Supporting Information

Electrochemical and chemical tuning of the surface wettability in tetrathiafulvalene self-assembled monolayers

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Experimental Section

Synthesis of 1. Compound **3** (0.065g 0.229 mmol) and α-lipoic acid **4** were dissolved in distilled DCM (4 ml). The solution was stirred for 15 min at 0°C. Then, a solution of DCC (32 mg, 0,158 mmol) and DMAP (4 mg, 0,032 mmol) in distilled CH₂Cl₂ (3 ml) was added and the reaction stirred at 0°C for 15 min. The mixture was left stirring overnight at room temperature and the residue was purified by a chromatography column hexane/CH₂Cl₂ (1/1) in order to give a yellow powder **1** (0.039 g, 60%). Rf (TLC) (hexane/CH₂Cl₂, 1/1): 0,54; M.P. = 89 - 93°C; ¹H-NMR (250 MHz, CDCl₃) δ (ppm): 7.24-7.21 (m, 2H, Ar-H), 7.12 -7.08 (m, 2H, Ar-H), 6.34 (s, 1H, -SCH), 4.83 (s, 2H, -CH₂O-), 3.59-3.54 (m, 1H), 3.17-3.08 (m, 2H), 2.40-2.34 (m, 3H), 2.00-1.85 (m, 1 H), 1.71-1.65 (m, 4H), 1.49-1.43 (m, 2H); ¹³C-NMR (62.5 MHz, CDCl₃) δ (ppm): 172.8 (C=O), 136.9, 136.8, 131.0, 125.9-119.0 (C-Ar), 113.4, 108.2, 60.6, 56.3, 40.2, 38.5, 34.6, 33.8, 28.6, 24.6; FT-IR (v_{max}, cm⁻¹): 3067, 2941, 2919, 2850, 1725, 1567, 1445, 1432, 1407, 1376, 1347, 1275, 1166, 1117, 944, 781, 733; MALDI-TOF (pos) MS: Calcd. 471.979, Found: 471.854; UV (CH₂Cl₂) (λ/nm (logε)): 259 (3,92), 315 (4,09), 440 (2.45); CV (0.1 M LiClO₄ in ACN vs. DMFc): two reversible waves corresponding

to the TTF oxidation at $E_1^{1/2}$ = +0.61 V and $E_2^{1/2}$ = +0.96 V and a third one coming from the S-S oxidation at $E_3^{1/2}$ = +1.19 V.

Synthesis of 7. The dithiol-2-one 5 (1,135 g, 3.206 mmol) and dithiole-2-thione 6 (0.801 g, 3.206 mmol) were heated to reflux in freshly distilled P(OMe)₃ (5 ml) for 10 min. taking place the precipitation of an orange product. The mixture was kept in the freezer for 16 h. and then filtered. The solid was purified by chromatography on silica gel (CH₂Cl₂/hexane, 1/1). Compound 7 was obtained with a low yield (14%). Rf (TLC) (CH₂Cl₂/hexane, 1/1): 0.66; M.p.= 199 – 203°C; ¹H-NMR (250 MHz, CDCl₃) δ (ppm): 3.86 (s, 6 H; 2 x –OCH₃); ¹⁹F-NMR (376 MHz, CDCl₃) δ (ppm): –110.68 (t, 4F, J= 3.76 Hz); –126.79 (quint, 2F, J= 3.76 Hz); ¹³C-NMR (62.5 MHz,CDCl₃) δ (ppm): 159.5 (2 C=O), 131.7, 118.5, 115.8-111.0 (CF₂-CF₂-CF₂), 53.5. FT-IR (v_{max}, cm⁻¹): 2959, 2850, 1741, 1710, 1599, 1579, 1514, 1435, 1318, 1262, 1240, 1192, 1139, 1101, 1032, 996, 947, 908, 871, 841; MALDI-TOF (pos) MS: Calcd. 555.849, Found: 555.602; UV (CH₂Cl₂) (λ /nm (loge)): 242 (3,55), 302 (3,38), 327 (3.41), 414 (2.52); CV (0.1 M LiClO₄ in ACN vs. DMFc): two reversible waves at E₁^{1/2}= +0.92 V and E₂^{1/2}= +1.11 V.

