

The First Electrochemically Active Cuppedophanes: Bis(tetrathiafulvalene)cuppedophanes

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Supporting Information

Experimental: All reactions were carried out under an atmosphere of dry N_2 . THF was distilled from Na/benzophenone immediately prior to use. MeOH and EtOH was distilled from Mg. DMF was allowed to stand over molecular sieves (4 Å) for at least 3 days before use. All reagents were standard grade and used as received, except 2,6,2'',6''-tetrakis(bromomethyl)-1,1':3',1''-terphenyl (**2**)^{5b} and 2,3-bis(2-cyanoethylthio)-6,7-bis(thiocyanatomethyl)tetrathiafulvalene (**3**),⁷ which were prepared according to the literature.

Analytical Thin Layer Chromatography (TLC) was performed on Merck DC-Alufolien Kieselgel 60 F₂₅₄ 0.2 mm thickness pre-coated TLC plates, while column chromatography was performed using Merck Kieselgel 60 (0.040–0.063 mm, 230–400 mesh AST0000M). Melting points (mp) were determined on a Büchi melting point apparatus and are uncorrected. ¹H NMR spectra were recorded on a Gemini-300BB instrument at 300 MHz, using the deuterated solvent as lock and TMS or the residual solvent as internal standard. ¹³C NMR spectra were recorded at 75 MHz using Broad Band Decoupling. Electron Impact Ionisation Mass Spectrometry (EIMS) was performed on a Varian MAT 311A instrument and Plasma Desorption Mass Spectrometry (PDMS) was performed on a Bio-Ion 20K time of flight instrument from Applied Biosystem on the basis of 5.000.000 fission events. InfraRed (IR) spectra were recorded on a Perkin-Elmer 580 spectrophotometer. Cyclic Voltammetry (CV) was carried out on an Autolab/PGSTAT 10 instrument using CH_2Cl_2 as solvent employing Bu_4NPF_6 (0.10 M) as supporting electrolyte, with a sweep rate of 0.100 Vs⁻¹. Counter and working electrodes were made of Pt, and the reference electrode was Ag/AgCl. Microanalyses were performed at the Atlantic Microlab, inc., Atlanta, Georgia.

2-{4,5-Bis(2-cyanoethylthio)-1,3-dithiole-2-yliden}-4,6,11,13-tetrahydrobenzo[h]-(1,3)-dithiolo[4',5'-c]-(1,6)-dithiecin (**4**)

A mixture of compound **3** (0.23 g, 0.45 mmol) and α,α' -dibromo *o*-xylene (0.12 g, 0.45 mmol) dissolved in anhyd THF-EtOH (50 mL, 1:1) were added dropwise over a period of 5 h to a suspension of excess sodium borohydride (0.20 g, 5.3 mmol) in anhyd THF-EtOH (140 mL, 19:1) under bubbling N_2 with vigorous stirring at rt. After addition was completed the orange reaction mixture was stirred for further 30 min, whereupon the orange reaction mixture was concentrated in vacuo to approximately 60 mL. Ice containing sat. aq NH_4Cl solution (60 mL) was added to precipitate the product. The orange solid was collected by filtration, washed with H_2O (3 × 20 mL) and dried in vacuo. The crude product was purified by column chromatography (120 mL silica gel, 3 cm Ø, eluent: CH_2Cl_2). The orange band ($R_f = 0.2$) was collected and concentrated to give 0.12 g (47%) of **4** as an analytically pure orange solid. Recrystallization from toluene/cyclohexane gave **4** as orange needles: mp 230 °C (dec); ¹H NMR (CD_3SOCD_3) δ 2.88 (t, $J = 6.7$ Hz, 4H, CH_2CN), 3.16 (t, $J = 6.7$ Hz, 4H, SCH_2CH_2CN), 3.24 (bs, 4H, $TTFCH_2SCH_2Ar$), 3.69 (bs, 4H, $TTFCH_2SCH_2Ar$), 7.28 (m, 2H, Ar-3-H), 7.53 (m, 2H, Ar-2-H); ¹³C NMR (CD_3SOCD_3) δ 18.21 (CH_2CN), 26.03 (CH_2), 27.83 (CH_2), 30.86 (SCH_2CH_2CN), 105.35 (fulvene C=C), 112.19 (fulvene C=C), 119.00 (CN), 127.44 (arom. C-2/3), 127.74 (dithiole RS-C=C-SR), 129.58 (arom. C-2/3), 131.01 (dithiole $SH_2C-C=C-CH_2S$), 136.46 (arom. C-1); MS(EI) m/z 568 (M^+ , 69), 310 (75), 168 (88), 135 (93), 104 (100); IR (KBr) ν 3056, 3018, 2958, 2919, 2250 (CN), 1602, 1487, 1417 cm^{-1} . Anal. Calcd for $C_{22}H_{20}N_2S_8$ (568.9): C, 46.45; H, 3.54; N, 4.92; S, 45.08. Found: C, 46.35; H, 3.44; N, 4.88; S, 45.13.

