Supplementary Material (ESI) for Chemical Communications

Dibenzopentarylenebis(dicarboximide)s: Novel Near-Infrared Absorbing Dyes

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Supporting information

General: The solvents and chemicals used were of commercial grade. Compounds **6** and **7** were synthesised as described elsewhere.[14, 10] Column chromatography was performed on silica gel (Geduran Si60, Merck). Melting points (uncorrected) were determined using Büchi Melting Point B-545 apparatus. Thermal gravimetric analyses were performed using Mettler TGA851e apparatus. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DPX 250 and Bruker DRX500 spectrometers. Infrared spectra were obtained on a Nicolet FT IR320. FD mass spectra were recorded with a VG-instruments ZAB 2-SE-FPD instrument. MALDI-TOF mass spectra were recorded on a Bruker MALDI-TOF spectrometer. UV/Vis spectra were recorded on a Perkin-Elmer Lambda 900 spectrophotometer. Elemental analyses were performed by the Department of Chemistry and Pharmacy of the University of Mainz.

5,11-Dibromotetracene 5. A solution of NBS (708 mg, 4 mmol) in dry DMF (40 ml) was added at once into a stirred at 60 °C solution of tetracene (456 mg, 2 mmol) in chloroform (200 ml). The resulted solution was stirred at 60 °C for 5 h. After cooling to room temperature the chloroform was evaporated in vacuo. The residue was diluted with water (150 ml) and filtered. The obtained solid was crystallised from toluene, and then dried in *vacuo*. Yield 710 mg (92 %). mp 226 °C; R_f = 0.46 (pentane); ^{1}H-NMR (250 MHz, $C_2D_2Cl_4$, 25 °C): δ = 9.05 (s, 2H), 8.35 (d, 2H), 7.95 (d, 2H), 7.36-7.50 ppm (m, 4H); ^{13}C-NMR (62,9 MHz, $C_2D_2Cl_4$, 25 °C): 133.67, 130.64, 129.35, 128.72, 128.66, 128.62, 128.08, 127.38 ppm; IR (KBr): ν = 1655, 1558, 1458, 1382, 1311, 1270, 944, 876, 732, 676 cm^{-1}; MS (FD): m/z (rel.int.) 386.2 (100%), M+; Found: C, 56.12; H, 2.55%. Calc. for $C_{18}H_{10}Br_2$: C, 56.00; H, 2.61%, Br, 41.39%.

5,11-bis-(N-(2,6-diisopropylphenyl)-3,4-dicarboximide-perylen-9-yl)tetracene 8. 5,11-Dibromotetracene (193 mg, 0.5 mmol), and N-(2,6-diisopropylphenyl)-9-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-perylene-3,4-dicarboximide **6** (608 mg, 1 mmol) were dissolved in the mixture of toluene (30 ml) and ethanol (2 ml) in 100 ml Schlenk flask and flushed with argon. After stirring at 80 °C for 20 min $Pd_2(dba)_3$ (20 mg, 13 μmol), DPEPHos (40 mg, 800 μmol) and the 2 M solution of K_2CO_3 (2 ml) in water were added to the solution. The reaction mixture was stirred at 95 °C for 15 h under argon. After cooling the resulting mixture was washed with water and extracted with toluene. The combined organic extracts were evaporated *in vacuo* and purified by

column chromatography on silica gel using dichloromethane as eluent. First red fraction contained one time substituted tetracene - 5-(N-(2,6-diisopropylphenyl)-3,4-dicarboximide-perylen-9-yl)tetracene (dry weight - 80 mg). Then, there were two orange fractions of impurities (deboronated PMI etc.). The next big fraction contained the product, 424 mg (71 %). mp >400 °C; R_f = 0.5 (dichloromethane); ^{1}H-NMR (250 MHz, CD_2Cl_2, 25 °C): δ = 8.81 (s, 4H,); 8.70-8.62 (m, 6H), 8.57-8.50 (m, 4H), 8.36-8.33 (m, 2H). 8.15-8.10 (m, 2H), 7.85-7.81 (m, 4H), 7.56-7.47 (m, 6H), 7.40-7.36 (d, 2H), 7.33-7.35 (m, 4H), 2.80 (sep, 4H), 1.18 ppm (s, 24H); ^{13}C-NMR (62,9 MHz, CD_2Cl_2, 25 °C): 146.56, 134.61, 132.38, 132.34, 130.43, 129.85, 129.79, 129.66, 127.63, 124.40, 29.47, 24.12; IR (KBr): ν = 2956, 2920, 2857, 2361, 1701, 1663, 1591, 1567, 1356, 1239, 814 cm^{-1}; UV-Vis (chloroform) λ_{max}, nm (ε): 524 (97100), 355 (8500); MS (FD): m/z (rel.int.) 1188.5 (100%), M+; Found: C, 87.07; H, 5.14; N, 2.41%. Calc. for $C_{86}H_{62}N_2O_4$: C, 86.99; H, 5.26; N, 2.36%

