Self-Assembled Monolayers of Mono-Tetrathiafulvalene-Calix[4]pyrroles and Their Electrochemical Sensing of Chloride


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EXPERIMENTAL SECTION

Materials. All reagents were purchased from Aldrich. The starting materials $3^{[S1]}$ and $10^{[S2]}$ were prepared according to literature procedures.

General Methods. All reactions were carried out under an inert N$_2$ or Ar atmosphere. THF was distilled from sodium-benzophenone immediately prior to use. MeOH was distilled from Mg and I$_2$ immediately prior to use. Analytical thin layer chromatography (TLC) was performed on Merck DC-Alufolien Kiselgel 60 F$_{254}$ 0.2 mm thickness precoated TLC plates, which were inspected by UV-light prior to development with iodine vapor. Column chromatography was performed using Merck Kiselgel 60 (0.040–0.060 mm, 230–240 mesh ASTM). Melting points (M.p.) were determined on a Büchi melting point apparatus and are uncorrected. The $^1$H NMR spectra were recorded at room temperature on a Varian Gemini 300 MHz or a Bruker Advance III 400 MHz $^{13}$C NMR spectra were recorded on a Varian Gemini (75 MHz) or a Bruker Advance III (100 MHz). Chemical shifts are quoted on the $\delta$ scale and coupling constants ($J$) are expressed in Hertz (Hz). Samples for $^1$H NMR spectroscopic studies were prepared using solvents purchased from Cambridge Isotope Labs. All spectra were referenced using the residual solvent peak. Electron impact ionization mass spectrometry (EI-MS) was performed on a Varian MAT 311A instrument, whereas high resolution Fourier Transform matrix-assisted laser-desorption/ionization mass spectrometry (HiResFT-MALDI-MS) was performed on an IonSpec 4.7 tesla Ultima Fourier Transform mass spectrometer, utilizing a 2,5-dihydroxybenzoic acid (DHB) matrix. Absorption spectroscopic data were recorded using a Shimadzu UV-1601PC apparatus. Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, Georgia. Electrochemical experiments were carried out at room temperature in CH$_2$Cl$_2$.

Compound 5
A solution of 2-{4-(2-cyanoethylthio)-5-methylthio-1,3-dithiole-2-yliden}-5-tosyl-(1,3)dithiolo[4,5-c]pyrrole (3) (2.58 g, 4.88 mmol) and 1,10-dibromodecane (4.39 g, 14.62 mmol) in anhydrous THF (300 mL) was deoxygenated with N$_2$ (10 min) before a solution of CsOH·H$_2$O (860 mg, 5.12 mmol) in anhydrous MeOH (25 mL) was added dropwise via a syringe over a period of 2 h. The reaction mixture was stirred over night, after which time the solvent was evaporated in vacuo and the resulting yellow residue was dissolved in CH$_2$Cl$_2$ (300 mL), washed with H$_2$O.
(3 \times 200 \text{ mL}) and dried (MgSO}_4). Evaporation of the solvent gave a yellow oil, which was purified by column chromatography (500 mL SiO\textsubscript{2}, 6.0 cm \textphi, eluent hexanes/CH\textsubscript{2}Cl\textsubscript{2} 3:2). The yellow band ($R_f = 0.2$) was collected and concentrated to give 5 as a yellow solid (2.94 g, 87\%); M.p. 84–86\degree C; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): $\delta$ 1.25–1.36 (m, 8H), 1.35–1.50 (m, 4H), 1.64 (p, 2H, $J = 7.2$ Hz), 1.84 (p, 2H, $J = 7.2$ Hz), 2.41 (s, 3H), 2.42 (s, 3H), 2.80 (t, 2H, $J = 7.2$ Hz), 3.40 (t, 2H, $J = 7.2$ Hz), 6.92 (s, 2H), 7.27 (d, 2H, $J = 8.1$ Hz), 7.70 (d, 2H, $J = 8.1$ Hz); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): $\delta$ 19.3, 21.6, 28.3, 28.4, 28.9, 29.0, 29.5, 29.6, 29.8, 33.1, 34.1, 36.4, 111.3, 115.2, 117.4, 125.1, 126.8, 127.0, 127.4, 129.5, 130.1, 135.2, 144.9, one signal is missing or overlapping; HiResFTMALDI-MS: calcd for C\textsubscript{26}H\textsubscript{32}BrNO\textsubscript{2}S\textsubscript{7} •+; 692.9656; found: 692.9640; Elemental analysis calcd for C\textsubscript{26}H\textsubscript{32}BrNO\textsubscript{2}S\textsubscript{7}: C, 44.94; H, 4.64; N, 2.02; S, 32.30. Found: C, 44.77; H, 4.53; N, 2.11; S, 32.21.

