Novel Fluorescence Labels: The Synthesis of Perylene-3,4,9-tricarboxylic Imides

Frank Süßmeier[a] and Heinz Langhals*[a]

Dedicated to Prof. Dr. R. Huisgen on the occasion of his 80th birthday

Keywords: Dyes / Fluorescent labels / Heterocycles / Perylenes

Perylene-3,4,9-tricarboxylic imides are prepared in a one-step synthesis from perylene-3,4,9,10-tetracarboxylic 3,4-anhydride 9,10-imides by partial decarboxylation with copper powder. The imides are of interest as labels because of their intense fluorescence and lightfastness and their easy monofunctionalization. A derivatization of amines and alcohols with these compounds is demonstrated.

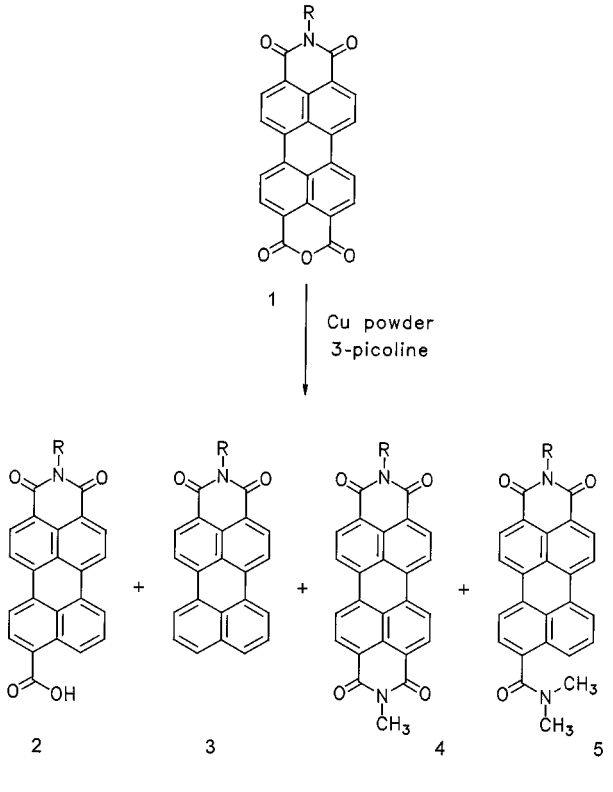
Introduction

Perylene imides are suitable chromophores for fluorescence labelling because of their high photostability and fluorescence quantum yield.[1] Monofunctionalization is required for such applications. Perylene-3,4,9-tricarboxylic-3,4-imides **2** are therefore interesting subjects, because a link to **2** may easily be obtained by reaction of the free carboxylic acid, whereas other properties such as the solubility can be controlled by the substituent (R) at the nitrogen atom (Scheme 1). However, compounds **2** are as yet unknown.

Results and Discussion

Suitable starting materials for **2** are the perylene-3,4,9,10-tetracarboxylic 3,4-anhydride 9,10-imides **1**,[2] in which two carboxylic functions are protected by the stable imide ring. A decarboxylation of the carboxylic groups constituting the anhydride moiety under standard reaction conditions[3,4] would lead directly to the imide **3**.[5] However, copper powder in boiling 3-picoline removes the carboxylic groups of the anhydride of **1** in a stepwise manner, according to Figure 1 and Table 1, respectively. Other solvents are either less efficient (4-picoline, for example) or cannot be used (such as 2-picoline or quinoline). Copper powder cannot be replaced by CuO (see Table 1).

Kinetic analysis[4,6] of the decarboxylation clearly shows a first-order reaction of **1a** to **2a**, followed by subsequent reaction to **3a**. The rate constants of the first ($k_{\mathbf{1a-2a}}$) and the second steps ($k_{\mathbf{2a-3a}}$) are 6.1×10^{-4} s^{-1} and 6.1×10^{-5} s^{-1}, respectively (see Figure 1 and Scheme 2). The calculated chemical yield for the reaction from the kinetic data is 75%, while an optimal reaction time for the preparation of **2a** is 1.5 h. The starting material **1a** need not be removed because it is completely converted; compound **3a** can be removed by chromatography.