4,6,11,13-Tetrahydro-2-{4,5-bis(methylthio)-1,3-dithiole-2-ylidene}benzo[*h*]- (1,3)-dithiolo[4',5'-*c*]- (1,6)-dithiecin (5)

Compound 4 (0.11 g, 0.19 mmol) suspended in anhyd DMF (20 mL) was purged with N₂ (20 min), before a solution of CsOH·H₂O (0.071 g, 0.42 mmol) in dry MeOH (5 mL) was added over a period of 5 min. The mixture was stirred for 20 min, causing the initially orange solution to become orange brown. MeI (0.30 mL, 0.68 g, 4.8 mmol) was added in one portion, causing a momentary colour change to orange. The reaction mixture was stirred for 20 min and then purged with N₂ (20 min). The solvent was removed in vacuo and the resulting orange residue was dissolved in CH₂Cl₂ (100 mL) and washed with H₂O (4 × 100 mL). After drying (MgSO₄) and evaporation of the solvent, the resulting orange solid was purified by column chromatography (100 mL silica gel, 3 cm Ø, eluent: CH₂Cl₂/cyclohexane 9:1). The orange yellow band (*R_f* = 0.6) was collected and concentrated to give 0.066 g (70%) of analytically pure 5 as a yellow solid: mp 196 °C (dec); ¹H NMR (CD₃SOCD₃) δ 2.42 (s, 6H, SCH₃), 3.21 (bs, 4H, TTFCH₂SCH₂Ar), 3.67 (bs, 4H, TTFCH₂SCH₂Ar), 7.24 (m, 2H, Ar-3-*H*), 7.51 (m, 2H, Ar-2-*H*); MS(EI) *m/z* 490 (M⁺, 100), 444 (41), 322 (45), 172 (33), 135 (42), 104 (31); IR (KBr) ν 3057, 3019, 2960, 2916, 1600, 1487, 1429 cm⁻¹. Anal. Calcd for C₁₈H₁₈S₈ (490.8): C, 44.05; H, 3.70; S, 52.26. Found: C, 44.30; H, 3.61; S 52.02.

Tetrakis(2-cyanoethylthio)-bis(TTF)cuppedophane (6)

A mixture of compound 3 (0.37 g, 0.72 mmol) and compound 2 (0.22 g, 0.37 mmol) in anhyd THF-EtOH (60 mL, 2:1) were added dropwise over a period of 4 h to a suspension of excess sodium borohydride (0.35 g, 9.3 mmol) in dry THF-EtOH (300 mL, 19:1) under bubbling N₂ with vigorous stirring at rt. After addition was finished the orange reaction mixture was stirred for further 30 min, whereupon it was concentrated in vacuo to approximately 100 mL. Ice containing sat. aq NH₄Cl solution (80 mL) was added to precipitate the product as an orange yellow solid, which was collected by filtration, washed with H₂O (3 × 20 mL) and dried in vacuo. The crude product was purified by column chromatography (150 mL silica gel, 4 cm Ø, eluent: CH₂Cl₂/EtOAc 24:1). The orange band (*R_f* = 0.15) was collected and concentrated to give an orange solid, which was repeatedly dissolved in CH₂Cl₂ (2 × 20 mL) and concentrated to give 0.13 g (31%) of analytically pure 6 as an orange solid. Recrystallization from CHCl₃/MeOH gave 6 as fine orange needles: mp 134–135 °C; ¹H NMR (CD₃SOCD₃) δ 2.87 (t, *J* = 6.7 Hz, 8H, CH₂CN), 3.15 (t, *J* = 6.7 Hz, 8H,

