Electronic Supplementary Information for

Redox interactions of Au(III) with carboxylated dithiafulvenes and tetrathiafulvalene analogues in polar organic media

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1. Experimental

1.1. General

Chemicals were purchased from commercial suppliers and used directly without purification. All reactions were conducted in standard, dry glassware and under an inert atmosphere of nitrogen unless otherwise noted. Evaporation and concentration were carried out with a water-aspirator. Flash column chromatography was performed with silica gel 60 (240-400 mesh). Thin-layer chromatography (TLC) was done with silica gel F254 coated on plastic sheets and visualized by UV light. Melting points were measured on an SRS OptiMelt melting point apparatus. $^1$H and $^{13}$C NMR spectra were measured on a Bruker Avance III 300 MHz multinuclear spectrometer. Chemical shifts ($\delta$) are reported in ppm downfield relative to the signal of either the internal reference SiMe$_4$ or residual solvent CHCl$_3$ (7.26 ppm for $^1$H and 77.2 ppm for $^{13}$C). Coupling constants ($J$) are given in Hz. Infrared spectra (IR) were recorded on a Bruker Alfa spectrometer. HRMS analyses were performed on an Agilent 6230 TOF LC/MS instrument using an APPI ionizer and a QSTAR XL hybrid quadrupole/TOF mass spectrometer equipped with an o-MALDI ion source. UV-Vis-NIR absorption spectra were measured on a Cary 6000i spectrophotometer. Scanning Electron Microscopes (SEM) were performed on JEOL JSM-7100F ($V_{\text{acc}}$ = 30 kV, $I_{\text{max}}$ = 400 nA). The Delsa Nano S particle analyzer (Beckman Coulter, Inc.) was used for dynamic light scattering (DLS) studies, where sample solutions were filtered through a 0.20 μm Millex-FG filter prior to the measurements. The calculations of the particle size distributions were performed with the Delsa Nano software 2.30 (Beckman Coulter, Inc). Cyclic voltammetric analyses were carried out in a standard three-electrode setup controlled by a BASi Epsilon potentiostat.
The synthesis of starting materials, dimethyl-5-formylisophthalate (6)\(^1\) and 1,3-dithole-2-thiones 7 and 8,\(^2\) was done according to the literature procedures with suitable modifications.

**Scheme S-1** Synthesis of carboxylated DTFs and TTFVs.

1.2 Synthetic Procedures

DTF 2a

A mixture of dimethyl-5-formylisophthalate 6 (1.00 g, 4.50 mmol) and thione 7 (3.01 g, 8.79 mmol) in P(OMe)₃ (15 mL) was stirred and heated at 105 °C for 3 h. The excess P(OMe)₃ was removed by vacuum distillation. The residue was purified by silica column chromatography (CH₂Cl₂/hexanes, 1:4) to afford compound DTF 2a (2.58 g, 3.36 mmol, 88%) as a yellow solid. m.p. > 145 °C (dec); ¹H NMR (300 MHz, CDCl₃) δ 8.44 (t, J = 1.5 Hz, 1H), 8.06 (d, J = 1.5 Hz, 2H), 6.51 (s, 1H), 3.96 (s, 6H), 2.83 (m, 4H), 1.69–1.59 (m, 4H), 1.45–1.22 (m, 28H), 0.91–0.81 (m, 6H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ 166.2, 137.1, 136.4, 131.4, 130.9, 128.3, 127.3, 124.7, 111.8, 52.4, 36.3, 36.1, 31.9, 30.9, 29.8, 29.7, 29.6, 29.5, 29.3, 29.2, 29.1, 28.57, 28.56, 22.7, 14.1 ppm; FTIR (neat) 2953, 2916, 2847, 1710, 1563, 1438, 1331, 1263, 1205, 1138, 1011, 886, 747 cm⁻¹; HRMS (APPI, positive) m/z calcd for C₃₄H₅₃O₄S₄ 653.2827, found 653.2814 [M + H]⁺.
TTFV 3a

DTF 2a (0.50 g, 0.76 mmol) and I₂ (0.58 g, 2.28 mmol) were added in CH₂Cl₂ (100 mL) and the mixture was stirred at rt overnight. Then a satd Na₂S₂O₃ aq. solution (90 mL) was added and the mixture was stirred for another 3 h at rt. The organic layer was separated, washed with H₂O, dried over MgSO₄, and concentrated under vacuum. The residue was purified by silica column chromatography (EtOAc/hexanes, 1:8) to afford TTFV 3a (0.40 g, 0.32 mmol, 86%) as a yellow gummy solid. \(^1\)H NMR (300 MHz, CDCl₃) δ 8.46 (t, \(J = 1.5\) Hz, 2H), 8.23 (d, \(J = 1.5\) Hz, 4H), 3.92 (s, 12H), 2.93–2.67 (m, 8H), 1.68–1.52 (m, 8H), 1.44–1.19 (m, 56H), 0.90–0.85 (m, 12H) ppm; \(^1\)^1C NMR (75 MHz, CDCl₃) δ 166.0, 140.6, 138.1, 131.8, 131.2, 128.9, 128.8, 125.9, 121.5, 52.4, 36.3, 36.2, 31.93, 31.91, 29.65, 29.58, 29.4, 29.3, 29.2, 28.6, 28.5, 22.7, 14.1 ppm; FTIR (neat) 2922, 2852, 1728, 1436, 1327, 1240, 1134, 1002, 757, 721 cm⁻¹; HRMS (APPI, positive) \(m/z\) calcd for C₆₈H₁₀₃O₅S₈ 1303.5419, found, 1303.5424 [M+H]^+.

