

Supplementary data

Redox-Active Self-Assembled Monolayers as Novel Solid Contacts for Ion-Selective

Electrodes

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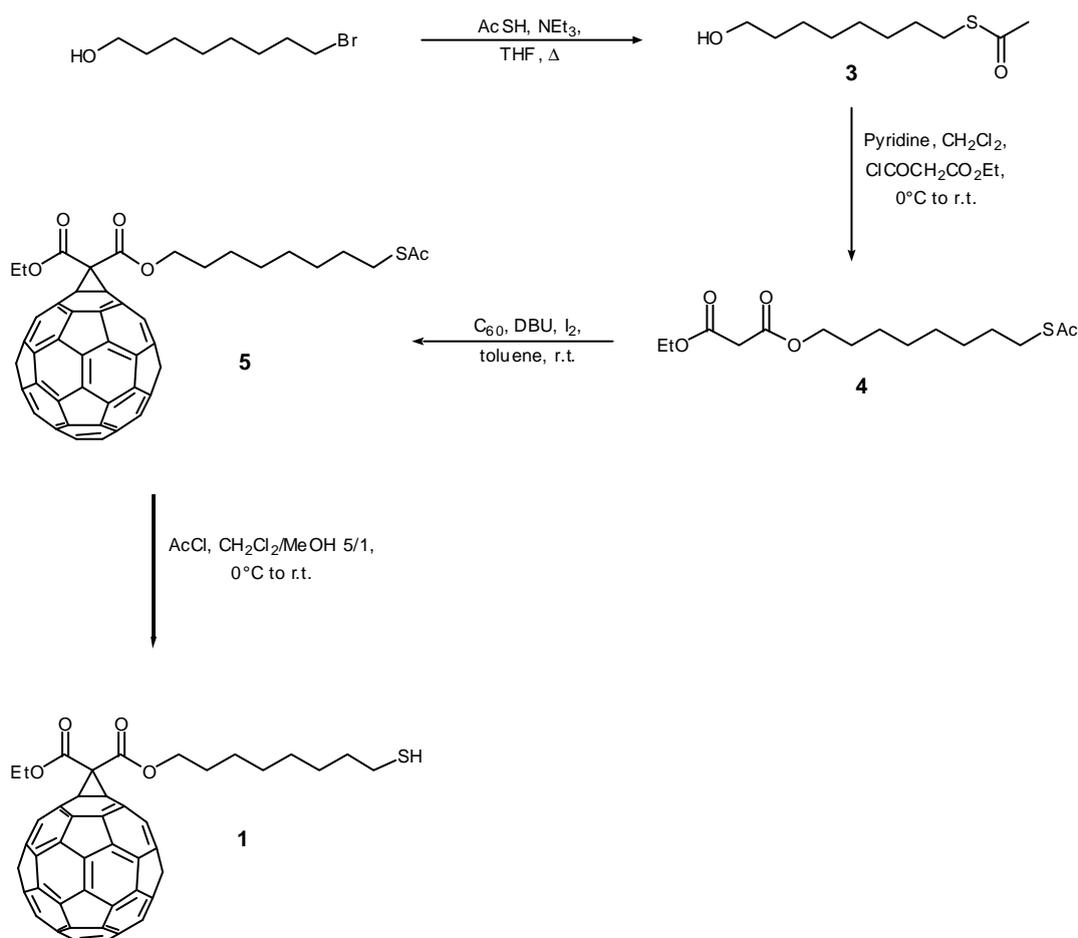
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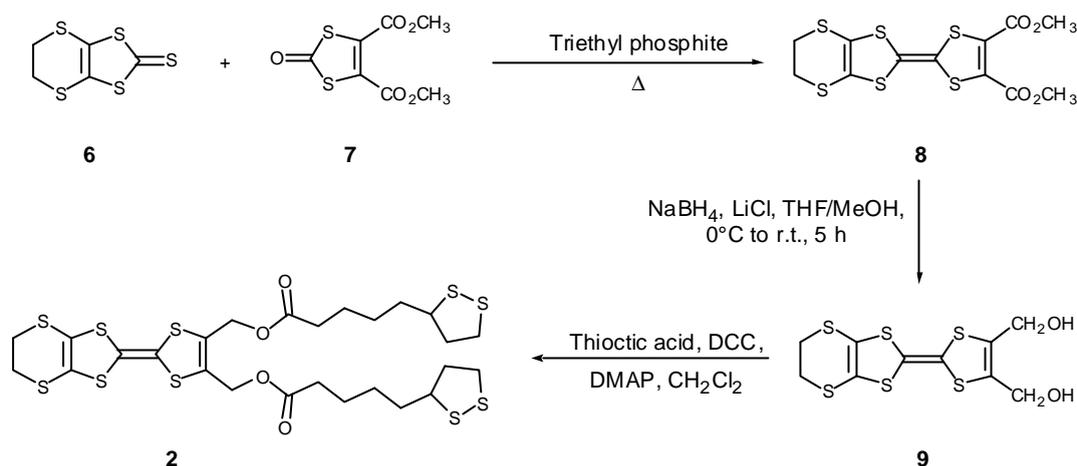
General experimental