**Compound 7**

A solution of the MPTTF derivative 5 (2.94 g, 4.23 mmol) in anhydrous THF (300 mL) and anhydrous MeOH (100 mL) was deoxygenated with N\textsubscript{2} (15 min) before sodium methoxide (25\% solution in MeOH, 9.6 mL, 2.28 g, 42.3 mmol) was added in one portion. The yellow solution was stirred for 2 h at room temperature. The reaction mixture was concentrated to approximately 50 mL before H\textsubscript{2}O (200 mL) was added and the mixture was extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 \times 100 mL). The combined organic phases were washed with H\textsubscript{2}O (3 \times 100 mL) and dried (MgSO\textsubscript{4}). After evaporation of the solvent, the yellow oil was purified by column chromatography (500 mL SiO\textsubscript{2}, 6.0 cm \textphi, eluent CH\textsubscript{2}Cl\textsubscript{2}/hexanes 2:1). The yellow band ($R_f = 0.4$) was collected and concentrated to give 7 as a pure orange solid (1.94 g, 85\%); M.p. 80–84\degree C; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): $\delta$ 1.25–1.35 (m, 8H), 1.35–1.50 (m, 4H), 1.63 (p, 2H, $J = 7.1$ Hz), 1.84 (p, 2H, $J = 7.1$ Hz), 2.42 (s, 3H), 2.81 (t, 2H, $J = 7.2$ Hz), 3.40 (t, 2H, $J = 7.2$ Hz), 6.60 (d, 2H, $J = 2.4$ Hz), 8.18 (bs, 1H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): $\delta$ 19.4, 28.3, 28.5, 28.9, 29.1, 29.4, 29.5, 29.8, 33.0, 34.2, 36.4, 109.9, 120.1, 120.2, 126.0, 129.1, three signals are missing or overlapping; HiRes-FT-MALDI-MS: calcd for C\textsubscript{19}H\textsubscript{26}BrNS\textsubscript{6} •+; 538.9567; found: 538.9593; Elemental analysis calcd for C\textsubscript{19}H\textsubscript{26}BrNS\textsubscript{6}: C, 42.20; H, 4.85; N, 2.59; S, 35.58. Found: C, 42.19; H, 4.74; N, 2.68; S, 35.72.
Potassium thioacetate (171 mg, 1.50 mmol) was added to a yellow solution of the MPTTF derivative 7 (270 mg, 0.50 mmol) in anhydrous THF (40 mL). The suspension was deoxygenated with N₂ (15 min) before it was heated under reflux for 2 h. After cooling to room temperature, the reaction mixture was concentrated to approximately 10 mL in vacuo and diluted with CH₂Cl₂ (100 mL), washed with H₂O (3 × 100 mL) and dried (MgSO₄). Evaporation of the solvent gave a yellow solid, which was purified by column chromatography (350 mL SiO₂, 3.5 cm Ø, eluent CH₂Cl₂/cyclohexane 3:1). The yellow band (Rₜ = 0.5) was collected and concentrated to give 9 as a yellow solid (255 mg, 95%); M.p. 67–68°C; ¹H NMR (300 MHz, CDCl₃): δ 1.25–1.45 (m, 12H), 1.55 (p, 2H, J = 7.2 Hz), 1.63 (p, 2H, J = 7.2 Hz), 2.32 (s, 3H), 2.42 (s, 3H), 2.81 (t, 2H, J = 7.2 Hz), 2.85 (t, 2H, J = 7.2 Hz), 6.60 (d, 2H, J = 2.7 Hz), 8.23 (bs, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 19.3, 28.5, 28.9, 29.2, 29.2, 29.3, 29.4, 29.5, 29.6, 29.8, 30.8, 36.4, 109.8, 120.1, 120.2, 125.9, 129.1, 196.3; three signals are missing or overlapping; HiRes-FT-MALDI-MS: calcd for C₂₁H₂₉NOS₇⁺⁺; 535.0289; found: 535.0296; Elemental analysis calcd for C₂₁H₂₉NOS₇: C, 47.06; H, 5.45; N, 2.61; S, 41.88. Found: C, 47.21; H, 5.48; N, 2.66; S, 41.74. CV (CH₂Cl₂, vs. Fc⁺/Fc): E₁/₂ = +0.010 V and +0.460 V.

