

*Electronic Supplementary Information for*

## **Computational investigations of electronic structure modifications of ferrocene-terminated self-assembled monolayers: Effects of electron donating/withdrawing functional groups attached on ferrocene moiety**

Yasuyuki Yokota,<sup>1,a)</sup> Sumito Akiyama,<sup>2</sup> Yukio Kaneda,<sup>2</sup> Akihito Imanishi,<sup>2</sup> Kouji Inagaki,<sup>3</sup>  
Yoshitada Morikawa,<sup>3,4,b)</sup> and Ken-ichi Fukui<sup>2,c)</sup>

<sup>1</sup>*Surface and Interface Science Laboratory, RIKEN, Wako, Saitama 351-0198, Japan*

<sup>2</sup>*Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan*

<sup>3</sup>*Department of Precision Science and Technology, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan*

<sup>4</sup>*Research Center for Ultra-Precision Science and Technology, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan*

### **Figure S1:**

Occupied-state molecular orbitals of ferrocene, C4(CO)Fc, C5Fc, C5OctFc molecules.

### **Figure S2:**

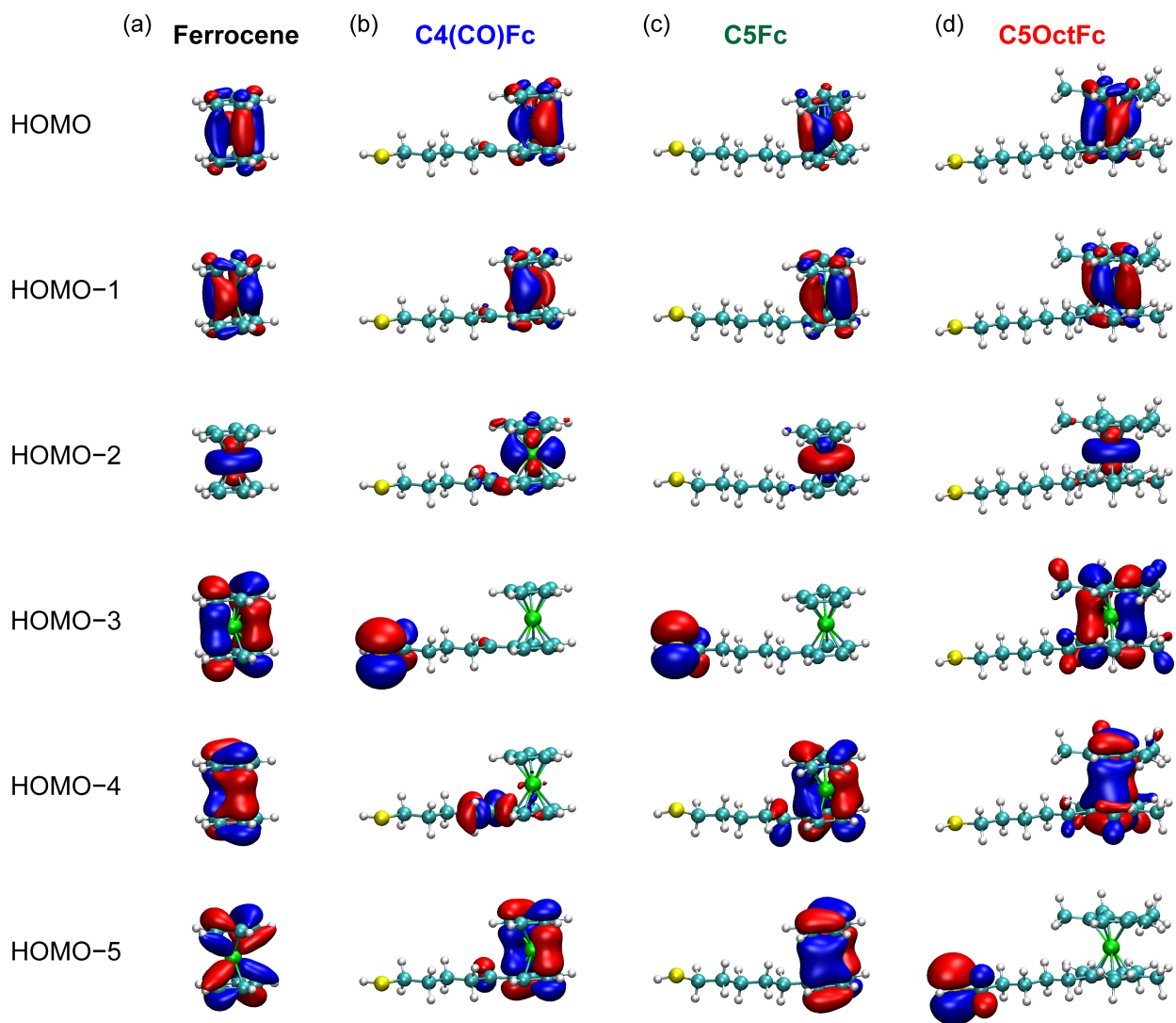
Comparisons between  $\Delta\text{HOMO}_{\text{SAM}}$  and  $\Delta\text{HOMO}_{\text{mol}}$ .