1 - 9	R
a	$CH(C_6H_{12})_2$
b	$CH(C_9H_{19})_2$
c	2,5-Di-*t*-C_4H_9-C_6H_3

Scheme 1. Synthesis of **2a**

CO_2 was identified (by aqueous $BaCl_2$ solution) as a product of the reaction of **1a** to **2a** and was gravimetrically determined with soda lime (79% with respect to decarb-

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

  1434–193X/01/0203–0607 $ 17.50+.50/0

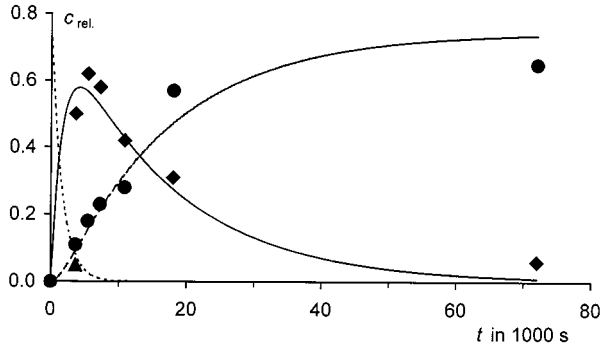
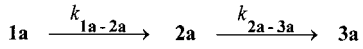


Figure 1. Kinetic analysis of the decarboxylation reaction of **1a** (···, ▲) via **2a** (—, ◆) to **3a** (—, ●) (Cu powder, refluxing 3-picoline, reaction conditions according to the general procedure); from left to right, relative concentrations of **1a**, **2a** and **3a**, respectively

Table 1. Synthesis of **2a**

Reaction time[a] [h]	Solvent	Reaction temperature [°C]	[%] 1a	2a	3a
1	3-Picoline	Refl. (143)	5	50	11
1.5	3-Picoline[b]	Refl. (143)	–	62	18
2	3-Picoline	Refl. (143)	–	58	23
3	3-Picoline[c]	Refl. (143)	–	42	28
5	3-Picoline	Refl. (143)	–	31	57
20	3-Picoline	Refl. (143)	–	6	65
4	4-Picoline	Refl. (≈150)	–	11	17
3	2-Picoline	Refl. (≈120)	95	–	–
5	Quinoline	190	58	–	33
5	Quinoline[d]	190	50	–	42
20	Quinoline[d]	190	40	–	42
4	3-Picoline[d]	Refl. (143)	30	–	2

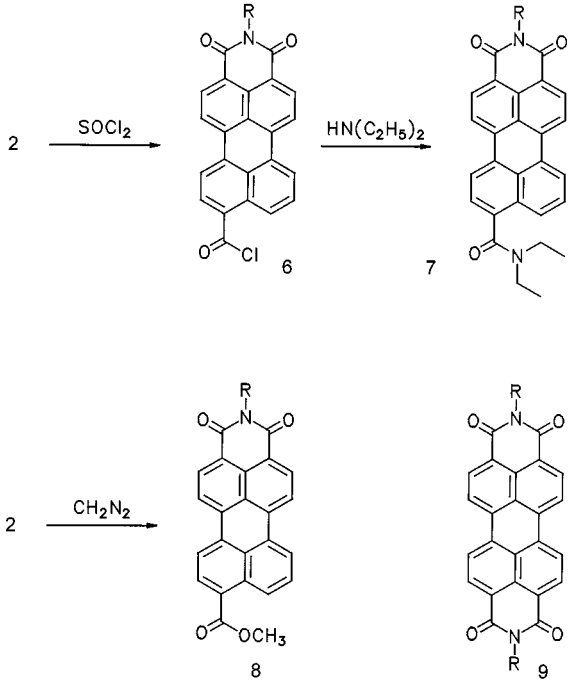
[a] 0.17 mmol **1a** and 1.0 mmol copper powder in 5 mL solvent. – [b] 2% **4** and 9% **5** were formed. – [c] 7% **4** and 7% **5** were formed. – [d] 1.38 mmol CuO instead of copper powder.



Scheme 2. Stepwise decarboxylation of **1**

oxylation). Minor by-products were the *N*-methylated bisimide **4a** (9%) and the dimethyl amide **5a** (2%); if no copper powder was added, **4a** and **5a** were not obtained. The methyl groups in **4a** and **5a** are not fragments from the substituent R in **1**, but from the solvent; since the same pattern of products was obtained from the aromatic derivative **1c**. Some of the decarboxylation proceeds with single C–C coupling to form traces of a bichromophore.[7] The total balance of isolated products was 91%. The additional aromatic hydrogen atoms in **2**, **3**, and **5** are not a consequence of product isolation; addition of deuterium oxide to the aqueous phase during isolation did not result in any incorporation of deuterium into the perylene nucleus. However, if the copper powder was treated with deuterium oxide (90 mg) before the reaction, then compound **2a** was obtained with 80% deuterium in the decarboxylated *peri* position (MS and ^{1}H NMR). All other perylene nucleus carbon atoms were free of deuteration. With **3a**, 18% was undeuterated, 57% was monodeuterated in the *peri* position and 25% was doubly deuterated in the *peri* positions. All other positions of the perylene nucleus were undeuterated.

