Pyrrolo- and Thiophenoperylenedicarboximides – Highly Fluorescent Heterocycles

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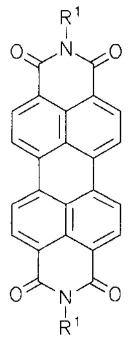
Pyrrolo- and thiophenoperylenedicarboximides **4** and **7** were prepared by reductive cyclization of 1-nitroperylenedicarboximides **3** and **5** with phosphorous acid esters and sulfur, respectively. The imides **4** and **7** are highly fluorescent and are easily monofunctionalized by nucleophilic substitution reactions which makes them useful for fluorescent labeling.

Perylene dyes (perylene-3,4,9,10-tetracarboxylic 3,4:9,10-diimides, **1**) are important pigments or fluorescent dyes[1–5], especially because of their photostability. A novel synthetic route[6] was recently developed for the similar perylene-3,4-dicarboximides (**2**). These dyes exhibit an even higher lightfastness than **1**. It is of interest to extend the chromophore of **2** by heterocyclic units and examine the effect of this on UV/Vis spectra and other properties. We therefore anellated pyrrole and thiophene rings at the positions 1 and 12 of **2**.



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1 - 7	R¹	R²
a	$CH(C_6H_{13})_2$	H
b	C_6H_3-2,5-(t-$C_4H_9)_2$	H
c	$CH(C_6H_{13})_2$	CH_3
d	$CH(C_6H_{13})_2$	$CH_2C_6H_5$
e	$CH(C_6H_{13})_2$	$COCH_3$
f	$CH(C_6H_{13})_2$	COC_6H_5
g	C_6H_3-2,5-(t-$C_4H_9)_2$	CH_3
h	C_6H_3-2,5-(t-$C_4H_9)_2$	COC_6H_5

Results and Discussion

Because the solubility of the extended perylene derivatives is very low, their synthesis, purification and investigation are difficult. To increase their solubility, the solubilizing 1-hexylheptyl (**a**)[7,8] or 2,5-di-*tert*-butylphenyl group (**b**)[9] was attached to the nitrogen atom of the starting material **2** according to ref.[1] either by a direct decarboxylating condensation of perylene-3,4,9,10-tetracarboxylic 3,4:9,10-dianhydride or via perylene-3,4-dicarboxylic anhydride.

2a or **2b** were nitrated[2] at position 1 (**3**) and reduced with triethyl phosphite (compare also ref.[10]) to the pyrrole derivative **4a** or **4b**, which exhibit brilliant colors and intense fluorescence both as solids (orange to red) and in solution (yellow). The UV/Vis spectra of **4a** are shown in Figure 1.

The thiophene-anellated dye **7b** was prepared by a reductive cyclization of the nitro compound **3b** with sulfur (compare "sulfur dyes"; see also ref.[11]) in 69% yield. **7b** is highly fluorescent both in solution (yellow) and in the solid state (orange to red) and exhibits a hypsochromic shift of 19 nm compared to **4**.

The dinitro compound **5a**[3] was prepared for a double anellation of five-membered rings. However, only one ring anellation proceeds with triethyl phosphite by reduction of the 1-nitro group. The 6-nitro group is also reduced, but forms the phosphoric amide ester **6a**. The twofold cyclization is probably inhibited by ring strain. Dye **6a**, however, is still of interest for analytical applications because of fluorescent labeling by transphosphorylation.

The dyes **4** with $R^2 = H$ may be reagents for fluorescent labeling in analytical applications because they can easily be monofunctionalized by a nucleophilic displacement reaction at the pyrrolo nitrogen atom (R^2), whereas the substituent at the imide nitrogen atom (R^1) can control the solubility. The labeling with **4a** and **4b** was demonstrated both for the alkylation with methyl iodide and benzyl chloride (**4c**, **4d**, and **4g**) and for the acylation with acetyl chloride and benzoyl chloride (**4e**, **4f** and **4h**). Both types of derivatives are highly fluorescent so that a sensitive fluorescent detection and determination of labeled alkyl and acyl groups are possible.

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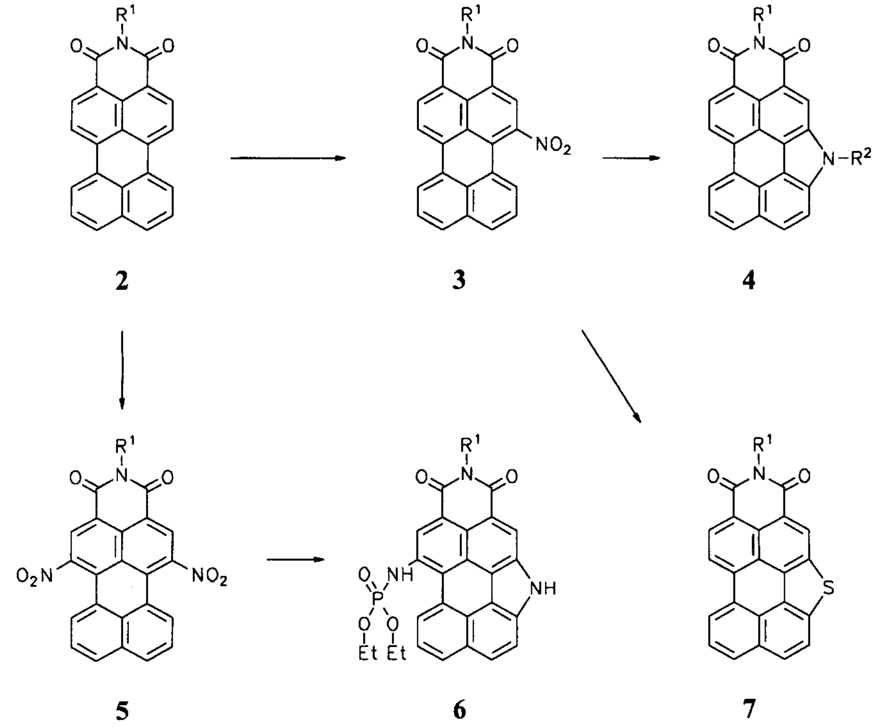
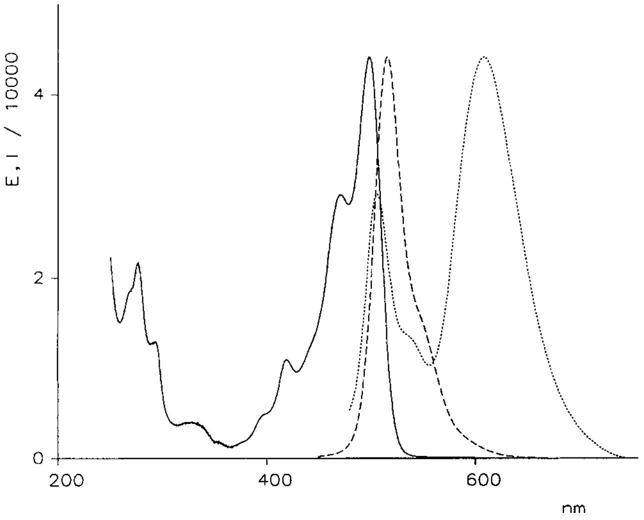