Synthesis of 8. A mixture of 7 (0.2 g, 0.36 mmol) and lithium bromide (0.56, 6.47 mmol) in 7 ml of dry DMF was stirred in a thermostitized bath at 90 °C. After 2h, 10 ml of a saturated solution of sodium chloride was added. The solid was then extracted in ethyl acetate (3x100 ml), washed with distilled water and dried with Na₂SO₄. The purification was carried out by chromatoghraphy in a silica gel column (CH₂Cl₂/ hexane (1/1)) to give 8 (0.113 g, 63%). Rf (TLC) (CH₂Cl₂/ hexane, 1/1): 0,79; M.p. = 205 – 208°C; ¹H-NMR (250 MHzCDCl₃) δ (ppm): 7.38 (s, 1 H, -SCH) , 3.84 (s, 3 H, -OCH₃); ¹⁹F-NMR (376 MHz,CDCl₃) δ (ppm): -110.72 (t, 4F, J= 3.76 Hz); -126.83 (quint, 2F, J= 3.76 Hz); ¹³C-NMR (100.4 MHz,CDCl₃) δ (ppm): 159.4 (C=O), 131.1,

128.2, 123.1, 115.9-108.6 ($\underline{C}F_2-\underline{C}F_2-\underline{C}F_2$), 53.0; FT-IR (v_{max} , cm⁻¹): 3105, 2964, 2922, 2853, 1706, 1600, 1561, 1536, 1439, 1319, 1260, 1240, 1198, 1122, 1106, 1059, 992, 915, 900, 870, 840; MALDI-TOF (pos) MS: Calcd. 497.844, Found: 497.659; UV (CH₂Cl₂) (λ /nm (log₈)): 242 (3,38), 311 (3,27), 324 (3.30), 403 (2.55); CV (0.1 M LiClO₄ in ACN *vs.* DMFc): two reversible waves at $E_1^{1/2}$ = +0.83 V and $E_2^{1/2}$ = +1.02 V.

Synthesis of 9. To a solution of TTF **8** (0.266 g, 0.534 mmol) in dry CH₂Cl₂ (20 ml), cooled at -78°C and under a Ar atmosphere, DIBAL-H (1 M, in CH₂Cl₂, 2,67 ml) was added dropwise. After 3 h., the mixture was treated with a 6 M aqueous solution 1:1 of HCl and MeOH (10 ml). CH₂Cl₂ (30 ml) was added and the organic layer was washed with 1 M aqueous HCl, then with water, dried with MgSO₄ and evaporated. The residue was purified by a chromatography column of silica gel (hexane/CH₂Cl₂ (1/1)) to give **9** as an orange solid (78%). Rf (TLC) (Hexane/CH₂Cl₂, 1/1): 0.24; M.p. = 197 - 200°C, ¹H-NMR (300 MHz, CDCl₃) δ (ppm): 6.28 (s, 1H, -SCH), 4.43 (s, 2H, -CH₂O-); ¹⁹F-NMR (235.25 MHz,CDCl₃) δ (ppm): -111.25 (t, 4F, J= 4.7 Hz); -127.38 (quint, 2F, J= 4.7Hz); ¹³C-NMR (100,4 MHz, CDCl₃) δ (ppm): 136.7, 125.4, 115.6-106.1 (CF₂-CF₂-CF₂), 60.6; FT-IR (v_{max}, cm⁻¹): 3248, 2923, 2853, 1608, 1597, 1421, 1321, 1266, 1241, 1200, 1136, 1027, 993, 872, 840; MALDI-TOF (pos) MS: Calcd. 469.849, Found: 469.820; UV (CH₂Cl₂) (λ/nm (logε)): 244 (3,99), 327 (4.03), 428 (2.85); CV (0.1 M LiClO₄ in ACN vs. DMFc): two reversible waves at E₁^{1/2} = +0.70 V and E₂^{1/2} = +0.95 V.

Synthesis of 2. The TTF alcohol 9 (0.07g 0.149 mmol) and α -lipoic acid (4) (0.037 g, 0.179 mmol) were dissolved in distilled CH₂Cl₂ (10 ml). The solution was stirred for 15 min at 0°C. Then, a solution of DCC (46 mg, 0,223 mmol) and DMAP (5.5 mg, 0,044 mmol) in distilled DCM (5 ml) was added and the reaction was stirred at 0°C for 15 min. The mixture was left stirring overnight at room temperature and the residue was

