FLUORESCENT LABELS FOR ALDEHYDES

Heinz LANGHALS[1,*] and Kerstin FUCHS[2]

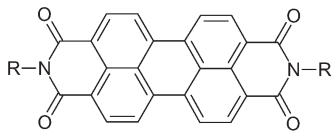
Department of Chemistry and Biochemistry, LMU Ludwig-Maximilians-University of Munich, Butenandtstr. 13, D-81377 Munich, Germany; e-mail: [1] Langhals@lrz.uni-muenchen.de, [2] fuchske@web.de

Received September 14, 2005
Accepted January 22, 2006

The fluorescence labeling of aldehydes with perylene bis(dicarboximide)s by the formation of acetals is described.

Keywords: Aldehydes; Fluorescence spectroscopy; Perylenes; Dyes; Acetals.

Aldehydes are important natural products and intermediates in chemical synthesis. They are also of interest concerning environmental pollution. A fluorescence labeling of aldehydes would be of general interest. The perylene bisimide chromophore **1** is suitable for such a labeling because of its high photostability and fluorescent quantum yield[1,2]. The formation of fluorescent hydrazones was described in preceding papers[3,4], however, this reaction is reversible[5]; an irreversible linkage would offer novel applications for such fluorescent structures.



1

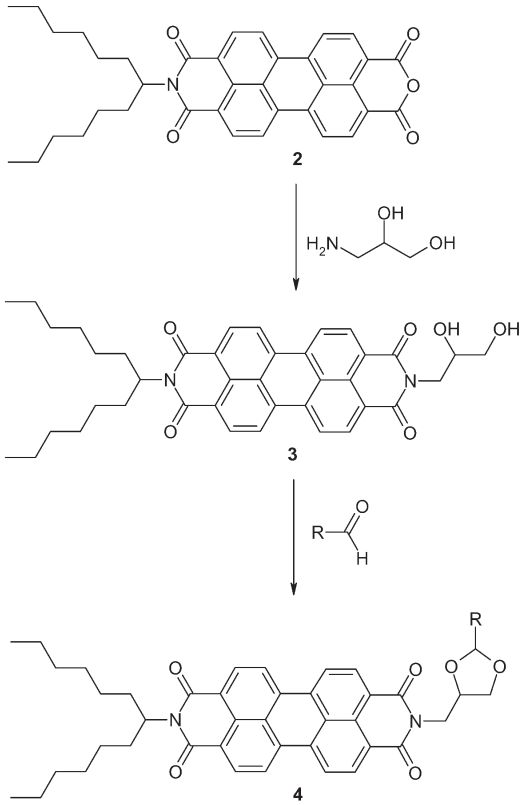
RESULTS AND DISCUSSION

The formation of cyclic acetals would be an efficient way for stable derivatization of aldehydes, however, up to now it has not attracted attention. Acetals can be easily prepared by acid catalysis and are very stable to alkaline conditions (Scheme 1). A cyclic structure of acetals would further favour their formation.

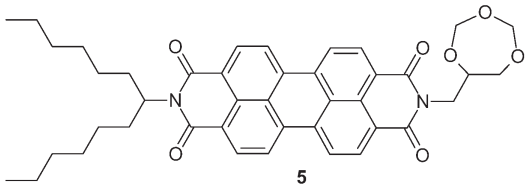
We have prepared the anhydride-imide **2** [6] as the first step for the synthesis of a derivatizing reagent. The nitrogen atom of **2** is attached to a long-

doi:10.1135/cccc20060625

chain secondary alkyl group ("swallow-tail substituent"), 1-hexylheptyl, to increase the solubility[7] and render the material hydrophobic. Compound **2** was condensed with 3-aminopropane-1,2-diol to form the diol **3** as the reagent for labeling aldehydes. Compound **3** reacts easily with aldehydes to cyclic acetals **4** under acid catalysis. The removal of water, for example with magnesium sulfate, is essential to complete the reaction. Aliphatic aldehydes such as acetaldehyde or propionaldehyde react more quickly compared with aromatic aldehydes such as benzaldehyde. Formaldehyde is an exception concerning the structure of the reaction product because two molecules of aldehyde are linked to one molecule of diol **3** forming the seven-membered ring compound **5**. This corresponds to the tendency of formaldehyde to form such rings.



SCHEME 1
Synthesis of fluorescent acetals



5

The cyclic acetals **4** are strongly fluorescent so that they can be determined with high sensitivity; for their UV/VIS spectra, see Fig. 1. The fluorescence quantum yields of **4** are close to 100%. This is remarkable because the acetal group contains two oxygen atoms which may cause fluorescence quenching by electron transfer to the excited perylene chromophore (cf. ref.[8]). Such a process seems to proceed only with the extraordinarily electron-rich trimethoxyphenyl derivative **4d**, however, a quantum yield of 60% is still attained even in this extreme case. The photostability of the acetals is so high that an intense light source can be applied for their determination and thus a high detection sensitivity may be obtained.