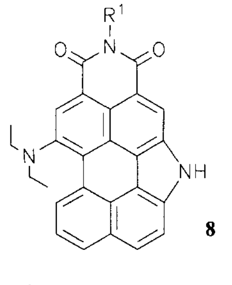
Figure 1. Absorption (———) (CHCl$_3$), fluorescence (– – –), and solid-state fluorescence (·····) spectra of **4a**



Experimental

IR: IFS 45, Bruker. – UV/Vis: OMEGA 20, Bruins Instruments. – Fluorescence spectra: FS 3000, Perkin-Elmer (excitation at the second vibration band of the UV/Vis absorption spectrum). – NMR: VXR 400S, Varian. MS: SN 1B, Varian MAT.

1-Hexylheptyl Derivative **4a**: *N*-(1-Hexylheptyl)-1-nitroperylene-3,4-dicarboximide (**3a**, 150 mg, 0.29 mmol)[4] was refluxed with triethyl phosphite (4 ml) under Ar until the color of the solution turned from red to orange-yellow (1.5 h). The solvent was removed in vacuo, and the residue was purified by column separation (silica gel/CHCl$_3$) to give 130 mg (93%) of **4a** as an orange powder with a strong solid-state fluorescence; m.p. >280°C, R_f (CHCl$_3$/silica gel): 0.36. – IR (KBr): $\tilde{\nu}$ = 3290 cm^{-1} (m), 3055 (w), 2956 (m), 2927 (m), 2857 (m), 1691 (m, C=O), 1679 (s, C=O), 1626 (s, C=O), 1601 (s), 1564 (m), 1557 (m), 1478 (w), 1458 (w), 1417 (m), 1392 (s), 1355 (m), 1321 (s), 1282 (m), 1200 (w), 1176 (w), 1128 (w), 1105 (w), 809 (s), 748 (m). – UV (CHCl$_3$): λ_{max} (lg ε) = 498 nm (4.646), 472 (4.467), 420 (4.055), 398 (3.732), 328 (3.663), 292 (4.127), 276 (4.343), 268 (4.278). – Fluorescence (CHCl$_3$): λ_{max} (I_{rel}) = 521 nm (1), 548 (0.36). – Solid-state fluorescence: λ_{max} = 617 nm. – ^{1}H NMR (CDCl$_3$): δ = 8.97 (br., 1 H), 8.75 (d, 1 H, J = 7.2 Hz), 8.69 (m, 2 H), 8.26 (d, 1 H, J = 7.8 Hz), 8.07 (br., 1 H), 7.92 (t, 1 H, J = 7.6 Hz), 7.88 (br., 1 H), 5.37 (m, 1 H, CHN), 2.32–2.37 (m, 2 H, CH$_2$), 1.92–1.97 (m, 2 H, CH$_2$), 1.23–1.44 (m, 16 H, CH$_2$), 0.81 (t, 6 H, CH$_3$, J = 6.9 Hz). – ^{13}C NMR (CDCl$_3$): δ = 164.09 (C=O), 135.01, 130.32, 128.82, 128.73, 128.73, 128.54, 127.93, 125.68, 125.06, 124.39, 124.06, 120.84, 117.07, 114.97, 54.52, 32.72 (br.), 31.84, 29.37, 27.15, 22.62, 14.05. – MS (70 eV), *m/z* (%): 518 (3), 517 (6), 516 (36) [M$^+$], 499 (4), 347 (4), 336 (7), 335 (38), 334 (100), 291 (2), 290 (3), 264 (4). – $C_{35}H_{36}N_2O_3$ (516.7): calcd. C 81.36, H 7.02, N 5.42; found C 81.05, H 6.89, N 5.19. – A second chromatographic fraction gave 5 mg (3%) of the diethylamino derivative **8** (R^1 = 1-hexylheptyl), R_f (CHCl$_3$/silica gel): 0.05. – UV (CHCl$_3$): λ_{max} (E_{rel}) = 530 nm (sh., 0.81), 500 (1), 467 (sh., 0.66), 418 (0.34). – Fluorescence (CHCl$_3$): λ_{max} (I_{rel}) = 516 nm (0.89), 570 (1). – MS (70 eV), *m/z* (%): 587 (1) [M$^+$], 560 (11), 559 (27), 542 (5), 532 (10), 531 (27), 514 (7), 379 (4), 378 (22), 377 (44), 351 (8), 350 (35), 349 (100), 304 (9). – $C_{39}H_{45}N_3O_2$ (587.4): calcd. 587.3512; found 587.3494 (MS).



