (m), 725 (w). − ^{1}H NMR ($CDCl_3$): δ = 0.79 (t, *J* = 6.8 Hz, 12 H, C*H*$_3$), 1.20−1.28 (m, 32 H, C*H*$_2$), 1.79−1.86 (m, 4 H, CH−C*H*$_2$), 2.20−2.27 (m, 4 H, CH−C*H*$_2$), 5.17−5.20 (m, 2 H, N−C*H*), 5.24 (s, 2 H, N*H*$_2$), 8.16 (s, 1 H, perylene), 8.40−8.47 (m, 3 H, perylene), 8.59 (m$_C$, 2 H, perylene), 8.81 (d, *J* = 8.2 Hz, 2 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.0, 22.6, 26.9, 29.2, 31.7, 32.4, 54.6, 115.5, 121.2, 122.8, 123.8, 127.3, 128.4, 129.7, 132.7, 135.1, 136.1, 146.1 (*C*−*N*H$_2$). − UV/Vis ($CHCl_3$): λ_{max} (ε) = 276 nm (24540), 420 (10090), 571 (31070). − Fluorescence (chloroform): λ_{max} = 684 nm. − MS (70 eV): *m/z* (%): 771 (11), 770 (39), 769 (75) [M$^+$], 753 (5), 752 (8) [M$^+$ − OH], 589 (7), 588 (22), 587 (23) [M$^+$ − $C_{13}H_{26}$], 570 (6), 418 (6), 407 (13), 406 (58), 405 (100) [M$^+$ − 2 × $C_{13}H_{26}$], 388 (5), 360 (6). − $C_{50}H_{63}N_3O_4$ (770.1): calcd. C 77.99, H 8.25, N 5.46; found C 77.77, H 8.07, N 5.47.

***N*,*N*′-Bis(1-hexylheptyl)-1-dimethylaminoperylene-3,4:9,10-bis(dicarboximide) (10a). − Methylation According to Eschweiler−Clarke (A):** 1-Amino-*N*,*N*′-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**9a**, 34.0 mg, 0.044 mmol) was dissolved in formic acid with the addition of small amounts of DMF; 35% aqueous formaldehyde solution (ca. 0.5 mL) was added. The mixture was heated under reflux with stirring (24 h, 85°C), precipitated with water, and made alkaline with Na_2CO_3. The dark precipitate was collected by vacuum filtration, dried, and purified by column separation (silica gel, chloroform). The yields varied considerably. Yield 21.0 mg (60%) of **10a**. Physical data see below.

1-Dimethylamino-*N*,*N*′-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (10a). − Methylation with Methyl Iodide: Compound **9a** (50.0 mg, 0.065 mmol) was dissolved in toluene (or dichloromethane). 85% KOH powder (15.0 mg, 0.228 mmol), benzyltriethylammonium chloride (5.00 mg, 0.022 mmol), and methyl iodide (0.040 mL, 0.091 mg, 0.642 mmol) were added. The mixture was stirred at room temperature for 16 h, diluted with the solvent used (or *tert*-butyl methyl ether), washed three times with water, dried with $MgSO_4$, and purified by column separation (silica gel, chloroform and silica gel, dichloromethane). The bluish-green monomethylated product and the blue starting material were obtained after elution of the main fraction. Yield 40.0 mg (77%) of **10a** as a dark green solid, m.p. 72−74°C. − R_f (silica gel, chloroform): 0.63. − R_f (silica gel, dichloromethane): 0.83. − IR (KBr): ṽ = 2954 cm^{-1} (m), 2925 (s), 2855 (s), 1694 (s), 1654 (s), 1612 (w), 1588 (s), 1509 (w), 1458 (w), 1405 (m), 1361 (w), 1332 (s), 1249 (m), 1192 (w), 1128 (w), 1058 (w), 948 (w), 846 (w), 809 (m), 750 (m), 724 (w), 702 (w). − ^{1}H NMR ($CDCl_3$): δ = 0.81 (t, *J* = 6.6 Hz, 12 H, C*H*$_3$), 1.21−1.29 (m, 32 H, C*H*$_2$), 1.84 (m$_C$, 4 H, CH−C*H*$_2$), 2.23 (m$_C$, 4 H, CH−C*H*$_2$), 3.02 (s, 6 H, N−CH$_3$), 5.17 (m$_C$, 2 H, N−C*H*), 8.50−8.63 (m, 6 H, perylene), 9.00 (d, *J* = 8.3 Hz, 1 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.01, 22.57, 26.90, 26.93, 29.21, 29.24, 31.75, 32.41, 43.54 [N(*C*H$_3$)$_2$], 54.53, 54.72, 120.23, 121.24, 123.75, 124.13, 124.72, 127.28, 128.54, 129.10, 129.40, 130.85, 131.31, 131.41, 132.02, 133.66, 135.04, 135.65, 152.06 (*C*−NMe$_2$), 163.92, 164.80. − UV/Vis ($CHCl_3$): λ_{max} ($E_{rel.}$) = 436 nm (0.62), 614 (1.0). − Fluorescence (chloroform): λ_{max} = 725 nm. − MS (70 eV): *m/z* (%): 799 (18), 798 (59), 797 (100) [M$^+$], 616 (9), 615 (8) [M$^+$ − $C_{13}H_{26}$], 434 (14), 433 (18) [M$^+$ − 2 × $C_{13}H_{26}$]. − $C_{52}H_{67}N_3O_4$ (798.1): calcd. C 78.26, H 8.46, N 5.26; found C 76.34, H 7.42, N 6.03.

***N*,*N*′-Bis(1-butylpentyl)-1-(dimethylamino)perylene-3,4:9,10-bis(dicarboximide) (10b):** Compound **6b** (100 mg, 0.146 mmol) was dissolved in THF. Iron (50.0 mg, 0.893 mmol) and concd. hydrochloric acid (0.5 mL) were added. The mixture was heated under reflux until no red, non fluorescent starting material was detectable by TLC (ca. 15 min). The dye was precipitated with water and a small amount of 2 N HCl, collected by vacuum filtration and dried (**9b**) and dissolved in dichloromethane. 85% KOH powder (30.0 mg, 0.456 mmol), benzyltriethylammonium chloride (10.0 mg, 0.044 mmol) and methyl iodide (0.10 mL, 0.228 mg, 1.61 mmol) were added. The mixture was vigorously stirred at room temperature for 16 h, diluted with dichloromethane, repeatedly washed with water, dried with $MgSO_4$, concentrated, and purified by column separation (silica gel, chloroform and silica gel, dichloromethane). Yield 70.0 mg (70%) of **10b** as a dark bluish-green powder, m.p. 170−172°C. − R_f (silica gel, chloroform): 0.50. − R_f (silica gel, dichloromethane): 0.76. − IR (KBr): ṽ = 2955 cm^{-1} (m), 2927 (m), 2858 (w), 1694 (s), 1654 (s), 1612 (w), 1588 (s), 1510 (w), 1458 (w), 1405 (m), 1361 (w), 1332 (s), 1253 (m), 1194 (w), 1128 (w), 1100 (w), 810 (m), 751 (w). − ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, *J* = 7.1 Hz, 12 H, C*H*$_3$), 1.20−1.40 (m, 16 H, C*H*$_2$), 1.87 (m$_C$, 4 H, CH−C*H*$_2$), 2.27 (m$_C$, 4 H, CH−C*H*$_2$), 3.04 (s, 6 H, N−CH$_3$), 5.20 (m$_C$, 2 H, N−C*H*), 8.48−8.72 (m, 6 H, perylene), 9.02 (d, *J* = 8.4 Hz, 1 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.06, 22.67, 29.15, 32.16, 43.58 [N(*C*H$_3$)$_2$], 54.49, 120.28, 121.28, 123.78, 124.18, 124.77, 127.32, 129.15, 129.45, 133.70, 135.08, 135.70, 152.10 (*C*−NMe$_2$). − UV/Vis ($CHCl_3$): λ_{max} (ε) = 278 nm (22490), 436 (15700), 615 (23570). − Fluorescence (chloroform): λ_{max} = 725 nm. − MS (70 eV): *m/z* (%): 687 (12), 686 (47), 685 (100) [M$^+$], 560 (13), 559 (2) [M$^+$ − C_9H_{19}], 435 (7), 434 (25), 433 (36) [M$^+$ − 2 × C_9H_{19}], 418 (5). − $C_{44}H_{51}N_3O_4$ (685.9): calcd. C 77.05, H 7.49, N 6.13; found C 77.05, H 7.84, N 5.80.

1-Amino-*N*-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic 3,4-Anhydride 9,10-Imide (17b) and 12-Amino-*N*-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic 3,4-Anhydride 9,10-Imide (18b) by Reduction with Iron and Hydrochloric Acid (A): A mixture (100 mg, 0.162 mmol) of 1-nitro-*N*-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic 3,4-anhydride 9,10-imide (**17a**) and 12-nitro-*N*-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic 3,4-anhydride 9,10-imide (**18a**) was dissolved in a mixture (30 mL) of chloroform/ethanol (1:3) or THF. Iron (64.0 mg, 1.14 mmol) and concd. HCl (0.5 mL) were added and the mixture was heated under reflux for 30 min, cooled and poured into 2 N HCl. Acetone was added to obtain a homogeneous solution (not necessary for THF). The solution was heated to boiling to remove chloroform, the precipitate (dark solid) was collected by vacuum filtration and dried. The thus obtained mixture of **17b** and **18b** as a dark blue powder was used without further purification. For physical data see B below.