The fluorescent labeling proceeds easily, even with an excess of **3**. This is shown for acetaldehyde. Thus, traces of aldehydes can be determined by the reaction with **3**. However, calibration is necessary because of incomplete conversion. A chromatographic separation was necessary, especially for mixtures of alehydes, for example by means of TLC. On the other hand,

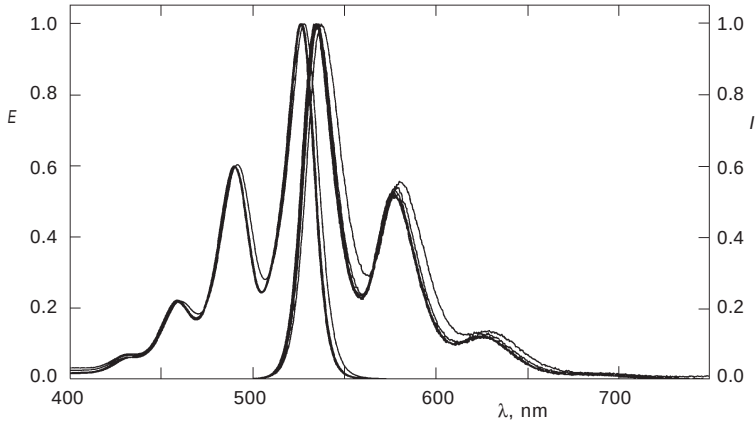


FIG. 1
UV/VIS absorption (left) and fluorescence (right) spectra of **3**, **4a**–**4d** and **5** in chloroform. The spectra of **4a**–**4d** and **5** are nearly identical, the spectra of **3** are bathochromically shifted

the reaction demonstrates that by-products of aldehydes can be detected, such as a propionaldehyde impurity in acetaldehyde.

The fluorescence spectra of **4a**–**4d** and **5** are nearly identical (see Fig. 1) so that the method for the determinaton of aldehydes becomes independent of the nature of the substrate, even for highly electron-rich derivatives such as the acetal of trimethoxybenzaldehyde **4d**. In contrast, the absorption spectrum of **3** is bathochromically shifted and the shift is even more pronounced for the fluorescence spectrum (see Fig. 1). Therefore, acetals **4** can be UV/VIS spectroscopically distinguished from the starting material **3**.

$$E(\lambda) = \sum E_o \exp\left[-\frac{(1/\lambda - 1/\lambda_o)^2}{2\sigma^2}\right] \qquad (1)$$

The spectroscopic differences between **3**, **4a**–**4d** and **5** have been investigated by Gaussian analysis using Eq. (*1*)[9,10], where λ is the wavelength and $E(\lambda)$ the molar absorption coefficient in the spectrum normalized to unity at the maximum. E_o, λ_o and σ are the parameters of Eq. (*1*) corresponding to the intensity, position and σ widths of the individual Gaussian bands. Five Gaussian functions are sufficient to describe the structured spectra both for absorption and fluorescence (see Table I and Fig. 2). Low *R* values have been obtained indicating the high quality of the fit for the experimen-

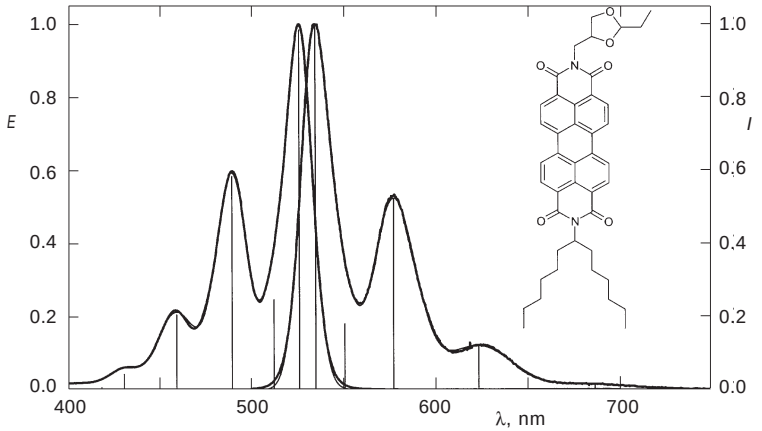


FIG. 2
UV/VIS absorption (thick line left) and fluorescence (thick line right) spectra of **4b** in chloroform and simulated spectra (thin lines) on the basis of five Gaussian functions. Bars: Line positions and intensities of the Gaussian functions

TABLE I
Gaussian analysis of absorption and fluorescence spectra (λ in nm)

