

SUPPORTING INFORMATION

Redox Stable SAMs in Water (pH 0 – 12) from 1,1'-Biferrocenylene-Terminated Thiols on Au

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^1H - ^1H -COSY and ^1H - ^1H -ROESY NMR assignments of the BFD derivatives 3a/b

ROESY NMR were recorded on a 600 MHz Varian spectrometer, all other NMR spectra on a 400 MHz Bruker Avance spectrometer. Chemical shifts (δ) are reported in ppm and are referenced with regard to the residual protiated solvent, tetrachloroethane- d_2 : δ 5.91 (^1H) and δ 74.2 (^{13}C). The atom numbering system applied to the BFD system was originally proposed by Goldberg and Matteson.¹

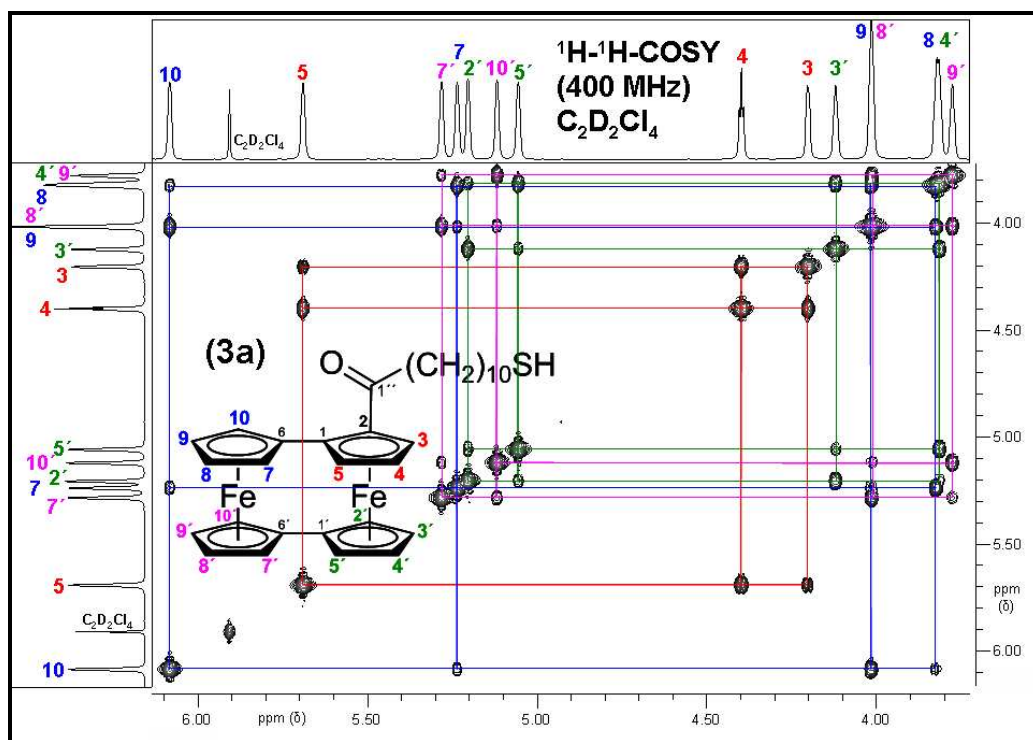


Figure S1. ¹H-¹H-COSY-NMR of **3a** (400 MHz, C₂D₂Cl₄, shown is the region relevant for the BFD proton signals)