Reagents and solvents were purchased reagent-grade and used without further purification, except for CH₂Cl₂ and THF which were distilled under N₂ in the presence of CaH₂ and sodium benzophenone ketyl, respectively. Fullerene soot extract was purchased from *MER Corporation*, Tucson, Arizona (AZ) 85706, USA. All reactions were performed in standard glassware. Evaporation and concentration *in vacuo* were done at water aspirator pressure, and compounds were dried at 10⁻² Torr. Flash column chromatography: SiO₂ 60 (230-400 mesh, 0.040-0.063 mm) from *E. Merck*, SiO₂ H (5-40 μm) from *Fluka*. TLC aluminum plates coated with SiO₂ 60 F₂₅₄ from *E. Merck*; visualization by UV light (254 or 366 nm). IR Spectra: *Perkin Ekmer 1600-FTIR or 2000-FTIR*. UV/VIS Spectra: *Varian-CARY-5 or Shimadzu UV-2101PC* spectrophotometer. NMR Spectra: *Varian Gemini 300 or 200* spectrometers at 296 or 300 °K, with solvent peaks as reference.

EI-MS: *VG Tribid* instrument, 70 eV. FAB-MS: *VG ZAB 2SEQ* or *VG MASSLAB TRIO-2* instrument, *m*-nitrobenzyl alcohol as matrix. MALDI-TOF-MS: *Bruker REFLEX* spectrometer; spectra with reflectron detection were measured in the positive-ion mode and acceleration voltage 15 kV, 3-indolacrylic acid as matrix. HR-FAB-MS: *micromass Quattro I* spectrometer in the positive FAB mode with a resolution of 10 K. Elemental analyses were performed by the Mikrolabor at the Laboratorium für Organische Chemie, ETH-Zürich. IR spectra for SAM with **1** and **2** were recorded at grazing incidence reflection on a *Bruker IFS 66 V* spectrometer equipped with a MCT detector. The measurements were performed at an incident angle of 80° with a fixed angle inset and at a pressure in the sample chamber of 1 mbar.



Synthetic pathway to fullerene derivative 1



Synthetic pathway to TTF derivative 2

S-(8-Hydroxyoctyl) thioacetate 3. NEt_3 (97%, 0.37 ml, 2.55 mmol) and thioacetic acid (96%, 0.19 ml, 2.55 mmol) were stirred in dry THF (20 ml) at r.t. for 1 h. To this solution, 8-bromo-1-octanol (0.3 ml, 1.70 mmol) was added dropwise over 30 min. The resulting slurry was stirred 12 h at r.t., then dist. H_2O (100 ml) was added followed by extraction with AcOEt (2 \times 50 ml). The combined organic layers were washed with dist. H_2O (2 \times 50 ml). The crude mixture was subjected to flash column chromatography (SiO_2 H, hexane/AcOEt 9:1) to afford (248 mg, 71%) **3** as a colorless oil: (Found: C, 58.89; H, 10.01; S, 15.48. $\text{C}_{10}\text{H}_{20}\text{O}_2\text{S}$ requires C, 58.78; H, 9.87; O, 15.66; S, 15.69%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2993, 2856, 1686, 1461, 1356, 1136, 1111, 956; δ_{H} (300 MHz, CDCl_3) 1.28-1.40 (8 H, m, CH_2), 1.51-1.58 (4 H, m, CH_2), 2.31 (3 H, s, S(O)C-CH_3), 2.85 (2 H, t, J 7.5, $-\text{CH}_2\text{-S-}$), 3.62 (2 H, t, J 6.6, $-\text{CH}_2\text{-OH}$); δ_{C} (50 MHz, CDCl_3) 23.17, 26.22, 26.53, 26.63, 26.72, 26.98, 28.15, 30.25 (CH_2 and S(O)C-CH_3), 60.53 ($-\text{CH}_2\text{-OH}$), 193.88 (S(O)C-CH_3); m/z (EI-MS) 43 ($[\text{C(O)CH}_3]^+$, 100%), 143 ($[\text{M} - \text{SCH}_2\text{CH}_2]^+$, 14%), 161 ($[\text{M} - \text{C(O)CH}_3]^+$, 3%), 186 ($[\text{M} - \text{H}_2\text{O}]^+$, 0.3%), 204 (M^+ , 0.4%).