The MPTTF derivative 7 (1.08 g, 2.00 mmol), tripyrane 10 (1.13 g, 4.00 mmol), and TBACl (0.556 g, 2.0 mmol) were dissolved in anhydrous CH₂Cl₂ (1.2 L) and anhydrous Me₂CO (400 mL) and deoxygenated with N₂ (10 min), before trifluoroacetic acid (0.8 mL) was added to the yellow solution. The reaction was stirred in the dark at room temperature for 20 h, whereupon triethylamine (2 mL) was added slowly. The reaction mixture was concentrated to approximately 400 mL, whereupon CH₂Cl₂ (150 mL) was added and the mixture was washed with H₂O (3 × 400 mL) before being dried (MgSO₄). Evaporation of the solvent gave a yellow oil, which was purified by column chromatography (800 mL SiO₂, 6.0 cm Ø, eluent CH₂Cl₂/hexanes 3:2). The second yellow band (Rₜ = 0.6) was collected and concentrated to give 12 as a yellow solid (398 mg, 22%); M.p. 68–72°C; ¹H NMR (300 MHz, CDCl₃): δ 1.25–1.35 (m, 8H), 1.35–1.50 (m, 4H), 1.51 (s, 12H), 1.53 (s, 12H), 1.64 (p, 2H, J = 7.1 Hz), 1.85 (p, 2H, J = 7.1 Hz), 2.43 (s, 3H), 2.83 (t, 2H, J = 7.2 Hz), 3.40 (t, 2H, J = 7.2 Hz), 5.89 (d, 2H, J = 3.2 Hz), 5.90–5.95 (m, 4H), 6.71 (bs, 1H),
6.94 (bs, 1H), 7.23 (bs, 2H); HiRes-FT-MALDI: calcd for C\textsubscript{43}H\textsubscript{57}BrN\textsubscript{4}S\textsubscript{6}Na\textsuperscript{+}; 923.1989; found: 923.1966;

