

Supplementary Information

The Supramolecular Structure of Self-Assembled Monolayers of Ferrocenyl Terminated n -Alkanethiolates on Gold Surfaces

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Fabrication of Au substrates

Preparation of the hydrogen flame annealed Au substrates. The Au substrates (250 nm of Au with a 2.5 nm Cr adhesion layer on glass) were purchased from Arrandee (Germany). The Au substrates were hydrogen flame annealed for 3-5 min to remove organic contaminants and to reconstruct the Au surface to yield large atomically-flat terraces of Au(111).^{1,2} After annealing, the surfaces were immediately used (after cooling down to room temperature) to minimize contamination from the ambient.

Preparation of the template stripped (TS) Au substrates. We followed procedures described in the literature³ to fabricate Au^{TS} surfaces for CV and HREELS measurements. Glass slides of $1 \times 1 \text{ cm}^2$ (7105 Microscope slide, 1 mm thick) were cleaned by a mixture solution of $\text{HCl}:\text{H}_2\text{O}_2:\text{H}_2\text{O} = 1:1:5$ at 70 °C for 20 min, then washed with H_2O and EtOH, and blown to dryness in a stream of stream of N_2 gas. We further cleaned the glass slides by a plasma of air for 5 min at a pressure of 0.7 mbar. Afterward, the glass slides were glued against the Au surface deposited on Si/SiO₂ wafer using an optical adhesive (OA; Norland, No. 61). The OA was cured in ultraviolet light for 1 h using a light source of 100 Watt at a distance of 40 cm from the substrate. The glass-OA-metal composite was cleaved off from the Si/SiO₂ wafer using a razor blade and use immediately to minimize contamination from the ambient.

Near edge X-ray absorption fine structure (NEXAFS) spectroscopy

We followed the previously reported procedure to acquire and process NEXAFS data.⁴ Here we gave a brief description. NEXAFS spectroscopy was carried out at the SINS (Surface, Interface and Nanostructure Science) beamline of the Singapore Synchrotron Light Source (SSLS). The base pressure of the ultrahigh vacuum (UHV) chamber was 1×10^{-10} mbar and all the

measurements were performed at room temperature. We collected the angular dependent C *K*-edge NEXAFS spectra. At least 90% linear polarization factor of the X-ray beam was generated by synchrotron light source. The photon energy of the incident X-ray was calibrated using sputtering cleaned gold foil as reference with the photon energy resolution of 200 meV. We used two different angles to determine the molecular orientations: normal incidence ($\theta = 90^\circ$) and grazing incidence ($\theta = 20^\circ$). The two NEXAFS spectra were first normalized to the clean NEXAFS spectrum monitored using the same mode on fresh sputtering cleaned Au foil, and then normalized to have the same absorption edge jump between 280 eV and 320 eV. The two lowest resonances located at 285.4 eV ($4e_{1g}$) and 286.9 eV ($3e_{2u}$) are attributed to the transition to the π^* orbitals associated with the cyclopentadiene (Cp) rings of Fc with different symmetry. The molecular axis of Fc is perpendicular to the Cp ring plane. The angular dependence of the intensity of the Fc π^* resonances can be expressed by eq. 1, where α is the tilt angle of Fc unit with respect to the surface normal, corresponding to the angle between the plane of Cp ring and the substrate surface plane, A is the normalization factor, P ($= 0.9$) is the degree of linear polarization. By evaluating the intensity ratio at normal incidence ($\theta = 90^\circ$) and grazing incidence ($\theta = 20^\circ$), the tilt angle of Fc unit, α can be derived.

$$I(\theta) = \frac{1}{3}AP \left[1 + \frac{1}{2}(3\cos^2\theta - 1)(3\cos^2\alpha - 1) \right] + \frac{1}{2}A(1 - P)\sin^2\alpha \quad (1)$$

X-ray single crystal diffraction

Experimental details of the crystal structure determination of HSC₃Fc and HSC₄Fc by X-ray single crystal diffraction are summarized in Table S1.

Table S1. Crystal data and structure refinement for HSC₃Fc and HSC₄Fc.

Crystal data		
Identification code	HSC ₃ Fc	HSC ₄ Fc
Empirical formula	C ₁₃ H ₁₆ FeS	C ₁₄ H ₁₈ FeS
Formula weight	260.17	274.19
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c
Unit cell dimensions	a = 12.134(2) Å, α = 90°. b = 7.6542(14) Å, β = 108.447(3)° c = 12.877(2) Å, γ = 90°.	a = 7.1738(6) Å, α = 90°. b = 8.6460(6) Å, β = 98.756(3)°. c = 20.1903(16) Å, γ = 90°.
Volume	1134.4(4) Å ³	1237.70(17) Å ³
Z	4	4
Density (calculated)	1.523 Mg/m ³	1.471 Mg/m ³
Absorption coefficient	1.474 mm ⁻¹	1.355 mm ⁻¹
F(000)	544	576
Crystal size	0.20 x 0.10 x 0.02 mm ³	0.36 x 0.20 x 0.10 mm ³
Theta range for data collection	1.77 to 27.50°.	2.57 to 27.49°.
Index ranges	-15 ≤ h ≤ 9, -9 ≤ k ≤ 9, -15 ≤ l ≤ 16	-9 ≤ h ≤ 9, -11 ≤ k ≤ 11, -26 ≤ l ≤ 26
Reflections collected	7409	20744
Independent reflections	2605 [R _(int) = 0.0395]	2836 [R _(int) = 0.0496]
Completeness to theta = 27.50°	100.00%	99.60%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9711 and 0.7569	0.8372 and 0.6860
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	2605 / 0 / 139	2836 / 0 / 149
Goodness-of-fit on F ²	1.14	1.112
Final R indices [I > 2sigma(I)]	R ₁ = 0.0467, wR ₂ = 0.1092	R ₁ = 0.0508, wR ₂ = 0.1636
R indices (all data)	R ₁ = 0.0516, wR ₂ = 0.1186	R ₁ = 0.0609, wR ₂ = 0.1693
Largest diff. peak and hole	0.955 and -0.607 e.Å ⁻³	1.776 and -0.537 e.Å ⁻³