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2,5-Di-tert-butylphenyl Derivative **4b**: 0.37 g (0.67 mmol) of *N*-(2,5-di-*tert*-butylphenyl)-1-nitroperylen-3,4-dicarboximide[5] (**3b**) was heated in triethyl phosphite (15 ml) for 3 h during which time the color of the solution turned from wine-red to orange-yellow. The solvent was removed in vacuo and the residue purified by column separation ($CHCl_3$/silica gel). 50 mg (14%) of the starting material was recovered (R_f = 0.89; $CHCl_3$/silica gel), and the main fraction (610 mg, R_f = 0.52) was further purified by a column separation with toluene/acetone (4 : 1), washed with *n*-pentane and collected with a glass filter (D5) to give 280 mg (80%) of **4b** as a red powder with an intense orange solid-state fluorescence; m.p. >360°C, R_f (toluene/acetone, 4 : 1; silica gel): 0.89. – IR (KBr): $\tilde{\nu}$ = 3270 cm^{-1} (m, NH), 3055 (w), 2962 (m, CH_3), 2933 (m, CH_3), 2870 (w, CH_3), 1697 (s, C=O), 1682 (s, C=O), 1644 (s), 1599 (s), 1563 (m), 1556 (m), 1479 (m), 1458 (m), 1417 (m), 1390 (s), 1355 (m), 1321 (s), 1289 (m), 1176 (m), 1126 (m), 1075 (m), 811 (m), 750 (m). – UV ($CHCl_3$): λ_{max} (lg ε) = 499 nm (4.654), 419 (4.027), 397 (br., 3.682). – Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 518 nm (1), 544 (0.28). – Solid-state fluorescence: λ_{max} (I_{rel}) = 518 nm (1), 638 (0.38). – ^1H NMR ($CDCl_3$): δ = 9.46 (br., 1 H, NH), 9.09 (s, 1 H), 8.91 (d, 1 H, *J* = 7.9 Hz), 8.89 (d, 1 H, *J* = 8.2), 8.86 (d, 1 H, *J* = 8.1), 8.34 (d, 1 H, *J* = 7.9), 8.18 (d, 1 H, *J* = 7.8), 8.00 (t, 1 H, *J* = 7.8), 7.95 (d, 1 H, *J* = 8.8 Hz), 7.63 (d, 1 H, *J* = 8.5 Hz), 7.48 (dd, 1 H, J_1 = 2.2, J_2 = 8.5 Hz), 7.12 (d, 1 H, *J* = 2.3 Hz), 1.54 [s, 9 H, $C(CH_3)_3$], 1.34 [s, 9 H, $C(CH_3)_3$]. – MS (70 eV), *m/z* (%): 523 (2), 522 (6) [M^+], 505 (3), 467 (7), 466 (37), 465 (100), 451 (4), 450 (10), 449 (21), 264 (4), 205 (14). – $C_{36}H_{30}N_2O_2 \cdot 0.5\ H_2O$ (531.6): calcd. C 81.34, H 5.88, N 5.27; found C 81.57, H 5.98, N 5.36.

Dye **6a**: *N*-(1-Hexylheptyl)-1,6-dinitroperylene-3,4-dicarboximide[7] (**5a**, 50 mg, 80 μmol) was refluxed with triethyl phosphite (5 ml) for 100 min during which time the color changed from wine-red to orange, and no starting material could be detected by TLC ($CHCl_3$/silica gel). The solvent was removed in vacuo. A little toluene was added to the residue and removed in vacuo to eliminate traces of triethyl phosphite. The orange-colored residue consisting of several compounds was purified by column separation (chloroform/silica gel). The main fraction was concentrated, the residue was washed with pentane, dissolved in chloroform, the solution was filtered through a glass filter (D5) and concentrated to give 20 mg (45%) of **6a** as a light red powder with a strong, red solid-state fluorescence; m.p. 96–98°C (dec.), R_f ($CHCl_3$/silica gel): 0.11. – IR (KBr): $\tilde{\nu}$ = 3280 cm^{-1} (m, br., NH), 2957 (w, CH_3) 2927 (m, CH_2), 2856 (w, CH_2), 1691 (m, C=O), 1680 (s, C=O), 1646 (m), 1636 (m), 1594 (m), 1557 (w), 1483 (w), 1420 (m), 1394 (m), 1294 (s), 1233 (w), 1208 (w), 1052 (m, br.), 1029 (m, br.), 978 (w), 811 (m). – UV ($CHCl_3$): λ_{max} (E_{rel}) = 501 nm (0.94), 474 (0.62), 424 (0.36), 278 (0.85), 252 (1). – Fluorescence ($CHCl_3$): λ_{max} = 526 nm. – Solid-state fluorescence: λ_{max} = 697 nm. – ^1H NMR ($CDCl_3$): δ = 11.08 (br., 1 H, NHP), 9.60 (br., 1 H), 8.83 and 8.77 (1 H), 8.68 (m, 2 H), 7.97 and 7.92 (1 H), 7.53 (d, 1 H, *J* = 8.1 Hz), 7.25 (d, 1 H, *J* = 8.3 Hz), 6.55 (br., 1 H, NH), 5.34 (m, 1 H, CHN), 4.63 (m, 4 H, OCH_2), 2.39 (m, 2 H, CH_2), 2.11 (m, 2 H, CH_2), 1.65 (t, 6 H, CH_2CH_3), 1.46–1.32 (m, 16 H, CH_2), 0.85 (t, 6 H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 166.26 (C=O), 165.35 (C=O), 164.50 (C=O), 134.02, 133.20, 129.53, 127.97, 127.69, 127.63, 126.92, 126.38, 124.95, 123.52, 121.95, 121.57, 120.83, 119.97, 119.55, 118.11, 117.31, 115.20, 113.76, 64.21 ($POCH_2$), 64.13 ($POCH_2$), 54.54 (CHN), 54.25 (CHN), 32.82 (CH_2), 31.95 (CH_2), 29.50 (CH_2), 27.48 (CH_2), 22.68 (CH_2), 16.67 ($POCH_2CH_3$), 16.58 ($POCH_2CH_3$), 14.09 (CH_3). – MS (70 eV), *m/z* (%): 426 (4), 425 (31), 424 (100) [$M^+ - C_{13}H_{26} - C_2H_5O_2$], 382 (5), 324 (14), 323 (63), 322 (11), 296 (6), 295 (15), 278 (6). – MS (FAB, matrix: 3-nitrobenzyl alcohol), *m/z* (%): 669 (3), 668 (12), 667 (15) [M^+], 666 (4), 486 (2), 485 (3) [$M^+ - C_{13}H_{16}$], 350 (7), 349 (6). – $C_{39}H_{46}N_3O_5P$: calcd. 667.3175; found 667.3118 (MS).