The free acid **2** reacts with thionyl chloride to give in high yield the acid chloride **6** as an reactive derivative of **2** (Scheme 3). This can be used without further purification. Compound **6** labels nucleophiles such as amines and alcohols to form highly fluorescent carboxylic amides and esters (**8a**), respectively. For example, **6a** reacts with diethylamine to form **7a**, and with the polymeric hydroxy compound cellulose (DMF as solvent) to give a highly fluorescent coloration on paper at room temperature. The covalent source of this coloration is proved by its fastness with regard to any solvent; it is only altered by prolonged refluxing with methanol (transesterification reaction).



Scheme 3. Derivatives of **2** and reference **9**

The UV/Vis absorption spectrum of **2** is intermediate between the only slightly structured spectrum of **3** and the strongly structured spectrum of **9** (see Figure 2). It seems that the structural details of the spectra depend on the elec-

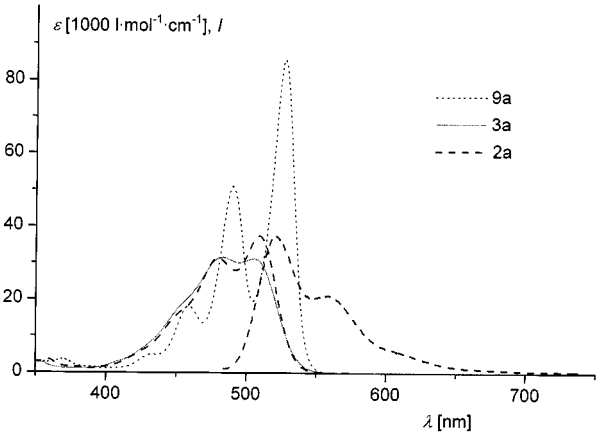


Figure 2. UV/Vis absorption spectra in chloroform: **2a** (- - -), **9a** (···) and **3a** (—); corrected fluorescence spectrum of **2a** (- - -)

tronic properties of the carboxyl substituent: an electron-withdrawing group such as a carboxylic acid chloride (**6a**) favours the fine structure, and this diminishes in the substituent sequence: carboxylic acid (**2a**) to carboxamide (**7a**) to hydrogen (**3a**). The molar absorptivity of **2a** is 37000. The fluorescence spectrum of **2** mirrors the absorption spectrum and the fluorescence quantum yield is about 84%. This indicates that dyes **2** are suitable precursors for fluorescence labelling; the acid chloride **6a** is a suitably reactive derivative for this, and forms the strongly fluorescent (Φ = 92%) amide **7a** with diethyl amine. The methyl ester **8a** is also strongly fluorescent (Φ = 87%).

Experimental Section

Preparation of Perylene-3,4,9-tricarboxylic 3,4-Imides 2: Perylene-3,4,9,10-tetracarboxylic 3,4-anhydride 9,10-imides (0.34 mmol), copper powder (130 mg, 2.0 mmol) and 3-picoline (10 mL) were refluxed under nitrogen for 1.5 h (complete conversion of **1**; TLC monitoring; silica gel, chloroform). The mixture was cooled down, stirred with hydrochloric acid (2 N, 100 mL), collected by filtration, washed with water, dried in air (90 °C), separated from **3** (first fraction) by column chromatography (silica gel, chloroform), eluted by addition of glacial acetic acid, purified by a second column separation (silica gel, chloroform/ethanol 10:1) and obtained as the last fraction.