1-Amino-*N*-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic 3,4-Anhydride 9,10-Imide (17b) and 12-Amino-*N*-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic 3,4-Anhydride 9,10-Imide (18b) by Reduction with Triethylammonium Formate and Palladium/Carbon (B): A mixture (100 mg, 0.162 mmol) of **17a** and **18a** was dissolved in THF. Triethylamine (1.30 mL, 0.940 mg, 9.33 mmol) and palladium/carbon (15 mg) were added, and the mixture was heated under reflux for 30 min (removing catalyst poison). Formic acid (0.26 mL, 316 mg, 6.87 mmol) and a second portion of palladium/carbon (30 mg) were added. The mixture was refluxed until no starting material could be detected by TLC (ca. 30 min), filtered and purified as is described for A above. The thus obtained mixture of **17b** and **18b** (a dark blue powder) was used without further purification. M.p. 292−294°C. − R_f (silica gel, dichloromethane/2% acetic acid): 0.15−0.40. − R_f (silica gel, chloroform/10% acetic acid): 0.60. − IR (KBr): ṽ = 2955 cm^{-1} (m), 2927 (m), 2856 (m), 1764 (s), 1725 (m), 1698 (s), 1655 (s), 1617 (m), 1604 (m), 1590 (s), 1561 (m), 1509 (w), 1459 (w), 1428 (m), 1399 (w), 1373 (m), 1351 (m), 1327 (s), 1284 (w), 1249 (m), 1202 (w), 1175 (w), 1135 (w), 1110 (w), 1035 (m), 100 (m), 805 (m), 742 (m). − ^{1}H NMR ($CDCl_3$): δ = 0.83 (t, *J* = 6.4 Hz, 6 H, C*H*$_3$), 1.23- 1.40 (m, 16 H, C*H*$_2$), 1.86 (m$_C$, 2 H, CH−C*H*$_2$), 2.23 (m$_C$, 2 H, CH−C*H*$_2$), 5.12−5.19 (m, 1 H, N−C*H*), 5.35 (s, 2 H, N*H*$_2$), 8.16 (br. s, 1 H, perylene), 8.46−8.66 (m, 5 H, perylene), 8.87 (br. s, 1 H, perylene). − UV/Vis ($CHCl_3$): λ_{max} ($E_{rel.}$) = 416 nm (0.38), 568 (1.0). − Fluorescence (chloroform): λ_{max} = 664 nm. − MS (70 eV): *m*/*z* (%): 590 (5), 589 (23), 588 (50) [M^+], 571 (5) [M^+ − OH], 408 (15), 407 (56), 406 (100) [$M^+ - C_{13}H_{26}$], 391 (6) [$M^+ - C_{13}H_{26} + H^+ - NH_2$], 362 (6) [$M^+ - C_{13}H_{26} - CO_2$], 334 (10) [$M^+ - C_{13}H_{26} - C_2O_3$].

1-Dimethylamino-*N*-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic 3,4-Anhydride 9,10-Imide (17c) and 12-Dimethylamino-*N*-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxylic 3,4-Anhydride 9,10-Imide (18c): A mixture (58.0 mg, 0.099 mmol) of **17b** and **18b** was dissolved in dimethylformamide (7 mL). Formic acid (2 mL) and aqueous formaldehyde solution (1 mL, 37%) were added under argon. The mixture was heated under reflux, under argon, with stirring (24 h, 105 °C) and poured into 1 N HCl (bluish-green precipitate). The precipitate was collected by vacuum filtration, washed with water, dried and purified by column separation (silica gel, chloroform/5% acetic acid) with the exclusion of daylight. Yield 43 mg (71%) of **17c** and **18c**. − R_f (silica gel, chloroform/3% acetic acid): 0.50. − The separation of the two isomers proceeded by column chromatography (silica gel, chloroform/1% acetic acid). − **First Fraction: 17c**. − R_f (silica gel, chloroform/1% acetic acid): 0.17. − UV/Vis ($CHCl_3$): λ_{max} ($E_{rel.}$) = 442 nm (0.70), 626 (1.0). − ^{1}H NMR ($CDCl_3$): δ = 0.83 (t, *J* = 6.4 Hz, 6 H, C*H*$_3$), 1.23−1.32 (m, 16 H, C*H*$_2$), 1.81−1.91 (m, 2 H, CH−C*H*$_2$), 2.22−2.29 (m, 2 H, CH−C*H*$_2$), 3.05 (s, 6 H, N−C*H*$_3$), 5.21 (m$_C$, 1 H, N−C*H*), 8.48−8.57 (m, 4 H, perylene), 8.64−8.68 (m$_C$, 2 H, perylene), 8.95 (d, *J* = 8.3 Hz, 1 H, perylene). − MS (70 eV): *m*/*z* (%): 618 (9), 617 (43), 616 (100) [M^+], 599 (8) [M^+ − OH], 436 (11), 435 (49), 434 (93) [$M^+ - C_{13}H_{26}$]. − **Second Fraction: 18c**. − R_f (silica gel, chloroform/1% acetic acid): 0.11. − UV/Vis ($CHCl_3$): λ_{max} ($E_{rel.}$) = 442 nm (0.71), 483 (0.35), 634 (1.0). − ^{1}H NMR ($CDCl_3$): δ = 0.84 (t, *J* = 6.4 Hz, 6 H, C*H*$_3$), 1.24−1.26 (m, 16 H, C*H*), 1.80−1.90 (m, 2 H, CH−C*H*$_2$), 2.21−2.27 (m, 2 H, CH−C*H*$_2$), 3.08 (s, 6 H, N−C*H*$_3$), 5.19 (m$_C$, 1 H, N−C*H*), 8.51−8.68 (m, 6 H, perylene), 8.80 (d, *J* = 8.3 Hz, 1 H, perylene). − *m*/*z* (%): 618 (8), 617 (36), 616 (100) [M^+], 435 (25), 434 (49) [$M^+ - C_{13}H_{26}$].

Reaction of *N*,*N'*-Bis(1-butylpentyl)-1-nitroperylene-3,4:9,10-bis(dicarboximide) (6b) with Sulfur: Sulfur (20.0 mg, 0.63 mmol) was completely dissolved in DMF (10 mL) by heating (80−90 °C). Compound **6b** (100 mg, 0.15 mmol) was added under argon. The mixture was heated under reflux (10 h, 120−130 °C) until no starting material could be detected by TLC, cooled down to below 100 °C, and poured into a mixture of water and 2 N HCl (2:1, ca. 100 mL; dark precipitate). The precipitate was collected by vacuum filtration, washed with water, dried at 70 °C, and purified by column separation (silica gel, $CHCl_3$). − **First Fraction:** This fraction was dissolved in petroleum ether and the excess sulfur was completely removed by column separation (silica gel, petroleum ether, ca. 2 L, until no sulfur could be detected if the eluent was evaporated). The green, main fraction was then eluted with chloroform. Yield 42 mg (42%) of **13b**, m.p. > 300 °C. − R_f (silica gel, chloroform): 0.63. − IR (KBr): ṽ = 2958 cm^{-1} (m), 2928 (m), 2856 (m), 1697 (s), 1660 (s), 1653 (s), 1590 (m), 1466 (s), 1457 (s), 1415 (w), 1402 (w), 1384 (m), 1339 (w), 1305 (m), 1263 (w), 1251 (m), 1187 (w), 1112 (w), 848 (w), 810 (m), 747 (w). − ^{1}H NMR ($CDCl_3$): δ = 0.83 (t, *J* = 7.0 Hz, 12 H, C*H*$_3$), 1.29 (m$_C$, 16 H, C*H*$_2$), 2.21 (m$_C$, 4 H, CH−C*H*$_2$), 2.52 (m$_C$, 4 H, CH−C*H*$_2$), 5.12 [tt, $^3J_1$ = 9.4 Hz, $^3J_2$ = 5.7 Hz, 2 H, C*H*−(CH_2)$_2$], 8.44 (s, 2 H, perylene), 8.51−8.58 (m, 4 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.4, 23.0, 29.5, 32.4, 55.3, 124.4, 127.1, 129.0, 129.2, 131.3, 131.9, 1132.9, 133.1, 133.2, 162.9, 163.6, 164.1, 164.6, 168.1. − UV/Vis ($CHCl_3$): λ_{max} (ε) = 403 nm (8580), 426 (12290), 450 (18390), 478 (29080), 611 (12030). − MS (70 eV): *m*/*z* (%): 707 (6), 706 (20), 705 (49), 704 (100) [M^+], 687 (5) [M^+ − OH], 581 (5), 580 (13), 579 (29), 578 (23) [$M^+ - C_9H_{18}$], 561 (6), 466 (5), 465 (11), 455 (11), 454 (31), 453 (69), 452 (89) [$M^+ - 2 \times C_9H_{18}$], 435 (6), 422 (10), 421 (29), 420 (40) [$M^+ - 2 \times C_9H_{18} - S$], 410 (6), 409 (14), 408 (7), 407 (17), 403 (14), 382 (8), 381 (6), 376 (8), 375 (10), 332 (5). − $C_{42}H_{44}N_2O_4S_2$ (705.0): calcd. C 71.56, H 6.29, N 3.97, S 9.10; found C 71.75, H 6.31, N 3.93, S 9.18. − **Second Fraction:** Yield 49 mg (47%) of **11b** as a bright orange powder, m.p. > 300 °C. − R_f (silica gel, chloroform): 0.54. − IR (KBr): ṽ = 2957 cm^{-1} (s), 2929 (s), 2860 (s), 1698 (s), 1660 (s), 1622 (w), 1598 (m), 1561 (m), 1467 (w), 1453 (w), 1428 (m), 1403 (w), 1364 (w), 1350 (m), 1307 (s), 1247 (m), 1200 (w), 1183 (w), 1171 (w), 1155 (w), 1121 (w), 1106 (m), 1089 (w), 915 (w), 850 (m), 808 (s), 743 (s), 736 (w), 633 (w), 599 (w), 592 (w), 540 (w). − ^{1}H NMR ($CDCl_3$): δ = 0.87 (t, *J* = 7.0 Hz, 12 H, C*H*$_3$), 1.44−1.31 (m, 16 H, C*H*$_2$), 1.94−2.00 (m, 4 H, CH−C*H*$_2$), 2.32−2.40 (m, 4 H, CH−C*H*$_2$), 5.28 [m, 2 H, C*H*−(CH_2)$_2$], 8.64 (d, *J* = 8.1 Hz, 2 H, perylene), 8.72 (br. d, *J* = 8.1 Hz, 2 H, perylene), 9.10 (s, 2 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 22.7, 29.3, 32.2, 55.0, 122.7, 123.2, 126.0, 128.6, 130.8, 131.0, 132.7, 137.9 (*C*−S−*C*). − UV/Vis ($CHCl_3$): λ_{max} (ε) = 391 nm (3020), 415 (10000), 440 (27400), 469 (48990), 501 (83110). − Fluorescence (chloroform): λ_{max} ($I_{rel.}$) = 511 nm (1.0), 548 (0.57), 590 (0.13). − Fluorescence quantum yield ($CHCl_3$, 7.67 × 10^{-7} mol/l in $CHCl_3$, reference *N*,*N'*-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**1a**) with Φ = 100%, $\lambda_{excit.}$ = 490 nm): 71%. − Solid-state fluorescence: λ_{max} = 584 nm. − MS (70 eV): *m*/*z* (%): 673 (12), 672 (25) [M^+], 655 (7) [M^+ − OH], 548 (8), 547 (25), 546 (29) [$M^+ - C_9H_{18}$], 529 (7), 433 (7), 422 (18), 421 (57), 420 (100) [$M^+ - 2 \times C_9H_{18}$], 404 (8), 403 (21), 376 (9), 375 (15). − $C_{42}H_{44}N_2O_4S$ (672.9): calcd. C 74.94, H 6.59, N 4.16, S 4.77; found C 74.69, H 6.60, N 4.95, S 4.95.

