Supplemental Information

The Supramolecular Structure Affects the Electronic Structure of Ferrocenyl-Alkanethiolate SAMs on Gold and Silver Electrodes

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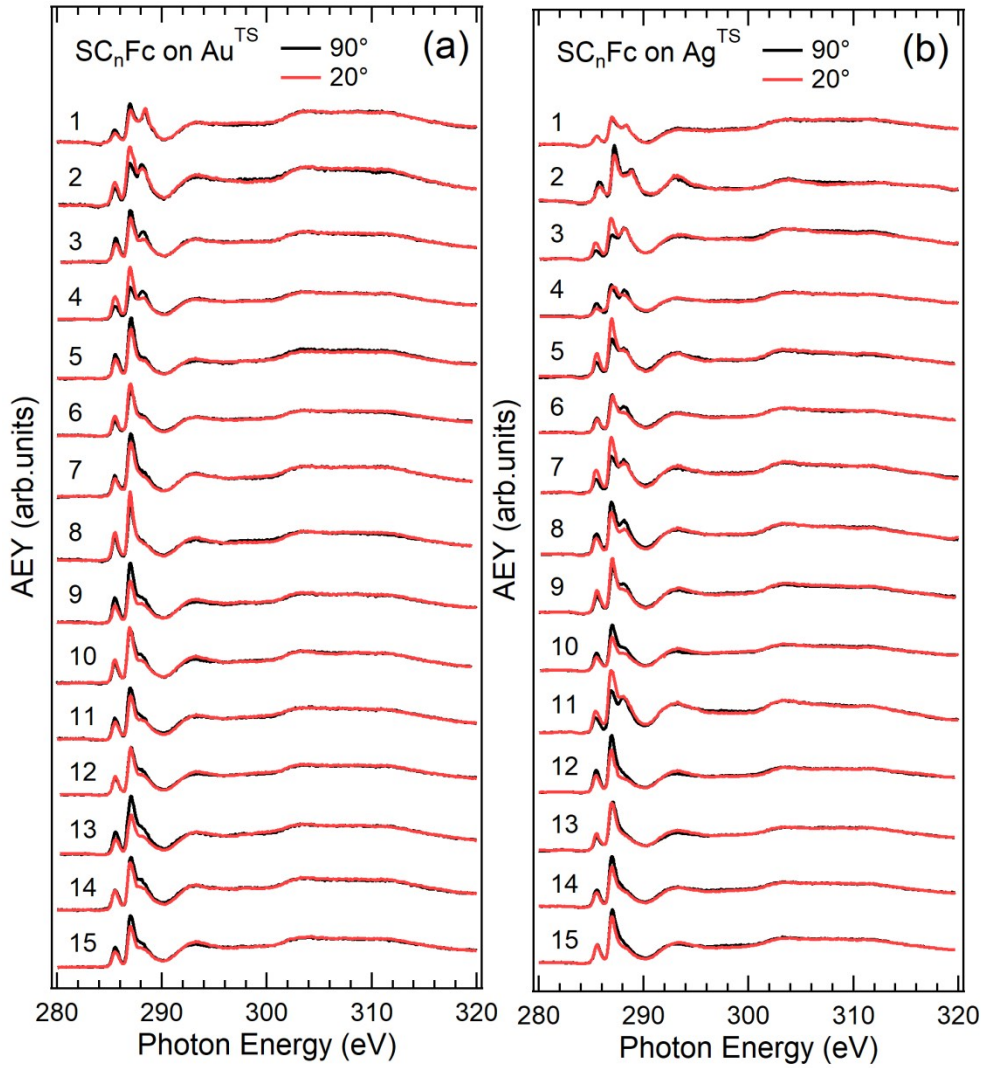

Figure S1. NEXAFS spectra for SC_nFC SAMs on Au^{TS} (a) and on Ag^{TS} (b). Data for n = 3 and 4 for SAMs on Au were taken from ref[1]. Data for n = 6-15 were taken from supporting information of ref[2].