***N*-(1-Hexylheptyl)perylene-3,4,9-tricarboxylic 9-Acid 3,4-Imide (2a):** Yield 118 mg (62%) of **2a** as a carmine red powder, m.p. 233−234 °C. − R_f (silica gel, chloroform/ethanol 10:1) = 0.38. − IR (KBr): $\tilde{\nu}$ = 3435 cm^{-1} (m), 2954 (s), 2856 (s), 1695 (s), 1655 (s), 1615 (m), 1593 (s), 1578 (m), 1508 (w), 1459 (w), 1353 (s), 1294 (w), 1247 (m), 1176 (w), 810 (m), 753 (m), 669 (w). − UV/Vis ($CHCl_3$): λ_{max} (ε) = 509.0 nm (37400), 479.4 (31300), 458 sh (18200). − Fluorescence ($CHCl_3$): λ_{max} ($I_{rel.}$) = 530 nm (1), 564 (0.55). − Fluorescence quantum yield ($c = 0.96 \times 10^{-6}$ mol·L^{-1} in $CHCl_3$, reference *N,N′*-(1-hexylheptyl)perylene-3,4:9,10-bis-(dicaboximide) (**9a**) with Φ = 100%, $\lambda_{excit.}$ = 484 nm) = 84%. − ^{1}H NMR ($CDCl_3$): δ = 0.83 (t, J = 6.9 Hz, 6 H, 2 CH_3), 1.22 (m, 16 H, CH_2), 1.87 (m, 2 H, CH_2), 2.25 (m, 2 H, CH_2), 5.19 (m, 1 H, CH), 7.76 (t, J = 7.6 Hz, 1 H), 8.43−8.49 (m, 5 H), 8.59 (br, 2 H), 9.14 (d, J = 8.6 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 14.0, 22.6, 27.0, 29.3, 31.8, 32.4, 54.6, 120.4, 121.0, 121.8, 122.0, 123.8, 126.3,126.8, 128.5,128.6, 129.4, 129.6, 131.9, 132.9, 135.4, 134.2, 136.5, 169.6 (COOH). − MS (70 eV): *m/z* (%) = 548 (9), 547 (23) [M$^+$], 530 (4) [M$^+$ − OH], 367 (10), 366 (47), 367 (100) [M$^+$ − $C_{13}H_{26}$], 321 (8), 320 (7), 85 (15), 83 (25), 55 (10). − $C_{36}H_{37}NO_4$ (547.2): calcd. C 78.95, H 6.81, N 2.56; found C 78.61, H 6.90, N 2.54.

***N*-(1-Nonyldecyl)perylene-3,4,9-tricarboxylic 9-Acid 3,4-Imide (2b):** Yield 125 mg (59%) of **2b** as a dark red powder, m.p. 226−227 °C. − R_f (silica gel, chloroform/ethanol 10:1) = 0.43. − IR (KBr): $\tilde{\nu}$ = 3436 cm^{-1} (br, s), 2923 (s), 2853 (s), 1697 (s), 1656 (s), 1638 (s), 1615 (m), 1592 (s), 1508 (w), 1458 (w), 1419 (w), 1354 (s), 1293 (w), 1249 (m), 1180 (m), 1124 (w), 809 (m), 749 (m), 669 (w). − UV/Vis ($CHCl_3$): λ_{max} (ε) = 509 nm (35300), 479.5 (29900), 457 (sh, 16900). − Fluorescence ($CHCl_3$): λ_{max} ($I_{rel.}$) = 531 nm (1.00), 563 (0.57). − Fluorescence quantum yield ($c = 0.97 \times 10^{-6}$ mol/l in $CHCl_3$, reference *N,N′*-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicaboximide) with Φ = 100%, $\lambda_{excit.}$ = 484 nm) = 91%. − ^{1}H NMR ($CDCl_3$): δ = 0.83 (t, 6 H), 1.39−1.21 (m, 28 H), 1.89 (m, 2 H), 2.27 (m, 2 H), 5.19 (m, 1 H), 7.68 (t, J = 8.1 Hz, 1 H), 8.37−8.27 (m, 5 H), 8.50 (br, 1 H), 8.56 (br, 1 H), 9.09 (d, J = 8.6 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 13.1, 21.6, 26.1, 28.3, 28.55, 28.58, 30.9, 31.4, 53.6, 119.8, 120.3, 120.7, 120.8, 122.0, 122.6, 125.1, 125.8, 127.3, 127.5, 128.2, 128.5, 129.9, 130.14, 130.6, 130.9, 131.8, 133.1, 134.2, 135.2, 162.9 (CO), 163.9 (CO), 169.8 (COOH). − MS (70 eV): *m/z* (%) = 632 (11), 631 [M$^+$] (86), 614 [M$^+$ − OH] (4), 587 (3), 367 (9), 366 (57), 365 [M$^+$ − $C_{19}H_{38}$] (100), 322 (7), 321 (16), 320 (4). − $C_{42}H_{49}NO_4$ (631.3): calcd. C 79.84, H 7.82, N 2.22; found C 79.15, H 7.64, N 2.13. − $C_{42}H_{49}NO_4$: calcd. 631.3662, found 631.3679 (MS).

