

Supplementary data

Facile synthetic approach to novel core-extended perylene carboximide dyes

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General

Melting points were performed on a Büchi melting point apparatus and are not corrected. ¹H NMR and ¹³C NMR spectra were recorded in deuterated tetrachloroethan on a Bruker AMX 300 and Bruker Avance 700, using the residual proton resonance or the carbon signal of the solvent as the internal standard. For ¹³C J-modulated spin-echo NMR measurements, the abbreviations q and t represent quaternary carbons, CH₂, and CH₃, CH groups, respectively. Infrared spectra were obtained on a Nicolet FT-IR 320. UV/vis spectra were recorded on a Perkin-Elmer Lambda 40 spectrophotometer at room temperature. Fluorescence spectra were recorded on a Spex Fluorolog 3 spectrometer. FD mass spectra were obtained on a VG Instruments ZAB 2-SE-FPD. The elemental analyses were carried out by the Microanalytical Laboratory of Johannes Gutenberg University, Mainz. 1,7-Dibromo-3,4:9,10-perylene tetracarboxdianhydride and N-(2,6-diisopropylphenyl)-9-bromo-3,4-perylene dicarboxmonoimide were provided by the BASF AG. All other starting materials were purchased from Aldrich, Acros, ABCR, or Lancaster, and used as received.

***N,N'*-Bis(2,6-diisopropylphenyl)-1,7-di-(2-bromophenyl)-3,4:9,10-perylene tetracarboxdiimide 7:** A Schlenk flask was charged with *N,N'*-bis(2,6-diisopropylphenyl)-1,7-dibromo-3,4:9,10-perylene tetracarboxdiimide (1.00 g, 1.15 mmol), 2-bromophenylboronic acid (500 mg, 2.49 mmol), tetrakis(triphenylphosphine)palladium(0) (150 mg, 0.130 mmol), toluene (75 mL), ethanol (5 mL) and a 2 M solution of potassium carbonate (25 mL) under argon. The mixture was heated to 75 °C with vigorous stirring for 12 h. The mixture was cooled to room temperature, the organic phase separated and washed twice with water. After drying with magnesium sulfate, the solvent was removed *in vacuo*. The crude product was dissolved in methylene chloride and filtered over silica gel. Evaporation of the solvent gave 620 mg (53%) of red crude product, which was used without further purification.

***N,N'*-Bis(2,6-diisopropylphenyl)-5,6:11,12-dibenzocoronene-2,3:8,9-tetracarboxdiimide 6:** Bis-(triphenylphosphine)palladium(II)dichloride (15 mg 0.021 mmol) was added to a solution of *N,N'*-bis(2,6-diisopropylphenyl)-1,7-di-(2-bromophenyl)-3,4:9,10-perylene tetra-

carboxdiimide (100 mg, 0.098 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (60 mg, 0.39 mmol) in dry dimethylacetamide (3 mL) under argon. The mixture was heated to 160 °C with stirring for 24 h, cooled to room temperature, and diluted with methylene chloride. The mixture was washed twice with water, dried over magnesium sulfate and the solvent removed *in vacuo*. The crude product was purified by column chromatography (silica gel, methylene chloride) to yield 40 mg (46%) of an orange solid. mp 240 °C (decomposition); ¹H NMR (700 MHz, C₂D₂Cl₄, 293 K): δ = 10.66 (s, 4H); 9.56 (d, ³J = 3.43 Hz, 4H); 8.22 (dd, ³J = 3.43, 2.59 Hz, 4H); 7.53 (dd, ³J = 7.7, 7.7 Hz, 2H); 7.40 (d, ³J = 8.54 Hz, 4H); 2.99 (sept, ³J = 6.79 Hz, 4H); 1.26 (d, ³J = 6.79 Hz, 24H); ¹³C NMR (J-modulated spin-echo; 175 MHz, C₂D₂Cl₄, 373 K): δ = 164.77 (q, C=O); 146.39 (q); 131.67 (q); 130.12 (q); 129.76 (t); 129.68 (t); 129.35 (q); 125.24 (q); 125.22 (q); 124.96 (t); 124.87 (t); 124.31 (t); 124.01 (q); 122.72 (q); 29.73 (t, isopropyl); 24.29 (t, isopropyl); IR (KBr): ν = 2962, 2927, 2869, 1698, 1663, 1655, 1581, 1541, 1459, 1363, 1351, 1278, 1214, 1175 cm⁻¹; UV/vis (CH₃Cl₃): λ_{max} (ε) = 432 (10,000), 460 (32,000), 494 nm (66,000 M⁻¹ cm⁻¹); MS (FD, 8 kV) : *m/z* (%): 554.8 (100) [M⁺], 429.3 (23) [M²⁺]; Found: C, 83.66; H, 5.38; N, 3.12%. Calc. for C₆₀H₄₆N₂O₄: C, 83.89; H, 5.40; N, 3.26%.