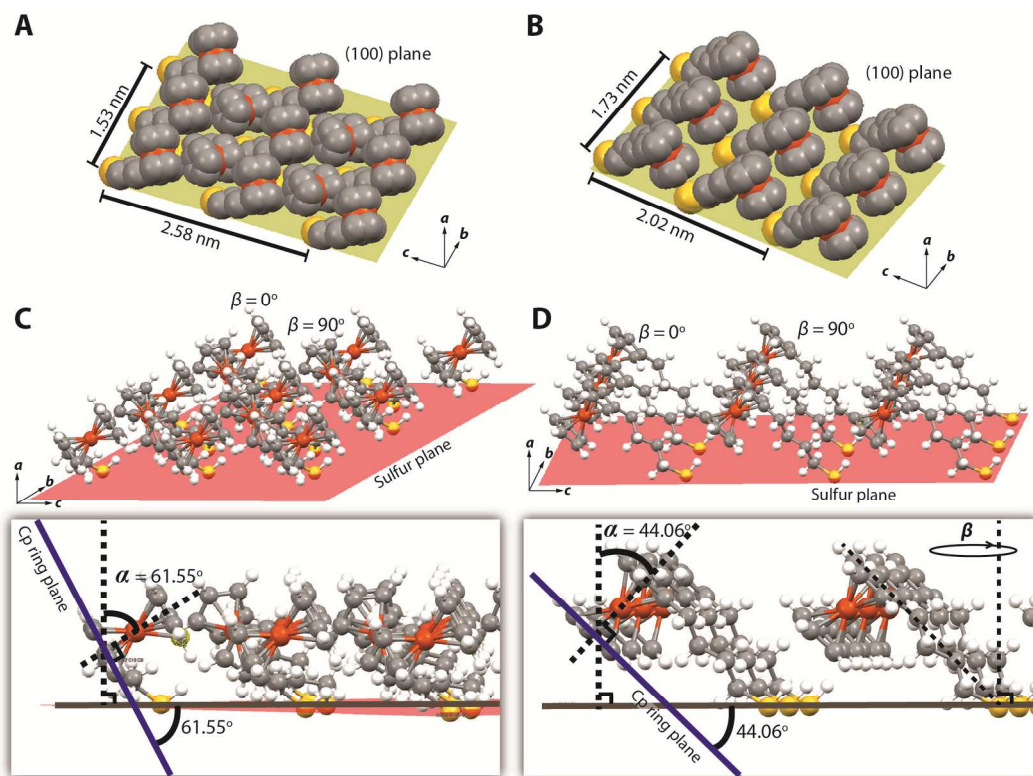


Figure S1. The crystal structures of the HSC₃Fc (A) and the HSC₄Fc (B) molecules obtained by single-crystal X-ray diffraction. The molecules are projected in the *bc*-plane showing the sulfur plane and Cp ring plane. The α values for HSC₃Fc (C) and HSC₄Fc (D) are 61.55° and 44.06°, respectively. The β values change by 90° between rows of molecules.

Figure S1 shows the crystal structures of HSC₃Fc (Fig. S1A and C) and HSC₄Fc (Fig. S2B and D) as determined by X-ray crystallography and shows the arrangement of the molecules of the bulk crystal in the *bc*-plane, also referred as the (100)-crystal plane. The unit cells of both HSC₃Fc and HSC₄Fc in their crystal structure are rectangles (the dihedral angle between two sides of the unit cell, defined as γ (°), is 90°). The Fc units pack edge-to-face (EF), in the so-called T shape conformation, for the HSC₃Fc bulk crystal, whereas they pack in a nearly parallel face-to-face (FF) alignment for the HSC₄Fc bulk crystal. The different Fc orientations between

rows of molecules in the crystal of both HSC₃Fc and HSC₄Fc are caused by the difference in azimuthal, or twist angle (β)⁵, angle of the carbon back-bone chain. The unit cell of HSC₃Fc occupies an area of 3.95 nm² (a dimension of 1.53 nm \times 2.58 nm) with eight molecules, while the unit cell of HSC₄Fc occupies an area of 3.49 nm² (a dimension of 1.73 \times 2.02 nm) with only four molecules. The packing density of HSC₃Fc (2.03 molecule/nm² or 3.4×10^{-10} mol/cm²) is about two times higher than that of HSC₄Fc (1.17 molecule/nm² or 1.9×10^{-10} mol/cm²).

References

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