Energy-Level Alignment and Orbital-Selective Femtosecond Charge Transfer Dynamics of Redox-Active Molecules on Au, Ag and Pt Metal Surfaces

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**S1. Fabrication of template-stripped metal surfaces and formation of self-assembled monolayers (SAMs).**

Template-stripped (TS) metal surfaces were made following established procedures. 400 nm Ag and 200 nm Au were deposited on silicon wafers using a thermal evaporator (Shen Yang Ke Yi, China). 40 nm Pt was deposited using an electron beam evaporator (Denton Vacuum Explorer, NJ USA). Clean glass slides were glued to the metal surface using EPOTEK 353ND thermal glue. The systems were heated to 80 °C and kept for 3 hours for the glues to cure, after which the glass–metal surfaces were removed from the silicon wafers. The freshly prepared Ag<sup>TS</sup>, Au<sup>TS</sup> and Pt<sup>TS</sup> surfaces were immersed in a solution of the SAM compound Fc-(CH<sub>2</sub>)<sub>n</sub>-Ph-CC-Ph-CH<sub>2</sub>-SH in THF/ethanol (1:5). The systems were kept in Argon atmosphere for 8 hours at room temperature to allow the SAMs to form. The samples were rinsed with THF and ethanol immediately after being taken out of the solutions, and then dried in a gentle flow of N<sub>2</sub> gas.

**S2. Photoemission spectroscopy**

The X-Ray Photoemission Spectroscopy (XPS), Near-edge X-ray Absorption Fine Structure (NEXAFS) and Resonant Photoemission Spectroscopy (RPES) were conducted at the soft X-ray beamline of the Australian Synchrotron. The equipment and measurement setup was described in our previous work. In this study, we recorded high resolution scans for C 1s, S 2p and Fe 2p spectra for all the SAMs and Ag 3d, Au 4f and Pt 4f spectra for the corresponding metal surfaces. For each region we measured the signals at take-off angles of 90° (normal emission, NE) and 40° (grazing emission, GE).

Figures S1-S3 show the S 2p spectra for all samples. On all three surfaces, the S 2p peak at 161.9-162.3 eV (S1, blue line) with minor contribution of another peak at ~163.4 eV (S2,
magenta line) are present. Peak S1 is attributed to the metal-bound sulphur and peak S2 is attributed to the S-H of physisorbed molecules. The shift of peak S1 on different metals is due to the differences in the electronic structure of the metal-sulfur bonds as has been detailed in the literature.\(^3\) In one SAM only, specifically with n=1 on Pt (i.e., Pt-S-CH\(_2\)-Ph-CC-Ph-(CH\(_2\))\(_1\)-Fc), an extra peak appears which corresponds to disulphide species, S3 at ~164.0 eV (orange line). This could be due to a small amount of impurities in the molecules. We determined the SAM thickness using the peak intensities of S1 at two take-off angles.\(^2\) The results are summarized in Table S1.

On Ag surface, another peak S0 at ~161.1 eV (green line) is present along with S1 and S2. This peak can be attributed to either atomic sulphur or disordered phase of chemisorbed thiol.\(^4\)–\(^6\) Here we believe it likely arise from disordered bound thiol, as they are present on Ag but not on Au or Pt. Such metal-dependent behaviour rules out the possibility of atomic sulphur impurities in the SAM precursor, but given the high affinity of Ag for sulphur we cannot rule possible contamination from the ambient since all of our samples were prepared under ordinary laboratory conditions.

Figures S4-S6 show the C 1s spectra for all samples. There are two peaks, C1 at ~284.8 eV (green line) and C2 at ~285.5 eV (blue line) in all spectra. C1 is attributed to the C=\(\text{C}/\text{C}=\text{C}\) in the diphenyl acetylene unit and C2 is attributed to the C=C in the Cp rings of the ferrocenyl head group. The ratio of these two peaks was fixed at C1:C2 = 14:10, based on the number of carbons in the molecular structure. The binding energy of C2 is used as a reference to align the VB and NEXAFS in Figure 2.
**Figure S1.** S 2p spectra of SAMs S-CH₂-Ph-CC-Ph-(CH₂)ₙ-Fc on Ag for n = 0-3.
Figure S2. S 2p spectra of SAMs $\text{S-CH}_2\text{-Ph-CC-Ph-(CH}_2\text{)_n-Fc}$ on Au for $n = 0-3$. 
Figure S3. S 2p spectra of SAMs S-CH$_2$-Ph-CC-Ph-(CH$_2$)$_n$-Fc on Pt for $n = 0-3$. 
Figure S4. C 1s spectra of SAMs S-CH$_2$-Ph-CC-Ph-(CH$_2$)$_n$-Fc on Ag for n = 0-3.
Figure S5. C 1s spectra of SAMs S-CH$_2$-Ph-CC-Ph-(CH$_2$)$_n$-Fc on Au for n = 0-3.
Figure S6. C 1s spectra of SAMs S-CH$_2$-Ph-CC-Ph-(CH$_2$)$_n$-Fc on Pt for n = 0-3.
Table S1. The thickness of the molecular films calculated from the S 2p spectra.

| n  | Ag  | Au  | Pt  |
|----|-----|-----|-----|
| n = 0 | 15.6 (16.8) | 15.9 (17.0) | 13.4 (17.0) |
| n = 1 | 16.6 (17.2) | 16.2 (17.3) | 14.2 (18.0) |
| n = 2 | 15.5 (19.1) | 14.9 (19.2) | 15.4 (19.2) |
| n = 3 | 16.0 (19.7) | 16.0 (19.4) | 14.5 (19.9) |

a The error for $d_{\text{SAM}}$ is 2Å, estimated from 5% fitting error.

b Values in parentheses are the calculated maximum heights of the Fe Fe atom above the 111 surface, taken from the single-molecule DFT models in which the S-CH$_2$-Ph-CC-Ph unit adopts a fully-upright orientation normal to the 111 plane.