Reaction of *N*,*N'*-Bis(1-hexylheptyl)-1-nitroperylene-3,4:9,10-bis(dicarboximide) (6a) with Sulfur in DMF: Sulfur (16 mg, 0.50 mmol) was allowed to react with compound **6a** (0.10 g, 0.13 mmol) in DMF (10 mL, 130 °C) analogously to **6b**. Yield 43.0 mg (40%) of **13a** and 47.0 mg (45%) of **11a** as a bright orange powder. Physical data see below.

Reaction of *N*,*N'*-Bis(1-hexylheptyl)-1-nitroperylene-3,4:9,10-bis(dicarboximide) (6a) with Sulfur in *N*-Methylpyrrolidone: Sulfur (160 mg, 4.9 mmol) was dissolved in *N*-methylpyrrolidone (12 mL, 70 °C). Compound **6a** (0.50 g, 0.62 mmol) was added under argon. The mixture was heated (130 °C, ca. 75 min, until the starting material **6a** could not be detected by TLC) and poured into water (150 mL). The precipitate was collected by vacuum filtration, washed with water, dried, and purified by column separation (silica gel, chloroform). − **First Fraction:** Yield 130 mg (25%) of **13a** as a dark green powder (residues of sulfur were removed as was described for **13b**), m.p. 158−160 °C. − R_f (silica gel, chloroform): 0.72. − IR (KBr): ṽ = 2955cm^{-1} (s), 2926 (s), 2856 (s), 1701 (s), 1699 (s), 1660 (s), 1589 (m), 1467 (w), 1457 (m), 1415 (w), 1401 (m), 1385 (m), 1337 (m), 1303 (m), 1252 (m), 1182 (w), 1115 (w), 923 (w), 850 (m), 810 (m), 747 (w). − ^{1}H NMR ($CDCl_3$): δ = 0.81 (t, *J* = 7.0 Hz, 12 H, C*H*$_3$), 1.21−1.33 (m, 32 H, C*H*$_2$), 1.78−1.85 (m, 4 H, CH−C*H*$_2$), 2.18−2.25 (m, 4 H, CH−C*H*$_2$), 5.14 [tt, $^3J_1$ = 9.4 Hz, $^3J_2$ = 5.6 Hz, 2 H, C*H*−(CH_2)$_2$], 8.49 (br. s, 2 H, perylene), 8.60 (br. s, 4 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 22.6, 26.9, 29.2, 31.8, 32.3, 55.0, 124.1, 126.8, 128.6, 131.6, 132.8, 133.0. − UV/Vis ($CHCl_3$): λ_{max} (ε) = 397 nm (9250), 424 (12580), 450 (18660), 478 (29550), 611 (13540). − MS (70 eV): *m/z* (%): 819 (8), 818 (24), 817 (56), 816 (100) [M^+], 799 (6), 637 (5), 636 (14), 635 (28), 634 (27) [$M^+ - C_{13}H_{26}$], 455 (9), 454 (24), 453 (47), 452 (64) [$M^+ - 2\times C_{13}H_{26}$], 422 (7), 421 (20), 420 (21) [$M^+ - 2\times\cdot C_{13}H_{26} - S$], 409 (6), 407 (7), 403 (8). − $C_{50}H_{60}N_2O_4S_2$ (817.2): calcd. C 73.49, H 7.40, N 3.43, S 7.85; found C 73.38, H 7.26, N 3.36, S 7.91. − **Second Fraction:** Yield 295 mg (60%) of **11a** as a bright orange powder, m.p. 263−265°C. − R_f (silica gel, chloroform): 0.67. − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1} (s), 2927 (s), 2857 (s), 1701 (s), 1662 (s), 1625 (w), 1560 (m), 1467 (w), 1456 (w), 1428 (m), 1402 (w), 1363 (m), 1347 (m), 1306 (s), 1246 (m), 1199 (w), 1167 (w), 1110 (w), 911 (w), 846 (w), 807 (s), 741 (m), 629 (w), 597 (w), 582 (w), 535 (w), 512 (w). − ^{1}H NMR ($CDCl_3$): δ = 0.81 (t, *J* = 7.0 Hz, 12 H, CH_3), 1.23−1.36 (m, 32 H, CH_2), 1.95 (m_C, 4 H, $CH{-}CH_2$), 2.30 (m_C, 4 H, $CH{-}CH_2$), 5.28 [m_C, 2 H, $CH{-}(CH_2)_2$], 8.62 (d, *J* = 8.1 Hz, 2 H, perylene), 8.71 (br. d, 2 H, perylene), 9.09 (br. s, 2 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 13.8, 22.74, 26.9, 29.1, 31.6, 32.4, 54.9, 122.5, 122.9, 125.7, 126.7, 127.3, 128.9, 129.6, 130.7, 132.5, 137.7 ($C{-}S{-}C$), 163.3, 163.6, 164.4, 164.8. − UV/Vis ($CHCl_3$): λ_{max} (ε) = 284 nm (14620), 316 (4750), 392 (2800, sh.), 415 (9850), 439 (26980), 468 (49580), 501 (84720). − Fluorescence (chloroform): λ_{max} ($I_{rel.}$) = 511 nm (1.0), 548 (0.36), 590 (0.10). − Solid-state fluorescence: λ_{max} = 650 nm. − MS (70 eV): *m/z* (%): 786 (5), 785 (13), 784 (24) [M^+], 767 (5) [$M^+ - OH$], 604 (11), 603 (29), 602 (29) [$M^+ - C_{13}H_{26}$], 433 (6), 423 (5), 422 (19), 421 (57), 420 (100) [$M^+ - 2\times C_{13}H_{26}$], 403 (12), 375 (6). − $C_{50}H_{60}N_2O_4S$ (785.1): calcd. C 76.49, H 7.70, N 3.57, S 4.08; found C 76.21, H 7.56, N 3.56, S 4.08.

Reaction of *N,N′*-Bis(2,5-di-*tert*-butylphenyl)-1-nitroperylene-3,4:9,10-bis(dicarboximide) (6c) with Sulfur: Sulfur (24.0 mg, 0.750 mmol) was dissolved in DMF (10 mL, 90°C). Compound **6c** (100 mg, 0.123 mmol) was added under argon. The mixture was heated at 120°C (17 h, until the starting material, **6c,** could not be detected by TLC), cooled down to below 100°C and poured, while still warm, into a mixture of water and 2 N HCl (100 mL, 2:1). The precipitate was collected by vacuum filtration, dried, and purified by column separation (silica gel, dichloromethane). − **First Fraction:** 56.0 mg (55%) of **13c**. If the reaction temperature was 153°C, the yield of **13c** dropped to 0%. M.p. > 300°C. − R_f (silica gel, chloroform): 0.36. − R_f (silica gel, dichloromethane): 0.47. − IR (KBr): $\tilde{\nu}$ = 2962 cm^{-1} (m), 2869 (w), 1710 (s), 1673 (s), 1589 (s), 1500 (w), 1464 (w), 1394 (s), 1363 (w), 1340 (m), 1314 (m), 1296 (w), 1252 (s), 1201 (m), 1169 (w), 1134 (w), 983 (w). 821 (w), 810 (m), 755 (w), 740 (w), 629 (w). − ^{1}H NMR ($CDCl_3$): δ = 1.31 (s, 18 H, CH_3), 1.33 (s, 9 H, CH_3), 1.34 (s, 9 H, CH_3), 7.01 and 7.03 (each d, $^4J_{CH}$ = 2.0 Hz, 2 H, phenyl), 7.485 and 7.488 (each dd, $^3J_{CH}$ = 8.5 Hz, $^4J_{CH}$ = 2.0 and 2.3 Hz, 2 H, phenyl), 7.61 and 7.62 (each d, $^3J_{CH}$ = 8.5, 2 H, phenyl), 8.61 and 8.62 (each s, 2 H), 8.71−8.76 (m, 4 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 31.62, 32.18, 34.69, 35.97, 123.71, 124.29, 124.39, 126.51, 127.04, 127.10, 127.59, 127.63, 128.75, 128.86, 131.42, 131.93, 131.96, 132.23, 133.26, 133.32, 133.4, 133.46, 143.74, 150.28, 163.56, 164.04. − UV/Vis ($CHCl_3$): λ_{max} (ε) = 271 nm (17510), 400 (5730), 426 (8480), 451 (13730), 480 (22740), 612 (9490). − MS (70 eV): *m/z* (%): 830 (7), 829 (17), 828 (28) [M^+], 774 (7), 773 (23), 772 (53), 771 (100) [$M^+ - C_4H_9$], 739 (7) [$M^+ - S$]. − $C_{52}H_{48}N_2O_4S_2$: calcd. 828.3055; found 828.3097 (MS). − $C_{52}H_{48}N_2O_4S_2$ (829.1): calcd. C 75.33, H 5.84, N 3.38, S 7.74; found C 74.59, H 5.69, N 3.30, S 7.09. − **Second Fraction:** Yield 29.0 mg (30%; at a reaction temperature of 153°C: 139 mg, 71%) of **10c** as a bright orange powder, m.p. > 300°C. − R_f (silica gel, chloroform): 0.32. − R_f (silica gel, dichloromethane): 0.43. − IR (KBr): $\tilde{\nu}$ = 2962 cm^{-1} (m), 2869 (w), 1708 (s), 1673 (s), 1597 (m), 1562 (w), 1501 (w), 1429 (m), 1399 (w), 1365 (m), 1351 (w), 1316 (m), 1242 (m, br.), 1184 (w), 1168 (w), 1130 (w), 820 (w), 810 (w), 746 (w), 732 (w), 606 (w). − ^{1}H NMR ($CDCl_3$): δ = 1.32, 1.33, 1.34, and 1.35 (each s, 36 H, CH_3), 7.12 and 7.17 (each d, $^4J_{CH}$ = 2.1 and 2.2 Hz, 2 H, phenyl), 7.48 and 7.50 (each dd, $^3J_{CH}$ = 8.5 Hz, $^4J_{CH}$ = 2.3 and 2.5 Hz, 2 H, phenyl), 7.62 and 7.63 (each d, $^3J_{CH}$ = 8.5 and 8.8 Hz, 2 H, phenyl), 8.96−9.06 (m, 4 H, perylene), 9.41 and 9.44 (each s, 2 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 31.21, 31.79, 34.28, 35.58, 35.61, 122.83, 122.86, 123.19, 123.25, 123.50, 123.64, 123.78, 123.83, 126.33, 126.39, 126.47, 126.61, 127.80, 127.99, 128.12, 128.79, 128.89, 130.06, 130.13, 131.82, 131.96, 132.90, 133.62, 133.77, 138.41 ($C{-}S{-}C$), 138.44 ($C{-}S{-}C$), 143.68, 143.76, 150.18, 150.24, 164.42, 164.50, 164.89, 164.98. − UV/Vis ($CHCl_3$): λ_{max} (ε) = 283 nm (16070), 416 (11440), 441 (29980), 469 (54950), 503 (93610). − Fluorescence (chloroform): λ_{max} ($I_{rel.}$) = 514 nm (1.0), 545 (0.50), 587 (0.11). − MS (70 eV): *m/z* (%): 796 (3) [M^+], 742 (5), 741 (18), 740 (53), 739 (100) [$M^+ - C_4H_9$], 682 (3) [$M^+ - 2\times C_4H_9$]. − $C_{52}H_{48}N_2O_4S$: calcd. 796.3335, found 796.3328 (MS). − $C_{52}H_{48}N_2O_4S$ (797.0): calcd. C 78.36, H 6.07, N 3.51, S 4.02; found C 77.60, H 6.17, N 3.43, S 3.84.