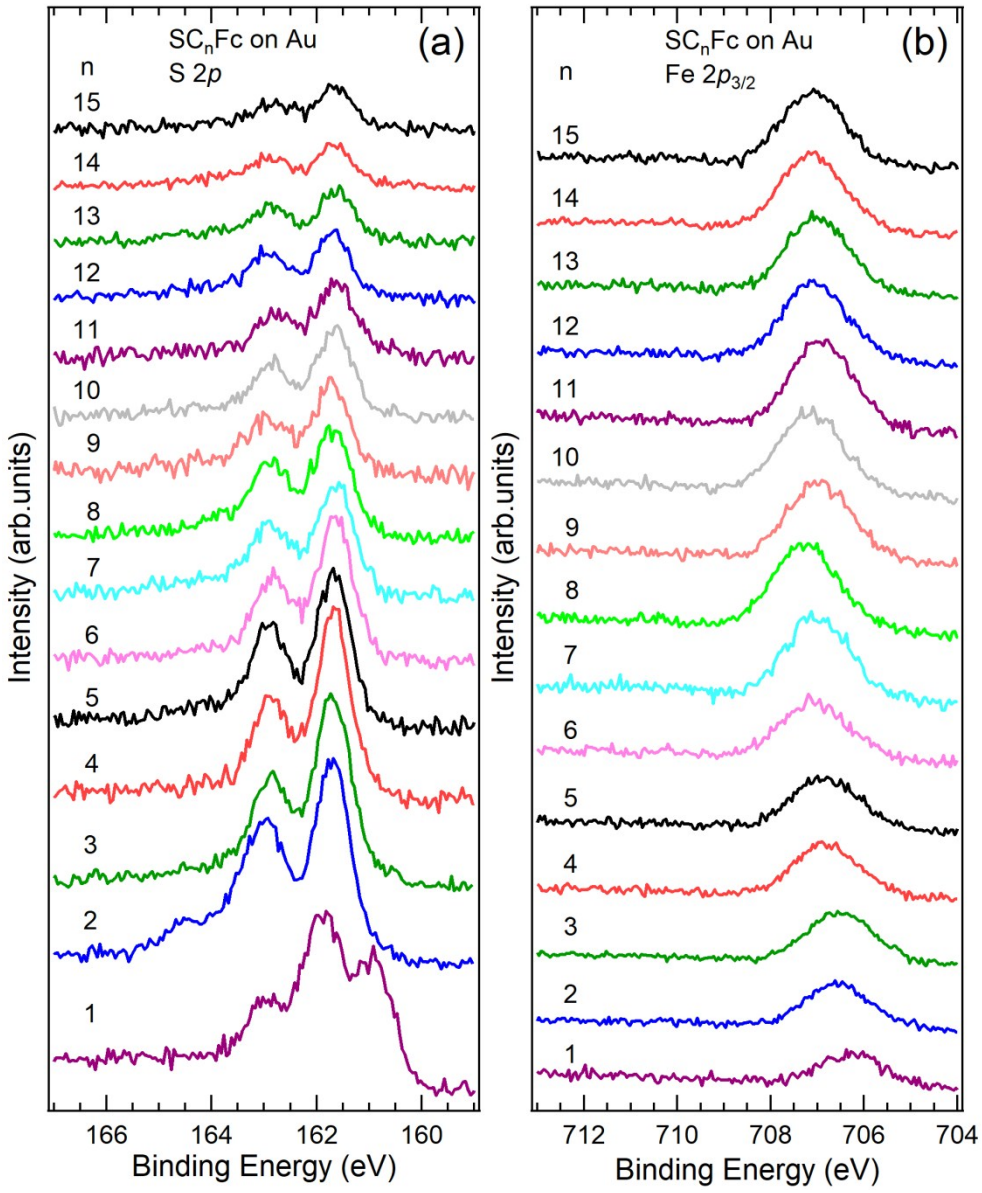

Figure S2. S 2*p* (a) and Fe $2p_{3/2}$ spectra for SC_nFc on Au^{TS} measured normal emission angle. The intensity of the S 2*p* component that is exclusively associated with the S-Au bonds (~161.7 eV) was used to evaluate the d_{SAM}. S 2*p* spectra were taken from supporting information of ref[3]. Fe $2p_{3/2}$ spectra for n = 6-15 were taken from supporting information of ref[4]. All data are shown together for the sake of clarity.