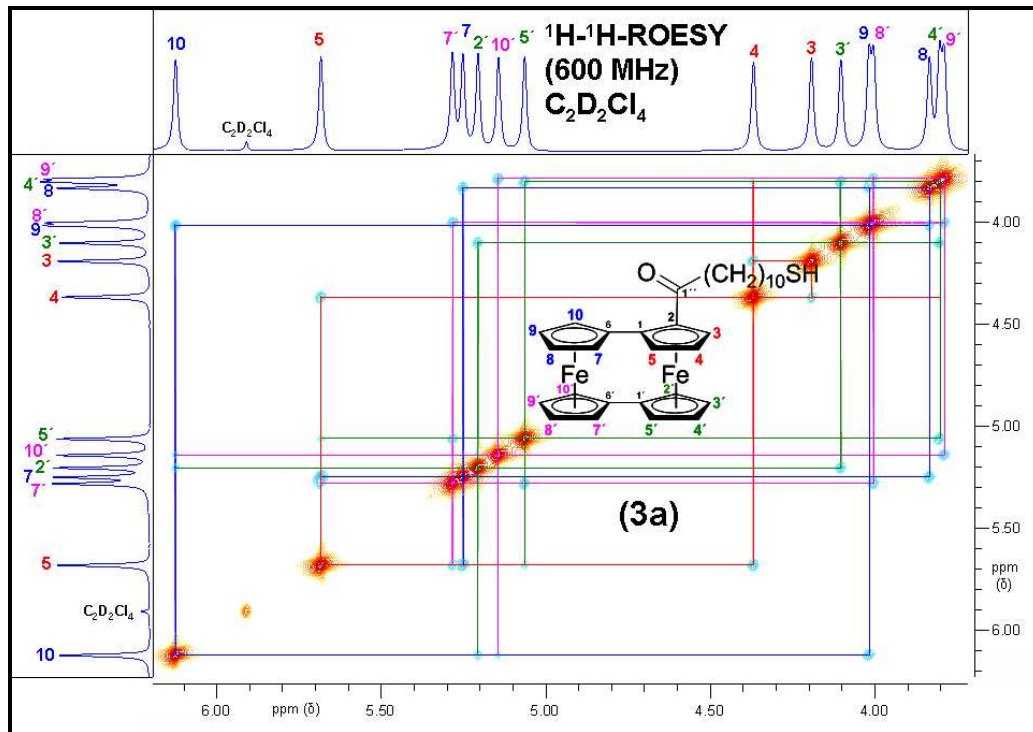


Figure S2. ¹H-¹H-ROESY-NMR of **3a** (600 MHz, C₂D₂Cl₄, shown is the region relevant for the BFD proton signals)

