

Large amplitude conductance gating in a wired redox molecule

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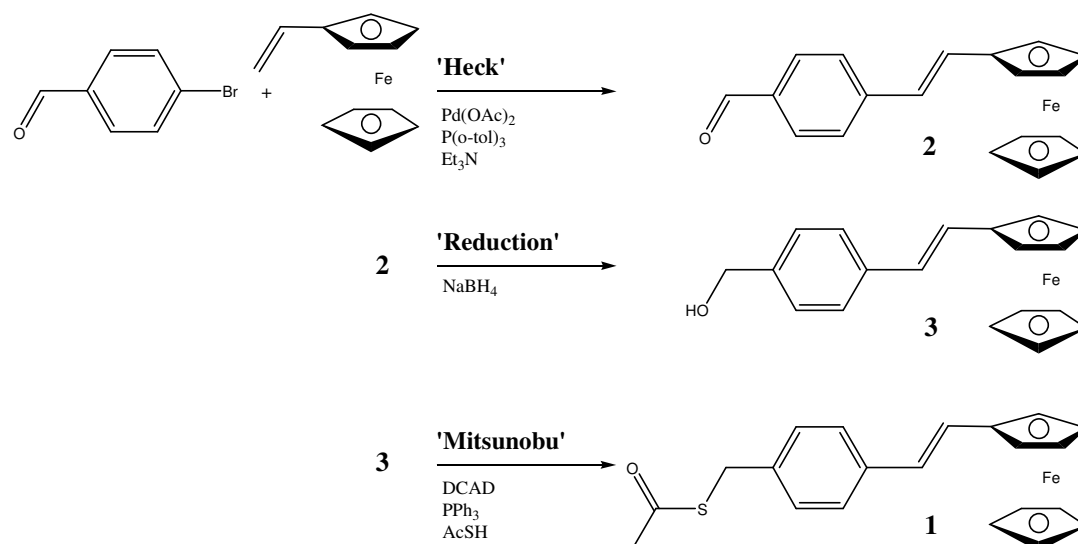
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Supplementary data

General materials and methods.

All reagents and solvents were commercial products purchased from Aldrich or Biosolve Ltd and used as received. Column chromatography was performed on silica gel 60 (Fluka, 230-400 mesh). TLC analysis was conducted on TLC-plastic sheets 60 F₂₅₄ (Merck) with detection by UV absorption where applicable. LC-MS spectra were recorded on a Finnigan LCQ Advantage Max/Surveyor system (Thermo Scientific) equipped with a Gemini C18 column (Phenomenex, particle size 3 μm, pore size 110 Å), LC eluent: H₂O/acetonitrile/ 0.1%TFA, LC gradient: 10-90% acetonitrile. ¹H-NMR and ¹³C-NMR spectra were measured with a Bruker AV-400 (400 and 100 MHz respectively). Chemical shifts are reported in ppm downfield from internal tetramethylsilane (0.00 ppm). In the case of the ¹³C spectra, the solvent peak was used as a reference (CDCl₃: 77.7 ppm). Abbreviations used are s = singlet, d = doublet, dd = doublet of doublets, m = multiplet, br = broad.

1. Synthesis of the ferrocene wire



4-((E)-2-(ferrocenyl-4-yl)vinyl)benzaldehyde (**2**)

2 was synthesized from 4-bromobenzaldehyde and vinylferrocene via Heck coupling. Vinylferrocene (Aldrich, 500 mg, 2.36 mmol, 1 equiv.), 4-bromobenzaldehyde (Aldrich, 440 mg, 2.36 mmol, 1 equiv.), triethylamine (Aldrich, 360 mg, 3.54 mmol, 1.5 equiv.) and tri-*o*-tolylphosphine (Aldrich, 72 mg, 0.47 mmol, 0.1 equiv.) were added to a dry schlenk flask in a glove box with an argon atmosphere. Dry *N,N*-dimethylformamide (Aldrich, 7.5 ml) was added as a solvent. Palladium(II) acetate (Acros Organics, 27 mg, 0.12 mmol, 0.05 equiv.) dissolved in dry *N,N*-dimethylformamide (2.5 ml) were added last to the reaction mixture, which was then stirred in the glove box for four hours at room temperature. The reaction mixture was then taken out of the glove box, to react further under nitrogen at 95 °C over night. Ethyl acetate (Biosolve, 30 ml) was then added to the reaction mixture and the organic phase was washed three times with water. Silica gel 60 (Aldrich, ~ 0.5 g) was added to the organic phase, after which the organic solvent was removed by rotary evaporation. The dark red solid bound to the silica gel was mounted on a silica gel 60 column and **1** was purified using a hexane, 5 % v/v ethyl acetate eluent. Yield: 50-75%. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 4.17 (s, Fc, 5 H), 4.36 (s, Fc, 2 H), 4.52 (s, Fc, 2 H), 6.72 (d, vinyl, $J = 16.0$ Hz, 1 H), 7.07 (d, vinyl, $J = 16.0$ Hz, 1 H), 7.56 (d, aromatic, $J = 8.4$ Hz, 2 H), 7.83 (d, aromatic, $J = 8.4$ Hz, 2 H), 9.97 (s, aldehyde, 1 H). LCMS: 316.05 and 317.06 g/mol.