***N,N′*-Bis(1-hexylheptyl)benzoperylene-1′,2′:3,4:9,10-hexacarboxylic 1′,2′-Anhydride 3,4:9,10-Bis(imide) (2a):** Compound **1a** (1.50 g, 1.99 mmol) was dissolved in molten maleic anhydride (95°C) with the addition of a few ml of acetone (or chloroform; for removing crystals of maleic anhydride from the reflux condenser). Chloranil (970 mg, 3.98 mmol) was added. The mixture was heated (bath 140°C) in an open reaction vessel until the reaction temperature reached 125°C and heated for 4 d in a flask fitted with a reflux condenser (the solvent removed any crystals of maleic anhydride from the condenser while refluxing). The reaction was cooled, dispersed in acetone while still warm, poured into 2 N HCl (250 mL) and stirred at room temperature for 16 h (ageing of the precipitate). The precipitate was collected by vacuum filtration, repeatedly washed with water, dried, dissolved in chloroform and purified by column separation (silica gel). The excess of chloranil and **1a** were completely eluted with chloroform, while the main fraction was eluted with a mixture of chloroform and 1−5% acetic acid. Yield 1.20 g (71%) of **2a** as a dark yellow powder, m.p. > 200°C (dec.). − R_f (silica gel, chloroform/acetic acid, 10:1): 0.81. − R_f (silica gel, chloroform): 0.00−0.70. − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1} (m), 2927 (s), 2857 (m), 1847 (w), 1776 (w), 1703 (s), 1661 (s), 1625 (w), 1597 (m), 1487 (w), 1419 (m), 1396 (w), 1366 (w), 1320 (s), 1268 (m), 1171 (m), 1016 (w), 954 (w), 912 (w), 847 (w), 812 (m), 763 (w), 749 (w), 718 (w). − ^{1}H NMR ($CDCl_3$): δ = 0.80 (t, *J* = 6.8 Hz, 12 H, CH_3), 1.10−1.42 (m, 32 H, CH_2), 1.88−2.00 (m, 4 H, $CH{-}CH_2$), 2.23−2.41 (m, 4 H, $CH{-}CH_2$), 5.28 (m_C, 2 H, $N{-}CH$), 9.22 (br. s, 2 H, perylene), 9.45 (d, *J* = 8.4 Hz, 2 H, perylene), 10.25 (s, 2 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.0, 22.6, 27.0, 29.2, 31.7, 32.4, 55.5, 123.3, 124.6, 124.9, 127.3, 127.9, 128.7, 129.0, 129.5, 130.9, 131.6, 133.5, 162.2. − UV/Vis ($CHCl_3$): λ_{max} (ε) = 332 nm (18060), 370 (8380), 413 (10970), 438 (30610), 468 (44930). − Fluorescence (chloroform): λ_{max} ($I_{rel.}$) = 481 nm (0.99), 508 (1.0), 550 (0.56). − Fluorescence quantum yield ($1.13\cdot 10^{-6}$ mol/L in $CHCl_3$, reference tetramethyl perylene-3,4,9,10-tetracarboxylate with Φ = 100%, $\lambda_{excit.}$ = 440 nm) = 74%. − MS (70 eV): *m/z* (%): 850 (7), 849 (21), 848 (36) [M^+], 669 (20), 668 (64), 667 (100), 666 (25) [$M^+ - C_{13}H_{26}$], 497 (7), 488 (5), 487 (24), 486 (87), 485 (91), 484 (27) [$M^+ - 2\times C_{13}H_{26}$], 468 (5), 467 (16), 415 (5), 414 (14), 413 (24), 412 (10), [$M^+ - 2\times C_{13}H_{26} - C_2O_3$], 395 (12).

***N,N*′-Bis(1-butylpentyl)benzoperylene-1′,2′:3,4:9,10-hexacarboxylic 1′,2′-Anhydride 3,4:9,10-Bis(imide) (2b):** Compound **1b** (500 mg, 0.779 mmol), dissolved in molten maleic anhydride (95°C), a few ml of acetone (or chloroform) and chloranil (380 mg, 1.56 mmol) were allowed to react, and purified as was described for **2a**. Yield 450 mg (77%) of **2b** as a bright orange powder, m.p. > 300°C. − R_f (silica gel, chloroform): 0.00−0.12. − R_f (silica gel, chloroform/acetic acid 10:1): 0.83. − IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1} (m), 2930 (m), 2870 (m), 1848 (w), 1777 (w), 1732 (m), 1705 (s), 1664 (s), 1626 (w), 1597 (m), 1488 (w), 1466 (w), 1417 (m), 1372 (m, sh), 1320 (s), 1297 (w), 1267 (m), 1217 (m, sh), 1172 (m), 1123 (w), 1017 (w), 847 (w), 812 (m), 761 (w), 748 (w). − ^{1}H NMR (CDCl$_3$): δ = 0.86 (t, J = 7.0 Hz, 12 H, C*H*$_3$), 1.27−1.42 (m, 16 H, C*H*$_2$), 1.90−2.02 (m, 4 H, CH−C*H*$_2$), 2.28−2.38 (m, 4 H, CH−C*H*$_2$), 5.29 (m$_C$, 2 H, N−C*H*), 9.22 (d, J = 8,1 Hz, 2 H, perylene), 9.43 (d, J = 8.5 Hz, 2 H, perylene), 10.24 (s, 2 H, perylene). − ^{13}C NMR (CDCl$_3$): δ = 14.0, 22.6, 29.2, 32.1, 55.4, 123.3, 124.6, 124.9, 127.3, 127.9, 129.0, 133.5, 162.2. − UV/Vis (CHCl$_3$): λ_{max} (ε) = 304 nm (21010), 332 (18180), 370 (5350), 412 (11220), 437 (33900), 467 (54190). − Fluorescence (chloroform): λ_{max} ($I_{rel.}$) = 477 nm (1.0), 504 (0.81), 548 sh (0.23). − Fluorescence quantum yield (1.13·10^{-6} mol/L in CHCl$_3$, reference tetramethyl perylene-3,4,9,10-tetracarboxylate with Φ = 100%, $\lambda_{excit.}$ = 440 nm) = 73%. − MS (70 eV): *m*/*z* (%): 738 (5), 737 (19), 736 (38) [M$^+$], 679 (6) [M$^+$ − C$_4$H$_9$], 613 (12), 612 (49), 611 (100), 610 (28) [M$^+$ − C$_9$H$_{18}$], 497 (9), 487 (16), 486 (60), 485 (96), 484 (42) [M$^+$ − 2 × C$_9$H$_{18}$], 467 (10) [M$^+$ − 2 × C$_9$H$_{18}$ − OH], 414(9), 413 (21), 412 (10) [M$^+$ − 2 × C$_9$H$_{18}$ − C$_2$O$_3$], 395 (8).

***N,N*′-Bis(2,5-di-*tert*-butylphenyl)benzoperylene-1′,2′:3,4:9,10-hexacarboxylic 1′,2′-Anhydride 3,4:9,10-Bis(imide) (2c):** Compound **1c** (300 mg, 0.392 mmol), dissolved in molten maleic anhydride (95°C), a few ml of acetone (or chloroform) and chloranil (240 mg, 0.984 mmol) were allowed to react as was described for **2a,** and purified by column separation (silica gel). The forerun was eluted with chloroform/10% ethanol and the main fraction with chloroform/10% acetic acid. Yield 230 mg (67%) of **2c** as a dark yellow powder, m.p. > 300°C. − R_f (silica gel, chloroform/10% ethanol): 0.00−0.16. − R_f (silica gel, chloroform/10% acetic acid): 0.55. − IR (KBr): $\tilde{\nu}$ = 3437 cm^{-1} (s), 2964 (m), 2871 (w), 1847 (w), 1778 (w), 1714 (s), 1674 (s), 1627 (w), 1598 (m), 1486 (w), 1413 (m), 1365 (m), 1330 (m), 1297 (w), 1264 (m), 1216 (m), 812 (m), 764 (w), 746 (w). − ^{1}H NMR (CDCl$_3$): δ = 1.35−1.36 (m, 36 H, C*H*$_3$), 7.13 and 7.18 (each s, 2 H, phenyl), 7.54 (d, $^3J_{CH}$ = 8.1 Hz, 2 H, phenyl), 7.67 (d, $^3J_{CH}$ = 8.5 Hz, 2 H, phenyl), 9.35 and 9.38 (each d, J = 7.7 and 7.4 Hz, 2 H, perylene), 9.57 and 9.62 (each d, J = 8.4 Hz, 2 H, perylene), 10.40 and 10.45 (each s, 2 H, perylene). − ^{13}C NMR (CDCl$_3$): δ = 31.23, 31.84, 34.35, 35.66, 123.71, 123.80, 124.98, 125.04, 125.19, 126.21, 126.27, 126.73, 127.58, 127.67, 128.21, 128.35, 128.85, 129.02, 129.07, 129.42, 129.67, 129.74, 131.61, 131.66, 132.17, 132.59, 134.01, 134.18, 143.77, 143.81, 150.43, 150.48, 162.18, 162.25, 163.81 163.86, 164.28, 164.34. − UV/Vis (CHCl$_3$): λ_{max} (ε) = 288 nm (17560), 333 (16460), 367 (5460), 413 (11020), 438 (31590), 468 (47990). − Fluorescence (chloroform): λ_{max} ($I_{rel.}$) = 479 nm (1.0), 508 (0.87), 547 (0.39). − MS (70 eV): *m*/*z* (%): 806 (6), 805 (27), 804 (58), 803 (100) [M$^+$ − C$_4$H$_9$].