***N*-(2,6-Diisopropylphenyl)-9-(2-bromophenyl)-3,4-perylene dicarboxmonoimide 9:** A Schlenk flask was charged with *N*-(2,6-diisopropylphenyl)-9-bromo-3,4-perylene dicarboxmonoimide (1.00 g, 1.78 mmol), 2-bromophenylboronic acid (715 mg, 3.56 mmol), tetrakis(triphenylphosphine)palladium(0) (205 mg, 0.177 mmol), toluene (75 mL), ethanol (5 mL) and a 2 M solution of potassium carbonate (25 mL) under argon. The mixture was heated to 75 °C with vigorous stirring for 4 h. The mixture was cooled to room temperature, the organic phase separated and washed twice with water. After drying with magnesium sulfate, the solvent was removed *in vacuo*. The crude product was dissolved in methylene chloride and filtered over silica gel. Evaporation of the solvent gave 620 mg (53%) of red crude product, which was used without further purification.

***N*-(2,6-Diisopropylphenyl)-indeno[1,2,3-cd]-3,4-perylene dicarboxmonoimide 5:** Bis-(triphenylphosphine)palladium(II)dichloride (55 mg 0.078 mmol) was added to a solution of *N*-(2,6-diisopropylphenyl)-9-(2-bromophenyl)-3,4-perylene dicarboxmonoimide (500 mg, 0.785 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (240 mg, 1.58 mmol) in dry dimethylacetamide (15 mL) under argon. The mixture was heated to 160 °C with stirring for 24 h, cooled to room temperature, and diluted with methylene chloride. The mixture was washed twice with water, dried over magnesium sulfate and the solvent removed *in vacuo*. The crude product was purified by column chromatography (silica gel, methylene chloride) to yield 126 mg (30%) of a violet solid. mp >300 °C; ¹H NMR (300 MHz, C₂D₂Cl₄, 373 K): δ =

8.58 (d, $^3J = 7.95$ Hz, 2H); 8.40 (d, $^3J = 8.19$ Hz, 2H); 8.31 (d, $^3J = 7.68$ Hz, 2H); 7.88 (d, $^3J = 7.68$ Hz, 2H); 7.82 (dd, $^3J = 5.64, 3.06$ Hz, 2H); 7.41 (dd, $^3J = 8.19, 7.17$ Hz, 1H); 7.35 (dd, $^3J = 5.64, 3.06$ Hz, 2H); 7.27 (d, $^3J = 7.41$ Hz, 2H); 2.75 (sept, $^3J = 6.66$ Hz, 2H); 1.16 (d, $^3J = 6.9$ Hz, 12H); ^{13}C NMR (J-modulated spin-echo; 75 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): $\delta = 163.92$ (q, C=O); 146.18 (q); 139.55 (q); 139.06 (q); 136.63 (q); 133.49 (q); 131.88 (t); 131.68 (q); 130.85 (q); 129.87 (q); 129.36 (t); 128.70 (t); 126.92 (q); 125.62 (q); 124.44 (t); 124.07 (t); 122.54 (t); 122.42 (q); 121.65 (t); 121.50 (t); 29.48 (t, isopropyl); 24.16 (t, isopropyl); IR (KBr): $\nu = 2961, 2928, 2869, 1712, 1672, 1607, 1467, 1437, 1383, 1324, 1253, 1214, 1193$ cm^{-1} ; UV/vis (CH_3Cl_3): λ_{max} (ϵ) = 477 (21,000), 506 (47,000), 542 nm (65,000 $\text{M}^{-1} \text{cm}^{-1}$); MS (FD, 8 kV): m/z (%): 554.8 (100) [M^+]; Found: C, 84.78; H, 5.36; N, 2.35%. Calc. for $\text{C}_{60}\text{H}_{46}\text{N}_2\text{O}_4$: C, 86.46; H, 5.26; N, 2.52%.