Parameter	3	4a	4b	4c	4d	5
			Absorption			
$\lambda_{(1)}$	528.0	526.4	526.2	526.6	526.9	526.5
$\sigma_{(1)}$	0.152	0.125	0.127	0.126	0.128	0.127
$E_{(1)}$	0.988	0.983	0.984	0.983	0.984	0.982
$\lambda_{(2)}$	513.2	512.6	512.4	512.8	512.9	512.7
$\sigma_{(2)}$	0.0787	0.0843	0.0845	0.0850	0.0829	0.0847
$E_{(2)}$	0.200	0.247	0.246	0.247	0.240	0.244
$\lambda_{(3)}$	491.6	489.6	489.5	489.8	490.2	489.8
$\sigma_{(3)}$	0.295	0.269	0.271	0.270	0.271	0.270
$E_{(3)}$	0.558	0.583	0.584	0.584	0.582	0.582
$\lambda_{(4)}$	461.2	459.4	459.2	459.5	459.8	459.6
$\sigma_{(4)}$	0.535	0.508	0.512	0.511	0.505	0.510
$E_{(4)}$	0.209	0.204	0.205	0.204	0.203	0.203
$\lambda_{(5)}$	432.5	430.7	430.8	431.0	431.0	430.8
$\sigma_{(5)}$	0.356	0.327	0.298	0.296	0.339	0.329
$E_{(5)}$	0.0444	0.0446	0.0429	0.0431	0.0446	0.0440
R^a	0.025	0.027	0.026	0.025	0.027	0.027
			Fluorescence			
$\lambda_{(1)}$	537.5	534.3	534.9	534.9	535.8	535.0
$\sigma_{(1)}$	0.169	0.150	0.150	0.149	0.152	0.147
$I_{(1)}$	0.983	0.991	0.993	0.986	0.984	0.980
$\lambda_{(2)}$	552.9	550.2	550.7	550.8	551.6	550.6
$\sigma_{(2)}$	0.0995	0.0765	0.0800	0.0800	0.0820	0.0824
$I_{(2)}$	0.212	0.176	0.180	0.180	0.181	0.189
$\lambda_{(3)}$	580.7	576.7	577.3	577.6	578.2	577.7
$\sigma_{(3)}$	0.294	0.253	0.248	0.249	0.250	0.256
$I_{(3)}$	0.543	0.511	0.521	0.506	0.528	0.504
$\lambda_{(4)}$	627.2	623.0	623.2	623.7	624.5	624.2
$\sigma_{(4)}$	0.481	0.435	0.445	0.448	0.461	0.437
$I_{(4)}$	0.132	0.118	0.119	0.117	0.124	0.116
$\lambda_{(5)}$	690.0	686.4	686.4	687.5	686.5	686.4
$\sigma_{(5)}$	0.332	0.267	0.275	0.245	0.244	0.250
$I_{(5)}$	0.0152	0.0131	0.0140	0.0125	0.0154	0.0132
R^a	0.014	0.017	0.017	0.017	0.018	0.017

[a] Residual $R = \sqrt{\int [E(\lambda)_{calc} - E(\lambda)_{exp}]^2 d\lambda \,/\, \int [E(\lambda)_{exp}]^2 d\lambda}$.

tal spectra (see Table I). The absorptivity *E* has to be replaced by the intensity *I* for the fluorescence spectra.

The parameters thus obtained are very similar for all acetals **4a**–**4d** and even for **5**. All bands of **3** are bathochromically shifted compared with **4** and **5**. The other parameters are also different from the parameters of the acetals. Therefore, the Gaussian analysis offers an efficient method to distinguish between acetals and the starting material employing only a small set of data.

EXPERIMENTAL

N-(2,3-Dihydroxypropyl)-N′-(1-hexylheptyl)perylene-2,3:9,10-bis(dicarboximide) (**3**): Perylene-3,4,9,10-tetracarboxylic acid 3,4-anhydride 9,10-(1-hexylheptylimide) (**2**; 101 mg, 183 μmol), 3-aminopropane-1,2-diol (64 mg, 700 μmol) and imidazole (10 g) were heated under argon to 105 °C for 4 h and quenched by addition of 2 M HCl (80 ml). The dark red precipitate was collected by vacuum filtration, dried at 100 °C in air and purified by column chromatography (silica gel, chloroform/ethanol 10:1). Yield 104 mg (92.0%) of **3**, m.p. > 250 °C. R_F (silica gel, chloroform/ethanol 5:1) 0.56. IR (KBr, cm^{-1}): 3436 m, 2925 m, 2855 m, 1697 s, 1656 s, 1594 s, 1578 m, 1507 w, 1438 m, 1404 m, 1343 s, 1251 m, 1171 w, 1127 w, 1106 w, 1035 w, 854 w, 810 m, 747 m, 432 w. ^{1}H NMR ($CDCl_3$, 300 MHz): 0.83 (t, *J* = 7, 6 H, CH_3); 1.16–1.43 (m, 16 H, CH_2); 1.81–1.97 (m, 2 H, N-CH-(C**H**H)$_2$); 2.18–2.32 (m, 2 H, N-CH-(CH**H**)$_2$); 2.80 (s br, 1 H, OH); 3.16 (s br, 1 H, OH); 3.63–3.78 (m, 2 H, CH(OH)-C**H**$_2$OH); 4.10–4.23 (m, 1 H, C**H**(OH)-CH_2OH); 4.40 (dd, ^2J = 14, ^3J = 5, 1 H, N-C**H**H-CH(OH)); 4.51 (dd, ^2J = 14, ^3J = 6.5, 1 H, N-C**H**H-CH(OH)); 5.10–5.25 (m, 1 H, N-C**H**-$(CH_2)_2$); 8.45–8.69 (m, 8 H, perylene). ^{13}C NMR ($CDCl_3$, 75 MHz): 14.1, 22.6, 27.0, 29.2, 31.8, 32.4, 42.9, 54.9, 63.9, 70.7, 122.4, 122.9, 123.3, 126.1, 126.3, 129.3, 131.8, 133.8, 135.1, 164.5. UV/VIS ($CHCl_3$, nm), λ_{max} (ε): 460 (16 800), 491 (44 700), 528 (73 700). Fluorescence ($CHCl_3$, nm), λ_{max}: 536, 579. Fluorescence quantum yield (λ_{exc} = 489 nm, *c* = 6.9 μmol l^{-1}, ref. *N,N′*-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide)) 100%. MS (70 eV), *m/z* (%): 646 (19) [M^+], 629 (8), 615 (11) [$M^+ - CH_3O$], 614 (10), 586 (6), 572 (11) [$M^+ - C_3H_6O_2$], 465 (18) [$M^+ - C_{13}H_{25}$], 446 (15), 433 (43) [$M^+ - C_{13}H_{26} - CH_3O$], 415 (12), 404 (100), 390 (68) [$M^+ - C_{13}H_{26} - C_3H_6O_2$], 373 (21), 345 (14), 207 (16), 55 (17), 44 (22). For $C_{40}H_{42}N_2O_6$ (646.8) calculated: 74.28% C, 6.55% H, 4.33% N; found: 73.96% C, 6.51% H, 4.29% N.

