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# Temperature Dependent Charge Transport across Tunnel Junctions of Single-Molecules and Self-Assembled Monolayers: A Comparative Study

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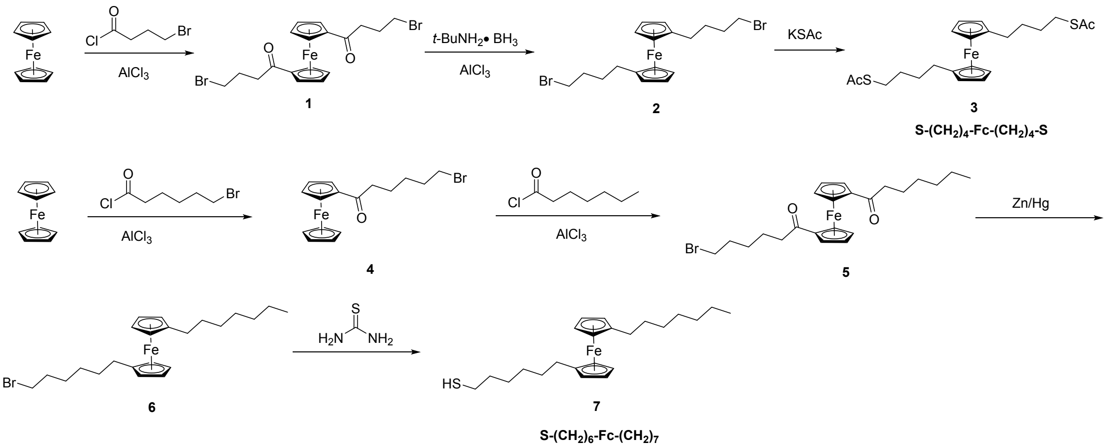
# Synthesis Details

**Scheme 1.** Synthetic route to prepare S-$(CH_2)_4$-Fc-$(CH_2)_4$-S and S-$(CH_2)_6$-Fc-$(CH_2)_7$. Compounds 4-7 have been reported before in reference 20 of the main text, but the preparation details are included here for the sake of completion.



## General Procedures:

The 4-bromobutanoyl chloride, borane-tert-butylamine complex, ferrocene, anhydrous aluminum chloride, mercury (II) choride, thiourea and potassium ethanethioate were purchased from Sigma-Aldrich. The heptanoyl chloride, 6-bromohexanoyl chloride, zinc granules (~20 Mesh) were purchased from Alfa Aesar. Chemicals were used without further purification. Solvents for chemical synthesis were freshly distilled prior to use. Dichloromethane (DCM) was distilled from calcium chloride, Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Deionized water (18.2 MΩcm) was generated from a water purifier (Purelab Option). All moisture sensitive reactions were performed under a $N_2$-atmosphere. Thin layer chromatography (TLC) glass plates coated with 0.25 mm thickness of silica gel 60 and fluorescent indication $UV_{254}$ (Macherey-Nagel) were used to monitor the progress of the reactions. The products were purified by column chromatography over silica gel (pore size 60 Å, 230-400 mesh particle size, 40-63 μm particle size, Sigma-Aldrich). $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker Avance 300 MHz (AV300) and Bruker Avance 500 MHz (AV500) spectrometer using chloroform-d as a solvent. Electrospray ionization (ESI) mass spectra and ESI high resolution mass spectra were recorded on a Finnigan LCQ mass spectrometer.

**Compound 1.** We followed a acylation procedure described in the literature[1] to synthesize ω-bromo aliphatic-1,1′-diacylferrocenes. In a 100 ml Schlenk flask, ferrocene (1.3g, 7mmol) and anhydrous $AlCl_3$ (2.8g, 21mmol) were dissolved in anhydrous DCM (30mL), next a solution of 4-bromobutanoyl chloride (2mL, 17mmol) in anhydrous DCM (25mL) was added to the reaction mixture dropwise at room temperature. The reaction mixture was stirred for 3 h at room temperature under a nitrogen atmosphere. After addition of deionized water (30mL), the reaction mixture was stirred for an additional 10 min. The dark red colored organic layer was separated from the blue colored aqueous layer. The aqueous layer was extracted three times with DCM (25mL) and the combined organic layers were washed with saturated sodium chloride, dried over sodium sulfate, filtered, and concentrated using rotary evaporation. The crude product was purified by column chromatography (hexane/DCM = 1:3) to yield the product (1,5g, 45% yield) as a dark red oil.