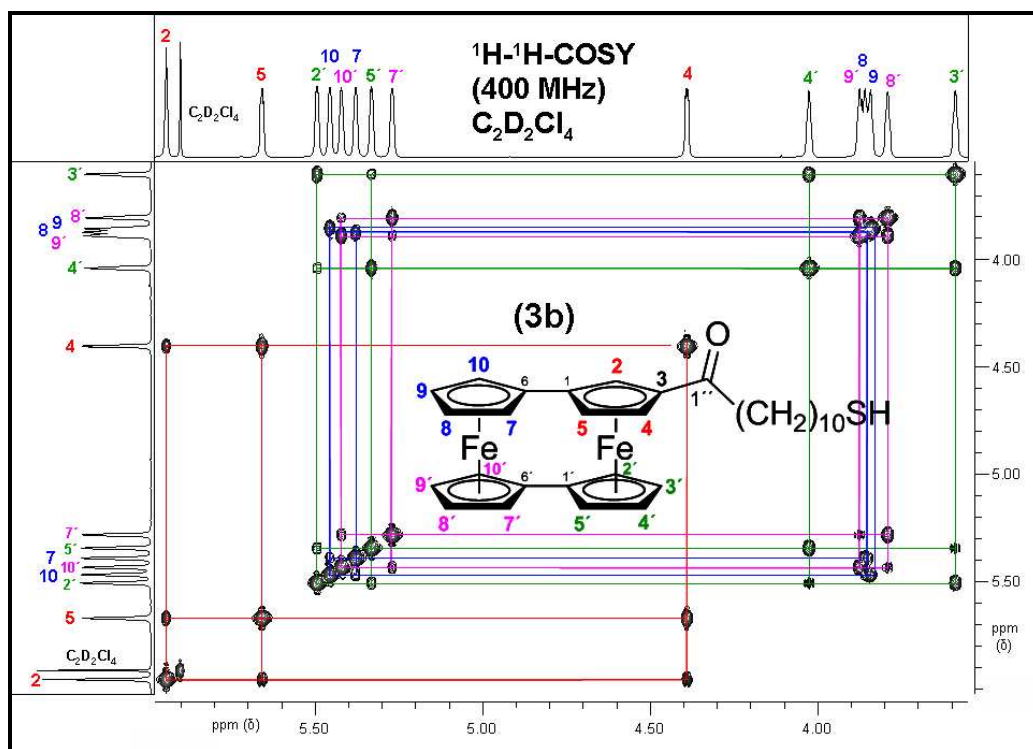


Figure S3. ^1H - ^1H -COSY-NMR of **3b** (400 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, shown is the region relevant for the BFD proton signals)

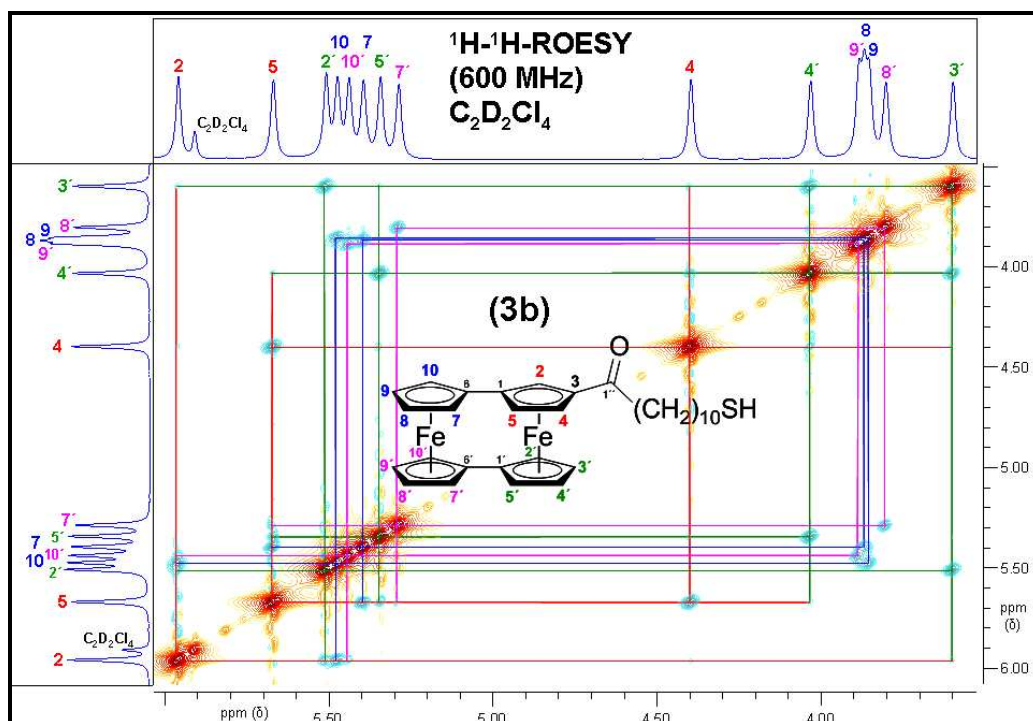


Figure S4. ^1H - ^1H -ROESY-NMR of **3b** (600 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, shown is the region relevant for the BFD proton signals)

Synthesis of 11''-Bromoundecanoylferrocene (Fc-(C=O)-C₁₀-Br).²

Under nitrogen atmosphere, ferrocene (9.76 g, 52.5 mmol) was dissolved in 40 mL of dry dichloromethane (CH₂Cl₂). At 0 °C a solution of 11-bromoundecanoyl chloride (13.2 g, 46.5 mmol) in 20 mL of dry CH₂Cl₂ was added. To the stirred solution solid AlCl₃ (7.21 g, 54.0 mmol) was inserted in small portions. After completed addition of AlCl₃ the ice-bath was removed and the deep red solution was stirred at room temperature for 8 hours. The reaction mixture was carefully quenched with ice-water (100 mL) at 0 °C. After addition of CH₂Cl₂ (50 mL) and subsequent phase separation in a separatory funnel, the aqueous phase was acidified with hydrochloric acid to pH 1 and extracted with CH₂Cl₂ (2 x 50 mL). The combined organic layer was washed twice with sat. NaHCO₃-solution and brine and finally dried over Na₂SO₄. After evaporation of the solvent under reduced pressure the solid was purified by silica column chromatography.