**Compound 2**

Potassium thioacetate (133 mg, 1.16 mmol) was added to a solution of 12 (350 mg, 0.388 mmol) in anhydrous THF (100 mL). The suspension was deoxygenated with N\textsubscript{2} (15 min) before it was heated under reflux for 4 h. After cooling to room temperature, the reaction mixture was concentrated to approximately 20 mL in vacuo and diluted with CH\textsubscript{2}Cl\textsubscript{2} (100 mL), washed with H\textsubscript{2}O (3 × 50 mL) and dried (MgSO\textsubscript{4}). Evaporation of the solvent gave a yellow solid, which was purified by column chromatography (150 mL SiO\textsubscript{2}, 3.5 cm Ø, eluent CH\textsubscript{2}Cl\textsubscript{2}/hexanes 3:2). The yellow band (R\textsubscript{f} = 0.4) was collected and concentrated to give 2 as a yellow solid (240 g, 69%); M.p. 72–75°C; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) 1.25–1.35 (m, 8H), 1.35–1.50 (m, 4H), 1.51 (s, 12H), 1.53 (s, 12H), 1.55–1.70 (m, 4H), 2.31 (s, 3H), 2.43 (s, 3H), 2.83 (t, 2H, \(J = 7.4\) Hz), 3.86 (t, 2H, \(J = 7.4\) Hz), 5.89 (d, 2H, \(J = 2.8\) Hz), 5.90–5.95 (m, 4H), 6.68 (bs, 1H), 6.93 (bs, 1H), 7.22 (bs, 2H); HisRes-FT-MALDI-MS: calcd for C\textsubscript{45}H\textsubscript{60}N\textsubscript{4}O\textsubscript{7}\textsuperscript{•}+; 896.2807; found: 896.2787; Elemental analysis calcd for C\textsubscript{45}H\textsubscript{60}N\textsubscript{4}O\textsubscript{7}: C, 60.22; H, 6.74; N, 6.24; S, 25.01. Found: C, 59.26; H, 6.68; N, 6.04; S, 25.17; CV (CH\textsubscript{2}Cl\textsubscript{2}, vs. Fc\textsuperscript{+}/Fc): \(E_{1/2} = +0.030\) V and +0.465 V.

**Compound 4**

A solution of 2-{4-(2-cyanethylthio)-5-methylthio-1,3-dithiole-2-yliden}-5-tosyl-(1,3)dithiolo[4,5-c] pyrrole 3 (2.38 g, 4.50 mmol) and 1,6-dibromohexane (3.29 g, 13.5 mmol) in anhydrous THF (450 mL) was deoxygenated with N\textsubscript{2} (10 min) before a solution of CsOH•H\textsubscript{2}O (793 mg, 4.73 mmol) in anhydrous MeOH (2.5 mL) was added dropwise via a syringe over a period of 1.5 h. The solvent was evaporated in vacuo and the resulting yellow residue was dissolved in CH\textsubscript{2}Cl\textsubscript{2} (300 mL), washed with H\textsubscript{2}O (3 × 200 mL) and dried (MgSO\textsubscript{4}). Evaporation of the solvent gave a yellow oil which was purified by column chromatography (500 mL SiO\textsubscript{2}, 6.0 cm Ø, eluent CH\textsubscript{2}Cl\textsubscript{2}/hexanes 2:1). The yellow band (R\textsubscript{f} = 0.3) was collected and concentrated to give 4 as a yellow solid (2.26 g, 79%); M.p. 109–110°C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 1.42–1.47 (m, 4H), 1.60–1.68 (m, 2H), 1.80–1.89 (m 2H), 2.40 (s, 3H), 2.41 (s, 3H), 2.80 (t, 2H, \(J = 7.2\) Hz), 3.39 (t, 2H, \(J = 7.2\) Hz), 6.93 (s, 2H), 7.29 (d, 2H, \(J = 8.8\) Hz), 7.72 (d, 2H, \(J = 8.8\) Hz); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 19.3, 21.8, 27.6, 27.7, 29.6,
32.7, 33.8, 36.2, 111.4, 115.0, 117.0, 125.3, 127.1, 127.3, 129.6, 130.3, 135.5, 145.6, one signal is missing or overlapping; HiRes-FT-MALDI: calcd for C_{22}H_{24}BrNO_2S_7^{+}; 636.9030; found: 636.9051.