$^1$H NMR ($CDCl_3$, 300 MHz) δ 4.83 (s, 4H), 4.54 (s, 4H), 3.58 (t, 4H, J=6.0 Hz), 2.88 (t, 4H, J=6.6 Hz), 2.26 (m, 4H); $^{13}$C NMR ($CDCl_3$, 75 MHz) δ 202.1, 80.1, 73.6, 70.6, 37.5, 33.8, 26.6; ESI HRMS *m/z* calcd for $C_{18}H_{21}FeBr_2O_2$ 482.9253, found 482.9249 ($M^+$+H).

**Compound 2.** The reduction was performed according to a literature[2] reported procedure. Borane-tert-butylamine complex (1.56g, 18mmol) in anhydrous DCM (50mL) was added at 0 °C to a suspension of $AlCl_3$ (1.2g, 9 mmol) in anhydrous DCM (50mL), the resulting mixture was allowed to stir at 0 °C for 1h until a clear solution was obtained. A solution of compound **1** (1.45g, 3mmol) in anhydrous DCM (25mL) was added dropwise. The reaction mixture was stirred at 0 °C for 2 h and then hydrolyzed with deionized water (30mL). The aqueous layer was extracted three times with DCM (25mL) and the combined organic layers were washed with 0.1 M HCl, water and saturated sodium chloride, dried over sodium sulfate, filtered, and concentrated using rotary evaporation. The crude product was purified by column chromatography (hexane/DCM = 10:1) to provide product (1.2g, 88% yield) as a yellow oil.

$^1$H NMR ($CDCl_3$, 300 MHz) δ 4.07 (s, 8H), 3.41 (t, 4H, J=6.6 Hz), 2.29 (t, 4H, J=6.9 Hz), 1.88 (t, 4H, J=6.9 Hz), 1.65 (m, 4H); $^{13}$C NMR ($CDCl_3$, 75 MHz) δ 89.3, 69.3, 68.5, 33.8, 32.5, 29.6, 28.5; ESI HRMS *m/z* calcd for $C_{18}H_{24}FeBr_2$ 453.9589, found 453.9596 ($M^+$).

**Compound 3.** In a 100 ml Schlenk flask, potassium thioacetate (0.72g, 6.25mmol) and compound **2** (1.15g, 2.5mmol) were dissolved in anhydrous THF (50mL). The solution was refluxed for 2 hour, and then allowed to cool to room temperature overnight. The resulting mixture was poured into water and extracted with ethyl acetate. The combined organic layers were washed with saturated sodium chloride, dried over sodium sulfate, filtered, and concentrated using rotary evaporation. The crude product was purified by column chromatography (hexane/DCM = 3:1) to provide product (1g, 95% yield) as a yellow oil.

$^1$H NMR (CDCl$_3$, 300 MHz) δ 4.04 (s, 8H), 2.87 (t, 4H, J=6.9 Hz), 2.32 (s, 6H), 2.27 (t, 4H, J=7.2 Hz), 1.58 (m, 8H); $^{13}$C NMR (CDCl$_3$, 75 MHz) δ 195.9, 89.4, 69.2, 68.3, 30.6, 30.3, 29.3, 28.9, 28.8; ESI HRMS *m/z* calcd for $C_{22}H_{31}FeO_2S_2$ 447.1109, found 447.1107 ($M^+$+H). To determine the purity more quantitatively, we recorded a GC-MS spectrum using an Agilent GC system 7890A shown in Fig. S1. From the GC-MS spectrum and the other results we conclude the compound was pure within the detection limits of our GC-MS, and we did not find any major impurities, such as disulfides or sulfonates.