Chromatography (silica: *n*-hexane/ethylacetate, v/v = 95/5; *R_f* = 0.25). Yield: 19.6 g (86%). Mp 56 °C (Lit.:² 57-58 °C). IR (KBr, cm⁻¹): 3127 (w, C-H_{Ar}), 3088 (w, C-H_{Ar}), 2918 (s), 2850 (s), 1659 (s, C=O), 1471 (m), 1456 (s), 1410 (m), 1379 (m), 1341 (w), 1282 (w), 1256 (m), 1234 (w), 1106 (m), 1074 (w), 1029 (w), 1001 (m), 971 (w), 894 (m), 824 (m), 751 (w), 718 (m), 633 (w), 560 (w), 545 (w), 534 (w), 499 (m), 482 (m), 466 (m), 434 (w). ¹H NMR (400 MHz, C₂D₂Cl₄): δ 4.67 (dd, ³*J* = 2 Hz, ⁴*J* = 1 Hz, 2H, 2-H, 5-H), 4.41 (dd, ³*J* = 2 Hz, ⁴*J* = 1 Hz, 2H, 3-H, 4-H), 4.11 (s, 5H, H-1'), 3.33 (t, ³*J* = 7 Hz, 2H, 11''-H), 2.59 (t, ³*J* = 7 Hz, 2H, 2''-H), 1.76 (tt, ³*J* = 8 Hz, ³*J* = 7 Hz, 2H, 10''-H), 1.58 (tt, ³*J* = 8 Hz, ³*J* = 7 Hz, 2H, 3''-H), 1.32 (m, 2H, 9''-H), 1.25-1.21 (m, 10H, 4''-H, 5''-H, 6''-H, 7''-H, 8''-H). ¹³C NMR (100 MHz, C₂D₂Cl₄): δ 205.0 (C=O), 79.5, 72.6, 70.1, 69.6, 39.9, 35.0, 33.1, 29.8 (2C), 29.7 (2C), 29.0, 28.5, 24.8.

Synthesis of 11''-Bromoundecylferrocene (Fc-C₁₁-Br).³

To a suspension of AlCl₃ (3.72 g, 27.9 mmol) in 80 mL of dry dichloromethane (CH₂Cl₂) was added *t*-BuNH₂·BH₃ (4.85 g, 55.8 mmol) at 0 °C under nitrogen atmosphere. After stirring for 15 min, a solution of 11''-bromoundecanoylferrocene (4.10 g, 9.46 mmol) in CH₂Cl₂ (40 mL) was added dropwise to this mixture. After completion of the addition, stirring was continued for 1 h at room temperature. Finally, the reaction mixture was quenched carefully with 0.1 M hydrochloric acid (100 mL). After extraction of the aqueous phase with 50 ml of CH₂Cl₂, the combined organic phase was washed with brine (3 x 75 mL) and dried over Na₂SO₄. After solvent evaporation under reduced pressure the residue was purified by column chromatography on silica.