**Compound 6**

A solution of MPTTF the derivative 4 (1.80 g, 2.82 mmol) in anhydrous THF (200 mL) and anhydrous MeOH (100 mL) was deoxygenated with N_2 (30 min) before sodium methoxide (25% solution in MeOH, 3.2 mL, 0.76 g, 14.1 mmol) was added in one portion. The yellow solution was stirred for 1 h at 30 °C, whereupon H_2O (100 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic phases were washed with H_2O (3 × 100 mL) and dried (MgSO_4). After evaporation of the solvent, the yellow oil was purified by column chromatography (500 mL SiO_2, 6.0 cm Ø, eluent CH_2Cl_2/cyclohexane 2:1). The yellow band (R_t = 0.4) was collected and concentrated to give 6 as a pure yellow solid (1.22 g, 89%); M.p. 105−108°C. ^1H NMR (400 MHz, CDCl_3): δ 1.42−1.48 (m, 4H), 1.60−1.70 (m, 2H), 1.82−1.90 (m, 2H), 2.43 (s, 3H), 2.82 (t, 2H, J = 7.4 Hz), 3.41 (t, 2H, J = 7.4 Hz), 6.60 (d, 2H, J = 2.8 Hz), 8.19 (bs, 1H); ^13C NMR (100 MHz, CDCl_3): δ 19.3, 27.7, 27.8, 29.6, 32.7, 33.9, 36.2, 109.8, 120.1, 120.1, 125.4, 129.6, three signals are missing or overlapping.

**Compound 8**

Potassium thioacetate (462 mg, 4.00 mmol) was added to a solution of the MPTTF derivative 6 (642 mg, 1.30 mmol) in anhydrous THF (100 mL). The suspension was deoxygenated with N_2 (15 min) before it was heated under reflux for 24 h. After cooling to room temperature, H_2O (50 mL) was added and the mixture was extracted with CH_2Cl_2 (150 mL). The organic phase was washed with H_2O (3 × 200 mL) and dried (MgSO_4). Evaporation of the solvent gave a yellow oil, which was purified by column chromatography (500 mL SiO_2, 5.5 cm Ø, eluent CH_2Cl_2/hexanes 2:1). The yellow band (R_t = 0.5) was collected and concentrated to give 8 as a yellow/orange solid (444 mg, 70%); M.p.113−115 °C; ^1H NMR (300 MHz, CDCl_3): δ 1.30−1.45 (m, 4H), 1.55−1.65 (m, 4H), 2.31 (s, 3H), 2.43 (s, 3H), 2.80−2.90 (m, 4H), 6.60 (d, 2H, J = 2.7 Hz), 8.20 (bs, 1H); MS(EI): m/z (%) 479 (M^{+}, 100); Elemental analysis calcd for C_{17}H_{21}NOS_7: C, 42.55; H, 4.41; N, 2.92; S, 46.78. Found: C, 42.66; H, 4.41; N, 2.91; S, 46.95. CV (CH_2Cl_2, vs. Fc^{+}/Fc): E_{1/2} = +0.020 V and +0.450 V.
**Compound 11**

The MPTTF derivative 6 (600 mg, 1.24 mmol) and tripyrane 10 (800 mg, 2.84 mmol) were dissolved in anhydrous CH₂Cl₂ (0.6 L) and anhydrous Me₂CO (0.21 L) and deoxygenated with N₂ (30 min), before trifluoroacetic acid (0.4 mL) and TBACl (482 mg, 1.73 mmol) was added to the yellow solution. The reaction was stirred in the dark at room temperature for 24 h, whereupon triethylamine (1 mL) was added slowly. The reaction mixture was concentrated to approximately 20 mL, whereupon CH₂Cl₂ (200 mL) was added and the mixture was washed with H₂O (3 × 100 mL) before being dried (MgSO₄). Evaporation of the solvent gave a yellow oil, which was purified by column chromatography (700 mL SiO₂, 6.0 cm Ø, eluent CH₂Cl₂/cyclohexane 3:2). The yellow band (Rf = 0.6) was collected and concentrated to give 11 as a yellow solid (236 mg, 23%); M.p. 87–88°C; ¹H NMR (300 MHz, CDCl₃): δ 1.42–1.50 (m, 4H), 1.51 (s, 12H), 1.53 (s, 12H), 1.60–1.74 (m, 2H), 1.82–1.93 (m, 2H), 2.44 (s, 3H), 2.83 (t, 2H, J = 7.1 Hz), 3.41 (t, 2H, J = 6.8 Hz), 5.90 (d, 2H, J = 2.8 Hz), 5.90–5.95 (m, 4H), 6.68 (bs, 1H), 6.92 (bs, 1H), 7.22 (bs, 2H); HiRes-FT-MALDI-MS: calcd for C₃₉H₄₅BrN₄S₆; 844.1460; found: 844.0816; Elemental analysis calcd for C₃₉H₄₅BrN₄S₆: C, 55.36; H, 5.84; N, 6.62; S, 22.74. Found: C, 54.95; H, 5.91; N, 5.81; S, 22.94.