***N,N*′-Bis(1-hexylheptyl)benzoperylene-1′,2′:3,4:9,10-hexacarboxylic 1′,2′-Bis(ethyl ester) 3,4:9,10-Bis(imide) (4a). − Preparation from the Free Acid:** *N,N*′-Bis(1-hexylheptyl)benzoperylene-1′,2′:3,4:9,10-hexacarboxylic acid 3,4:9,10-bis(imide) (110 mg, 0.127 mmol, by hydrolysis of **2a**) was dissolved in THF and deprotonated with DBU (60.0 mg, 0.395 mmol). Ethyl iodide (100 mg, 0.641 mmol) was added. The mixture was stirred at room temperature for 16 h, poured into water (150 mL), weakly acidified with 2 N HCl, and stirred at room temperature for 16 h (for the ageing of the precipitate). The precipitate was collected by vacuum filtration, dried, and purified by column separation (silica gel, chloroform). Yield 100 mg (85%) of **4a** as a bright orange powder. Physical data see below.

***N,N*′-Bis(1-hexylheptyl)benzoperylene-1′,2′:3,4:9,10-hexacarboxylic 1′,2′-Bis(ethyl ester) 3,4:9,10-Bis(imide) (4a) from 2a:** Compound **2a** (108 mg, 0.127 mmol) was dissolved in chloroform. Ethanol (ca. 2 mL) was added. The mixture was concentrated and allowed to react with DBU and ethyl iodide as was described above. Yield 100 mg (85%) of **4a** as a bright orange powder, m.p. 273−275°C. − R_f (silica gel, chloroform): 0.65. − IR (KBr): $\tilde{\nu}$ = 2956 cm^{-1} (m), 2927 (s), 2857 (m), 1727 (m, ester C=O), 1705 (s), 1662 (s), 1626 (w), 1597 (m), 1466 (w), 1415 (m), 1372 (m), 1345 (w), 1320 (s), 1297 (w), 1273 (m), 1216 (m), 1168 (m), 1129 (w), 1074 (w), 1019 (w), 846 (w), 810 (m), 759 (w), 747 (w). − ^{1}H NMR (CDCl$_3$): δ = 0.81 (t, J = 6.8 Hz, 12 H, C*H*$_3$), 1.20−1.36 (m, 32 H, C*H*$_2$), 1.59 (t, J = 7.1 Hz, 6 H, O−CH$_2$−C*H*$_3$), 1.95−1.99 (m, 4 H, CH−C*H*$_2$), 2.29−2.36 (m, 4 H, CH−C*H*$_2$), 4.73 (q, J = 7.2 Hz, 4 H, O−C*H*$_2$−CH$_3$), 5.26 (tt, $^3J_1$ = 6.0 Hz, $^3J_2$ = 8.8 Hz, 2 H, N−C*H*), 9.01 (br. d, 2 H, perylene), 9.12 (d, J = 8.4 Hz, 2 H, perylene), 9.44 (s, 2 H, perylene). − ^{13}C NMR (CDCl$_3$): δ = 14.0, 14.3 (O−CH$_2$−C*H*$_3$), 22.6, 27.1, 29.3, 31.8, 32.5, 55.2, 63.1 (O−C*H*$_2$−CH$_3$), 122.8, 123.3, 125.2, 126.3, 131.5, 132.8, 166.6 (*C*OOEt). − UV/Vis (CHCl$_3$): λ_{max} (ε) = 388 nm (5360), 411 (16700), 436 (43460), 466 (69070). − Fluorescence (chloroform): λ_{max} ($I_{rel.}$) = 476 nm (1.0), 506 (0.57), 547 (0.08). − Fluorescence quantum yield (1.18 × 10^{-6} mol/L in CHCl$_3$, reference tetramethyl perylene-3,4,9,10-tetracarboxylate with Φ = 100%, $\lambda_{excit.}$ = 440 nm) = 85%. − MS (70 eV): *m*/*z* (%): 924 (13), 923 (39), 922 (66) [M$^+$], 905 (7) [M$^+$ − OH], 743 (6), 742 (26), 741 (63), 740 (56) [M$^+$ − C$_{13}$H$_{26}$], 667 (9) [M$^+$ − C$_{13}$H$_{26}$ − C$_3$H$_5$O$_2$], 577 (6), 560 (21), 559 (55), 558 (100) [M$^+$ − 2 × C$_{13}$H$_{26}$], 486 (18), 485 (50) [M$^+$ − 2 × C$_{13}$H$_{26}$ − C$_3$H$_5$O$_2$], 467 (8), 466 (8), 414 (6), 413 (7), 397 (8), 396 (14), 368 (6), 339 (7), 322 (10), 313 (7). − $C_{58}H_{70}N_2O_8$ (923.2): calcd. C 75.46, H 7.64, N 3.03; found C 75.34, H 7.52, N 3.04.

***N,N*′-Bis(1-butylpentyl)benzoperylene-1′:2′,3:4,9:10-hexacarboxylic 1′,2′-Bis(ethyl ester) 3,4:9,10-Bis(imide) (4b). − Preparation from the Free Acid:** *N,N*′-Bis(1-butylpentyl)benzoperylene-1′,2′:3,4:9,10-hexacarboxylic acid 3,4:9,10-bis(imide) (30 mg, 0.04 mmol, by hydrolysis of **2b**) was dissolved in THF and allowed to react with DBU (65 mg, 0.42 mmol) and ethyl iodide (65 mg, 0.42 mmol) as was described for **4a** and purified by column separation (silica gel activity III .. IV, chloroform). Yield 27 mg (84%) of **4b** as a high orange powder, m.p. > 300°C. − R_f (silica gel, chloroform): 0.41. − IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1} (m), 2930 (m), 2871 (m), 1732 (m, ester C=O), 1705 (s), 1663 (s), 1626 (w), 1597 (m), 1466 (w), 1415 (m), 1372 (m), 1362 (w), 1320 (s), 1296 (w), 1270 (m), 1214 (m), 1173 (w), 1131 (w), 1020 (w), 811 (m), 760 (w), 748 (w). − ^{1}H NMR (CDCl$_3$): δ = 0.88 (t, J = 6.7 Hz, 12 H, C*H*$_3$), 1.36−1.40 (m, 16 H, C*H*$_2$), 1.59 (t, J = 7.2 Hz, 6 H, O−CH$_2$−C*H*$_3$), 1.94−2.03 (m, 4 H, CH−C*H*$_2$), 2.30−2.39 (m, 4 H, CH−C*H*$_2$), 4.69 (q, J = 7.2 Hz, 4 H, O−C*H*$_2$−CH$_3$), 5.27 (m$_C$, 2 H, N−C*H*), 9.00 (br. d, J = 7.4 Hz, 2 H, perylene), 9.10 (d, J = 8.5 Hz, 2 H, perylene), 9.43 (s, 2 H, perylene). − ^{13}C NMR (CDCl$_3$): δ = 14.1, 14.3 (O−CH$_2$−C*H*$_3$), 22.7, 29.3, 32.2, 55.1, 63.1 (O−C*H*$_2$−CH$_3$), 122.8, 123.3, 125.1, 126.3, 127.1, 131.5, 132.8, 163.3, 163.6, 164.5, 166.6 (*C*OOEt). − UV/Vis (CHCl$_3$): λ_{max} (ε) = 302 nm (30880), 334 (20880), 388 (2620), 411 (13980), 437 (40500), 466 (65340). − Fluorescence (chloroform): λ_{max} (I$_{rel.}$) = 478 nm (1.0), 508 (0.60), 548 (0.09). − MS (70 eV): *m*/*z* (%): 812 (8), 811 (28), 810 (51) [M$^+$], 793 (8) [M$^+$ − OH], 753 (6), 745 (6), 686 (19), 685 (49), 684 (46)

$[M^+ - C_9H_{18}]$, 667 (5), 612 (7), 611 (15) $[M^+ - C_9H_{18} - C_3H_5O_2]$, 560 (18), 559 (59), 558 (100) $[M^+ - 2 \times C_9H_{18}]$, 487 (5), 486 (22), 485 (57) $[M^+ - 2 \times C_9H_{18} - C_3H_5O_2]$, 484 (5), 467 (7), 442 (5), 414 (8), 413 (13). − $C_{50}H_{54}N_2O_4$ (811.0): calcd. C 74.05, H 6.71, N 3.45; found C 74.09, H 6.77, N 3.38.