***N*-(2,5-Di-*tert*-butylphenyl)perylene-3,4,9-tricarboxylic 9-Acid 3,4-Imide (2c):** Yield 110 mg (57%) of **2c** as a light red, crystalline powder, m.p. > 270 °C. − R_f (silica gel, chloroform/ethanol 10:1) = 0.32. − IR (KBr): $\tilde{\nu}$ = 3436 cm^{-1} (br, m), 2963 (m), 1706 (s), 1664 (s), 1593 (s), 1508 (w), 1459 (w), 1411 (w), 1359 (s), 1294 (w), 1248 (m), 1201 (w), 1180 (w), 1121 (w), 812 (m), 756 (m), 735 (w). − UV/Vis ($CHCl_3$): λ_{max} (ε) = 510.4 nm (36200), 480.5 (31000), 458 (sh, 17400). − Fluorescence ($CHCl_3$): λ_{max} ($I_{rel.}$) = 533 nm (1.00), 567 (0.55). − Fluorescence quantum yield ($c = 0.92 \times 10^{-6}$ mol/l in $CHCl_3$, reference *N,N′*-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicaboximide) with Φ = 100%, $\lambda_{excit.}$ = 484 nm) = 86%. − ^{1}H NMR ([D$_6$]DMSO): δ = 1.18 (m, 9 H), 1.26 (m, 9 H), 7.23 (d, J = 2.2 Hz, 1 H), 7.41 (dd, ^3J = 8.6 Hz, ^4J = 2.4 Hz, 1 H), 7.53 (d, J = 8.5 Hz, 1 H), 7.76 (t, J = 8.1 Hz, 1 H), 8.19 (d, J = 8.0 Hz, 1 H), 8.47 (2 d, 2 H), 8.70−8.63 (m, 4 H), 8.90 (d, J = 8.6 Hz, 1 H). − ^{13}C NMR ([D$_6$]DMSO): δ = 31.5, 31.8, 34.5, 35.6, 121.6, 122.1, 122.3, 122.8, 123.8, 125.1, 125.9, 126.3, 128.0, 128.6, 128.7, 128.8, 128.9, 129.1, 129.7, 130.4, 130.8, 131.6, 131.76, 132.1, 132.4, 133.8, 136.1, 137.0, 143.8, 149.8, 164.58, 164.59, 168.6. − MS (70 eV): *m/z* (%) = 554 (3), 553 [M$^+$] (7), 536 [M$^+$ − OH] (2), 498 (7), 497 (38), 496 [M$^+$ − C_4H_9] (100), 482 (4), 481 (7), 480 (14), 452 (3). − $C_{37}H_{31}NO_4$ (553.2): calcd. C 80.27, H 5.64, N 2.53; found C 78.38, H 5.64, N 2.53. − $C_{37}H_{31}NO_4$: calcd. 553.2253, found 553.2265 (MS).

***N*-(1-Hexylheptyl)perylene-3,4,9-tricarboxylic 9-Chloride 3,4-Imide (6a): 2a** (100 mg, 0.18 mmol) and thionyl chloride (10 mL) were refluxed for 4 h, evaporated (a small amount of benzene may be added as a carrier and evaporated in order to remove traces of thionyl chloride), dried in medium vacuum at 50 °C and used without further purification. Dark red solid **6a**. − IR (KBr): $\tilde{\nu}$ = 2954 cm^{-1} (m), 2925 (s), 2855 (m), 1756 (m), 1698 (s), 1655 (s), 1592 (s), 1506 (w), 1457 (w), 1409 (w), 1351 (s), 1320 (w), 1294 (w), 1245 (m), 1217 (m), 1158 (w), 1096 (w), 90 (w), 840 (w), 808 (m), 771 (m), 751 (m), 678 (w). − UV ($CHCl_3$): λ_{max} ($E_{rel.}$) = 512.7 nm (1.00), 487.7 (0.82), 456 sh (0.45), 430 sh (0.19). − ^{1}H NMR ($CDCl_3$): δ = 0.83 (t, 6 H), 1.37−1.23 (m, 16 H), 1.87 (m, 2 H), 2.25 (m, 2 H), 5.19 (m, 1 H), 7.76 (t, J = 7.8 Hz, 1 H), 8.47−8.39 (m, 4 H), 8.64−8.57 (m, 3 H), 8.77 (d, J = 8.6 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 14.0, 22.6, 27.0, 29.2, 31.8, 32.4, 54.7, 121.5, 121.6, 122.6, 124.0, 127.5, 126.2, 128.4, 129.5, 129.6, 129.8, 130.4, 131.9, 135.1, 135.8, 163.8, 164.8, 167.0. − MS (70 eV): *m/z* (%) = 567 (29), 566 (25), 565 (76) [M$^+$], 548 (9) [M$^+$ − OH], 531 (7), 530 (8) [M$^+$ − Cl], 386 (22), 385 (50), 384 (67), 383 (100) [M$^+$ − $C_{13}H_{26}$], 350 (10), 349 (38), 348 (94) [383 − Cl], 322 (10), 321 (44), 320 (33) [348 − CO], 275 (8), 207 (33). $C_{36}H_{36}NO_3Cl$: calcd. 565.2383, found 565.2394 (MS).