**Compound 1**

Potassium thioacetate (42 mg, 0.37 mmol) was added to a solution of the MPTTF derivative 11 (96 mg, 0.11 mmol) in anhydrous THF (75 mL). The suspension was deoxygenated with N₂ (15 min) before it was heated under reflux for 24 h. After cooling to room temperature, H₂O (20 mL) was added and the mixture extracted with CH₂Cl₂ (150 mL). The organic phase was washed with H₂O (3 × 200 mL) and dried (MgSO₄). Evaporation of the solvent gave a yellow oil, which was purified by column chromatography (500 mL SiO₂, 5.5 cm Ø, eluent CH₂Cl₂/hexanes 2:1). The yellow band (Rf = 0.5) was collected and concentrated to give 1 as a yellow solid (84 mg, 88%); ¹H NMR (300 MHz, CDCl₃): δ 1.36–1.48 (m, 4H), 1.51 (s, 12H), 1.54 (s, 12H), 1.55–1.70 (m, 4H), 2.30 (s, 3H), 2.44 (s, 3H), 2.82 (t, 2H, J = 7.1 Hz), 2.87 (t, 2H, J = 7.1 Hz), 5.89 (d, 2H, J = 2.8 Hz), 5.90–5.95 (m, 4H), 6.70 (bs, 1H), 6.94 (bs, 1H), 7.23 (bs, 2H); HiRes-FTMALDI-MS: calcd for C₄₁H₅₂N₄O₇⁺⁺; 840.2181; found: 840.1767; Elemental analysis calcd for C₄₁H₅₂N₄O₇: C, 58.53; H, 6.23; N, 6.66; S, 26.68. Found: C, 58.19; H, 6.36; N, 6.22; S, 25.96; CV (CH₂Cl₂, vs. Fe⁺/Fe⁺): E₁/₂ = +0.030 V and +0.460 V.
Figure S1. CV recorded in CH$_2$Cl$_2$ of the SAM prepared from the TTF-calix[4]pyrrole 2 (Reference electrode Fc/Fc$^+$ with n-Bu$_4$NPF$_6$ (0.1 M) as supporting electrolyte on Pt). The insert is showing the linear dependence between the oxidation peak intensities and the scan rate.
Figure S2. CVs recorded in CH$_2$Cl$_2$ of the SAM prepared from the MPTTF model compound 9 after additions of successive aliquots of $n$-Bu$_4$NCl (Reference electrode Fe/Fe$^+$ with $n$-Bu$_4$PF$_6$ (0.1 M) as supporting electrolyte on Pt at 0.2 V s$^{-1}$).
Figure S3. Frequency variations as a function of time of the gold coated quartz crystal during the addition of a 1 mM CH$_2$Cl$_2$ solution of 8 into the QCM cell in the presence of 20 mM of Cl$^-$ (top) and without Cl$^-$ (bottom). The data points have been fitted according to the Langmuir adsorption isotherm model.$^{[S3]}$ The deposition kinetics for the MPTTF model compound 8 does not change when chloride anions is added into the CH$_2$Cl$_2$ solution of 8 before adsorption ($k_{obs} = 0.035 \pm 0.001$ s$^{-1}$ with and without chloride anions).
REFERENCES