***N,N′*-Bis(2,5-di-*tert*-butylphenyl)benzoperylene-1′:2′,3:4,9:10-hexacarboxylic 1′,2′-Bis(ethyl ester) 3,4:9,10-Bis(imide) (4c). − Preparation from the Free Acid:** *N,N′*-Bis(2,5-di-*tert*-butylphenyl)benzoperylene-1′,2′:3,4:9,10-hexacarboxylic acid 3,4:9,10-bis(imide) (50 mg, 0.060 mmol, by hydrolysis of **2c**) was dissolved in THF and allowed to react with DBU (35 mg, 0.23 mmol) and ethyl iodide (45 mg, 0.29 mmol) as was described for **6a**, and purified by column separation (silica gel, chloroform/3% ethanol). Yield 41 mg (78%) of **4c** as a yolk-yellow powder, m.p. > 300 °C. − R_f (silica gel, chloroform): 0.24. − R_f (Al_2O_3/chloroform): 0.88. − R_f (silica gel, chloroform/3% ethanol): 0.67. − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1} (w), 2963 (m), 2907 (w), 2870 (w), 1732 (m, Ester-C=O), 1715 (s), 1675 (s), 1628 (w), 1598 (m), 1486 (w), 1466 (w), 1411 (s), 1372 (s), 1363 (m), 1330 (s), 1296 (w), 1270 (m), 1255 (m), 1212 (s), 1182 (w), 1164 (w), 1142 (w), 1131 (w), 1094 (w), 1075 (w), 1019 (w), 820 (w), 812 (m), 761 (w), 746 (w). − ^{1}H NMR ($CDCl_3$): δ = 1.27 (s, 12 H, CH_3), 1.32−1.35 (m, 24 H, CH_3), 1.57 and 1.61 (each t, J = 7.1 Hz, 6 H, O−CH_2−CH_3), 4.66−4.78 (m, 4 H, O−CH_2−CH_3), 7.12 (d, $^4J_{CH}$ = 2.3 Hz, 0.8 H, phenyl), 7.35 (br. d, 1.2 H, phenyl), 7.47 and 7.50 (each dd, $^3J_{CH}$ = 8.5 Hz, $^4J_{CH}$ = 2.2 Hz, 2 H, phenyl), 7.60 (d, $^3J_{CH}$ = 8.5 Hz, 1.2 H, phenyl), 7.64 (d, $^3J_{CH}$ = 8.5 Hz, 0.8 H, phenyl), 9.07−9.15 (m, 2.8 H, perylene), 9.22 (d, J = 8.2 Hz, 0.8 H, perylene), 9.45 (d, J = 8.3 Hz, 0.8 H, perylene), 9.58 (s, 1.0 H, perylene), 9.723 (s, 0.6 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.53 (O−CH_2−$\mathit{C}H_3$), 14.62 (O−CH_2−$\mathit{C}H_3$), 31.42, 31.48, 32.01, 34.54, 34.60, 35.78, 35.87, 63.49 (O−$\mathit{C}H_2$−CH_3), 63.62 (O−$\mathit{C}H_2$−CH_3), 123.02, 123.19, 123.27, 123.88, 123.99, 124.18, 124.44, 124.58, 125.65, 126.29, 126.57, 126.77, 126.99, 127.23, 127.85, 127.94, 128.47, 128.90, 129.17, 130.29, 130.58, 131.69, 132.20, 132.27, 132.40, 132.64, 132.74, 133.26, 134.09, 143.79, 144.06, 150.52, 150.60, 164.36, 164.49, 164.67, 164.88, 166.90 (*C*OOEt), 167.02 (*C*OOEt). − UV/Vis ($CHCl_3$): λ_{max} (ε) = 289 nm (30820), 300 (31060), 334 (27410), 386 (4860), 411 (17630), 437 (47320), 467 (76150). − Fluorescence (chloroform): λ_{max} ($I_{rel.}$) = 476 nm (1.0), 509 (0.50), 549 (0.08). − MS (70 eV): *m/z* (%): 887 (5), 879 (20), 878 (60), 877 (100) $[M^+ - C_4H_9]$, 57 (9) $[C_4H_9]$. − $C_{56}H_{49}N_2O_8$ (878.01): calcd. 877.3489; found 877.3428 (MS). − $C_{60}H_{58}N_2O_8$ (935.1): calcd. C 77.07, H 6.25, N 3.00; found C 76.38, H 6.50, N 2.99.

***N,N′′*-Bis(1-hexylheptyl)-N′-cyclohexylbenzoperylene-1′,2′:3,4:9,10-tris(dicarboximide) (3a):** Compound **2a** (100 mg, 0.118 mmol), cyclohexylamine (114 mg, 1.15 mmol) and quinoline (10 mL) were refluxed (6 h, bath 160 °C), cooled, poured into 2 N HCl (100 mL), stirred at room temperature for several h (ageing of the brown precipitate), collected by vacuum filtration, dried, and purified by column separation (silica gel, chloroform). Yield 71 mg (66%) **3a** as an orange yellow powder, m.p. > 300 °C. − R_f (silica gel, chloroform): 0.63. − IR (KBr): $\tilde{\nu}$ = 2954 cm^{-1} (s), 2928 (s), 2857 (s), 1765 (m, C=O of the 5-membered-ring imide), 1709 (s), 1666 (s), 1625 (w), 1596 (m), 1523 (w), 1456 (m), 1414 (m), 1366 (s), 1348 (w), 1318 (s), 1272 (w), 1240 (m), 1203 (w), 1175 (m), 1107 (w), 945 (m), 846 (w), 811 (m), 766 (m), 747 (w), 660 (w), 640 (w), 529 (w), 436 (w). − ^{1}H NMR ($CDCl_3$): δ = 0.83 (t, J = 7.0 Hz, 12 H, CH_3), 1.27−1.43 (m, 37 H, CH_2), 2.04−2.12 (m, 8 H, CH_2), 2.33−2.51 (m, 6 H, CH_2), 4.37 (tt, $^3J_{CH\text{-}AE}$ = 3.5 Hz, $^3J_{CH\text{-}AA}$ = 12.2 Hz, 1 H, N−C$H_{cyclohexyl}$), 5.30 (m_C, 2 H, N−C$H_{tridec.}$), 8.89−8.98 (m, 4 H, perylene), 10.02 (s, 2 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 22.6, 25.4 (cyclohexyl), 26.3 (cyclohexyl), 27.1, 29.3, 30.1 (cyclohexyl), 31.8, 32.5, 51.9 (N−*C*$H_{cyclohexyl}$), 55.3, 122.6, 123.3, 124.0, 126.6, 126.8, 127.2, 132.4, 167.8 (5-ring-*C*=O). − UV/Vis ($CHCl_3$): λ_{max} (ε) = 274 nm (28070), 316 (14660), 332 (16940), 358 (28370), 372 (37350), 410 (15310), 435 (38930), 465 (60230). − Fluorescence (chloroform): λ_{max} ($I_{rel.}$) = 480 nm (1.0), 509 (0.60), 548 (0.11). − Fluorescence quantum yield (7.92×10^{-7} mol/L in $CHCl_3$, reference tetramethyl perylene-3,4,9,10-tetracarboxylate with Φ = 100%, $\lambda_{excit.}$ = 440 nm) = 45%. − MS (70 eV): *m/z* (%): 931 (12), 930 (18), 929 (52) $[M^+]$, 913 (5), 912 (11) $[M^+ - OH]$, 845 (8), 844 (16) $[M^+ - C_6H_{13}]$, 760 (6), 751 (6), 750 (23), 749 (66), 748 (100), 747 (39) $[M^+ - C_{13}H_{26}]$, 730 (8), 664 (5), 663 (7), 662 (5),568 (25), 567 (60), 566 (74), 565 (63) $[M^+ - 2 \times C_{13}H_{26}]$, 522 (7), 486 (5), 485 (25), 484 (59), 483 (32) $[M^+ - 2 \times C_{13}H_{26} - C_6H_{10}]$, 466 (13), 441 (8), 182 (7). − $C_{60}H_{71}N_3O_6$ (930.2): calcd. C 77.47, H 7.69, N 4.52; found C 77.27, H 7.57, N 4.49.

***N,N′′*-Bis(1-hexylheptyl)-N′-2,5-di-*tert*-butylphenylbenzoperylene-1′,2′:3,4:9,10-tris(dicarboximide) (3b):** Compound **2a** (60.0 mg, 0.0710 mmol), 2,5-di-*tert*-butylaniline (100 mg, 0.488 mmol), and DCC (75.0 mg, 0.364 mmol) were dissolved in chloroform. Trifluoroacetic acid (1 drop) was added. The mixture was heated under reflux (24 h), diluted with chloroform, repeatedly washed with water, concentrated, and purified by column separation (silica gel, chloroform followed by neutral alumina, petroleum ether/3% chloroform). Yield 50 mg (70%; Yield 50% after 4 days reaction time, if only DCC or only trifluoroacetic acid were applied) **3b** as a bright yellow solid, m.p. 285−287 °C. − R_f (silica gel, chloroform): 0.66. − IR (KBr): $\tilde{\nu}$ = 2956 cm^{-1} (m), 2927 (m), 2858 (w), 1774 (w, C=O 5-membered-ring-imide), 1720 (s, C=O 5-membered-ring-imide), 1707 (m), 1664 (s), 1627 (w), 1596 (w), 1523 (w), 1505 (w), 1459 (w), 1413 (m), 1366 (m), 1320 (s), 1272 (w), 1241 (w), 1204 (w), 1169 (w), 1112 (w), 972 (w), 946 (w), 848 (w), 813 (w), 767 (w), 749 (w), 725 (w), 662 (w). − ^{1}H NMR ($CDCl_3$): δ = 0.80 (t, J = 6.6 Hz, 12 H, CH_3), 1.20−1.43 (m, 50 H, CH_2 of the alkyl side-chain + CH_3 of the *tert*-butyl groups at 1.34 and 1.40 ppm), 1.92 (m_C, 4 H, CH−CH_2), 2.32 (m_C, 4 H, CH−CH_2), 5.28 (m_C, 2 H, N−C$H_{tridec.}$), 7.19 (d, $^4J_{CH}$ = 1.9 Hz, 1 H, phenyl), 7.53 (dd, $^3J_{CH}$ = 8.6 Hz, ^4J_H = 2.1 Hz, 1 H, phenyl), 7.64 (d, $^3J_{CH}$ = 8.6 Hz, 1 H, phenyl), 9.16 (br. d, 2 H, perylene), 9.40 (d, J = 8.4 Hz, 2 H, perylene), 10.52 (s, 2 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.03, 22.57, 26.99, 29.23, 31.19, 31.76 (*C*Me_3), 31.81 (*C*Me_3), 32.42, 34.33 (CMe_3), 35.32 (CMe_3), 55.27, 123.51, 124.07, 125.19, 127.27, 127.74, 127.95, 128.20, 128.30, 128.54, 128.94, 129.94, 130.70, 133.35, 146.24 ($R_{aromatic}$), 150.45 ($R_{aromatic}$), 163.07, 163.60, 164.31, 164.69, 168.64 (5-ring-*C*=O). − UV/Vis ($CHCl_3$): λ_{max} (ε) = 264 nm (27410), 273 (29750), 376 (40280), 410 (15240), 436 (38980), 466 (60980). − Fluorescence (chloroform): λ_{max} ($I_{rel.}$) = 478 nm (1.0), 510 (0.62), 550 (0.17). − Fluorescence quantum yield (1.13×10^{-6} mol/L in $CHCl_3$, reference tetramethyl perylene-3,4,9,10-tetracarboxylate with Φ = 100%, $\lambda_{excit.}$ = 440 nm) = 45%. − MS (70 eV): *m/z* (%): 1037 (19), 1036 (49), 1035 (67) $[M^+]$, 1020 (6), 1019 (6), 1018 (8) $[M^+ - OH]$, 856 (19), 855 (58), 854 (100), 853 (52) $[M^+ - C_{13}H_{26}]$, 838 (6), 836 (6), 674 (19), 673 (56), 672 (75), 671 (40) $[M^+ - 2 \times C_{13}H_{26}]$, 658 (6), 657 (22), 656 (48) $[M^+ - 2 \times C_{13}H_{26} - OH]$, 638 (8), 617 (8), 616 (15), 615 (6), 614 (11) $[M^+ - 2\ C_{13}H_{26} - C_4H_9]$, 601 (7), 600(14), 583 (8), 582 (19), 561 (14), 560 (34) $[M^+ - 2 \times C_{13}H_{26} - C_4H_9 - C_4H_7]$, 558 (8) $[M^+ - 2 \times C_{13}H_{26} - C_4H_9 - C_4H_9]$, 542 (5), 419 (5). − $C_{68}H_{81}N_3O_6$ (1036.4): calcd. C 78.81, H 7.88, N 4.05; found C 78.63, H 8.12, N 4.04.