Dye **4c**: To a dispersion of **4a** (60 mg, 0.12 mmol) in anhydrous ethanol (5 ml), sodium methoxide was added (30 mg, 0.56 mmol). The mixture was refluxed for 1 h, the solvent was evaporated, and the remaining red-violet sodium salt was dissolved in *N*-methylpyrolidone (5 ml). Methyl iodide (0.20 ml, 3.2 mmol) was added to the solution, and the mixture was stirred for 2 h. The solvent was removed in vacuo, the residue was dispersed in distilled water, and the orange-yellow solid was collected by vacuum filtration, dried at 120°C and purified by column separation ($CHCl_3$/silica gel) to give 60 mg (96%) of **4c** as an orange-red powder with a dark orange solid-state fluorescence; m.p. 180–181°C, R_f ($CHCl_3$/silica gel): 0.88. – IR (KBr): $\tilde{\nu}$ = 3055 cm^{-1} (w, Ar), 2955 (m, CH_2), 2926 (s, CH_2), 2855 (m, CH_3), 1693 (m, CO), 1680 (s, CO), 1643 (s, CO), 1596 (m), 1562 (w), 1556 (w), 1548 (w), 1482 (w), 1458 (w), 1415 (w), 1395 (m), 1367 (m), 1328 (s), 1313 (s), 1210 (w), 1127 (w), 806 (s), 747 (m). – UV ($CHCl_3$): λ_{max} (lg ε) = 504 nm (4.633), 476 (4.444), 438 (4.149), 411 (3.785), 330 (br., 3.568), 297 (4.055), 282 (4.055), 282 (4.270), 274 (4.230). – Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 524 nm (1), 550 (0.36), 595 (br., 0.04). – Solid-state fluorescence: λ_{max} = 619 nm. – ^1H NMR ($CDCl_3$): δ = 8.56 (br., 2 H), 8.42 (d, 1 H, *J* = 7.6 Hz), 8.36 (d, 1 H, *J* = 8.0 Hz), 7.98 (d, 1 H, *J* = 8.1 Hz), 7.81 (d, 1 H, *J* = 8.9 Hz), 7.73 (t, 1 H, *J* = 7.8 Hz), 7.43 (d, 1 H, *J* = 8.8 Hz), 5.36 (m, 1 H, CHN), 4.08 (s, 3 H, NCH_3), 2.40 (m, 2 H, CH_2), 2.00 (m, 2 H, CH_2), 1.57–1.26 (m, 16 H, CH_2), 0.85 (t, 6 H, *J* = 6.9 Hz, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 165.6 (C=O), 136.01, 131.53, 128.12, 127.90, 127.83, 127.46, 125.03, 124.37, 123.49, 120.65, 120.20, 115.54, 112.66, 54.40 (CHN), 32.75 (CH_2), 31.91 (CH_2), 31.40 (CH_3N), 29.42 (CH_2), 27.24 (CH_2), 22.67 (CH_2), 14.08 (CH_3). – MS (70 eV), *m/z* (%): 531 (15), 530 (37) [M^+], 514 (4), 513 (10.1), 361 (4), 350 (7), 349 (36), 348 (100), 331 (6), 304 (6), 303 (9), 277 (4). – $C_{36}H_{38}N_2O_2$ (530.7): calcd. C 81.47, H 7.22, N 5.28; found C 81.23, H 7.70, N 5.11.