***N′*,*N′*-Diethyl-*N*-(1-hexylheptyl)perylene-3,4,9-tricarboxylic 9-Amide 3,4-Imide (7a):** A solution of diethylamine (0.20 mL, 1.9 mmol) in anhydrous 1,4-dioxane (5 mL) was added to a solution of **6a** (prepared from **2a**, 100 mg, 0.18 mmol) in anhydrous 1,4-dioxane (5 mL), stirred at room temperature for 15 min, refluxed for 15 min, cooled down, and treated with 2 N HCl. The

precipitate was collected by vacuum filtration, washed with water, dried in vacuo (KOH), purified by two column separations (silica gel, chloroform) and then highly purified by preparative TLC. (silica gel, dichloromethane). Yield 85 mg (83%) of **7a** as a red, amorphous powder, m.p. 80−81 °C. − R_f (silica gel, chloroform/ethanol 20:1) = 0.7. − IR (KBr): $\tilde{\nu}$ = 2954 cm^{-1} (m), 2926 (s), 2856 (m), 1693 (s), 1653 (s), 1633 (s), 1592 (s), 1577 (m), 1506 (w), 1461 (m), 1436 (m), 1352 (s), 1319 (m), 1294 (m), 1278 (m), 1245 (m), 1214 (w), 1112 (w), 842 (w), 811 (m), 752 (m). − UV ($CHCl_3$): λ_{max} (ε) = 505.9 nm (35100), 480.5 (33600). − Fluorescence ($CHCl_3$): λ_{max} ($I_{rel.}$) = 535 nm (1.00), 568 (0.61). − Fluorescence quantum yield ($c = 0.83 \cdot 10^{-6}$ mol/l in $CHCl_3$, reference *N*,*N*′-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**9a**) with Φ = 100%, $\lambda_{excit.}$ = 468 nm) = 92%. − ^{1}H NMR ($CDCl_3$): δ = 0.75 (t, 3 H), 0.98 (t, 3 H), 1.25−1.16 (m, 16 H), 1.34 (t, 3 H), 1.80 (m, 2 H), 2.19 (m, 2 H), 3.10 (m, 2 H), 3.52 (br, 1 H), 3.79 (br, 1 H), 5.12 (m, 1 H), 7.72 (d, *J* = 8.3 Hz, 1 H), 7.40 (d, *J* = 7.6 Hz, 1 H), 7.50 (t, *J* = 7.9 Hz, 1 H), 8.19 (d, *J* = 8.3 Hz, 1 H), 8.20 (d, *J* = 8.3 Hz, 1 H), 8.21 (d, *J* = 7.8 Hz, 1 H), 8.23 (d, *J* = 7.8 Hz, 1 H), 8.42 (br, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 13.1, 14.0, 14.4, 22.6, 27.0, 29.3, 31.8, 32.4, 39.2, 43.2, 54.4, 120.4, 120.5, 121.1, 121.86, 122.8, 123.8, 124.3, 126.4, 127.5, 127.7, 128.0, 129.5, 129.7, 129.7, 130.6, 131.0, 131.8, 136.0, 136.4, 137.4, 164.02, 165.0, 169.3. − MS (70 eV): *m*/*z* (%) = 604 (10), 603 (43), 602 (100) [M^+], 586 (7), 585 (15) [M^+ − OH], 531 (4), 530 (4), 422 (11), 421 (45), 420 (79) [$M^+ - C_{13}H_{26}$], 419 (10), 350 (11), 349 (29), 348 (36), 322 (9), 321 (25), 320 (20). − $C_{40}H_{50}N_2O_3$ (602.7): calcd. C 79.70, H 7.69, N 4.65; found C 78.90, H 7.84, N 4.48.

