

Supplementary material

Fullerodendrimers with a tris-isothiocyanate core allowing their anchoring onto gold electrodes

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General. All manipulations were performed under a dry argon atmosphere using Schlenk-tube techniques. Solvents were dried by standard methods and distilled under argon immediately prior to use. All the chemicals used in this work have been purchased from Aldrich Chemicals and used as received.

Physical Measurements. Carbon and hydrogen analyses were performed with a Perkin-Elmer 2400 microanalyzer. Mass spectra were recorded in a VG Autospec double-focusing mass spectrometer operating in the FAB⁺ mode. Ions were produced with the standard Cs⁺ gun at ca. 30 kV; 3-nitrobenzyl alcohol (NBA) was used as matrix. ¹H and ¹³C{¹H} spectra were recorded on a Varian UNITY, Bruker ARX 300, and Varian Gemini 300 spectrometers operating at 299.95 and 75.47 MHz, 300.13 and 75.47 MHz, and 300.08 and 75.46 MHz,

respectively. Chemical shifts are reported in ppm and referenced to Me₄Si using the signal of the deuterated solvent (¹H and ¹³C) as external reference. Molecular weights were determined with a Knauer osmometer using chloroform solution of the complexes.

Synthesis of BzOCH₂CH₂OCH₂C(CH₂OTs)₃ (2). To a solution of **1** (7.57 g, 28.00 mmol) in pyridine (38 mL) cooled at -5 °C, solid *p*-toluenesulfonic chloride (21.35 g, 111.99 mmol) was added in small portions to keep the reaction temperature below 0 °C. Upon stirring for 2 h at 0 °C and then at room temperature for 24 h, the pink-coloured reaction mixture was poured into crushed-iced water. The precipitate thus obtained was filtered off, washed with cold diethyl ether and dried under vacuum to afford **2** as a white solid (16.20 g, 80 %). ¹H NMR (300 MHz, CDCl₃) δ: 7.67 (d, ³J = 8.28 Hz, 6H, C₆H₄CH₃), 7.31 (m, 11H, C₆H₅ + C₆H₄CH₃), 4.44 (s, 2H, PhCH₂O), 3.90 (s, 6H, C(CH₂OTs)₃), 3.38 (s, 4H, PhCH₂OCH₂CH₂), 3.31 (s, 2H, PhCH₂OCH₂CH₂OCH₂), 2.42 (s, 9H, CH₃). ¹³C NMR (75 MHz, CDCl₃): δ = 145.1 (s, C_{ipso} Ts), 131.7 (s, C_{ipso} Bn), 129.9 (s, C_m+C_p Ts), 128.3 (s, C_m Bn), 127.8 (s, C_o Ts), 127.5 (s, C_p Bn), 127.4 (s, C_o Bn), 73.0 (s, PhCH₂OCH₂CH₂OCH₂), 70.8 (s, OCH₂CH₂), 68.9 (s, CH₂OTs), 67.4 (s, OCH₂CH₂), 66.9 (s, CH₂Ph), 43.6 (s, C(CH₂OTs)₃), 21.5 (s, CH₃). MS (EI): m/z = 547 (M⁺ - 2 OTs, 15%). Anal. Calcd. for C₃₄H₃₈O₁₁S₃. C 56.81, H 5.33. Found: C 56.28, H 4.81.

Synthesis of HOCH₂CH₂OCH₂C(CH₂OTs)₃. A mixture of **2** (6.00 g, 8.35 mmol) and Pd/C (108 mg) was stirred in THF under an atmosphere of H₂ (1 bar) for 12 h at room temperature. The reaction mixture was then filtered through celite, and upon removal of the solvent by distillation under vacuum, a white solid was isolated (4.20 g, 78%). ¹H NMR (300 MHz, CDCl₃) δ: 7.71 (d, ³J = 8.40 Hz, 6H), 7.35 (d, ³J = 8.10 Hz, 6H) (C₆H₄CH₃), 3.92 (s, 6H, CCH₂OTs), 3.55 (br s, 1H, OH), 3.36 (s, 4H, HOCH₂CH₂), 3.32 (s, 2H, HOCH₂CH₂OCH₂), 2.45 (s, 9H, CH₃). ¹³C NMR (75 MHz, CDCl₃) δ: 145.3 (s, C_{ipso} Ts), 129.9 (s, C_m+C_p Ts), 127.8 (s, C_o Ts), 72.8 (s, HOCH₂CH₂OCH₂), 66.7 (s, HOCH₂CH₂), 66.4 (s, CH₂OTs), 61.2 (s, HOCH₂CH₂), 43.9 (s, C(CH₂OTs)₃), 21.5 (s, CH₃). MS (EI) m/z: 522 (M⁺ - C₆H₄CH₃ - 2 CH₃, 44%). Anal. Calcd. for C₂₈H₃₄O₁₁S₃: C 55.32, H 5.33. Found: C 55.28, H 5.36.