Dye **4f**: To a solution of **4a** (50 mg, 0.10 mmol) in acetone (10 ml) 85% KOH powder was added (50 mg, 0.9 mmol). During the addition a color change from yellow-orange to red occurred, and the mixture was heated at reflux for 30 min. Benzoyl chloride (77 μl, 1.0 mmol) was added to the hot solution the color of which changed to yellow again. The mixture was further refluxed for 1 h, cooled to room temp. and hydrolyzed with distilled water (10 ml). The precipitated solid was collected by vacuum filtration, washed with water, dried in a drying cabinet at 120°C and purified by column separation (chloroform/silica gel) to give 50 mg (83%) of **4f** as an orange powder with a brilliant red solid-state fluorescence; m.p. 268–269°C, R_f ($CHCl_3$/silica gel): 0.89. – IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1} (w, CH_2), 2925 (m, CH_2), 2855 (w, CH_3), 1693 (s, C=O), 1646 (s, C=O), 1602 (m), 1550 (w), 1468 (w), 1456 (w), 1392 (w), 1380 (w), 1358 (m), 1315 (m), 1323 (s), 1308 (s), 1262 (s), 1204 (w), 955 (w), 814 (m), 748 (m), 725 (w), 700 (w), 665 (w). – UV ($CHCl_3$): λ_{max} (lg ε) = 492 nm (4.582), 465 (4.460), 403 (4.207), 382 (3.846), 284 (4.480), 272 (4.462). – Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 514 nm (1), 542 (0.43). – Solid-state fluorescence: λ_{max} = 594 nm. – ^1H NMR ($CDCl_3$): signal doubling by two conformers in a ratio of 58 : 42 (20°C) marked as [a] and [b]; δ = 8.52[a] (br., 1 H), 8.44[a] (br.), 8.37[a] (br.), 8.27 (d, 1 H, *J* = 7.7 Hz), 8.25 (d, 1 H, *J* = 8.1 Hz), 7.92 (d, 1 H, *J* = 8.2 Hz), 7.89 (d, 2 H, *J* = 7.1 Hz), 7.81 (t, 1 H, *J* = 7.3 Hz), 7.70–7.64 (m, 4 H), 7.41[b] (d, br., *J* = 8.2 Hz), 7.32[b] (d, br.), 5.25 (m, 1 H, CHN), 2.32–2.25 (m, 2 H, CH_2), 1.94–1.91 (m, 2 H, CH_2), 1.35–1.25 (m, 16 H, CH_2), 0.84 (t, 6 H, CH_3, *J* = 6.7 Hz). – ^{13}C NMR ($CDCl_3$): δ = 169.44 (PhC=O), 163.05 (C=O), 162.50 (C=O), 135.29, 135.22, 135.04, 134.25, 133.12, 131.38, 129.86, 129.28, 129.09, 128.67, 128.51 (br.), 128.03, 126.83, 125.92, 123.90, 123.16, 121.01, 120.90, 118.64, 117.99 (br.), 54.55 (CHN), 32.60 (CH_2), 31.85 (CH_2), 29.35 (CH_2), 27.17 (CH_2), 22.63 (CH_2), 14.06 (CH_3). – MS (70 eV), *m/z* (%): 622 (4), 621 (18), 620 (36) [M^+], 604 (5), 603 (11) [M^+ – OH], 451 (4) [M^+ – $C_{12}H_{25}$], 440 (8), 439 (34), 438 (68) [M^+ – $C_{13}H_{26}$], 421 (2) [438 – OH], 335 (3), 334 (5) [438 – PhC=O], 105 (100) [PhC=O^+]. – $C_{42}H_{40}N_2O_3$ (620.8): calcd. C 81.26, H 6.49, N 4.51; found C 81.25, H 6.69, N 4.71. – 10 mg (15%), of **4a** was recovered.

Dye **4e**: Dye **4a** (70 mg, 0.14 mmol), acetone (10 ml), KOH powder (70 mg, 1.3 mmol), and acetyl chloride (90 µl, 1.3 mmol) were allowed to react and worked up as described for **4f**. The oily reaction product was extracted (chloroform) and purified by column separation (chloroform/silica gel) to give 40 mg of **4e** as an orange powder with a bright red solid-state fluorescence; m. p. 202–203 °C, R_f ($CHCl_3$/silica gel): 0.68. – IR (KBr): $\tilde{\nu}$ = 2955 cm^{-1} (m), 2927 (s), 2856 (m), 1711 (s, C=O), 1693 (s, C=O), 1669 (m, C=O), 1646 (s, br.), 1602 (m), 1554 (w), 1469 (w), 1457 (w), 1410 (w), 1385 (m), 1370 (s), 1324 (s), 1308 (m), 1263 (m), 1243 (w), 1225 (w), 1111 (w), 1027 (w), 975 (w), 845 (w), 814 (m), 747 (s). – UV ($CHCl_3$): λ_{max} (lg ε) = 496 nm (4.550), 470 (4.432), 404 (4.135), 383 (3.782), 328 (3.556), 281 (4.340), 261 (4.373), 255 (4.368). – Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 520 nm (1), 544 (sh., 0.43). – Solid-state fluorescence: λ_{max} (I_{rel}) = 612 nm (1), 681 (0.13). – ^1H NMR ($CDCl_3$): δ = 8.39 and 8.27 (2 H, br.), 7.87 (d, 1 H, *J* = 7.5 Hz), 7.83 (s, 1 H, *J* = 8.1 Hz), 7.69 (d, 1 H, *J* = 8.0 Hz), 7.60 (br., 1 H), 7.48 (d, 1 H, *J* = 7.9 Hz), 7.43 (d, 1 H, *J* = 7.8 Hz), 5.25 (m, 1 H, CHN), 2.75 (s, 3 H, CH_3C=O), 2.32–2.28 (m, 2 H, CH_2), 2.03–1.99 (m, 2 H, CH_2), 1.43–1.31 (m, 16 H, CH_2), 0.88 (t, 6 H, *J* = 6.8 Hz, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 169.53 (CH_3C=O), 165.72 (C=O), 164.72 (C=O), 163.80 (C=O), 134.10, 133.61 (br.), 130.84, 129.54, 129.17, 128.79, 128.37, 127.74, 127.59, 126.45, 124.97, 123.26, 122.64, 122.01, 120.34, 120.11 (br.), 119.83, 119.37, 117.68 (br.), 117.30, 54.56 (CH-N), 32.66 (CH_2), 31.91 (CH_2), 29.38 (CH_2), 27.30 (CH_2), 25.64 (CH_3C=O), 22.68 (CH_2), 14.09 (CH_3). – MS (70 eV), *m/z* (%): 560 (7), 559 (33), 558 (79) [M^+], 542 (6), 541 (15) [M^+ – OH], 473 (4) [M^+ – C_3H_{13}], 389 (5) [M^+ – $C_{12}H_{25}$], 378 (9), 377 (47), 376 (100) [M^+ – $C_{13}H_{26}$], 336 (6), 335 (34), 334 (80) [376 – CH_2=C=O], 317 (9) [334 – OH], 290 (10), 289 (14) [334 – HCO_2]. – $C_{37}H_{38}N_2O_2$ (558.8): calcd. C 79.54, H 6.86; found C 79.66, H 6.94. – 30 mg (43%) of the starting material **4a** was recovered.