Chromatography (silica: *n*-hexane; *R_f* = 0.30). Yield: 3.81 g (96%). Mp 40 °C (Lit.:² 38-42 °C). IR (KBr, cm⁻¹): 3093 (w, C-H_{Ar}), 2922 (s), 2848 (s), 1467 (s), 1438 (w), 1408 (w), 1366 (w), 1335 (w), 1317 (w), 1292 (m), 1265 (m), 1240 (m), 1214 (m), 1198 (w), 1103 (s), 1038 (m), 1023 (m), 1001 (s), 920 (w), 857 (w), 835 (m), 819 (s), 722 (s), 644 (s), 518 (m), 497 (s), 477 (s), 439 (m). ¹H NMR (400 MHz, C₂D₂Cl₄): δ 4.03 (s, 5H, 1'-H), 4.00 (m, 2H, 2-H, 5-H), 3.97 (m, 2H, 3-H, 4-H), 3.36 (t, ³*J* = 7 Hz, 2H, 11''-H), 2.24 (t, ³*J* = 8 Hz, 2H, 1''-H), 1.79 (tt, ³*J* = 8 Hz, ³*J* = 7 Hz, 2H, 10''-H), 1.43 (tt, ³*J* = 8 Hz, ³*J* = 7 Hz, 2H, 2''-H), 1.35 (m, 2H, 9''-H), 1.22 (m, 12H, 3''-H, 4''-H, 5''-H, 6''-H, 7''-H, 8''-H). ¹³C NMR (100 MHz, C₂D₂Cl₄): δ 89.9, 68.9, 68.4, 67.4, 34.9, 33.1, 31.4, 30.0, 29.9, 29.9, 29.8, 29.8, 29.8, 29.1, 28.5.

Synthesis of 11''-Mercaptoundecanoylferrocene (6, Fc-(C=O)-C₁₀-SH).²

Under nitrogen atmosphere, a mixture of 11''-bromoundecanoylferrocene (3.00 g, 6.93 mmol) and thiourea (0.63 g, 8.31 mmol) was refluxed in 50 mL of dry ethanol for 6 hours. After the reflux was stopped and a solution of NaOH (0.55 g, 13.9 mmol) in 1.5 mL of water was added, the reflux was continued for additional 2 hours. Finally the reaction mixture was cooled to room temperature, quenched by adding 50 mL of 0.1 M hydrochloric acid and extracted with ethylacetate (200 mL). In a separatory funnel the combined organic phase was washed with brine (2 x 50 mL) and dried over Na₂SO₄. After solvent evaporation under reduced pressure the residue was purified by column chromatography on silica.

Chromatography (silica: *n*-hexane/ethylacetate, v/v = 90/10; *R_f* = 0.35). Yield: 1.74 g (65%). Mp 56 °C (Lit.:⁴ 57-58 °C). IR (KBr, cm⁻¹): 3095 (C-H_{Ar}, w), 2919 (s), 2850 (s), 2558 (w, S-H), 1662 (C=O, s), 1472 (m), 1456 (m), 1406 (w), 1379 (w), 1341 (w), 1286 (w), 1256 (w), 1236 (w), 1218 (w), 1107 (m), 1080 (w), 1048 (w), 1027 (w), 1000 (m), 972 (w), 893 (m), 820 (m), 715 (w), 533 (w), 498 (m), 478 (m). ¹H NMR (400 MHz, C₂D₂Cl₄): δ 4.67 (dd, ³*J* = 2 Hz, ⁴*J* = 1 Hz, 2H, 2-H, 5-H), 4.41 (dd, ³*J* = 2 Hz, ⁴*J* = 1 Hz, 2H, 3-H, 4-H), 4.11 (s, 5H, 1'-H), 2.59 (t, ³*J* = 7 Hz, 2H, 2''-H), 2.43 (dt, ³*J* = 8 Hz, ³*J* = 7 Hz, 2H, 11''-H), 1.58 (tt, ³*J* = 8 Hz, ³*J* = 7 Hz, 2H, 3''-H), 1.51 (tt, ³*J* = 8 Hz, ³*J* = 7 Hz, 2H, 10''-H), 1.28 (t, ³*J* = 8 Hz, 1H, S-H), 1.27 (m, 4H, 4''-H, 9''-H), 1.20 (m, 8H, 5''-H, 6''-H, 7''-H, 8''-H). ¹³C NMR (100 MHz, C₂D₂Cl₄): δ 205.0 (C=O), 79.5, 72.6, 70.1, 69.6, 39.9, 34.3, 29.8, 29.8 (2C), 29.8, 29.4, 28.7, 25.1, 24.8.