4-((E)-2-(ferrocenyl-4-yl)vinyl)phenylmethanol (**3**)

In a glove box **2** (344 mg, 1.09 mmol, 1 equiv.) was added to a dry schlenk flask and dissolved in tetrahydrofuran (Aldrich, 20 ml) and 0.25 M NaOH (2 ml). Slowly, sodium borohydride (Aldrich, 41 mg, 1.09 mmol, 1 equiv.) was added to the reaction mixture which was then stirred in the glove box for two hours at room temperature. Ethyl acetate (30 ml) was then added to the reaction mixture and the organic phase was washed three times with water. The organic solvent was removed by rotary evaporation and NMR showed that purification was not necessary. Yield: >95%. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 2.04 (s, alcohol, 1 H), 4.13 (s, Fc, 5 H), 4.28 (t, Fc, $J = 1.8$ Hz, 2 H), 4.46 (t, Fc, $J = 1.8$ Hz, 2 H), 4.67 (s, benzyl, 2 H), 6.69 (d, vinyl, $J = 16.0$ Hz, 1

H), 6.88 (d, vinyl, $J = 16.0$ Hz, 1 H), 7.32 (d, aromatic, $J = 8.0$ Hz, 2 H), 7.42 (d, aromatic, $J = 8.0$ Hz, 2 H). LCMS: 318.07 g/mol.

S-4-((E)-2-(ferrocenyl-4-yl)vinyl)benzyl ethanethioate (1)

1 was synthesized from **3** and thioacetic acid via a Mitsunobu reaction. In a glove box triphenylphosphine (Aldrich, 224 mg, 0.86 mmol, 2 equiv.) and di-(4-chlorobenzyl) azodicarboxylate (Aldrich, 314 mg, 0.86 mmol, 2 equiv.) were added to a dry three neck flask. Dry tetrahydrofuran (Aldrich, 2 ml) was added and the reaction mixture was chilled under nitrogen for thirty minutes. **3** (137 mg, 0.43 mmol, 1 equiv.), thioacetic acid (Aldrich, 33 mg, 0.43 mmol, 1 equiv.) and dry tetrahydrofuran (2 ml) were added to a separate three neck flask in the glove box. This reaction mixture was transferred with a syringe to the triphenylphosphine, di-(4-chlorobenzyl) azodicarboxylate reaction mixture one drop at a time. This combined mixture was stirred under nitrogen at 0°C for one hour and then at room temperature for one hour. The reaction mixture was then transferred to a separatory funnel. Chloroform (10 ml) was added and the organic phase was washed three times with water. The solvent was removed by rotary evaporation and replaced by 80% pentane - 20% dichloromethane. **1** was purified over a HPLC silica column (Alltech, Alltima silica 5u) with a pentane/dichloromethane eluent, gradient (20-50%). Yield: ~20%. ¹H NMR (400 MHz, CDCl₃, ppm): δ 2.35 (s, SCOCH₃, 3 H), 4.12 (d, $J = 10.4$ Hz, Fc, 5 H), 4.29 (s, Fc, 2 H), 4.46 (s, Fc, 2 H), 6.65 (d, vinyl, $J = 16.4$ Hz, 1 H), 6.84 (d, vinyl, $J = 16.4$ Hz, 1 H), 7.24 (d, aromatic, $J = 8.4$ Hz, 2 H), 7.35 (d, aromatic, $J = 8.0$ Hz, 2 H). LCMS: 376.06 g/mol.

2. Ferrocene wire assembly and voltammetry

Cyclic voltammetric data was obtained using on gold disk electrodes prepared by a process of reductive stripping of surface impurities, mechanical polishing with alumina slurry, pirhana treatment and electrochemical polishing.¹ A platinum electrode served as counter, with an SCE reference. All electrodes were supplied by CH Instruments. CV was performed in 100mM phosphate buffer, pH7.0, deoxygenated by bubbling nitrogen for at least 30 minutes, at sweep rates ranging from 0.1-240Vs⁻¹. Five cycles were taken successively and the last one selected for analysis. Electroactive monolayer modification was achieved by co-adsorption of the ferrocene wire with dodecanethiol by incubation of the electrode in a 1mM mixed ethanolic solution, or post-adsorption into a pre-formed dodecanethiol monolayer with a 1mM pure ethanolic ferrocene wire solution. Both adsorptions were performed overnight at room temperature. The ferrocene wire thiol moiety was protected by an acetyl group, which was hydrolyzed in the incubating solution by the addition of 0.5% ammonia by volume. After incubation electrodes were washed with absolute ethanol and deionized water (Millipore).