### **Table S1:**

Geometry Parameters of Optimized SAM Structures.

### **Table S2:**

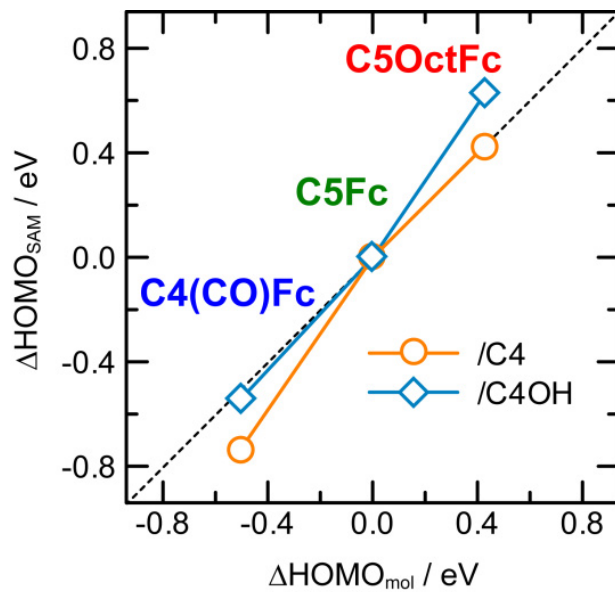
Electronic Properties of SAMs.



(e)

	Ferrocene	C4(CO)Fc	C5Fc	C5OctFc
HOMO	1.22	0.72	1.21	1.66
HOMO-1	1.20	0.67	1.19	1.64
HOMO-2	1.05	0.64	1.08	1.47
HOMO-3	-0.69	<b>0.00</b>	<b>0.00</b>	0.26
HOMO-4	-0.69	-0.14	-0.51	0.21
HOMO-5	-1.12	-1.03	-0.69	<b>0.00</b>
HOMO <sub>SAM</sub>	1.17	0.67	1.17	1.60
$\Delta$ HOMO <sub>SAM</sub>	0.00	-0.50	0.00	0.43

**Fig. S1** Occupied-state molecular orbitals of (a) ferrocene, (b) C4(CO)Fc, (c) C5Fc, and (d) C5OctFc molecules. HOMO and HOMO-1 of the ferrocene molecule are degenerate and those of the others have almost the same energy. HOMO, HOMO-1, and HOMO-2 orbitals contribute to the first peak of DOS curves in Fig. 1. (e) Orbital energies (in eV) with respect to the localized -SH state (see main text for details).



**Fig. S2** Comparisons between  $\Delta\text{HOMO}_{\text{SAM}}$  and  $\Delta\text{HOMO}_{\text{mol}}$  of C4(CO)Fc, C5Fc, and C5OctFc systems.  $\Delta\text{HOMO}_{\text{SAM}}$  is presented with respect to each matrix SAM. The dotted line indicates a slope of 1 for comparison.