***N*-(1-Hexylheptyl)perylene-3,4,9-tricarboxylic 3,4-Imide 9-(Methyl ester) (8):** A saturated solution of diazomethane in diethyl ether was added to a solution of **2a** (100 mg, 0.18 mmol) in a mixture of diethyl ether (15 mL) and methanol (2 mL) until no further evolution of gas could be observed. The mixture was stirred for 15 min, evaporated and purified by column separation (silica gel, chloroform). Yield 0.85 g (83%) of methyl *N*-(1-hexylheptyl)perylene-3,4-dicarboximide-9-carboxylate as fine, light red needles, m.p. 187−188 °C. − R_f (silica gel, chloroform) = 0.32. − IR (KBr): $\tilde{\nu}$ = 2926 cm^{-1} (s), 2856 (m), 1715 (m), 1694 (s), 1653 (s), 1592 (s), 1507 (w), 1434 (w), 1411 (w), 1354 (s), 1295 (m), 1258 (m), 1203 (m), 1124 (w), 809 (m), 752 (m). − UV ($CHCl_3$): λ_{max} (ε) = 508.0 nm (38800), 479.7 (34000), 455 sh (19000). − Fluorescence ($CHCl_3$): λ_{max} ($I_{rel.}$) = 531 nm (1.00), 567 (0.55). − Fluorescence quantum yield ($c = 1.01 \times 10^{-6}$ mol/l in $CHCl_3$, reference *N*,*N*′-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**9a**) with Φ = 100%, $\lambda_{excit.}$ = 468 nm) = 87%. − ^{1}H NMR ($CDCl_3$): δ = 0.83 (t, 6 H), 1.39−1.23 (m, 16 H), 2.27 (m, 2 H), 1.88 (m, 2 H), 5.19 (m, 1 H), 4.05 (s, 3 H), 7.63 (t, *J* = 7.7 Hz, 1 H), 8.14 (d, *J* = 8.0 Hz, 1 H), 8.24 (d, *J* = 8.3 Hz, 1 H), 8.32−8.29 (m, 3 H), 8.52 (br, 2 H), 8.92 (d, *J* = 8.6 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 22.6, 27.0, 29.3, 31.8, 32.4, 52.5, 54.5, 120.7, 121.4, 121.9, 123.6, 126.2, 128.2, 128.3, 128.5, 128.5, 129.1, 129.6, 130.5, 130.9, 131.1, 131.6, 132.0, 132.5, 133.1, 135.43, 136.4, 164.0, 165.07, 167.2. − MS (70 eV): *m*/*z* (%) = 562 (13), 561 (35) [M^+], 544 (7) [M^+ − OH], 409 (3), 380 (13), 379 (100) [$M^+ - C_{13}H_{26}$], 348 (4), 321 (3), 320 (5). − $C_{37}H_{39}NO_4$ (561.7): calcd. C 79.11, H 7.00, N 2.49; found C 78.88, H 6.96, N 2.49.

By-products of the Synthesis of 2a

***N*-(1-Hexylheptyl)-*N*,*N*′-dimethylperylene-3,4,9-tricarboxylic 9-Amide 3,4-Imide (5a):** Isolated by column separation (see above) as a red, amorphous powder, m.p.: softens at about 50 °C, m.p. 94/95 °C. − R_f (silica gel, CH_2Cl_2): 0.04. − IR (KBr): $\tilde{\nu}$ = 2924 cm^{-1} (s), 2855 (m), 1693 (s), 1652 (s), 1592 (s), 1577 (m), 1508 (w), 1457 (w), 1390 (w), 1352 (s), 1292 (w), 1245 (w), 1109 (w), 1067 (w), 843 (w), 811 (w), 753 (w). − ^{1}H NMR ($CDCl_3$): δ = 0.81 (t, 6 H), 1.29−1.19 (m, 16 H), 1.82 (m, 2 H), 2.23 (m, 2 H), 2.86 (s, 3 H), 3.25 (s, 3 H), 5.15 (m, 1 H), 7.49 (d, *J* = 7.6 Hz, 1 H), 7.58 (t, *J* = 7.9 Hz, 1 H), 7.78 (d, *J* = 8.2 Hz, 1 H), 8.33 (m, 4 H), 8.51 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 14.0, 22.6, 26.9, 29.23, 31.8, 32.4, 34.9, 38.8, 54.5, 120.5, 120.6, 121.4, 121.9, 122.8, 123.8, 124.9, 126.5, 127.6, 127.86, 128.1, 129.7, 129.8, 130.0, 130.6, 131.1, 131.9, 136.1, 136.5, 137.0, 164.0, 165.1, 169.9. − UV/Vis ($CHCl_3$): λ_{max} (ε) = 505.1 nm (34900), 479.6 (33100), 457.5 (sh, 21000). − Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 533 nm (1), 568 (0.6). − Fluorescence quantum yield ($c = 1.1 \times 10^{-6}$ mol/L in $CHCl_3$, reference *N*,*N*′-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**9a**) with Φ = 100%, $\lambda_{excit.}$ = 484 nm) = 80%. − MS (70 eV): *m*/*z* (%) = 576 (6), 575 (28), 574 (77) [M^+], 557 (12) [M^+ − OH], 394 (10), 393 (50), 392 (100) [$M^+ - C_{13}H_{26}$], 349 (15), 348 (46) [392−C_2H_6N], 321 (15), 320 (17) [348−CO], 275 (4). − $C_{38}H_{42}N_2O_3$ (574.7): calcd. C 79.41, H 7.37, N 4.87; found C 79.20, H 7.41, N 4.91.