Synthesis of 11''-Mercaptoundecylferrocene (7, Fc-C₁₁-SH).²

Under nitrogen atmosphere, a mixture of 11''-bromoundecylferrocene (3.00 g, 7.16 mmol) and thiourea (0.65 g, 8.59 mmol) was refluxed in 30 mL of dry ethanol for 5 hours. After the reflux was stopped and a solution of NaOH (0.57 g, 14.3 mmol) in 1.5 mL of water was added, the reflux was continued for additional 2 hours. Finally the reaction mixture was cooled to room temperature, quenched by adding 50 mL of 0.1 M hydrochloric acid and extracted with ethylacetate (200 mL). In a separatory funnel the combined organic phase was washed with brine (2 x 50 mL) and dried over Na₂SO₄. After solvent evaporation under reduced pressure the residue was purified by column chromatography on silica.

Chromatography (silica: *n*-hexane; *R_f* = 0.20). Yield: 1.69 g (63%). Mp 39 °C (Lit.:² 40-41 °C). IR (KBr, cm⁻¹): 3090 (C-H_{Ar}, w), 2918 (s), 2849 (m), 2560 (S-H, w), 1469 (s), 1296 (w), 1268 (w), 1242 (w), 1104 (s), 1038 (m), 1025 (m), 998 (m), 924 (w), 812 (s), 719 (s), 515 (s), 496 (s), 481 (s). ¹H NMR (400 MHz, CDCl₃): δ 4.11 (s, 5H, 1'-H), 4.07 (m, 2H, 2-H, 5-H), 4.05 (m, 2H, 3-H, 4-H), 2.53 (dt, ³*J* = 8 Hz, ³*J* = 7 Hz, 2H, 11''-H), 2.32 (t, ³*J* = 8 Hz, 2H, 1''-H), 1.62 (tt, ³*J* = 8 Hz, ³*J* = 7 Hz, 2H, 10''-H), 1.51 (tt, ³*J* = 8 Hz, ³*J* = 7 Hz, 2H, 2''-H), 1.39 (m, 2H, 9''-H), 1.34 (t, ³*J* = 8 Hz, 1H, S-H), 1.29 (m, 12H, 3''-H, 4''-H, 5''-H, 6''-H, 7''-H, 8''-H). ¹³C NMR (100 MHz, CDCl₃): δ 89.5, 68.4, 68.0, 66.9, 34.0, 31.1, 29.6, 29.5 (3C), 29.5 (2C), 29.0, 28.3, 24.6.

CV of **5a**-SAM (α -BFD- C_{11} -S-Au) in 1 M HClO₄ (pH 0)