[8-(Acetylsulfanyl)octyl] ethyl malonate 4. Ethyl-3-chloro-3-oxopropanoate (95%, 0.83 ml, 6.18 mmol) was added dropwise to a solution of **3** (631 mg, 3.9 mmol) and pyridine (0.50 ml, 6.18 mmol) in dry CH_2Cl_2 (30 ml) at 0 $^\circ\text{C}$ over 15 min. The reaction was allowed to warm slowly

up to r.t. for 10 h, then washed with sat. aq. NH_4Cl solution (3×30 ml) and dist. H_2O (2×100 ml). The organic phase was dried over MgSO_4 and concentrated under reduced pressure. The resulting yellow oil was purified by distillation under reduced pressure (bp 120-122 °C at 0.1 mm Hg) to yield 696 mg (2.19 mmol, 70%) of **4** as a colorless oil: (Found: C, 56.57; H, 8.00; S, 9.94. $\text{C}_{15}\text{H}_{26}\text{O}_5\text{S}$ requires C, 56.58; H, 8.23; O, 25.12; S, 10.07%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3011, 2934, 2858, 1707, 1728, 1686, 1332, 1148, 1032, 957; δ_{H} (200 MHz, CDCl_3) 1.25-1.33 (15 H, t, J 7.2, and br s, $\text{CH}_3\text{-CH}_2\text{-O-}$ and CH_2), 2.33 (3 H, s, S(O)C-CH_3), 2.87 (2 H, t, J 7.0, $-\text{CH}_2\text{-S-}$), 3.37 (2 H, s, $(\text{O})\text{C-CH}_2\text{-C(O)}$), 4.14 (2 H, t, J 6.6, $-\text{CH}_2\text{-CH}_2\text{-O-}$), 4.21 (2 H, q, J 7.0, $\text{CH}_3\text{-CH}_2\text{-O-}$); δ_{C} (50 MHz, CDCl_3) 14.08 ($\text{CH}_3\text{-CH}_2\text{-O-}$), 25.70, 28.42, 28.68, 28.95, 29.02, 29.10, 29.47 (CH_2), 30.65 (S(O)C-CH_3), 41.7 ($(\text{O})\text{C-CH}_2\text{-C(O)}$), 61.50, 65.61 ($-\text{CH}_2\text{-O-C(O)}$), 166.73 ($-\text{O-C(O)}$), 196.06 ($-\text{S-C(O)}$); m/z (EI-MS) 43 ($[\text{C(O)CH}_3]^+$, 100%), 258 ($[\text{M} - \text{SCH}_2\text{CH}_2]^+$, 3%), 275 ($[\text{M} - \text{C(O)CH}_3]^+$, 4%), 318 (M^+ , 2%).