N-[(2-Ethyl-1,3-dioxolan-4-yl)methyl]-N′-(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**4b**): *N*-(2,3-Dihydroxypropyl)-*N′*-(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**3**; 29 mg, 45 μmol) was dissolved in chloroform (5 ml), propionaldehyde (0.10 ml, 1.8 mmol), *p*-toluenesulfonic acid monohydrate (one load of a microspatula) and anhydrous magnesium sulfate were added and stirred for 8 h. Magnesium sulfate was removed by filtration and the filtrate was evaporated. The residue was purified by column chromatography (alumina, chloroform/acetone 10:1). Yield 30 mg (96%) of **4b**, m.p. > 250 °C. R_F (silica gel, chloroform/acetone 10:1) 0.45. IR (KBr, cm^{-1}): 3436 m, 2927 m, 2857 m, 1698 s, 1659 s, 1595 s, 1579 w, 1507 w, 1465 w, 1437 w, 1405 m, 1344 s, 1252 w, 1175 w, 1126 w, 1108 w, 1084 w, 934 w, 853 w, 810 m, 748 m, 625 w, 431 w. ^{1}H NMR ($CDCl_3$, 300 MHz): 0.84 (t, *J* = 7, 6 H, CH_3); 0.95 (t, *J* = 7.5, 3 H, C**H**$_3$-CH_2); 0.98 (t, *J* = 7.5, 3 H, C**H**$_3$-CH_2); 1.16–1.48 (m,

16 H, CH_2); 1.62–1.70 (m, 2 H, CH_3-C**H**$_2$); 1.70–1.82 (m, 2 H, CH_3-C**H**$_2$); 1.82–1.98 (m, 2 H, N-CH-(C**H**H)$_2$); 2.07–2.35 (m, 2 H, N-CH-(CH**H**)$_2$); 3.79–3.86 (m, 1 H, C**H**HO); 3.97–4.00 (m, 2 H, C**H**HO + CH**H**O); 4.16–4.28 (m, 3 H, CH**H**O + 2 × N-C**H**H); 4.50–4.62 (m, 3 H, 2 × N-CH**H** + N-CH_2-C**H**); 4.62–4.71 (m, 1 H, N-CH_2-C**H**); 4.90 (t, J = 5, 1 H, OCHO); 5.11–5.26 (m, 2 H, N-C**H**-$(CH_2)_2$ + OC**H**O); 8.36–8.69 (m, 8 H, perylene). ^{13}C NMR ($CDCl_3$, 75 MHz): 7.9, 8.0, 14.0, 22.6, 27.0, 27.2, 29.2, 31.8, 32.4, 41.8, 43.1, 54.8, 68.3, 68.5, 73.5, 104.9, 106.3, 122.7, 122.8, 122.9, 123.0, 126.1, 126.2, 129.3, 129.4, 131.0, 131.4, 134.0, 134.6, 163.3. H,H-gDQCOSY-NMR (cross peaks): (0.8, 1.3), (1.3, 1.9, 2.3), (1.9, 2.3, 5.2), (1.0, 1.7), (1.0, 1.8), (1.7, 5.2), (1.8, 4.9), (3.8, 4.1, 4.2, 4.7) (4.0, 4.2, 4.6). C,H-gHSQC-NMR (cross peaks): (0.8, 14.0), (1.2–1.5 22.6, 27.0, 29.2, 31.9), (1.9, 2.3, 32.4), (5.2, 54.8), (0.95, 7.9), (0.98, 8.0), (1.7, 1.8, 27.2), (3.8, 4.0, 4.1, 68.3, 68.5), (4.2, 43.1), (4.6, 41.8), (4.5, 4.7, 73.5), (4.9, 106.3), (5.2, 104.9). UV/VIS ($CHCl_3$, nm), λ_{max} (ε): 458 (17 500), 490 (48 400), 526 (80 400). Fluorescence ($CHCl_3$, nm), λ_{max}: 533, 575. Fluorescence quantum yield (λ_{exc} = 489 nm, c = 8.9 μmol l^{-1}, ref. *N,N′*-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide)) 100%. MS (70 eV), *m/z* (%): 687 (39), 686 (100) [M^+], 657 (35), 628 (15) [$M^+ - C_3H_6O$], 572 (15) [$M^+ - C_6H_{10}O_2$], 505 (25) [$M^+ - C_{13}H_{25}$], 504 (12), 475 (12), 446 (21), 430 (20), 415 (14), 404 (18), 390 (54) [$M^+ - C_6H_{10}O_2 - C_{13}H_{26}$], 373 (12), 345 (9), 55 (6). For $C_{43}H_{46}N_2O_6$ (686.9) calculated: 75.19% C, 6.75% H, 4.08% N; found: 74.89% C, 6.94% H, 3.94% N.