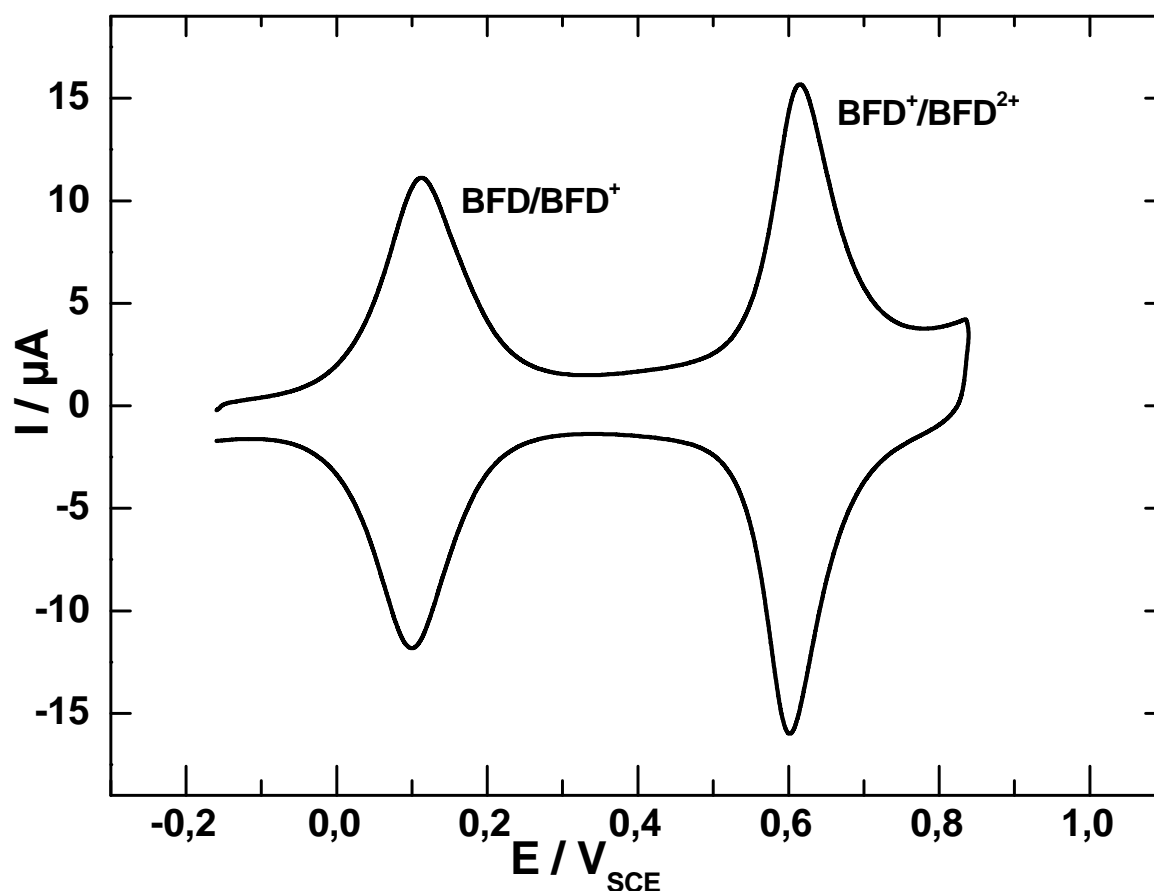


Figure S5. CV of **5a**-SAM (α -BFD- C_{11} -S-Au; diluted with *n*-decanethiol, $\Gamma \approx 1.9 \pm 0.1 \cdot 10^{-10} \text{ mol} \cdot \text{cm}^{-2}$) in 1 M HClO₄ (pH 0; NaClO₄, 0.1 M), representing the monocationic state (BFD/BFD⁺) and the dicationic state (BFD⁺/BFD²⁺).

Additional remarks:

Figure S5 displays a CV of **5a**-SAM (α -BFD- C_{11} -S-Au; diluted with *n*-decanethiol, $\Gamma \approx 1.9 \pm 0.1 \cdot 10^{-10} \text{ mol} \cdot \text{cm}^{-2}$) in 1 M HClO₄ (pH 0; supporting electrolyte: NaClO₄, 0.1 M). The first redox wave represents the monocationic state (BFD/BFD⁺), whereas the second redox wave corresponds to the dicationic state (BFD⁺/BFD²⁺). Both redox waves span a distance of 510 mV ($^1E_{1/2} = 0.10 \text{ V}_{\text{SCE}}$, $^2E_{1/2} = 0.61 \text{ V}_{\text{SCE}}$). The integrated charges (Q_{CV}) of each voltammetric peak are of equal amount within a deviation of $\pm 2.5\%$. The full width at half maximum (FWHM) of the dicationic redox wave is $\sim 25\%$ smaller than in case of the monocationic redox wave. This effect can be explained by an increased lateral interaction between dicationic BFD²⁺ groups next to each other, stronger than in a monolayer of monocationic BFD⁺ groups. In general, the effect of decreasing FWHM-values due to lateral interactions within a redox active monolayer has been discussed in detail in the literature.⁵

References

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