S3. Least-squares peak fitting for the RPES and NEXAFS spectra

Figure S7. NEXAFS spectra for SAMs M-S-CH$_2$-Ph-CC-Ph-(CH$_2$)$_n$-Fc and the corresponding fitting curves. Metal substrate is (a) Ag, (b) Au and (c) Pt. The intensity for each photon energy is the integral of VB spectra from binding energy 0 eV to 20 eV. The fitted peak denotes resonance I (blue), II (green), III (purple) and IV (pink).

To extract the accurate intensity of each resonance, the least-squares peak fitting was performed using a linear background. The position and full width at half maximum for each
resonant component in NEXAFS and integrated RPES spectra were fixed during fitting. Because
the coupling strength between the DPA unit and the substrate does not change with \( n \), we believe
the CT time from resonance I remains constant for a given metal surface. Thus, the integrated
intensity ratio values of \( I_{\text{RPES}}/I_{\text{NEXAFS}} \) for resonant I for SAMs on each metal film were used as an
internal reference for the peak fitting. We treat the SAMs of \( n = 3 \) as the isolated system where no
charge transfer occurs between the Fc moieties and substrates within the core-hole lifetime. The
charge transfer time (\( \tau_{\text{CT}} \)) for coupled systems with \( n < 3 \) may thus be obtained from the relation
\[ \tau_{\text{CT}} = \tau_{\text{CH}} \frac{I_{\text{RPES}}^{\text{coup}}/I_{\text{NEXAFS}}^{\text{coup}}}{I_{\text{RPES}}^{\text{iso}}/I_{\text{NEXAFS}}^{\text{iso}} - I_{\text{RPES}}^{\text{coup}}/I_{\text{NEXAFS}}^{\text{coup}}} \]
# (1)
in which \( \tau_{\text{CH}} \) is the core-hole lifetime, which is 6 fs for C 1s, \( F^{\text{coup}} \) and \( F^{\text{iso}} \) represent the fitting area
of resonance for the isolated system (\( n = 3 \)) and the coupled system (\( n < 3 \)).

**S4. Full DFT dataset on M-S-CH\(_2\)-Ph-CC-Ph-(CH\(_2\))\(_n\)-Fc for M=Au, Ag, Pt and n = 0-3**

Twelve DFT simulation cells were constructed, to model all the experimental variants of
the methylene-based DPA-Fc linker moiety and the metal substrate.

The SAM electronic structure calculations were carried out using density-functional theory
(DFT) performed with the Vienna *ab initio* simulation package (VASP).\(^8\) The periodic SAM
models were described using periodic plane wave DFT with the GGA-PBE functional,\(^9\) projector
augmented wave (PAW)\(^10\) pseudopotentials with a plane wave cut-off of 400 eV. The molecule-
surface complexes were calculated under periodic boundary conditions with a 30 Å vacuum
spacing in the direction normal to the four-layer gold surface. All atoms except the gold atoms in
the bottom layer were allowed to relax unconstrained until the forces on each atom were <3
meV/Å. The conductance gaps and positions of the PDOS peaks were converged to below 100 meV for all SAMs using a 441 k-point grid.

The computed conductance gaps are given in Table S2 and the full set of calculated PDOS plots are given in Figures S8-S10. All bands are aligned according to the C core 1s levels to allow comparison between PDOS distributions for the different SAMs. Finally, the M=Au, n=3 PDOS (Fig. S9d and main text Fig. 2d) is decomposed into the Cp and DPA contributions to the C atom populations (Fig. S11) and the Fe 3d suborbital contributions (Fig. S12), identifying the components of the peaks labelled A, B and I-III in main text Fig. 2.

**Table S2.** The computed HOMO-LUMO band gap in the SAMs of M-S-CH₂-Ph-CC-Ph-(CH₂)ₙ-Fc for M=Au, Ag, Pt and n = 0-3

| n   | Ag | Au | Pt |
|-----|----|----|----|
| n = 0 | 2.2 | 2.3 | 2.4 |
| n = 1 | 2.2 | 2.1 | 2.3 |
| n = 2 | 2.2 | 2.3 | 2.7 |
| n = 3 | 2.3 | 2.2 | 2.6 |

*a The computed band gaps are similar, in the range 2.1–2.7 eV, with no obvious n-dependence and only a very small n-averaged increase of <0.3 eV on switching to Pt, from Ag or Au, due to shifting of the top of the valence band below the Fermi level. The values are also consistent with the gaps estimated from spectroscopy (Fig. 2, main text).
Figure S8. Calculated PDOS distributions for Ag-S-CH$_2$-Ph-CC-Ph-(CH$_2$)$_n$-Fe with n=0-3.
Figure S9. Calculated PDOS distributions for Au-S-CH$_2$-Ph-CC-Ph-(CH$_2$)$_n$-Fc with $n=0$-$3$. 
Figure S10. Calculated PDOS distributions for Pt-S-CH\(_2\)-Ph-CC-Ph-(CH\(_2\))\(_n\)-Fc with n=0-3.
Figure S11. Calculated DPA and Cp components of C-atom contribution to PDOS in Au-S-CH$_2$-Ph-CC-Ph-(CH$_2$)$_3$-Fc.
Figure S12. Calculated Fe 3d suborbital components of Fe-atom contribution to PDOS in Au-S-CH$_2$-Ph-CC-Ph-(CH$_2$)$_3$-Fc.
Figure S13. Calculated electron density surface for the frontier molecular orbitals. The peak labelling follows main text Figure 2: peak B and A in the VB spectra and peak I-III in the NEXAFS spectra.

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