Dye **4d**: Dye **4a** (70 mg, 0.13 mmol), sodium methoxide (30 mg, 0.56 mmol), and benzyl chloride (70 µl, 0.63 mmol) were allowed to react and worked up as described for **4c**. The reaction product was purified by column separation (toluene/silica gel) to give 60 mg (73%) of **4d** as a dark red powder with a medium strong solid-state fluorescence; m. p. 139–141 °C, R_f ($CHCl_3$/silica gel): 0.88. – IR (KBr): $\tilde{\nu}$ = 2968 cm^{-1} (m, CH_2), 2925 (m, CH_2), 2856 (w, CH_3), 1678 (s, C=O), 1643 (s, br., C=O), 1598 (m), 1564 (w), 1545 (w), 1476 (w), 1457 (w), 1417 (w), 1394 (m), 1365 (w), 1311 (m, br.), 1238 (w), 1170 (w), 806 (m), 747 (m), 702 (w), 668 (m). – UV ($CHCl_3$): λ_{max} (lg ε) = 503 nm (4.610), 475 (4.427), 435 (4.140), 409 (sh, 3.789), 329 (br., 3.580), 297 (4.080), 282 (4.269), 273 (4.254). – Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 522 nm (1), 549 (0.34). – Solid-state fluorescence: λ_{max} = 614 nm. – ^1H NMR ($CDCl_3$): δ = 8.58 (s, 1 H), 8.51 (br., 1 H), 8.27 (d, 1 H, *J* = 7.7 Hz), 8.23 (d, 1 H, *J* = 8.0 Hz), 7.96 (d, 1 H, *J* = 8.0 Hz), 7.72 (d, 1 H, *J* = 8.9 Hz), 7.63 (t, 1 H, *J* = 7.8 Hz), 7.34 (d, br., 1 H, *J* = 8.9 Hz), 7.30–7.23 (m, 3 H), 7.19–7.16 (m, 2 H), 5.57 (s, 2 H, CH_2N), 5.37 (m, 1 H, CHN), 2.40–2.35 (m, 2 H, CH_2), 2.11–2.01 (m, 2 H, CH_2), 1.48–1.26 (m, 16 H, CH_2), 0.96 (t, 6 H, CH_3, *J* = 6.9 Hz). – ^{13}C NMR ($CDCl_3$): δ = 166.91 (C=O), 165.98 (C=O), 165.69 (C=O), 164.82 (C=O), 136.79, 135.68, 134.07, 131.21, 129.01, 128.55, 128.22, 128.15, 127.94, 127.84, 127.38, 127.10, 125.09, 124.45, 123.47, 123.39, 120.74, 120.48, 120.20, 119.71, 119.03, 118.24, 115.84, 113.19, 54.45 (N-CH), 49.56 (CH_2Ph), 33.72 (CH_2), 32.79 (CH_2), 31.87 (CH_2), 29.41 (CH_2), 27.27 (CH_2), 22.69 (CH_2), 14.06 (CH_3). – MS (70 eV), *m/z* (%): 608 (8), 607 (38), 606 (82) [M^+], 590 (5), 589 (11) [M^+ – OH], 437 (4) [M^+ – $C_{12}H_{25}$], 426 (11), 425 (52), 424 (100) [M^+ – $C_{13}H_{26}$], 334 (5) [424 – PhCH_2], 333 (6), 91 (27) [$C_7H_7^+$]. – $C_{42}H_{42}N_2O_2$ (606.8): calcd. C 83.13, H 6.98, N 4.62; found C 83.02, H 7.30, N 4.38. – 10 mg (14%) of **4a** was recovered.