**Table S1 Geometry Parameters of Optimized SAM Structures.**

SAMs	$d_{\text{SAM}}$ (Å) <sup>a</sup>	$h_{\text{S}}$ (Å) <sup>b</sup>	$r(\text{S}-\text{C})$ (Å)	$\theta(\text{S}-\text{C})$ (°) <sup>c</sup>	$r(\text{Au}-\text{S})$ (Å) <sup>d</sup>	$h4-h3$ (Å) <sup>e</sup>	$h3-h2$ (Å) <sup>e</sup>	$h2-h1$ (Å) <sup>e</sup>	$r(\text{Fe}-\text{C})$ (Å)	$r(\text{C}-\text{H})$ (Å)	$r(\text{C}-\text{C})$ (Å)
Au(111)	-	-	-	-	-	2.50	2.47	2.40	-	-	-
C4	7.97	2.19	1.84	55.0	2.48	2.49	2.49	2.40	-	-	-
C4OH	9.05	2.19	1.84	55.0	2.48	2.49	2.49	2.40	-	-	-
C4(CO)Fc/C4	12.76	2.21	1.84	57.2	2.48	2.50	2.50	2.40	2.04	1.09	-
C4(CO)Fc/C4OH	12.78	2.16	1.84	56.8	2.48	2.48	2.48	2.40	2.04	1.09	-
C5Fc/C4	12.75	2.19	1.84	55.2	2.48	2.49	2.49	2.40	2.04	1.08	-
C5Fc/C4OH	12.81	2.18	1.84	55.5	2.48	2.49	2.48	2.40	2.04	1.09	-
C5OctFc/C4	14.39	2.18	1.84	55.8	2.48	2.49	2.49	2.40	2.04	-	1.49
C5OctFc/C4OH	14.44	2.18	1.84	55.7	2.48	2.49	2.49	2.40	2.04	-	1.49

<sup>a</sup> The SAM thickness  $d_{\text{SAM}}$  is defined as the height of the farthest atom from the ideal bulk terminated Au(111) surface.

<sup>b</sup> The height of sulfur atoms  $h_{\text{S}}$  is defined as the average height of the sulfur atoms from the ideal bulk terminated Au(111) surface.

<sup>c</sup> The angle  $\theta(\text{S}-\text{C})$  is defined as the average angle of S-C bond with respect to the surface normal.

<sup>d</sup> The length  $r(\text{Au}-\text{S})$  is defined as the average length of the sulfur atom and two gold atoms that constitute the bridge site; the position of sulfur atom is slightly shifted to the FCC-hollow site.

<sup>e</sup> The spacing of Au layers;  $h4$  represents the average height of the topmost Au layers.

**Table S2 Electronic Properties of SAMs.**

SAMs	HOMO <sub>SAM</sub> (eV) <sup>a</sup>	$\Delta\text{HOMO}_{\text{SAM}}$ (eV) <sup>b</sup>	$W$ (eV)	$\Delta W$ (eV) <sup>b</sup>	$\mu$ (Debye) <sup>c</sup>	$\Delta V_{\text{ES}}(\text{S})$ (V) <sup>b,d</sup>	$V_{\text{ES}}(\text{O})$ (V) <sup>e</sup>	$\Delta V_{\text{ES}}(\text{Fe})$ (V) <sup>b,f</sup>	$\Delta I_{\text{p}}$ (V) <sup>b,g</sup>
Au(111)	-	-	5.16	1.35	-0.20	-	-	-	-
C4	-	-	3.80	-0.01	3.46	-0.01	-	-	-
C4OH	-	-	3.18	-0.63	4.96	0.00	0.00	-	-
C4(CO)Fc/C4	-1.30	-0.73	3.22	-0.59	4.90	0.03	-	-0.72	0.14
C4(CO)Fc/C4OH	-1.38	-0.81	2.95	-0.86	5.16	-0.16	-0.80	-0.91	-0.05
C5Fc/C4	-0.57	0.00	3.81	0.00	3.40	0.00	-	0.00	0.00
C5Fc/C4OH	-0.84	-0.27	3.41	-0.40	4.05	-0.16	-0.11	-0.39	-0.13
C5OctFc/C4	-0.14	0.43	3.73	-0.08	3.37	-0.10	-	0.45	-0.51
C5OctFc/C4OH	-0.21	0.36	3.60	-0.21	3.69	-0.03	-0.21	0.38	-0.57

<sup>a</sup> The peak top energy of the first peak in Fig. 4.

<sup>b</sup> Relative value with respect to the C5Fc/C4 SAM.

<sup>c</sup> Dipole moment of the unit cell perpendicular to the surface.

<sup>d</sup> Average electrostatic potential energy at the positions of sulfur atoms.

<sup>e</sup> Differences of average electrostatic potential at the positions of oxygen atom in the C4OH molecule before and after C4(CO)Fc, C5Fc, and C5OctFc substitutions.

<sup>f</sup> Electrostatic potential at the position of the iron atom.

<sup>g</sup> Ionization potential  $I_{\text{p}}$  is defined as the difference between the vacuum level and HOMO<sub>SAM</sub>.