Dye 15a: Compound **2a** (100 mg, 0.115 mmol) and 1,8-diaminonaphthalene (180 mg, 1.14 mmol) were dissolved in diethylene glycol monomethyl ether (15 ml; or quinoline), heated under reflux

(5 h, 150°C), poured into water (150 ml; or into 2 N HCl if quinoline is used), stirred at room temperature for 16 h (dark brown precipitate). The precipitate was collected by vacuum filtration, dried, and purified by column separation (silica gel, added to the column with pure chloroform, eluted with 1. chloroform, 2. dichloromethane 3. petroleum ether/chloroform, 4:1). Yield 80 mg (71%) of **15a** as a dark red powder, m.p. > 300°C. − R_f (silica gel, chloroform): 0.60. − R_f (silica gel, dichloromethane): 0.53. − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1} (m), 2926 (s), 2856 (m), 1707 (s), 1661 (s), 1625 (w), 1595 (w), 1524 (w), 1456 (m), 1408 (m), 1367 (m), 1350 (m), 1347 (w), 1322 (s), 1260 (w), 1238 (m), 1170 (w), 827 (m), 812 (m), 770 (m), 759 (w), 748 (w), 664 (w. − ^1H NMR ($CDCl_3$): δ = 0.87 (t, *J* = 6.7 Hz, 12 H, CH_3), 1.34 (m_C, 16 H, CH_2), 1.51 (m_C, 16 H, CH_2), 2.12 (m_C, 4 H, CH−CH_2), 2.47 (m_C, 4 H, CH−CH_2), 5.36 (m_C, 2 H, N−C*H*), 6.84 (br. d, *J* = 28.3 Hz, 1 H, naphthalene), 7.15 (dd, $^3J_1$ = $^3J_2$ = 7.8 Hz, 1 H, naphthalene), 7.26−7.37 (m, 3 H, naphthalene), 7.85 (br. d, 1 H, naphthalene), 8.70 (br. d, *J* = 8.5 Hz, 2 H, perylene), 8.78 (d, *J* = 8.3 Hz, 1 H, perylene), 8.82 (d, *J* = 8.3 Hz, 1 H, perylene), 10.02 (br. s, 1 H, perylene), 10.24 (br. s, 1 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.2, 22.8, 27.3, 29.5, 32.0, 32.6, 55.2 (only the signals of the alkyl side-chain even after 4096 scans at 75.47 MHz because of the low solubility of the amine). − UV/Vis ($CHCl_3$): λ_{max} (ε) = 277 nm (22410), 296 (22950), 322 (19280), 367 (32150), 379 (sh., 32150), 386 (44420), 410 (14230), 436 (31720), 464 (47670), 518 (br., 13240), 587 (sh., 6440). − MS (70 eV): *m/z* (%): 973 (8), 972 (29), 971 (76), 970 (100) [M^+], 790 (11), 789 (26), 788 (23) [$M^+ - C_{13}H_{26}$], 704 (6), 608 (20), 607 (71), 606 (60), [$M^+ - 2 \times C_{13}H_{26}$]. − $C_{64}H_{66}N_4O_5$ (971.3): calcd. C 79.15, H 6.85, N 5.77; found C 78.87, H 6.68, N 5.68.

***N,N'*-Bis(1-hexylheptyl)benzoperylene-3,4:9,10-bis(dicarboximide) (5a). − Decarboxylation of 2a with Copper Powder:** Compound **2a** (50 mg, 0.060 mmol) and copper powder (40 mg, 0.64 mmol) were heated in quinoline under argon (4 h, 180°C), cooled, poured into 2 N HCl, and stirred at room temperature for 16 h (dark brown precipitate). The precipitate was collected by vacuum filtration, dried and purified by column separation (silica gel, chloroform). Yield 17 mg (38%) of **5a** as a yellow to orange powder. Physical data see below.

***N,N'*-Bis(1-hexylheptyl)benzoperylene-3,4:9,10-bis(dicarboximide) (5a). − Decarboxylation of 2a with Copper(I) Oxide:** Compound **2a** (50 mg, 0.060 mmol) and copper(I) oxide (Cu_2O, 40 mg, 0.28 mmol) were heated in quinoline under argon at 180°C for 4 h, cooled, poured into 2 N HCl, and stirred at room temperature for 16 h (dark brown precipitate). The precipitate was collected by vacuum filtration, dried, and purified by column separation (silica gel, chloroform; the yields were very variable). Yield 16 mg (36%) of **5a** as a yellow to orange powder, m.p. 289−291°C. − R_f (silica gel, chloroform): 0.82. − IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1} (m), 2927 (s), 2857 (m), 1703 (s), 1662 (s), 1627 (w), 1597 (m), 1498 (w), 1460 (w), 1411 (w−m), 1362 (m), 1317 (s), 1258 (w−m), 1234 (w), 1179 (w), 1163 (w), 1119 (w), 930 (w), 844 (w), 809 (m), 790 (w), 747 (w−m), 724 (w), 642 (w), 590 (w), 456 (w). − ^1H NMR ($CDCl_3$): δ = 0.83 (t, *J* = 6.6 Hz, 12 H, CH_3), 1.25−1.38 (m, 32 H, CH_2), 1.93−2.02 (m, 4 H, CH−CH_2), 2.31−2.41 (m, 4 H, CH−CH_2), 5.32 [m, 2 H, C*H*(CH_2)$_2$], 8.61 (s, 2 H, perylene), 9.01 (br. d, 2 H, perylene), 9.16 (d, *J* = 8.6 Hz, 2 H, perylene), 9.29 (br. s, 2 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.0, 22.6, 27.0, 29.3, 31.8, 32.5, 55.0, 122.9, 123.5, 124.4, 127.1, 129.1, 130.0, 132.9. − UV/Vis ($CHCl_3$): λ_{max} (ε) = 279 nm (30160), 287 (33410), 300 (28250), 388 (4740), 413 (17100), 439 (46000), 468 (75910). − Fluorescence (chloroform): λ_{max} ($I_{rel.}$) = 477 nm (1.0), 510 (0.58), 549 (0.13). − Fluorescence quantum yield ($CHCl_3$, 5.34×10^{-7} mol/l in $CHCl_3$, reference tetramethyl perylene-3,4,9,10-tetracarboxylate with Φ = 100%, $\lambda_{excit.}$ = 440 nm) = 77%. − MS (70 eV): *m/z* (%): 780 (8), 779 (28), 778 (52) [M^+], 761 (6) [$M^+ - OH$], 598 (17), 597 (48), 596 (45) [$M^+ - C_{13}H_{26}$], 427 (6), 416 (20), 415 (70), 414 (100) [$M^+ - 2 \times C_{13}H_{26}$], 397 (11). − $C_{52}H_{62}N_2O_4$ (779.08): calcd. C 80.17, H 8.02, N 3.60; found C 80.08, H 8.11, N 3.59.