N-(1-Hexylheptyl)-N′-[(1,3,5-trioxepan-6-yl)methyl]perylene-3,4:9,10-bis(dicarboximide) (**5**): *N*-(2,3-Dihydroxypropyl)-*N′*-(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**3**; 55 mg, 85 μmol) was dissolved in chloroform (5 ml). Aqueous formaldehyde solution (35%; 0.10 ml, 1.3 mmol), anhydrous magnesium sulfate and a catalytic amount of *p*-toluenesulfonic acid monohydrate were added. The mixture was stirred at room temperature for 8 h, filtered, evaporated in vacuo and purified by column chromatography (alumina, chloroform/acetone 5:1). The solubility of the product is lower than that of other perylenebisimide acetals. Yield 47 mg (80%) of **5**, m.p. > 250 °C. R_F (silica gel, chloroform/aceton 5:1) 0.42. IR (KBr, cm^{-1}): 3436 m, 2925 m, 2855 m, 1699 s, 1657 s, 1595 s, 1578 m, 1506 w, 1438 m, 1405 m, 1344 s, 1252 m, 1174 m, 1143 m, 1108 w, 1059 w, 994 w, 856 w, 810 m, 746 m, 617 w, 432 w. ^{1}H NMR ($CDCl_3$, 300 MHz): 0.83 (t, J = 7, 6 H, CH_3); 1.17–1.47 (m, 16 H, CH_2); 1.81–1.97 (m, 2 H, N-CH-(C**H**H)$_2$); 2.18–2.35 (m, 2 H, N-CH-(CH**H**)$_2$); 3.80 (dd, ^2J = 12.5, ^3J = 7.5, 1 H, C**H**HO); 4.07 (dd, ^2J = 12.5, ^3J = 1.7, 1 H, CH**H**O); 4.15 (dd, ^2J = 13.3, ^3J = 4.8, 1 H, N-C**H**H); 4.22–4.34 (m, 1 H, CH_2-C**H**O); 4.64 (dd, ^2J = 13.3, ^3J = 8.0, 1 H, N-CH**H**); 4.86 (d, J = 6.5, 1 H, OC**H**HO); 4.93 (d, J = 5.5, 1 H, OC**H**HO); 4.97 (d, J = 5.5, 1 H, OCH**H**O); 5.13 (d, J = 6.5, 1 H, OCH**H**O); 5.14–5.26 (m, 1 H, N-C**H**-$(CH_2)_2$); 8.40–8.77 (m, 8 H, perylene). ^{13}C NMR ($CDCl_3$, 75 MHz): 14.1, 22.6, 27.0, 29.2, 29.7, 31.8, 32.4, 40.2, 54.9, 71.3, 73.4, 90.9, 93.2, 122.8, 122.9, 123.1, 126.2, 126.3, 129.4, 129.5, 131.0, 131.5, 134.1, 134.8, 163.4. H,H-gDQCOSY-NMR (cross peaks): (0.83, 1.3), (1.3, 1.9, 2.3), (1.9, 2.3, 5.2), (3.80, 4.07, 4.3), (4.15, 4.3, 4.64), (4.86, 5.13). C,H-gHSQC-NMR (cross peaks): (0.83, 14.0), (1.2–1.5 22.6, 27.0, 29.2, 31.9), (1.9, 2.3, 32.4), (5.2, 54.8), (3.80, 4.07, 71.3), (4.15, 4.64, 40.2), (4.3, 76.3), (4.86, 5.13, 90.9), (4.93, 4.97, 93.2). UV/VIS ($CHCl_3$, nm), λ_{max} (E_{rel}): 458 (0.23), 490 (0.60), 527 (1.0). Fluorescence ($CHCl_3$, nm), λ_{max}: 534, 575. MS (70 eV), *m/z* (%): 688 (65) [M^+], 671 (11) [M^+ – O], 658 (24) [$M^+ - CH_2O$], 628 (33) [$M^+ - C_2H_4O_2$], 572 (6) [$M^+ - C_5H_8O_3$], 507 (46) [$M^+ - C_{13}H_{25}$], 477 (15), 446 (63) [$M^+ - C_{13}H_{26} - C_2H_4O_2$], 430 (37), 415 (33), 404 (50), 390 (100) [$M^+ - C_{13}H_{26} - C_5H_8O_3$], 373 (22), 345 (15), 73 (12), 55 (16). HR MS ($C_{43}H_{46}N_2O_6$) calculated: 688.3149, found: 688.3156.