DTF 2b
DTF 2a (0.39 g, 0.59 mmol) and NaOH (0.76 g, 19 mmol) were added in THF/H$_2$O (240 mL, 3:1) and the mixture was stirred and heated at 75 °C overnight. The solvent THF was then removed under vacuum, and the residue was diluted to 50 mL with H$_2$O and acidified to pH 4 with HCl (aq). The precipitate formed was extracted with EtOAc, washed with H$_2$O, dried over MgSO$_4$, and concentrated under vacuum to afford compound 2b (0.32 g, 0.51 mmol, 87%) as a yellow solid. m.p. > 120 °C (dec); $^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.26 (t, $J$ = 1.5 Hz, 1H), 8.01 (d, $J$ = 1.3 Hz, 2H), 6.94 (s, 1H), 2.92–2.80 (m, 4H), 1.62–1.51 (m, 8H), 1.43–1.15 (m, 28H), 0.85–0.78 (m, 6H) ppm (one carboxylic proton signal not observed because of rapid proton exchange); Meaningful $^{13}$C NMR data was not acquired because of low solubility; FTIR (neat) 2920, 2849, 1687, 1559, 1436, 1301, 1262, 1217, 916, 795, 751, 608 cm$^{-1}$; HRMS (APPI, positive) m/z calcd for C$_{32}$H$_{49}$O$_4$S$_4$ 625.2514 found, 625.2513 [M+H]$^+$. 

TTFV 3b

TTFV 3a (0.10 g, 0.076 mmol) and NaOH (0.090 g, 2.3 mmol) were added in THF/H$_2$O (40 mL, 3:1) and the mixture was stirred and heated at 75 °C overnight. The solvent MeOH was then removed under vacuum, and the residue was diluted to 50 mL with H$_2$O and acidified to pH 4 with HCl (aq). The precipitate formed was extracted with EtOAc, washed with H$_2$O, dried over MgSO$_4$, and concentrated under vacuum to afford compound 3b (0.060 g, 0.048 mmol, 75%) as
a yellow solid. m.p. > 246 °C (dec); $^1$H NMR (300 MHz, acetone-$d_6$) $\delta$ 8.53 (t, $J = 1.5$ Hz, 2H), 8.36 (d, $J = 1.5$ Hz, 4H), 2.98-2.78 (m, 8H), 1.72-1.61 (m, 8H), 1.50-1.22 (m, 56H), 0.91-0.83 (m, 12H) ppm (one carboxylic proton signal not observed because of rapid proton exchange); Meaningful $^{13}$C NMR data was not acquired because of low solubility; FTIR (neat): 2922, 2851, 1729, 1528, 1436, 1260, 1103, 1021, 720, 668 cm$^{-1}$; HRMS (APPI, negative) m/z calcd for C$_{64}$H$_{93}$O$_8$S$_8$ 1245.4642, found, 1245.4633 [M−H]$^−$.

**DTF 4**

![Structure of DTF 4](image)

A mixture of dimethyl-5-formylisophthalate 6 (0.510 g, 2.25 mmol) and thione 8 (2.01 g, 8.87 mmol) in P(OMe)$_3$ (15 mL) was stirred and heated at 105 °C for 3 h. The excess P(OMe)$_3$ was removed by vacuum distillation. The residue was purified by silica column chromatography (CH$_2$Cl$_2$/hexanes, 1:2) to afford compound DTF 4 (1.97 g, 4.92 mmol, 86%) as a yellow solid. m.p. 167–198 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.45 (m, 1H), 8.06 (m, 2H), 6.53 (s, 1H), 3.96 (s, 6H), 2.46 (s, 3H), 2.44 (s, 3H), ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 166.4, 137.2, 136.2, 131.6, 131.1, 128.4, 127.5, 124.1, 112.4, 52.6, 19.3, 19.1 ppm; FTIR (neat) 2996, 2949, 2916, 1709, 1492, 1421, 1203, 1109, 725, 668, 547, 470 cm$^{-1}$; HRMS (APPI, positive) m/z calcd for C$_{16}$H$_{17}$O$_4$S$_4$, 401.0010, found 401.0010 [M+H]$^+$.
**TTFV 5**