SCH₂CH₂CN), 3.37 and 3.53 (AB q, *J* = 14.6 Hz, 8H, TTFCH₂SCH₂Ar), 3.52 and 3.76 (AB q, *J* = 11.4 Hz, 8H, TTFCH₂SCH₂Ar), 6.84 (t, *J* = 1.0 Hz, 1H, isolated Ar-*H* in the central *m*-terphenyl ring), 7.2–7.4 (m, 8H, Ar-*H* in the "outer" *m*-terphenyl rings [6H] and Ar-*H* meta to the isolated H in the central *m*-terphenyl ring [2H]), 7.48 (t, *J* = 7.6 Hz, 1H Ar-*H* para to the isolated H in the central *m*-terphenyl ring); ¹H NMR (CDCl₃) δ 2.74 (t, *J* = 7.2 Hz, 8H CH₂CN), 3.09 (t, *J* = 7.2 Hz, 8H, SCH₂CH₂CN), 3.26 (bs, 8H, TTFCH₂SCH₂Ar), 3.54 and 3.83 (AB q, *J* = 11.0 Hz, 8H TTFCH₂SCH₂Ar), 7.03 (t, *J* = 1.0 Hz, 1H, isolated Ar-*H* in the central *m*-terphenyl ring), 7.2–7.6 (m, 9H, Ar-*H* in the "outer" *m*-terphenyl rings [6H], Ar-*H* meta to the isolated H in the central *m*-terphenyl ring [2H] and Ar-*H* para to the isolated H in the central *m*-terphenyl ring [1H]); MS (PD) *m/z* 1212.4 (M⁺); Calcd for C₅₀H₄₂N₄S₁₆, 1211.9; IR (KBr) ν 3057, 3014, 2921, 2849, 2250 (CN), 1600, 1416 cm⁻¹. Anal. Calcd for C₅₀H₄₂N₄S₁₆ (1211.9): C, 49.56; H, 3.49; N, 4.62; S, 42.33. Found: C, 49.38; H, 3.49; N, 4.57; S, 42.17.

Tetrakis(methylthio)-bis(TTF)cuppedophane (7)

Compound 6 (0.059 g, 0.049 mmol) dissolved in anhyd DMF (15 mL) was purged with N₂ (20 min) before a solution of CsOH·H₂O (0.038 g, 0.23 mmol) in anhyd MeOH (5 mL) was added over a period of 5 min. The mixture was stirred for 45 min, causing the initially orange solution to become orange brown. MeI (0.20 mL, 0.46 g, 3.2 mmol) was added in one portion, causing a momentary colour change to orange yellow. The reaction mixture was stirred for 20 min and then purged with N₂ (20 min). The solvent was removed in vacuo and the resulting orange residue was dissolved in CH₂Cl₂ (75 mL) and washed with H₂O (4 × 50 mL). After drying (MgSO₄) and evaporation of the solvent, the resulting red solid was purified by column chromatography (100 mL silica gel, 3 cm Ø, eluent: CH₂Cl₂/cyclohexane 9:1). The orange yellow band (*R_f* = 0.6) was collected and concentrated to give 0.029 g (57%) of 7 as an orange yellow solid: mp 155.5–157.5 °C; ¹H NMR (CDCl₃) δ 2.42 (12H, SCH₃), 3.23 and 3.27 (AB q, *J* = 14.3 Hz, 8H, TTFCH₂SCH₂Ar), 3.50 and 3.83 (AB q, *J* = 11.0 Hz, 8H, TTFCH₂SCH₂Ar), 7.01 (bs, 1H, isolated Ar-*H* in the central *m*-terphenyl ring), 7.2–7.6 (m, 9H, Ar-*H* in the "outer" *m*-terphenyl rings [6H], Ar-*H* meta to the isolated H in the central *m*-terphenyl ring [2H] and Ar-*H* para to the isolated H in the central *m*-terphenyl ring [1H]); MS(PD) *m/z* 1056.2 (M⁺); Calcd for C₄₂H₃₈S₁₆, 1055.7; IR (KBr) ν 3058, 3012, 2916, 2848, 1600, 1428 cm⁻¹. Anal. Calcd for C₄₂H₃₈S₁₆ (1055.7): C, 47.78; H, 3.63; S, 48.59. Found: C, 47.01; H, 3.59; S, 47.66.