N-(1-Hexylheptyl)-N′-[(2-phenyl-1,3-dioxolan-4-yl)methyl]perylene-3,4:9,10-bis(dicarboximide) (**4c**): *N*-(2,3-Dihydroxypropyl)-*N′*-(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**3**;

50 mg, 77 μmol) was dissolved in chloroform (5 ml). Benzaldehyde (0.2 ml, 2 mmol), anhydrous magnesium sulfate and a catalytic amount of *p*-toluenesulfonic acid monohydrate were added. The mixture was stirred at room temperature for 8 h, filtered and evaporated. Residual benzaldehyde was removed with *n*-pentane. The solid was collected by vacuum filtration and purified by column chromatography (alumina, chloroform/acetone 5:1). Yield 32 mg (56%) of **4c**, m.p. > 250 °C. R_F (silica gel, chloroform/acetone 10:1) 0.54. IR (KBr, cm^{-1}): 3436 m, 3067 w, 2954 m, 2926 m, 2856 m, 1698 s, 1658 s, 1595 s, 1579 m, 1508 w, 1458 m, 1437 m, 1405, 1343 s, 1252 m, 1219 w, 1175 m, 1126 w, 1107 m, 1088 m, 1071 m, 1027 w, 985 w, 915 w, 853 w, 811 m, 748 m, 698 w, 642 w, 624 w, 591 w, 490 w, 431 w. ^{1}H NMR ($CDCl_3$, 300 MHz): 0.83 (t, J = 7, 6 H, CH_3); 1.17–1.45 (m, 16 H, CH_2); 1.82–1.98 (m, 2 H, N-CH-(C**H**H)$_2$); 2.19–2.34 (m, 2 H, N-CH-(CH**H**)$_2$); 3.97–4.04 (m, 1 H, C**H**HO); 4.13–4.24 (m, 3 H, C**H**HO, CH**H**O, N-C**H**H); 4.32–4.44 (m, 2 H, CH**H**O, N-C**H**H); 4.66–4.95 (m, 4 H, 2 × N-CH_2-C**H** + 2 × N-CH**H**); 5.13–5.25 (m, 1 H, N-C**H**-$(CH_2)_2$); 5.83 (s, 1 H, C**H**-phenyl); 6.16 (s, 1 H, C**H**-phenyl); 7.31–7.42 (m, 3 H, phenyl); 7.47–7.52 (m, 1 H, phenyl); 7.52–7.61 (m, 1 H, phenyl); 8.38–8.68 (m, 8 H, perylene). ^{13}C NMR ($CDCl_3$, 75 MHz): 14.1, 22.6, 27.0, 29.2, 31.8, 32.4, 41.9, 42.9, 54.9, 68.6, 68.9, 74.0, 74.3, 103.4, 104.7, 122.8, 123.1, 126.2, 126.6, 126.9, 128.3, 128.4, 129.3, 129.4, 131.4, 134.1, 134.7, 137.2, 137.7, 163.4. H,H-gDQCOSY-NMR (cross peaks): (0.83, 1.3), (1.3, 1.9, 2.3), (1.9, 2.3, 5.2), (4.0, 4.4, 4.7), (4.2, 4.8). UV/VIS ($CHCl_3$, nm), λ_{max} (ε): 459 (18 000), 490 (49 600), 527 (82 800). Fluorescence ($CHCl_3$, nm), λ_{max}: 533, 576. Fluorescence quantum yield (λ_{exc} = 488 nm, c = 5.6 μmol l^{-1}, ref. *N,N′*-bis(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide)) 100%. MS (70 eV), *m/z* (%): 735 (50), 734 (100) [M^+], 628 (44) [$M^+ - C_7H_6O$], 612 (11), 572 (9) [$M^+ - C_{10}H_{10}O_2$], 553 (33) [$M^+ - C_{13}H_{25}$], 446 (57), 430 (59) [$M^+ - C_{13}H_{26} - C_7H_6O_2$], 415 (48), 404 (39), 390 (74) [$M^+ - C_{13}H_{26} - C_{10}H_{10}O_2$], 373 (21), 345 (14), 149 (22), 105 (25), 91 (47), 55 (20). For $C_{47}H_{46}N_2O_6$ (734.9) calculated: 76.82% C, 6.31% H, 3.81% N; found: 76.62% C, 6.38% H, 3.62% N.