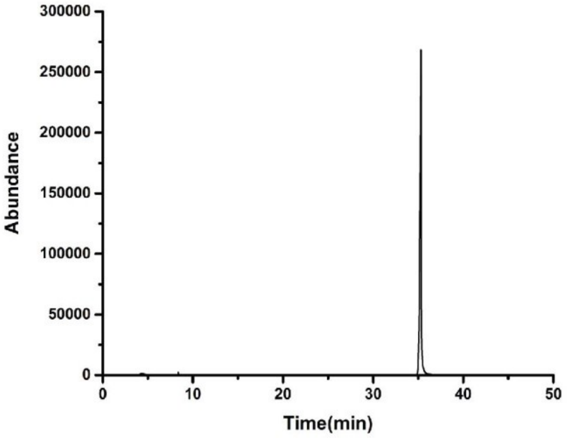


**Figure S1**. The GC-MS spectrum of $Ac_4FcC_4SAc$ compound.

**Compound 4.** ω-bromo aliphatic-1-monoacylferrocenes was functionalized via a Friedel-Crafts acylation with ω-bromo aliphatic chloride described in literature[3], To a cold (0 °C) stirred solution of anhydrous AlCl$_3$ (1.8g, 13.5mmol) in DCM (15mL) under nitrogen atmosphere was added 6-bromohexanoyl chloride (2.9g, 13.5mmol) and stirred for 20 min. This solution was added to a solution of ferrocene (5.0g, 26.9mmol) in DCM (135 mL) dropwise during which the Fc solution turned from orange to purple in color. After 2 h of stirring at room temperature, the deionized water (150 mL) were added slowly at 0 °C. The aqueous layer was extracted three times with DCM (50mL) and the combined organic layers were washed with were washed with 1.0 M HCl (50mL), saturated sodium chloride, dried over sodium sulfate, filtered, and concentrated using rotary evaporation. The crude product was purified by column chromatography (hexane/ethyl acetate = 9:1) to yield the product (3.2 g, 66% yield) as an orange oil.

$^1$H NMR ($CDCl_3$, 300 MHz): δ 4.77 (t, 2H, J = 2.0 Hz), 4.49 (t, 2H, J = 1.9 Hz), 4.19 (s, 5H), 3.43 (t, 2H, J = 6.8 Hz), 2.72 (t, 2H, J = 7.2 Hz), 1.94-1.87 (m, 2H), 1.76-1.68 (m, 2H), 1.57-1.47 (m, 2H); $^{13}$C NMR ($CDCl_3$, 75 MHz): δ 204.11, 78.99, 72.14, 69.71, 69.25, 39.34, 33.65, 32.63, 28.02, 23.53; ESI MS *m/z* calcd for $C_{16}H_{19}OBrFe$: 362; found: 363 ($M^{+}$+H).

**Compound 5.** A solution of anhydrous $AlCl_3$ (1.2g 9mmol) in DCM (10 mL) under nitrogen atmosphere was cooled to 0°C, then heptanoyl chloride (0.67 g, 4.5mmol) was added into the solution and the reaction mixture was stirred for an additional 20 min. Subsequently, we added this solution dropwise while stirring to a solution of compound **4** (3.2g, 8.9mmol) in DCM (20mL). After refluxing for 5h, the reaction mixture was quenched by the addition of deionized water (30mL) at 0°C. The aqueous layer was extracted three times with DCM (25mL) and the combined organic layers were washed with were washed with 1.0 M HCl (50mL), saturated sodium chloride, dried over sodium sulfate, filtered, and concentrated using rotary evaporation. The crude product was purified by column chromatography (hexane/ethyl acetate = 4:1) to yield the product (1.7g, 81% yield).

$^1$H NMR ($CDCl_3$, 500 MHz): δ 4.75-4.74 (m, 4H), 4.47-4.46 (m, 4H), 3.43 (t, 2H, J = 6.9 Hz), 2.67-2.61 (m, 4H), 1.94-1.64 (m, 4H), 1.55-1.30 (m, 8H,), 0.89 (t, 3H, J = 6.9 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz): δ 203.68, 203.15, 80.39, 80.26, 73.31, 73.27, 70.56, 70.48, 39.94, 39.51, 33.58, 32.59, 31.64, 29.08, 27.90, 24.23, 23.14, 22.49, 14.01.

**Compound 6.** Granulated Zn (7g, 108mmol), $HgCl_2$ (490mg, 1.8mmol) were taken into a round bottle flask and added a mixture of water and 12.0 M HCl (2:1 v/v, 10mL). To this mixture, we added a solution of compound **5** (1.7g, 3.6mmol) in toluene (25mL) after which this two-phase reaction mixture was refluxed overnight while vigorously stirring. The reaction mixture was allowed to cool down to room temperature and the organic layer was separated from the aqueous layer. The aqueous layer was extracted two times with diethylether (25mL) and the combined organic layers were washed with saturated sodium chloride, dried over sodium sulfate, filtered, and concentrated using rotary evaporation. The crude product was purified by column chromatography (hexane) to yield the product (1.5g, 94% yield) as a yellow oil.