The λ can be estimated from (for example) Laviron defined² k_{et} and scan rate ν based empirically on simulated data:³

$$\lambda = (T/1000)\{2.968 - 0.6581\log(|\nu|/k) + 5.300E_p - 0.2986E_p \log(|\nu|/k)\} \quad (1)$$

Ellipsometric and imaging analyses of the pure ferrocene appended film (**1**) were consistent with the presence of a disordered monolayer and previous reports of OPV films.⁴ Specifically, measurements were conducted with a computer-controlled Beaglehole Picometer Ellipsometer using a helium-neon laser ($\lambda = 632.8$ nm) at variable angle of incidence from 30° to 80°. The optical constants for the clean gold substrate were measured before each experiments and averaged over 5 scans. The substrates were cut to $\sim 2 \times 2$ cm² such that at least four regions of the surface could be interrogated and used to measure the average layer thickness. The model used to elucidate layer thickness assumed a single monolayer of refractive index $n = 1.45$ on the gold surface.

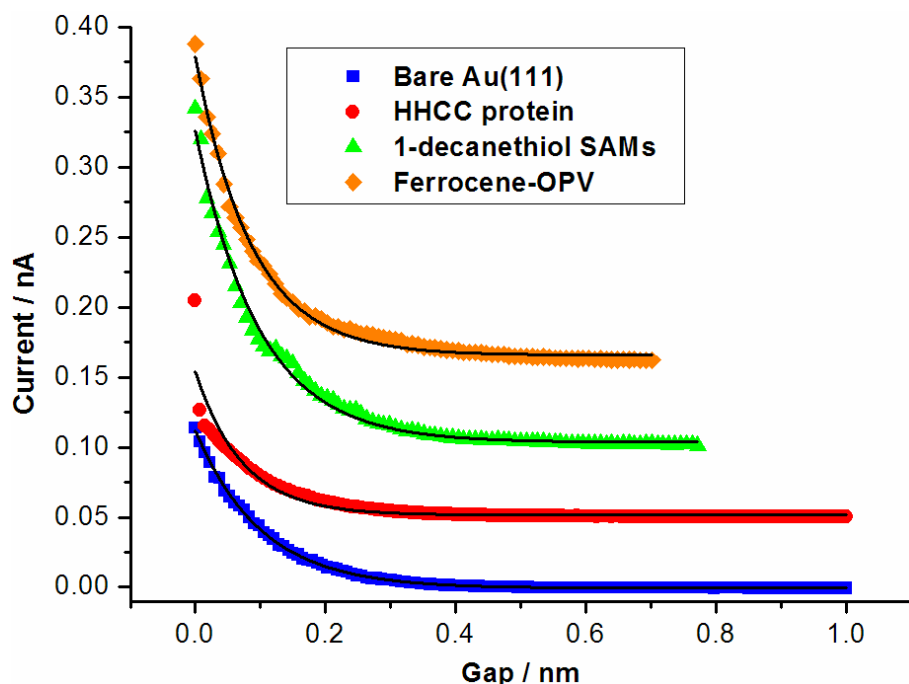


Figure S1: The *in situ* (10 mM potassium phosphate buffer, pH 7.0) determination of the tunnelling gap distance decay parameters over bare Au(111) (blue squares), protein (HHCC) modified Au(111) (red circles), 1-decanethiol modified Au(111) (green triangles) and wire (1) modified Au(111) (orange rhombus). The black solid lines are the best exponential fits to these data giving $1.10 \pm 0.05 \text{ \AA}^{-1}$ (dated averaged over 50 individual scans), $0.98 \pm 0.06 \text{ \AA}^{-1}$ (data averaged over 100 individual scans on different molecules), $0.97 \pm 0.04 \text{ \AA}^{-1}$ (dated averaged over 80 individual scans), and $1.03 \pm 0.08 \text{ \AA}^{-1}$ (averaged scans over 11 individual molecular wires) for the bare gold, protein, alkylthiol and wire modified surfaces respectively.

In all cases the initial tunneling junction resistance was set to 1.0 Giga Ohm. These decay trends are consistent with a clean tunneling junction and the absence of tip-molecule mechanical contact at these resistances. Anomalously low solution barrier heights have been measured only at tunnel resistances / bias an order of magnitude or more higher/lower than we use here.^{5,6}

- (1) Tkac, J.; Davis, J. J. *J. Electroanal. Chem.* **2008**, *621*, 117-120.
- (2) Laviron, E. *J. Electroanal. Chem.* **1979**, *101*, 19-28.
- (3) Honeychurch, M. J. *Langmuir* **1999**, *15*, 5158-5163.
- (4) Dudek, S. P.; Sikes, H. D.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **2001**, *123*, 8033-8038.
- (5) Vaught, A.; Jing, T. W.; Lindsay, S. M. *Chem. Phys. Lett.* **1995**, *236*, 306-310.
- (6) Akiyama, T.; Imahori, H.; Sakata, Y. *Chem. Lett.* **1994**, 1447-1450.