N-(1-Hexylheptyl)-N′-{[(2-(3,4,5-trimethoxyphenyl)-1,3-dioxolan-4-yl]methyl}perylene-3,4:9,10-bis(dicarboximide) (**4d**): *N*-(2,3-Dihydroxypropyl)-*N′*-(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**3**; 56 mg, 87 μmol), 3,4,5-trimethoxybenzaldehyde (68 mg, 350 μmol), a catalytic amount of *p*-toluenesulfonic acid monohydrate and chloroform (5 ml) were allowed to react analogously to **4c** for 16 h. Yield 39 mg (55%) of **4d**, m.p. 182 °C. R_F (silica gel, chloroform/acetone 5:1) 0.33. IR (KBr, cm^{-1}): 3436 m, 2927 m, 2856 m, 1697 s, 1659 s, 1595 s, 1579 w, 1507 w, 1464 w, 1436 w, 1404 m, 1343 s, 1252 w, 1175 w, 1158 w, 1126 m, 1106 w, 1007 w, 852 w, 810 m, 748 m, 624 w, 431 w. ^{1}H NMR ($CDCl_3$, 300 MHz): 0.83 (t, J = 7, 6 H, CH_3); 1.16–1.45 (m, 16 H, CH_2); 1.82–1.98 (m, 2 H, N-CH-(C**H**H)$_2$); 2.18–2.35 (m, 2 H, N-CH-(CH**H**)$_2$); 3.79 (s, 3 H, O-CH_3); 3.83 (s, 3 H, O-CH_3); 3.85 (s, 6 H, O-CH_3); 3.93 (s, 6 H, O-CH_3); 3.97–4.04 (m, 1 H, C**H**HO); 4.11–4.25 (m, 3 H, C**H**HO, CH**H**O, N-C**H**H); 4.28–4.41 (m, 2 H, CH**H**O + N-C**H**H); 4.71–4.82 (m, 3 H, 2 × N-CH**H** + N-CH_2C**H**); 4.83–4.86 (m, 1 H, N-CH_2-C**H**); 5.12–5.26 (m, 1 H, N-C**H**-$(CH_2)_2$); 5.76 (s, 1 H, C**H**-phenyl); 6.08 (s, 1 H, C**H**-phenyl); 6.75 (s, 2 H, phenyl); 6.85 (s, 1 H, phenyl); 8.32–8.67 (m, 8 H, perylene). ^{13}C NMR ($CDCl_3$, 75 MHz): 14.0, 22.6, 27.0, 29.2, 31.9, 32.4, 41.9, 43.1, 53.8, 54.8, 56.1, 56.1, 60.7, 68.5, 68.4, 69.5, 73.9, 103.3, 103.5, 103.9, 104.7, 122.8, 123.1, 124.1, 126.2, 129.3, 129.4, 131.3, 132.4, 133.1, 133.9, 134.7, 138.7, 153.2, 153.3, 163.4. H,H-gDQCOSY-NMR (cross peaks): (0.83, 1.3), (1.3, 1.9, 2.3), (1.9, 2.3, 5.2), (4.0, 4.3, 4.8), (4.2, 4.7), (1.7, 5.2), (1.8, 4.9), (3.8, 4.1, 4.2, 4.7) (4.0, 4.2, 4.3, 4.6). C,H-gHSQC-NMR (cross peaks): (0.8, 14.0), (1.2–1.5 22.6, 27.0, 29.2, 31.9), (1.9, 2.3, 32.4), (5.2, 54.8), (3.79, 60.7), (3.83, 60.7), (3,85, 56.1), (3.93, 56.1), (4.0, 4.3, 69.6), (4.2, 69.9), (4.2, 4.7, 41.9), (4.3, 4.7, 43.1), (4.7,

4.9, 73.9), (5.76, 104.7), (6.08, 103.3), (6.75, 103.5), (6.85, 103.9). UV/VIS ($CHCl_3$, nm), λ_{max} (ε): 458 (17 700), 490 (49 200), 527 (82 500). Fluorescence ($CHCl_3$, nm), λ_{max}: 533, 576. Fluorescence quantum yield (λ_{exc} = 489 nm, *c* = 10.3 μmol l^{-1}, ref. *N,N′*-bis(1-hexylheptyl)-perylene-3,4:9,10-bis(dicarboximide)) 50%. MS (70 eV), *m/z* (%): 825 (52), 824 (100) [M^+], 642 (9) [$M^+ - C_{13}H_{26}$], 628 (23) [$M^+ - C_{10}H_{12}O_4$], 612 (10), 447 (20) [$M^+ - C_{13}H_{25} - C_{10}H_{12}O_4$], 430 (44), 415 (33), 404 (19), 390 (30) [$M^+ - C_{13}H_{26} - C_{13}H_{16}O_5$], 373 (12), 239 (26), 212 (21), 195 (29), 181 (18), 168 (22), 55 (15). For $C_{50}H_{52}N_2O_9$ (825.0) calculated: 72.80% C, 6.35% H, 3.40% N; found: 72.96% C, 6.43% H, 3.30% N.