N,N'-Bis-(N-(2,6-diisopropylphenyl)-9,10:21,22-dibenzopentarylene-3,4:15,16-bis(dicarboximide) 11. 5,11-Bis-(N-(2,6-diisopropylphenyl)-perylendicarboximide-9-yl)tetracene **8** (120 mg, 0.1 mmol) was dissolved in 10 ml dry dichloromethane in 25 ml Schlenk tube and flushed with argon for 20 min. A solution of anhydrous iron (III) chloride (260 mg, 2 mmol) in dry nirtomethane (3 ml) was injected to the solution *via* a syringe. The reaction mixture was stirred under a slow argon flow for 3 h in the dark and then poured into methanol (50 ml). The precipitate was filtered, rinsed with methanol and dried *in vacuo* at room temperature

A 25 ml Schlenck flask with dried precipitate was charged with mixture of anhydrous potassium carbonate (2 g) and ethanolamine (3 ml). The mixture was stirred under argon at 120 °C for 2 h. The mixture was cooled to room temperature, diluted with water (25 ml) and filtered. The precipitate was filtered, rinsed with water, methanol and dichloromethane and dried *in vacuo*. The solid residue was extracted with chlorobenzene. Evaporation of chlorobenzene extract afforded 68 mg (58%) of the target material. mp (decomp., TGA data) 441 °C; IR (KBr): ν = 2954, 2925, 2886, 1700, 1662, 1559, 1501, 1326, 1306, 1273, 1207, 1169 cm^{-1}; UV-Vis (chlorobenzene) λ_{max} (rel.int., %): 1018 (100), 542 (43), 318 (62); MS (MALDI-TOF): m/z (rel.int., %) 1183 (100); Found: C, 87.44; H, 4.82; N, 2.45%. Calc. for $C_{86}H_{58}N_2O_4$: C, 87.29; H, 4.94; N, 2.37%.

Tetracene-5,11-bis-(N-(2,6-diisopropylphenyl)-1,6-bis[4-(1,1,3,3-tetramethylbutyl)phenoxy]-perylen-9-yl-3,4-dicarboximide) 9. N-(2,6-diisopropylphenyl)-1,6-bis(4-(1,1,3,3-tetramethylbutyl)phenoxy)-9-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-perylene-3,4-dicarboximide **7** (0.61 g, 0.6 mmol) and 5,11-dibromotetracene (116 mg, 0.3 mmol) were dissolved in the mixture of toluene (40 ml) and ethanol (4 ml) in 100 ml Schlenk flask and flushed with argon. After stirring at 80 °C for 20 min min $Pd_2(dba)_3$ (16 mg, 12 μmol), DPEPHos (30 mg, 60 μmol) and 2M aqueous K_2CO_3 (2.5 ml) were added to the solution. The reaction mixture was stirred at 85 °C for 15 h under argon. After cooling the resulting mixture was washed with water and extracted with toluene. The combined organic extracts were evaporated *in vacuo* and purified by column chromatography on silica gel using