Synthesis of TBDMSOCH₂CH₂OCH₂C(CH₂OTs)₃ (3). To a solution of HOCH₂CH₂OCH₂C(CH₂OTs)₃ (1.55 g, 2.41 mmol) in dichloromethane (30 mL) cooled at 0 °C, solid imidazol (0.25 g, 3.61 mmol) and then solid TBDMS (0.47 g, 3.13 mmol) were added. The resulting mixture was stirred at 0 °C for 30 min and at room temperature for 5 h, and then water (50 mL) was added. The solution thus obtained was extracted with dichloromethane (3 x 75 mL) and the combined organics fractions were washed with a saturated solution of NaCl, dried over sodium sulphate, and finally filtered through a pad of celite. After removal of the solvent by distillation under vacuum, a white solid was isolated (1.77 g, 99%). ¹H NMR (300 MHz, CDCl₃) δ: 7.70 (d, ³J = 8.40 Hz, 6H), 7.34 (d, ³J = 8.40 Hz, 6H) (C₆H₄CH₃), 3.88 (s, 6H, CCH₂OTs), 3.51 (t, ³J = 4.80 Hz, 2H, TBDMSOCH₂CH₂), 3.31 (s, 2H, TBDMSOCH₂CH₂OCH₂), 3.24 (t, ³J = 4.80 Hz, 2H, TBDMSOCH₂CH₂), 2.45 (s, 9H, CH₃Ts), 0.83 (s, 9H, (CH₃)₃C), -0.03 (s, 6H, Si(CH₃)₂). ¹³C NMR (75 MHz, CDCl₃) δ: 145.1 (s, C_{ipso} Ts), 132.0 (s, C_m+C_p Ts), 127.9 (s, C_o Ts), 72.8 (s, TBDMSOCH₂CH₂OCH₂), 67.6 (s, TBDMSOCH₂CH₂), 66.9 (s, CH₂OTs), 62.1 (s, TBDMSOCH₂CH₂), 43.7 (s, C(CH₂OTs)₃), 32.2 (s, C(CH₃)), 25.7 (s, C(CH₃)₃), 21.6 (s, CH₃Ts), -5.5 (s, Si(CH₃)₂). MS (EI) m/z: 574 (M⁺ - OTs, 27%). Anal. Calcd. for C₃₃H₄₈O₁₁S₃Si: C 53.20, H 6.49. Found: C 53.60, H 6.39.

Synthesis of BzOCH₂CH₂OCH₂C(SCN)₃ (4). To a solution of **3** (6.80 g, 9.11 mmol) in dry DMF (75 mL), solid KSCN (11.51 g, 118.48 mmol) was added and the resulting mixture was stirred at 140 °C for 6 h. The resulting dark coloured solution was poured into cold water and left overnight standing at 5 °C. The tan precipitate formed was separated by decantation, washed with water and then dissolved in methylene chloride (3 x 20 mL). The combined organic fractions were washed with a saturated solution of NaCl, dried over sodium sulphate and then filtered. The volatiles were removed under reduced pressure to afford a dark brown oil, which was purified by chromatography on silica gel eluting with acetone (1.50 g, 54%). ¹H NMR (300 MHz, CDCl₃) δ: 3.71 (br. s, 4H, HOCH₂CH₂), 3.67 (s, 2H, HOCH₂CH₂OCH₂), 3.29 (s, 6H, CCH₂SCN), 2.39 (br s, 4H, HO). ¹³C NMR (75 MHz, CDCl₃) δ: 111.4 (s, SCN), 73.0 (s, HOCH₂CH₂OCH₂), 70.9 (s, HOCH₂CH₂), 62.3 (s, HOCH₂CH₂), 46.1 (s, C(CH₂SCN)₃), 25.7 (s, CH₂SCN). Anal. Calcd. for C₁₀H₁₃N₃O₂S₃: C 39.59, H 4.32, N 13.85. Found: C 40.21, H 4.37, N 13.89.