8-(Acetylsulfanyl)octyl ethyl 1,2-methano[60]fullerene-61,61-dicarboxylate 5. DBU (1.04 ml, 6.94 mmol) was added to a solution of C_{60} (3.00 g, 4.16 mmol), I_2 (1.32 g, 5.20 mmol), and **4** (1.10 g, 3.47 mmol) in degassed toluene (3 l). The mixture was stirred overnight, then filtered through a short plug (SiO_2), eluting first with toluene to remove iodine and unreacted C_{60} and then with CH_2Cl_2 . This red-brown fraction was then purified by flash column chromatography (SiO_2 H, gradient CH_2Cl_2 /hexane 2:8 to CH_2Cl_2) to yield 1.83 g (1.76 mmol, 51%) of **5** as a red-brown solid: (Found: C, 85.14; H, 2.88. $\text{C}_{75}\text{H}_{24}\text{O}_5\text{S}\cdot\text{CH}_3\text{OH}$ requires C, 85.38; H, 2.64; O, 8.98; S, 3.00%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2922, 2844, 1742, 1687, 1461, 1428, 1232, 1094, 1056, 700, 622, 578, 528; $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ (ϵ) 687 (220), 490 (1590), 426 (2840), 414 (2570), 401 (3670), 394 (5290), 326 (39100), 258 (126400); δ_{H} (200 MHz, CDCl_3) 1.25-1.92 (15 H, m, $\text{CH}_3\text{-CH}_2\text{-O-}$ and CH_2), 2.33 (3 H, s, S(O)C-CH_3), 2.87 (2 H, t, J 7.2, $-\text{CH}_2\text{-S-}$), 4.50 (2 H, t, J 6.6, $-\text{CH}_2\text{-CH}_2\text{-O-}$), 4.57 (2 H, q, J 7.4, $\text{CH}_3\text{-CH}_2\text{-O-}$); δ_{C} (125 MHz, CDCl_3) 14.26 ($\text{CH}_3\text{-CH}_2\text{-O-}$), 25.90, 28.55, 28.71, 29.04, 29.09, 29.68 (CH_2), 30.65 (S(O)C-CH_3), 52.34 ($(\text{O})\text{C-CH}_2\text{-C(O)}$), 63.41, 67.39 ($-\text{CH}_2\text{-O-C(O)}$),

71.65 (C(fullerene)-C-(C(O)-)₂), 138.94, 139.08, 140.95, 141.91, 141.92, 142.21, 142.98, 143.00, 143.02, 143.08, 143.09, 143.89, 144.61, 144.65, 144.68, 144.69, 144.88, 145.17, 145.17, 145.18, 145.20, 145.26, 145.31, 145.40 (C(fullerene)), 163.57, 163.68 (-O-C(O)), 195.96 (-S-C(O)); *m/z* (MALDI-TOF-MS) 1038 ([MH]⁺, calc. for ¹²C₇₅H₂₄O₅S: 1037.1), 1060 ([M + Na]⁺).

Ethyl (8-Sulfanyloctyl) 1,2-methano[60]fullerene-61,61-dicarboxylate 1. To a solution of **5** (84 mg, 0.08 mmol) in a mixture of 3 ml of methanol and 45 ml of CH₂Cl₂ at 0 °C, was added dropwise acetyl chloride (98%, 2 ml, 27.57 mmol). The resulting mixture was stirred at r.t. for 5 h, then washed with H₂O (50 ml). The organic phase was evaporated and the brown residue was purified by flash column chromatography (SiO₂, CH₂Cl₂/hexane 1:1) to yield 77 mg (0.08 mmol, 96%) of **1** as a brown solid. *v*_{max}(KBr)/cm⁻¹ 2922, 2844, 1743, 1461, 1428, 1232, 1094, 1056, 806, 700, 578, 550, 526; *λ*_{max}(CH₂Cl₂)/nm (ε) 688 (230), 491 (1680), 426 (2860), 414 (2690), 401 (3880), 394 (5400), 326 (27500), 258 (92000); δ_H (300 MHz, CDCl₃) 1.25-1.63 (14 H, m, CH₃-CH₂-O- and CH₂), 1.85 (2 H, br quin., *J* 6.9, -CH₂-CH₂-SH), 2.53 (2 H, q, *J* 7.2, -CH₂-SH), 4.50 (2 H, t, *J* 6.6, -CH₂-CH₂-O-), 4.57 (2 H, q, *J* 6.9, CH₃-CH₂-O-); δ_C (125 MHz, CDCl₃) 14.26 (CH₃-CH₂-O-), 24.62, 25.93, 28.27, 28.57, 29.02, 29.69, 33.97 (CH₂), 52.52 ((O)C-CH₂-C(O)), 63.42, 67.40 (-CH₂-O-C(O)), 71.66 (C(fullerene)-C-(C(O)-)₂), 138.94, 139.10, 140.96, 141.92, 142.22, 142.99, 143.02, 143.04, 143.10, 143.90, 144.62, 144.70, 144.90, 145.20, 145.28, 145.31, 145.42 (C(fullerene)), 163.59, 163.70 (-O-C(O)). *m/z* (FAB-MS) 994 (M⁺, 35%), 720 (C₆₀⁺, 100%); *m/z* (HR-FAB-MS) 994.1243 (M⁺, C₇₃H₂₂O₄S calc. 994.1239).