Dye **4g**: Dye **4b** (70 mg, 0.13 mmol), potassium *tert*-butoxide (30 mg, 0.26 mmol), and methyl iodide (150 µl, 3.25 mmol) were allowed to react and worked up as described for **4c**. The reaction product was then further purified by column separation (chloroform/silica gel) and extractively recrystallized[12] from pentane and then from methanol to give 50 mg (70%) of **4g** as an orange powder with a strong solid-state fluorescence; m.p. >360 °C, R_f ($CHCl_3$/silica gel): 0.48. – IR (KBr): $\tilde{\nu}$ = 2963 cm^{-1} (w, CH_3), 2890 (ww, CH_3), 1698 (s, C=O), 1683 (s, C=O), 1652 (s), 1594 (m), 1563 (w), 1555 (w), 1483 (w), 1415 (w), 1393 (m), 1365 (m), 1332 (m), 1315 (m), 1215 (w), 1169 (w), 808 (m), 749 (m). – UV ($CHCl_3$): λ_{max} (lg ε) = 505 nm (4.629), 476 (4.429), 438 (4.120), 411 (3.763), 353 (3.230), 324 (3.519), 296 (4.007), 282 (4.195), 273 (4.186). – Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 522 nm (1), 552 (0.34). – Solid-state fluorescence: λ_{max} = 615 nm. – ^1H NMR ($CDCl_3$): δ = 9.02 (s, 1 H), 8.87 (d, 1 H, *J* = 7.4 Hz), 8.85 (d, 1 H, *J* = 7.9 Hz), 8.82 (d, 1 H, *J* = 8.1 Hz), 8.32 (d, 1 H, *J* = 8.0 Hz), 8.15 (d, 1 H, *J* = 8.9 Hz), 7.97 (t, 1 H, *J* = 7.7 Hz), 7.87 (d, 1 H, *J* = 8.8 Hz), 7.63 (d, 1 H, *J* = 8.5 Hz), 7.48 (dd, 1 H, *J* = 8.4/2.3 Hz), 7.14 (d, 1 H, *J* = 2.3 Hz), 4.44 (s, 3 H, CH_3), 1.37 [s, 9 H, C(CH_3)$_3$], 1.34 [s, 9 H, C(CH_3)$_3$]. – ^{13}C NMR ($CDCl_3$): δ = 166.93 (C=O), 165.60 (C=O), 149.88, 143.87, 137.00, 135.39, 134.14, 132.28, 128.69, 128.65, 128.59, 128.17, 128.15, 128.06, 125.89, 125.54, 125.42, 124.43, 124.32, 121.94, 121.52, 120.88, 120.58, 120.19, 119.85, 118.96, 118.65, 117.92, 116.51, 115.64, 113.42, 41.06 (N-CH_3), 34.27 (C(CH_3)$_3$), 32.11 (C(CH_3)$_3$), 31.81 (C(CH_3)$_3$), 31.32 (C(CH_3)$_3$). MS (70 eV), *m/z* (%): 538 (2), 537 (7), 536 (16) [M^+], 519 (3) [M^+ – OH], 481 (7), 480 (36), 479 (100) [M^+ – C_4H_9], 465 (3), 464 (10), 463 (19) [479 – OH], 277 (2). – $C_{37}H_{32}N_2O_2$: calcd. 536.2464; found 536.2472 (MS). – $C_{37}H_{32}N_2O_2$ (536.7): calcd. N 5.22; found N 5.26. – 5 mg (7%) of **4b** was recovered.

Dye **4h**: Dye **4b** (80 mg, 0.15 mmol), KOH powder (0.11 g, 2.0 mmol), and benzoyl chloride (300 µl, 2.60 mmol) were allowed to react and worked up as described for **4e**. The reaction product was further purified by extractive[1] recrystallization from methanol to give 40 mg (43%) of **4h** as an orange powder with a strong solid-state fluorescence; m. p. 179–181 °C, R_f ($CHCl_3$/silica gel): 0.36. – IR (KBr): $\tilde{\nu}$ = 3055 cm^{-1} (w), 2963 (m, CH_3), 2835 (w, CH_3), 1703 (s, C=O), 1679 (s, C=O), 1660 (s, C=O), 1601 (m), 1552 (m), 1468 (m), 1449 (w), 1409 (m), 1382 (s), 1357 (s), 1328 (s), 1263 (s), 1207 (w), 1178 (w), 955 (m), 836 (w), 816 (s), 757 (s), 750 (s), 730 (m), 700 (m), 668 (m). – UV ($CHCl_3$): λ_{max} (lg ε) = 488 nm (4.546), 461 (4.420), 437 (sh, 4.094), 402 (4.014), 382 (3.702). – Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 508 nm (1), 536 (0.48). – ^1H NMR ($CDCl_3$): δ = 8.74 (d, 1 H, *J* = 7.9 Hz), 8.59 (d, 1 H, *J* = 7.5 Hz), 8.56 (d, 1 H, *J* = 8.0 Hz), 8.46 (s, 1 H), 8.14 (d, 1 H, *J* = 8.1 Hz), 7.94 (d, 1 H, *J* = 8.8 Hz), 7.91 (d, 1 H), 7.90 (d, 1 H), 7.87 (t, 1 H, *J* = 7.9 Hz), 7.77 (dd, 2 H, *J* = 1.2/8.8 Hz), 7.72 (d, 1 H, *J* = 8.9 Hz), 7.65 (d, 2 H, *J* = 7.7 Hz), 7.59 (d, 1 H, *J* = 8.7 Hz), 7.45 (dd, 1 H, *J* = 2.2/8.6 Hz), 7.14 (d, 1 H, *J* = 2.3 Hz), 1.36 [s, 9 H, C(CH_3)$_3$]. 1.29 [s, 9 H, C(CH_3)$_3$]. – ^{13}C NMR ($CDCl_3$): δ = 169.71 (PhC=O), 165.74 (C=O), 164.93 (C=O), 149.92, 143.69, 136.04, 135.80, 134.22, 133.65, 133.19, 131.59, 130.25, 130.18, 130.15, 129.45, 129.19, 129.09, 129.03, 128.71, 128.46, 128.29, 127.99, 127.16, 126.61, 126.00, 124.69, 124.46, 122.99, 121.35, 120.51, 120.23, 119.12, 118.44, 35.55 $[C(CH_3)_3]$, 34.27 $[C(CH_3)_3]$, 31.77 $[C(CH_3)_3]$, 31.30 $[C(CH_3)_3]$. – MS (70 eV), *m/z* (%): 627 (3), 626 (8) $[M^+]$, 571 (5), 570 (39), 569 (100) $[M^+ - C_4H_9]$, 465 (6) [569 – PhC=O], 449 (7), 434 (8), 297 (9), 262 (4) $[465 - CO_2 - HCN]$, 105 (97) [PhC=O]. – $C_{43}H_{34}N_2O_3$: calcd. 626.2569; found 626.2478 (MS). – $C_{43}H_{34}N_2O_3$ (626.8): calcd. H 5.47, N 4.47; found H 5.81, N 4.28. – 40 mg (50%) of **4b** was recovered.