$^1$H NMR ($CDCl_3$, 500 MHz): δ 3.98-3.95 (m, 8H), 3.41 (t, 2H, J = 6.9 Hz), 2.33-2.29 (m, 2H), 1.89-1.83 (m, 2H), 1.54-1.42 (m, 2H), 1.37-1.28 (m, 16H), 0.89 (t, 3H, J = 6.9 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz): δ 89.45, 89.00, 68.61, 67.69, 67.63, 33.90, 32.77, 31.85, 31.29, 31.10, 29.61, 29.41, 29.31, 29.20, 28.66, 28.04, 22.66, 14.09; ESI MS *m/z* calcd for $C_{23}H_{35}BrFe$: 446; found: 446 ($M^+$)

**Compound 7.** Compound **6** (1.5g, 3.4mmol) and thiourea (0.52g 6.8mmol) were dissolved in absolute ethanol (10mL) and refluxed overnight under argon after which an aqueous solution of 2.0 M potassium hydroxide (3.4mL) was added and further refluxed for an additional 2 h nitrogen atmosphere. After the reaction mixture was cooled down to room temperature, the mixture was extracted three times with diethylether (5mL) and the combined organic layers were washed with saturated sodium chloride, dried over sodium sulfate, filtered, and concentrated using rotary evaporation. The crude product was purified by flash column chromatography (hexane) to yield the product (1.1g, 82% yield) as a yellow oil.

$^1$H NMR ($CDCl_3$, 500 MHz): δ 3.97-3.96 (m, 8H), 2.55-2.50 (q, 2H, J = 7.0 Hz), 2.32-2.28 (m, 4H), 1.64-1.59 (m, 2H) 1.52-1.26 (m, 16H), 0.89 (t, 3H, J = 7.0 Hz); $^{13}$C NMR ($CDCl_3$, 125 MHz): δ 89.47, 89.14, 68.63, 67.69, 67.64, 33.98, 31.86, 31.29, 31.17, 29.61, 29.41, 2936, 29.20, 28.99, 28.24, 24.61, 22.66, 14.10; ESI MS *m/z*: 400 ($M^+$); ESI HRMS *m/z* calcd for $C_{23}H_{36}SFe$: 400.1887; found: 400.1881 ($M^+$).

## X-ray photoelectron spectroscopy

We have published the high resolution XPS spectra of S 2p and Fe 2p of the compound 7 in reference 4. Here we show the full range XPS spectra (binding energy from 0 to 620 eV) and C 1s spectra of the SAM of compound 7. We do not observe any O 1s peak in the energy range of 525 to 545 eV or any oxidized carbons.

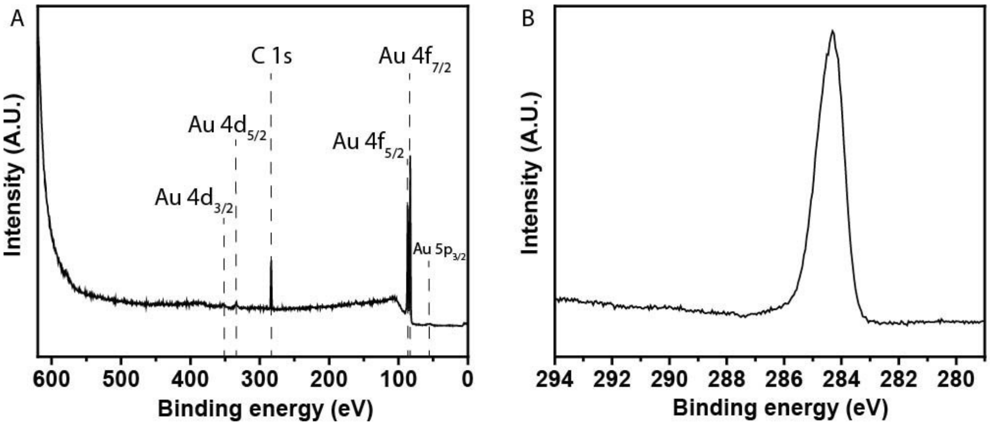


**Figure S2**. A) The XPS spectra of $SC_6FcC_7$ SAM with binding energy from 0 to 620 eV. B) The C1s spectra of $SC_6FcC_7$ SAM.

## References:

1. G. Vulugundam, K. Kumar, P. Kondaiah and S. Bhattacharya, *Org. Biomol. Chem.,* 2015, **13**, 4310-4320.
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4. Yuan, L.; Nerngchamnong, N.; Cao, L.; Hamoudi, H.; del Barco, E.; Roemer, M.; Sriramula, R.; Thompson, D.; Nijhuis, C. *Nat. Commun.* 2015, **6**, 6324.