toluene as eluent. Yield 354 mg (59 %); mp 318 °C; R_f = 0.62 (toluene); ^{1}H-NMR (250 MHz, CD_2Cl_2, 25 °C): δ = 9.68-9.75 (m, 2H), 9.49-9.52 (d, 2H), 9.40-9.44 (m, 2H), 8.35 (s, 2H), 8.32 (s, 2H), 7.66-7.93 (m, 4H), 7.42-7.52 (m, 12H), 7.34 (d, 4H), 7.12-7.23 (m, 16H), 2.75 (sep, 4H), 1.74 (s, 4H), 1.73 (s, 4H), 1.40 (s, 6H), 1.38 (s, 6H), 1.15 (s, 12H), 1.12 (s, 12H), 0.73 (s, 18H), 0.71 (s, 18H); ^{13}C-NMR (62,9 MHz, CD_2Cl_2, 25 °C): 163.68, 154.70, 154.61, 154.58, 153.71, 153.34, 147.06, 146.96, 146.91, 146.87, 146.45, 129.74, 129.33, 128.52, 128.48, 128.45, 125.59, 124.41, 124.21, 122.04, 119.02, 118.81, 118.75, 118.71, 118.65, 57.39, 38.64, 32.61, 31.83, 31.66, 29.44, 24.10 ppm; IR (KBr): ν = 2955, 2921, 2856, 2361, 1701, 1663, 1590, 1567, 1355, 1241, 815 cm^{-1}; UV-Vis (chloroform) λ_{max} (ε): 530 (94860), 420 (16960); MS (FD): m/z (rel.int.) 2005.0 (100%), M+, 1002.8 (14%), M/2; Found: C, 85.17; H, 7.05; N, 1.45%. Calc. for $C_{142}H_{142}N_2O_8$: C, 85.08; H, 7.14; N, 1.40%

N,N'-Bis-(N-(2,6-diisopropylphenyl)-1,6,13,18-tetrakis(4-(1,1,3,3-tetramethylbutyl)phenoxy)-9,10:21,22-dibenzopentarylene-3,4:15,16-bis(dicarboximide) 4. 5,11-Bis-(N-(2,6-diisopropylphenyl)-1,6-bis(4-(1,1,3,3-tetramethylbutyl)phenoxy)-9-yl)tetracene **9** (200 mg, 0.1 mmol) was dissolved in 10 ml dry dichloromethane in 25 ml Schlenk flask and flushed with argon for 20 min. A solution of anhydrous iron (III) chloride (260 mg, 2 mmol) in dry nitromethane (3 ml) was injected to the solution *via* a syringe. The reaction mixture was stirred under a slow argon flow for 3 h in the dark and then poured into methanol (50 ml). The precipitate was filtered, rinsed with methanol and dried *in vacuo* at room temperature

A mixture of anhydrous potassium carbonate (2 g) and ethanolamine (3 ml) was stirred in a 25 ml Schlenk flask under argon at 120 °C for 30 min. A solution of precipitate in 1 ml of anhydrous DMF was injected into the reaction flask and stirred for 2 h at the same temperature. The mixture was cooled to room temperature, diluted with water (25 ml) and filtered. The precipitate was filtered, rinsed with water and methanol and dried *in vacuo*. The crude product was purified by a column chromatography on silica gel (petroleum ether-dichloromethane, 1:1), and then by preparative TLC (the same eluent). Yield 105 mg (53%). mp (decomp., TGA data) 330 °C; R_f = 0.63 (toluene); ^{1}H-NMR (500 MHz, $C_2D_2Cl_4$, 100 °C): δ = 10.53-10.44 (dd, ^3J=9.62 and 9.66 Hz, 4H), 9.86 and 9.75 (dd, ^3J=9.73 and 9.79 Hz, 4H), 9.00-9.10 (m, 4H), 8.14 (s, 4H), 7.94 (d, ^3J=8.27 Hz, 4H), 7.65 (m, 2H), 7.42 (d, ^3J=7.78 Hz, 4H), 7.27 (d, ^3J=7.83 Hz, 8H), 7.19 (d, ^3J=8.63 Hz, 8H), 2.75 (sep, ^3J=6.78 Hz, 4H), 1.41 (s, 8H), 1.29 (s, 24H), 1.12 (d, ^3J=6.76 Hz, 24H), 0.74 (s, 36H); H, H-COSY-NMR (500 MHz, $C_2D_2Cl_4$, 100 °C): Coupling of δ = (10.53, 9.75), (10.45, 9.86), (9.06, 7.94), (7.65, 7.42), (7.28, 7.19); IR (KBr): ν = 2954, 2925, 2886, 1700, 1662, 1559, 1501, 1326, 1306, 1273, 1207, 1169 cm^{-1}; UV-Vis (dichloromethane) λ_{max} (ε): 1037 (149500), 567 (46700), 321 (84500); MS (FD): m/z (rel.int.) 1999.0 (100%), M+, 1000.6 (45%), M/2; Found: C, 85.31; H, 6.89; N, 1.46%. Calc. for $C_{142}H_{138}N_2O_8$: C, 85.25; H, 6.95; N, 1.40%.