Dye **7b**: Sulfur (250 mg, 7.8 mmol) was dispersed in DMF (30 ml), and the dispersion was heated at reflux until a homogeneous solution had formed which was cooled. A solution of **3b** (60 mg, 0.11 mmol) in DMF (12 ml) was added, and the solution was heated at 125–130°C for 30 h. The solvent was removed in vacuo (12 Torr) and the orange-red residue purified by column separation (chloroform/silica gel). Remaining sulfur was removed by a column separation with petroleum ether (silica gel). The dye **7b** was eluted with acetone and then extractively recrystallized[2] from methanol to give 40 mg (69%) of **7b** as orange-red crystals with a strong solid-state fluorescence; m.p. >360°C. R_f ($CHCl_3$/silica gel) = 0.69. – UV ($CHCl_3$): λ_{max} (lg ε) = 480 nm (4.570), 452 (4.438), 413 (4.144), 392 (3.749), 293 (4.260), 274 (4.359). – Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 498 nm (1), 527 (0.48). – ^1H NMR ($CDCl_3$): δ = 9.21 (s, 1 H), 8.77 (d, 1 H, *J* = 8.0 Hz), 8.64 (d, 1 H, *J* = 7.6 Hz), 8.61 (d, 1 H, *J* = 8.1 Hz), 8.20 (d, 1 H, *J* = 7.9 Hz), 8.12 (d, 1 H, *J* = 7.9 Hz), 8.07 (d, 1 H, *J* = 9.0 Hz), 7.90 (t, 1 H, *J* = 7.8 Hz), 7.63 (d, 1 H, *J* = 7.6 Hz), 7.50 (dd, 1 H, *J* = 8.7/2.2 Hz), 7.17 (d, 1 H, *J* = 2.1 Hz), 1.39 [s, 9 H, $C(CH_3)_3$], 1.33 [s, 9 H, $C(CH_3)_3$]. – ^{13}C NMR ($CDCl_3$): δ = 165.54 (C=O), 165.07 (C=O), 150.02, 143.83, 139.54, 135.56, 133.72, 133.48, 133.26, 130.47, 129.74, 128.79, 128.76, 128.64, 128.51, 127.98, 127.95, 126.88, 126.71, 126.60, 126.15, 125.09, 123.59, 123.28, 121.96, 120.76, 120.58, 120.45, 35.60 $[C(CH_3)_3]$, 34.31 $[C(CH_3)_3]$, 31.80 $[C(CH_3)_3]$, 31.33 $[C(CH_3)_3]$. – MS (70 eV), *m/z* (%): 540 (5), 539 (14) $[M^+]$, 485 (2), 484 (11), 483 (35), 482 (100) $[M^+ - C_4H_9]$, 468 (4), 467 (8), 466 (15), 452 (2), 450 (3). – $C_{36}H_{29}NO_2S$: calcd. 539.1919; found 539.1919 (MS). – Some violet 1-amino-*N*-(1-hexylheptyl)perylene-3,4-dicarboximide was obtained from the first column separation as a by-product with a lower R_f value. – R_f ($CHCl_3$/silica gel): 0.29. – UV ($CHCl_3$): λ_{max} (E_{rel}) = 534 (1), 507 (0.792), 407 (0.292), 276 (0.997). – Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 592 (1). – ^1H NMR ($CDCl_3$): δ = 8.79 (d, 1 H, *J* = 7.7 Hz), 8.48 (d, 1 H, *J* = 7.9 Hz), 8.39 (d, 1 H, *J* = 8.2 Hz), 8.39 (d, 1 H, *J* = 6.7 Hz, br.), 7.90 (d, 1 H, *J* = 7.9 Hz), 7.81 (d, 1 H, *J* = 8.1 Hz), 7.66 (t, 1 H, *J* = 7.8 Hz), 7.61 (t, 1 H, *J* = 7.8 Hz), 7.58 (d, 1 H, *J* = 8.5 Hz), 7.45 (dd, 1 H, *J* = 8.5/2.3 Hz), 7.01 (d, 1 H, *J* = 2.3 Hz), 4.79 (br. 2 H, NH_2), 1.33 [s, 9 H, $C(CH_3)_3$], 1.30 [s, 9 H, $C(CH_3)_3$]. – ^{13}C NMR ($CDCl_3$): δ = 165.20 (C=O), 164.83 (C=O), 149.98, 143.83, 143.20, 136.00, 134.46, 133.08, 130.48, 129.97, 129.82, 129.30, 128.67, 128.43, 128.29, 127.87, 126.99, 126.69, 126.11, 125.18, 124.67, 124.38, 122.24, 121.88, 121.30, 121.20, 119.29, 35.52 $[C(CH_3)_3]$, 34.25 $[C(CH_3)_3]$, 31.73 $[C(CH_3)_3]$, 31.25 $[C(CH_3)_3]$. – MS (70 eV), *m/z* (%): 526 (3), 525 (14), 524 (43) $[M^+]$, 507 (6) $[M^+ - NH_3]$, 469 (5), 468 (36), 467 (100) $[M^+ - C_4H_9]$, 453 (4), 452 (16), 451 (28) $[507 - C_4H_8]$. – $C_{36}H_{32}N_2O_2$: calcd. 524.2464; found 524.2306 (MS).

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