***N,N'*-Bis(1-butylpentyl)-1,3-dioxo-2-phenylbenzo[4,10]anthra[1,9,8-*cdef*][1,2,4]triazolo[1,2-*a*]cinnoline-5,6:11,12-bis(dicarboximide) (14b):** *N,N'*-Bis(1-butylpentyl)perylene-3,4:9,10-bis(dicarboximide) (**1b**, 100 mg, 0.156 mmol), 4-phenyl-1,2,4-triazoline-3,5-dione (273 mg, 1.56 mmol) and chloranil (38.0 mg, 0.156 mmol) in dried toluene were refluxed for 24 h, concentrated, and purified by column separation (silica gel, chloroform for removing **1b** and dichloromethane for the elution of **14b**; **14b** has a higher R_f value in chloroform than **1b**; the chromatography can be accelerated by the addition of 1% ethanol or acetone). Yield 32 mg (25%; the yield without the addition of chloranil is 6 mg, 5%) of **14b** as a green solid, m.p. > 300°C. − R_f (silica gel, chloroform): 0.18. − R_f (silica gel, dichloromethane): 0.39. − IR (KBr): $\tilde{\nu}$ = 3109 cm^{-1} (w, C−$H_{arom.}$), 2956 (m), 2929 (m), 2861 (w), 1773 (m, C=O triazole ring), 1726 (s, C=O triazole ring), 1702 (s), 1661 (s), 1600 (m), 1577 (m), 1502 (m), 1458 (w), 1421 (m), 1394 (s), 1378 (m), 1339 (m), 1301 (m), 1282 (w), 1241 (w), 1184 (w), 985 (w), 927 (w), 850 (w), 810 (m), 744 (m), 731 (w), 688 (w), 645 (w), 537 (w), 503 (w). − ^1H NMR ($CDCl_3$): δ = 0.84 (t, *J* = 7.0 Hz, 12 H, CH_3), 1.15−1.40 (m, 16 H, CH_2), 1.84 (m_C, 4 H, CH−CH_2), 2.15 (m_C, 4 H, CH−CH_2), 5.07 [tt, $^3J_1$ = 6.0 Hz, $^3J_2$ = 9.0 Hz, 2 H, C*H* (CH_2)$_2$], 7.48 (t, *J* = 7.2 Hz, 1 H, phenyl), 7.57 (t, *J* = 7.2 Hz, 2 H, phenyl), 7.70 (d, *J* = 7.2 Hz, 2 H, phenyl), 8.12 (d, *J* = 8.1 Hz, 2 H, perylene), 8.33 (br. d, *J* = 7.9 Hz, 2 H, perylene), 9.23 (s, 2 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.0, 22.6, 29.1, 31.9, 55.0, 116.9, 123.5, 125.0, 126.1, 126.4, 129.1, 129.4, 130.0, 132.6, 133.5, 143.3 (*C*=O triazole ring). − UV/Vis ($CHCl_3$): λ_{max} ($E_{rel.}$) = 291 nm (1.0), 346 (0.19), 396 (0.12), 419 (0.21), 443 (0.41), 649 (0.26). − Fluorescence (chloroform): λ_{max} = 756 nm, 866, 885 sh. − MS (70 eV): *m/z* (%): 817 (17), 816 (57), 815 (100) [M^+], 798 (8) [$M^+ - OH$], 691 (8), 690 (18), 689 (20) [$M^+ - C_9H_{18}$], 672 (6), 565 (11), 564 (27), 563 (33) [$M^+ - 2 \times C_9H_{18}$], 429 (6), 418 (12), 417 (43), 416 (53) [$M^+ - 2 \times C_9H_{18} - C_6H_5NCO - CO$], 399 (12), 391 (6), 390 (10), 388 (7). − $C_{50}H_{49}N_5O_6$ (816.0): calcd. C 73.60, H 6.05, N 8.58; found C 72.13, H 6.25, N 8.38.

***N,N'*-Bis(1-hexylheptyl)-1,3-dioxo-2-phenylbenzo[4,10]-anthra[1,9,8-*cdef*][1,2,4]triazolo[1,2-*a*]cinnoline-5,6:11,12-dis(dicarboximide) (14a):** *N,N'*-Bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**1a**, 100 mg, 0.133 mmol), 4-phenyl-1,2,4-triazolin-3,5-dion (180 mg, 1.03 mmol) and chloranil (32.5 mg, 0.133 mmol) were heated under reflux in dry toluene for 24 h, concentrated, and purified by column separation (silica gel, chloroform for removing of **1a** and dichloromethane for the elution of **14a**). Yield 32 mg (25%) of **14a** as a green solid, m.p. > 300°C. − R_f (silica gel, chloroform): 0.32. − R_f (silica gel, dichloromethane): 0.56. − IR (KBr): $\tilde{\nu}$ = 2954 cm^{-1} (m), 2927 (m−s), 2856 (m), 1773 (m, C=O triazole ring), 1726 (s, C=O triazole ring), 1702 (s), 1661 (s), 1600 (m), 1577 (m), 1502 (m), 1458 (w), 1421 (m), 1394 (s), 1378 (m), 1339 (m), 1300 (m−s), 1243 (w), 1178 (w), 1118 (w), 1028 (w), 975 (w), 928 (w), 851 (w), 809 (m), 744 (m), 730 (w), 694 (w), 645 (w), 536 (w), 503 (w). − ^1H NMR ($CDCl_3$): δ = 0.84 (t, *J* = 6.7 Hz, 12 H, CH_3), 1.22−1.40 (m, 32 H, CH_2), 1.84 (m_C, 4 H, CH−CH_2), 2.18 (m_C, 4 H, CH−CH_2), 5.09 [tt, $^3J_1$ = 6.2 Hz, ^3J = 9.0 Hz, 2 H, C*H*(CH_2)$_2$], 7.51 (t, *J* = 7.3 Hz, 1 H, phenyl), 7.60 (t, *J* = 7.5 Hz, 2 H, phenyl), 7.70 (d, *J* = 7.7 Hz, 2 H, phenyl), 8.13 (d, *J* = 8.2 Hz, 2 H, perylene), 8.33 (br. d, *J* = 7.3 Hz, 2 H, perylene), 9.24 (s, 2 H, perylene). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 22.6, 27.0, 29.2, 31.8, 32.2, 55.1, 116.9, 123.5, 125.0, 126.1, 126.4, 129.2, 129.4, 130.0, 132.6, 133.5, 143.4 (*C*=O triazole ring). − UV/Vis ($CHCl_3$): λ_{max} (ε) = 291 nm (53140), 347 (10900), 357 (10270), 396 (7030), 419 (12120), 443 (22870), 650 (14610). − Fluorescence (chloroform): λ_{max} = 753 nm, 868, 882 sh. − MS (70 eV): *m*/*z* (%): 930 (5), 929 (22), 928 (65), 927 (100) [M^+], 910 (6) [$M^+ - OH$], 747 (10), 746 (19), 745 (17) [$M^+ - C_{13}H_{26}$], 565 (12), 564 (25), 563 (25) [$M^+ - 2 \times C_{13}H_{26}$], 418 (7), 417 (25), 416 (30) [$M^+ - 2 \times C_{13}H_{26} - C_6H_5NCO - CO$], 399 (7). − $C_{58}H_{65}N_5O_6$ (928.2): calcd. C 75.05, H 7.06, N 7.55; found C 74.84, H 7.26, N 7.49.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Prof. Grätzel for the investigations with the TiO_2 cell.

---

[1] H. Langhals, *Heterocycles* **1995**, *40*, 477−500.

[2] H. Langhals, *D.O.S.* 3016764 (April 30, **1980**); *Chem. Abstr.* **1982**, *96*, P70417x.

[3] H. Langhals, S. Demmig, T. Potrawa, *J. Prakt. Chem.* **1991**, *333*, 733−748.

[4] U. Rohr, P. Schlichtling, A. Böhm, M. Groß, K. Merholz, C. Bräuchle, K. Müllen, *Angew. Chem.* **1998**, *110*, 1463−1467; *Angew. Chem. Int. Ed.* **1998**, *37*, 1434−1437.

[5] H. Langhals, S. Grundner, *Chem. Ber.* **1986**, *119*, 2373−2376.

[6] H. Langhals, L. Feiler, *Liebigs Ann.* **1996**, 1587−1591.

[7] E. Clar, M. Zander, *J. Chem. Soc.* **1957**, 4616−4625.

[8] H. Hopff, H. R. Schweizer, *Helv. Chim. Acta* **1959**, *42*, 2315−2333.

[9] V. I. Rogovik, *Zh. Org. Khim.* **1974**, *10*, 1072 −1075; *J. Org. Chem. USSR (Engl. Transl.)* **1974**, *10*, 1084−1087.

[10] R. C. Cookson, S. S. H. Gilani, J. D. R. Stevens, *J. Chem. Soc. C* **1967**, 1905−1909.

[11] J. Sauer, B. Schröder, *Chem. Ber.* **1967**, *100*, 678−684.

[12] M. Zander, *Chem. Ber.* **1974**, *107*, 1406−1408.

[13] M. Zander, *Chem.-Ztg.* **1975**, *99*, 92−93.

[14] W. Seidenfaden, D. Pawellek, D. Houben-Weyl, *Methoden der Org. Chem. (Houben-Weyl) 4. Aufl.* **1971**, vol. 10/1, p. 488.

[15] V. I. Rogovik, E. I. Shirokii, A. V. El'tsov, *Zh. Org. Khim.* **1980**, *16*, 867−872; *J. Org. Chem. USSR (Enlg. Transl.)* **1980**, *16*, 762−766.

[16] J. I. G. Cadogan, M. Cameron-Wood, *Proc. Chem. Soc.* **1962**, 361.

[17] L. Feiler, H. Langhals, K. Polborn, *Liebigs Ann.* **1995**, 1229−1244.

[18] I. D. Entwistle, A. E. Jackson, R. A. W. Johnstone, R. T. Telford, *J. Chem. Soc., Perkin Trans. 1* **1977**, 443−444.

[19] N. A. Cortese, R. F. Heck, *J. Org. Chem.* **1977**, *42*, 3491−3494.

[20] H. Kaiser, J. Lindner, H. Langhals, *Chem. Ber.* **1991**, *124*, 529−535.

[21] T. I. Solomentseva, V. I. Rogovik, T. A. Chibisova, V. F. Traven', B. I. Stepanov, *Zh. Org. Khim.* **1986**, *22*, 1050−1054; *J. Org. Chem. USSR (Engl. Transl.)* **1986**, *22*, 943−946.

[22] Free perylene-3,4:9,10-tetracarboxylic acid and its derivatives, have been reported for this synthesis. It is more probable that a ring closure to bis(anhydrides) proceeded under the reaction conditions because of the instability of the free acid; compare ref.[1]

[23] H. Langhals, J. Karolin, L. B.-Å. Johansson, *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2919−2922.

[24] J. Moser, M. Grätzel, *J. Am. Chem. Soc.* **1984**, *106*, 6557−6564.

[25] O. Enea, J. Moser, M. Grätzel, *J. Electroanal. Chem.* **1989**, *259*, 59−65.

[26] S. Ruile, Ph. D. Thesis, EPF Lausanne, **1997**.

[27] R. Borsdorf, H.-J. Hofmann, H.-J. Köhler, M. Scholz, J. Fabian, *Tetrahedron* **1970**, *26*, 3227−3231.

[28] W. Schroth, H. Langguth, F. Billig, *Z. Chem.* **1965**, *5*, 353−354.

[29] A. Y. Zheltov, V. Y. Rodinov, B. I. Stepanov, *Zh. Org. Khim.* **1975**, *11*, 1304−1311; *J. Org. Chem. USSR (Engl. Transl.)* **1975**, *11*, 1288−1294.

Received October 12, 1998
[O98450]