2,3-bis(hydroxymethyl)-6,7-(ethylenedithio) tetrathiafulvalene 9. To a 100 ml three-necked round-bottom flask was added **8** (1.0 g, 2.43 mmol), 60 ml of dry THF and 15 ml of methanol. The mixture was stirred and cooled to 0 °C. Then, NaBH₄ (0.8 g, 21.14 mmol) and LiCl (0.9 g, 21.23 mmol) were added slowly under nitrogen. After stirring at 0 °C for about 2 h, the cooling bath was removed and stirring continued for an additional 3 h at room temperature. The

reaction mixture was then cooled down again at 0 °C, and 30 ml of a sat. aq. NH₄Cl solution was added dropwise. After the addition, the mixture was extracted three times with AcOEt (3×100 ml) and the combined organic layers were washed with sat. aq. NaCl solution (2×40 ml), and dried over Na₂SO₄. After removal of the solvent, the crude product was collected and washed with CH₂Cl₂ (3×5 ml) to afford 650 mg (1.82 mmol, 75%) of **9** as pale-yellow powder. $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3257, 1007; δ_{H} (300 MHz, (CD₃)₂SO) 3.37 (4 H, s, CH₂-S), 4.22 (4 H, d, *J* 5.5, CH₂-OH), 5.53 (2 H, t, *J* 5.6, CH₂-OH); δ_{C} (75 MHz, (CD₃)₂SO) 29.50 (CH₂-S), 56.59 (CH₂-OH), 101.03, 112.83, 116.81, 131.57 (C(sp²)); *m/z* (FAB-MS) 354 (M⁺, 100%). Characterization in agreement with literature⁹.

2,3 - bis ({ [5 - (1,2 - dithiolan - 3 - yl) pentanoyl] oxy } methyl) - 6,7 - (ethylenedithio) tetrathiafulvalene 2. TTF derivative **9** (0.4 g, 1.13 mmol) was added to 15 ml of CH₂Cl₂ along with thioctic acid (0.53 g, 2.56 mmol). The mixture was stirred for 15 min at 0°C under N₂. Then DCC (0.95 g, 4.60 mmol) was added to the above solution along with DMAP (0.09 g, 0.736 mmol) in 10 ml cold CH₂Cl₂, and the mixture was stirred for another 15 min at 0 °C. The cooling bath was then removed and the solution allowed to warm to room temperature. After being stirred for 48 h under N₂, the reaction mixture was filtered to afford a clear filtrate and the insoluble urea by-product as a fine white-gray powder. The solvent was removed by evaporation, and the residue was subjected to column chromatography (SiO₂, CH₂Cl₂) to yield 694 mg (0.95 mmol, 84%) **2** as an orange-red oil. $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1007, 2928, 2852, 1733, 1709, 1628, 1538, 1228, 1157; δ_{H} (300 MHz, CDCl₃) 1.58-1.55 (4 H, m, -CH-CH₂-), 1.76-1.71 (8 H, m, CH₂), 1.93-1.90 (2 H, m, CH₂-CH(dithiolane)), 2.38-2.33 (4 H, m, CH₂-C(O)), 2.51-2.41 (2 H, m, CH₂-CH(dithiolane)), 3.23-3.15 (4 H, m, CH₂-S(dithiolane)), 3.29 (4 H, s, S-CH₂-CH₂-S), 3.56-3.54 (2 H, m, -CH(dithiolane)), 4.90 (4 H, s, CH₂-O-); δ_{C} (75 MHz, CDCl₃) 23.35, 25.07, 26.72, 27.47 (CH₂), 30.60 (S-CH₂-CH₂-S), 33.58, 35.28, 37.00 (CH₂), 58.30 (CH₂-O), 106.91, 114.36, 114.39, 129.95, 140.17 (C(TTF)), 173.10 (C=O); *m/z* (FAB-MS) 731 (M⁺, 100%); *m/z* (HR-FAB-MS) 730.9735 (M⁺, C₂₆H₃₄O₄S₁₀ calc. 730.9735).

IR of SAM with compound 1 and 2

1: 2922, 2850, 1745, 1462, 1235, 1096, 1060.

2: 2928, 2850, 1739, 1627, 1539.