Identification of traces of aldehydes: reaction of ***3*** *with acetaldehyde as the minor component; N-(1-hexylheptyl)-N′-[(2-methyl-1,3-dioxolan-4-yl)methyl]perylene-3,4:9,10-bis(dicarboximide)* (**4a**): *N*-(2,3-Dihydroxypropyl)-*N′*-(1-hexylheptyl)perylene-3,4:9,10-bis(dicarboximide) (**3**; 28 mg, 44 μmol) was dissolved in chloroform (5 ml) at 40 °C. 1 ml of a solution of acetaldehyde in chloroform (*c* = 18 mol l^{-1}, 18 μmol), anhydrous magnesium sulfate and a catalytic amount of *p*-toluenesulfonic acid monohydrate were added at room temperature. Samples were taken after 5, 15, 30 min, 2 h and 6 h and analyzed by TLC; the equilibrium was reached after 1 h. The mixture was filtered, evaporated and purified by column chromatography (alumina, chloroform/acetone 5:1). Yield 8 mg (66%) of **4a**. R_F (silica gel, chloroform/acetone 5:1) 0.65. IR (KBr, cm^{-1}): 3436 m, 2955 m, 2927 m, 2856 m, 1698 s, 1659 s, 1595 s, 1579 m, 1507 w, 1437 m, 1405 m, 1373 w, 1344 s, 1252 m, 1175 w, 1152 w, 1126 w, 1107 w, 1068 w, 854 w, 810 m, 748 m, 624 w, 431 w. ^{1}H NMR ($CDCl_3$, 400 MHz): 0.83 (t, *J* = 7, 6 H, CH_3); 1.18–1.42 (m, 19 H, C**H**$_2$ + CH-C**H**$_3$); 1.44 (d, *J* = 4.8, 3 H, CH-C**H**$_3$); 1.83–1.98 (m, 2 H, N-CH-(C**H**H)$_2$); 2.19–2.35 (m, 2 H, N-CH-(CH**H**)$_2$); 3.77–3.83 (m, 1 H, CH-C**H**HO); 3.91–3.98 (m, 1 H, CH-C**H**HO); 3.98–4.03 (m, 1 H, CH**H**O); 4.03–4.28 (m, 3 H, CH**H**O + 2 × N-C**H**H); 4.54–4.71 (m, 4 H, 2 × C**H**O + 2 × N-CH**H**); 5.06 (q, *J* = 4.8, 1 H, C**H**-CH_3); 5.13–5.24 (m, 1 H, N-C**H**-$(CH_2)_2$); 5.35 (q, *J* = 4.8, 1 H, C**H**-CH_3); 8.41–8.71 (m, 8 H, perylene). ^{13}C NMR ($CDCl_3$, 100 MHz): 14.0, 19.9, 20.1, 22.6, 26.8, 27.0, 29.2, 29.3, 29.7, 31.8, 32.4, 43.1, 43.2, 54.9, 67.9, 68.4, 68.6, 73.6, 73.7, 101.1, 102.5, 122.8, 122.9, 123.1, 126.2, 126.3, 129.4, 129.5, 131.4, 131.5, 134.1, 134.7, 163.4. H,H-gDQCOSY-NMR (cross peaks): (0.8, 1.3), (1.3, 1.9, 2.3), (1.9, 2.3, 5.2), (1.3, 5.3), (1.4, 5.0), (3.8, 4.2, 4.6), (3.9, 4.0, 4.5). UV/VIS ($CHCl_3$, nm), λ_{max} (E_{rel}): 459 (0.21), 490 (0.60), 527 (1.0). Fluorescence ($CHCl_3$, nm), λ_{max}: 532, 574. MS (70 eV), *m/z* (%): 686 (23), 672 (88) [M^+], 628 (21) [$M^+ - C_2H_4O$], 572 (16) [$M^+ - C_5H_8O_2$], 505 (12), 491 (27) [$M^+ - C_{13}H_{25}$], 446 (32) [$M^+ - C_{13}H_{26} - C_2H_4O$], 429 (19), 418 (14) [$M^+ - C_{13}H_{26} - C_3H_4O_2$], 404 (39), 390 (100) [$M^+ - C_{13}H_{26} - C_5H_8O_2$], 373 (18), 345 (12), 101 (11) [$(C_5H_9O_2)^+$], 55 (13).

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

REFERENCES

1. Langhals H.: *Helv. Chim. Acta* **2005**, *88*, 1309.
2. Langhals H.: *Heterocycles* **1995**, *40*, 477.
3. Langhals H., Jona W.: *Chem. Eur. J.* **1998**, *4*, 2110.
4. Langhals H., Jona W.: Eur. Pat. Appl. EP 896964 (July 15, 1998); *Chem. Abstr.* **1999**, *130*, 169525.
5. Mohr G. J., Spichiger U. E., Jona W., Langhals H.: *Anal. Chem.* **2000**, *72*, 1084.

6. Kaiser H., Lindner J., Langhals H.: *Chem. Ber.* **1991**, *124*, 529.
7. Langhals H., Demmig S., Potrawa T.: *J. Prakt. Chem.* **1991**, *333*, 733.
8. Langhals H., Saulich S.: *Chem. Eur. J.* **2002**, *8*, 5630.
9. Langhals H.: *Spectrochim. Acta, Part A* **2000**, *56*, 2207.
10. Langhals H.: *Anal. Bioanal. Chem.* **2002**, *374*, 573.