***N*-(1-Hexylheptyl)-*N*′-methylperylene-3,4:9,10-bis(dicarboximide) (4a):** Yield 27 mg (9%) as red violet plates, m.p. > 250 °C. − R_f (silica gel, $CHCl_3$/EtOH, 10:1): 0.85. − IR (KBr): $\tilde{\nu}$ = 2954 cm^{-1} (m), 2927 (m), 2857 (m), 1698 (s), 1659 (s), 1595 (s), 1578 (m), 1440 (m), 1404 (m), 1344 (s), 1287 (m), 1248 (m), 1176 (w), 1056 (w), 851 (w), 810 (m), 744 (m). − ^{1}H NMR ($CDCl_3$): δ = 0.84 (t, 6 H), 1.37−1.24 (m, 16 H), 1.91 (m, 2 H), 2.28 (m, 2 H), 5.19 (m, 1 H), 3.52 (s, 3 H), 8.37 (d, 2 H, *J* = 8.1 Hz), 8.44 (d, 2 H, *J* = 8.0 Hz), 8.46 (d, 2 H, *J* = 8.1 Hz), 8.60 (br, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 22.6, 27.0, 27.1, 29.3, 31.8, 32.4, 54.9, 122.8, 122.8, 122.9, 123.3, 124.1, 126.0, 126.1, 129.0, 129.4, 130.9, 131.1, 131.6, 134.0, 134.4, 163.3, 164.4. − UV/Vis ($CHCl_3$): λ_{max} (ε) = 524.9 nm (83000), 488.5 (50200), 457.5 (19000). − Fluorescence ($CHCl_3$): λ_{max} ($I_{rel.}$) = 532 (1), 572 (0.39). − Fluorescence quantum yield ($c = 1.1 \times 10^{-6}$ mol/L in $CHCl_3$, reference *N*,*N*′-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**9a**) with Φ = 100%, $\lambda_{excit.}$ = 484 nm) = 80%. − MS (70 eV): *m*/*z* (%) = 587 (14), 586 (34) [M^+], 569 (4) [M^+ − OH], 406 (11), 405 (48), 404 (100) [$M^+ - C_{13}H_{26}$], 387 (5), 376 (4), 359 (4). − $C_{38}H_{38}N_2O_4$ (586.7): calcd. C 77.79, H 6.53, N 4.77; found C 77.54, H 6.54, N 4.75.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

[1] For a review see: H. Langhals, *Heterocycles* **1995**, *40*, 477−500.
[2] H. Kaiser, J. Lindner, H. Langhals, *Chem. Ber.* **1991**, *124*, 529−535.
[3] A. F. Shepard, N. R. Winslow, J. R. Johnson, *J. Am. Chem. Soc.* **1930**, *52*, 2083−2094.
[4] T. Cohen, R. W. Berninger, J. T. Wood, *J. Org. Chem.* **1978**, *43*, 837−847.
[5] L. Feiler, H. Langhals, K. Polborn, *Liebigs Ann.* **1995**, 1229−1244.
[6] T. Cohen, R. A. Schambach, *J. Am. Chem. Soc.* **1970**, *92*, 3189−3191.
[7] H. Langhals, F. Süßmeier, *J. Prakt. Chem.* **1999**, *341*, 309−311.

Received February 15, 2000
[O00074]