A mixture of DTF 4 (0.34 g, 0.85 mmol) and I₂ (0.26 g, 3.07 mmol) in CH₂Cl₂ (100 mL) was stirred at rt overnight. Then a satd Na₂S₂O₃ aq. solution (90 mL) was added. The mixture was stirred for another 3 h at rt. The organic layer was separated, washed with H₂O, dried over MgSO₄, and concentrated under vacuum. The residue was purified by silica column chromatography (EtOAc/hexanes, 1:1) to afford compound 5 (0.68 g, 1.3 mmol, 80%) as a yellow gummy solid. ¹H NMR (300 MHz, CDCl₃) δ 8.46 (m, 2H), 8.23 (m, 4H), 3.93 (s, 12H), 2.44 (s, 6H), 2.41 (s, 6H) ppm; Meaningful ¹³C NMR data was not acquired because of low solubility; FTIR (neat) 2921, 2851, 1723, 1460, 1433, 1328, 1242, 1134, 1028, 720, 671, 467 cm⁻¹; HRMS (APPI, positive) m/z calcd for C₃₂H₃₁O₈S₈ 798.9785, found 798.9789 [M+H]⁺. X-ray.

**Preparation of HAuCl₄ and DTF/TTFV mixtures:** To a solution of DTF/TTFV (1.0 mg) in a chosen organic solvent (2 mL), HAuCl₄·3H₂O (1.0 mg) as added, and the resulting mixture was stirred at room temperature. Aliquots of the mixture were taken at different times for UV-Vis-NIR, SEM, and DLS analyses.
2. NMR Spectra for New Compounds

Fig. S-1 $^1$H NMR (300 MHz, CDCl$_3$) of compound 2a.
Fig. S-2 $^{13}$C NMR (75 MHz, CDCl$_3$) of compound 2a.
Fig. S-3 $^1$H NMR (300 MHz, CDCl$_3$) of compound 3a.
Fig. S-4 $^{13}$C NMR (75 MHz, CDCl$_3$) of compound 3a.
Fig. S-5 $^1$H NMR (300 MHz, DMSO-$d_6$) of compound 2b.
Fig. S-6 $^1$H NMR (300 MHz, acetone-$d_6$) of compound 3b.
Fig. S-7 $^1$H NMR (300 MHz, CDCl$_3$) of compound 4.
Fig. S-8 $^{13}$C NMR (75 MHz, CDCl$_3$) of compound 4.
Fig. S-9 $^1$H NMR (300 MHz, CDCl$_3$) of compound 5.
3. Electrochemical Analysis

![Cyclic voltammograms of (A) DTF 2a and (B) TTFV 3a measured in CH₂Cl₂ at rt.](image)

**Fig. S-10** Cyclic voltammograms of (A) DTF 2a and (B) TTFV 3a measured in CH₂Cl₂ at rt. Experimental conditions: supporting electrolyte: Bu₄NBF₄ (0.10 M), working electrode: glassy carbon, counter electrode: Pt wire, reference electrode: Ag/AgCl (3 M NaCl), scan rate: 50 mV/s.
Fig. S-11 Cyclic voltammograms of (A) DTF 2b and (B) TTFV 3b measured in CHCl$_3$ at room temperature. Experimental conditions: supporting electrolyte: Bu$_4$NBF$_4$ (0.10 M), working electrode: glassy carbon, counter electrode: Pt wire, reference electrode: Ag/AgCl (3 M NaCl), scan rate: 100 mV/s.
Fig. S-12 Cyclic voltammograms of (A) DTF 2b and (B) TTFV 3b measured in DMSO at room temperature. Experimental conditions: supporting electrolyte: Bu4NBF4 (0.10 M), working electrode: glassy carbon, counter electrode: Pt wire, reference electrode: Ag/AgCl (3 M NaCl), scan rate: 50 mV/s.
**Fig. S-13** Cyclic voltammograms of (A) DTF 4 and (B) TTFV 5 measured in CH$_2$Cl$_2$ at room temperature. Experimental conditions: supporting electrolyte: Bu$_4$NBF$_4$ (0.10 M), working electrode: glassy carbon, counter electrode: Pt wire, reference electrode: Ag/AgCl (3 M NaCl), scan rate: 100 mV/s.
4. Oxidative UV-Vis-NIR Titration Results

**Fig. S-14** UV-Vis-NIR spectra monitoring the titration of DTF 2b in CHCl₃ (1.0 × 10⁻⁶ M) with PhI(OAc)₂/CF₃SO₃H (1:4 molar ratio) as oxidant at room temperature. The amount of PhI(OAc)₂ increased from 0.0 to 2.6 molar equivalents.

**Fig. S-15** UV-Vis-NIR spectra monitoring the titration of TTFV 3b in CHCl₃ (8.2 × 10⁻⁷ M) with PhI(OAc)₂/CF₃SO₃H (1:4 molar ratio) as oxidant at room temperature. The amount of PhI(OAc)₂ increased from 0.0 to 6.2 molar equivalents.