purified by a chromatography column hexane/CH₂Cl₂ (1/1) in order to give a yellow powder **2** (0.071 g, 72%). Rf(TLC) (hexane/CH₂Cl₂, 1/1): 0,48; M.p. = 139 – 141°C; ¹H-NMR (250 MHz, CDCl₃) δ (ppm): 6.38(s, 1H, -SCH-), 4.83 (s, 2H, -CH₂O-), 3.59-3.52 (m, 1H), 3.19-3.11 (m, 2H), 2.50-2.34 (m, 3H), 1.94-1.87 (m, 1 H), 1.74-1.62 (m, 4 H), 1.56-1.43 (m, 2H); ¹⁹F-NMR (235.25 MHz,CDCl₃) δ (ppm): –111.25 (t, 4F, J= 4.7 Hz); –127.38 (quint, 2F, J= 4.7 Hz); ¹³C-NMR (90,36 MHz, CDCl₃) δ (ppm): 173.3 (C=O), 131.2, 125.1, 118.7, 115.6-106.5 (CF₂-CF₂-CF₂), 60.3, 56.3, 40.5, 38.6, 34.6, 33.9, , 28.6, 24.6; FT-IR (v_{max}, cm⁻¹): 3067, 2921, 2853, 1726, 1597, 1439, 1416, 1378, 1352, 1315, 1273, 1240, 1195, 1171, 1122, 992, 945, 903, 868, 841; MALDI-TOF (pos) MS: Calcd. 657.882, Found: 658.288; UV (CH₂Cl₂) (λ /nm (log ε)): 244 (4.10) 327 (4.12), 428 (2.85); CV (0.1 M LiClO₄ in ACN *vs*. DMFc): two reversible waves corresponding to the TTF oxidation at E₁^{1/2}= +0.74 V and E₂^{1/2}= +0.96 V and a third one coming from the S-S oxidation at E₁^{1/2}= +1.18 V.

SAM Preparation:

The solvents used in the surface chemistry experiments were c high purity grade for HPLC from ROMIL-SpS (Super Purity Solvent). Gold (111) substrates consisting of 300 nm of Au on mica were purchased from Georg Albert PVD-Beschichtungen. The substrates were first rinsed with dichloromethane, acetone and ethanol and dried under nitrogen stream. Then, these substrates were cleaned in a UV ozone chamber for 20 minutes and, afterwards, immediately immersed in ethanol HPLC for, at least, 30 minutes, rinsed with ethanol and isopropanol and dried under nitrogen stream. The substrates were immediately immersed in the solution of the desired TTF to prepare the SAM.

SAMs of both TTFs **1** and **2** were prepared on Au(111) substrates by incubating the freshly cleaned substrates in a 1 mM solution of the corresponding molecule in absence of light and under argon. In the case of TTF **1**, tetrahydrofuran (THF) was employed as a solvent and the samples were immersed for 48 h at room temperature, whereas for TTF **2** a toluene solution was used and the substrates were placed in for 72 h, the first three hours heating at 47°C and afterwards at room temperature. The substrates were then rinsed thoroughly with the same solvent employed for the SAM formation to remove the physisorbed material and dried under nitrogen stream.

Additional Characterization Data



Figure S1. XPS spectrum of S2p of SAM S1.



Figure S2. XPS spectra of S2p (top) and F1s (bottom) for SAM S2.

The XPS spectrum of S1 showed two doublets characteristic of the sulfur S2p_{3/2} and S2p_{1/2}, with a 2:1 intensity ratio and a splitting of 1.2 eV. The first doublet has one peak at 161.9 eV (S2p_{3/2}) and one at 163.1 eV (S2p_{1/2}) and is attributed to the S-Au bond, while the second one is centered at 163.5 eV (S2p_{3/2}) and 164.7 eV (S2p_{1/2}) and corresponds to the sulfurs of the TTF moiety. The intensity ratio between the doublets is 2.2:3.8, close to the expected value of 2:4. For S2, the Au-S doublet is observed at binding energies 161.9 eV and 163.1 eV, and TTF sulfurs at 163.7 eV and 164.9 eV. In this case, the Au-S and the TTF sulfur doublets have an intensity relation 2.1:5.9 (theoretical 2:6). In this SAM, the fluorine peak F1s is observed at 687.6 eV, and the S/F experimental ratio is 1.1, similar to the calculated one of 1.3.



Figure S3. ToF-SIMS spectrum of SAM S1.



Figure S4. ToF-SIMS spectrum of SAM S2.



Figure S5. CV of the TTF **1** using the Pt wire as the working electrode vs Ag(s) and a Pt wire as the counter electrode in 0.1 M LiClO₄ in acetonitrile at scan rate 300 mV/s.



Figure S6. CV of the TTF **2** using the Pt wire as the working electrode *vs* Ag(s) and a Pt wire as the counter electrode in 0.1 M LiClO₄ in acetonitrile at scan rate 300 mV/s.



Figure S7. CV of **S1** using the functionalised surface as the working electrode vs Ag(s) and a Pt wire as the counter electrode in 0.1 M LiClO₄ in acetonitrile at 100 mV/s.



Figure S8. CV of **S2** using the functionalised surface as the working electrode vs Ag(s) and a Pt wire as the counter electrode in 0.1 M LiClO₄ in acetonitrile at 500 mV/s.

NMR Spectra

Compound **1**



¹H-NMR





Compound **2**







¹³C-NMR



¹⁹F-NMR

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¹³C-NMR









¹H-NMR



δ **(ppm)**

¹⁹F-NMR

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Compound **9**











¹⁹F-NMR