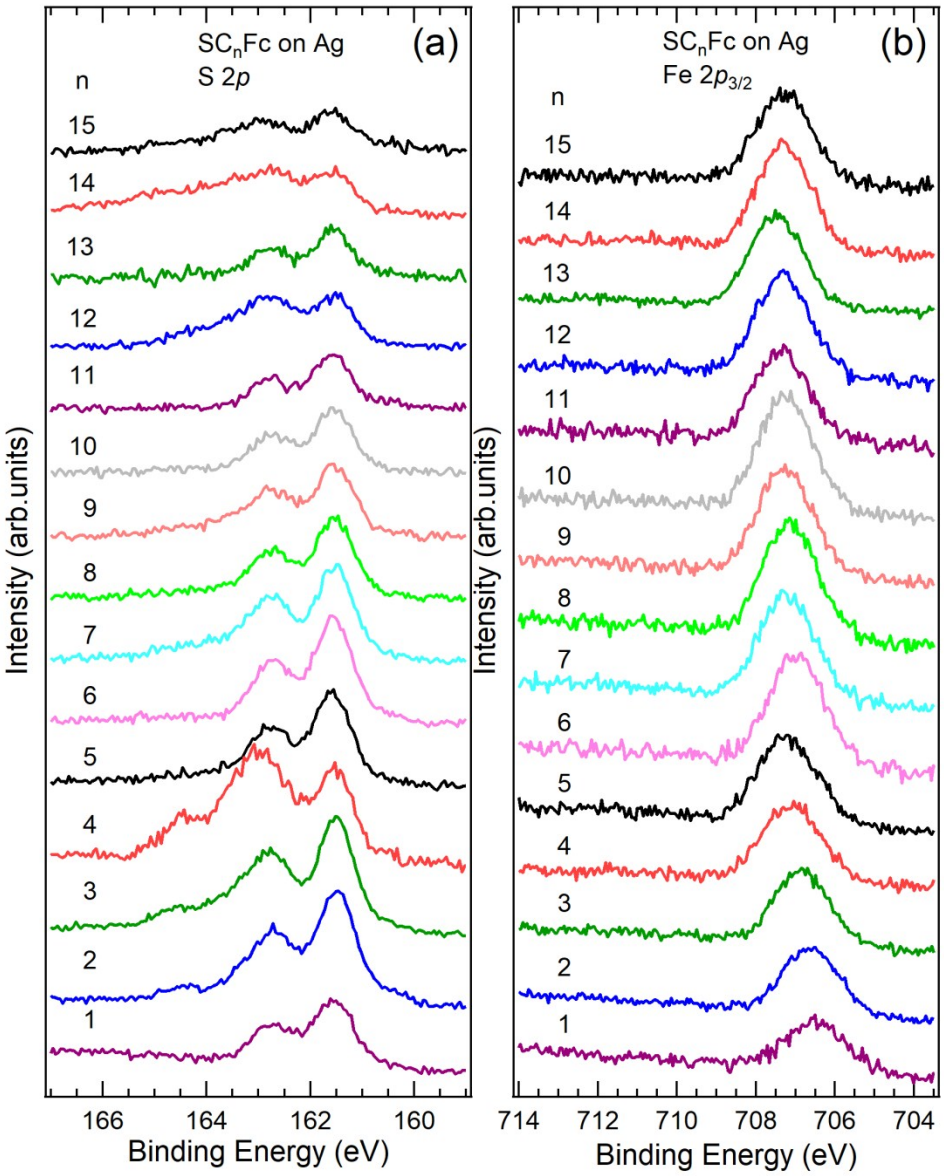

Figure S3. S 2*p* (a) and Fe $2p_{3/2}$ spectra for SC_nFc on Ag^{TS} measured normal emission angle. S 2*p* and Fe $2p_{3/2}$ spectra for n = 6-15 were taken from supporting information of ref[4]. All data are shown together for the sake of clarity.

Table S1: Relative intensities (I_{eff}) at 90º and 40º take-off angles for S 2*p* and Fe $2p_{3/2}$ components of SC_nFc SAMs on Au^{TS}. The d_S, d_{Fe}, and d_{SAM} are evaluated from angular dependent PES following the procedure reported in ref [4].[a] Average tilt angles of Fc (α) are estimated from angular dependent NEXAFS.

	S 2*p*			Fe $2p_{3/2}$				
n	I_{eff}(90º) (%)	I_{eff}(40º) (%)	d_S (Å)	I_{eff}(90º) (%)	I_{eff}(40º) (%)	d_{Fe} (Å)	d_{SAM} (Å)	α(°)
1	61.0	39.0	5.72	61.3	38.7	4.43	7.52	59.2
2	68.0	32.0	10.13	62.5	37.5	5.07	11.93	49.9
3	69.1	30.9	10.87	62.1	37.9	4.86	12.67	60.2
4	70.5	29.5	11.82	62.6	37.4	5.12	13.62	45.4
5	70.5	29.5	11.82	61.9	38.1	4.75	13.62	59.3
6	72.2	27.8	13.02	63.0	37.0	5.34	14.82	50.0
7	72.4	27.6	13.16	62.0	38.0	4.80	14.96	58.1
8	73.2	26.8	13.74	62.6	37.4	5.12	15.54	51.5
9	73.8	26.2	14.19	61.9	38.1	4.75	15.99	59.5
10	74.1	25.9	14.41	62.7	37.3	5.18	16.21	52.1
11	74.9	25.1	15.02	61.7	38.3	4.64	16.82	58.0
12	75.3	24.7	15.33	62.4	37.6	5.02	17.13	53.5
13	76.8	23.2	16.51	61.1	38.9	4.32	18.31	59.5
14	77.4	22.6	17.00	63.1	36.9	5.39	18.80	54.5
15	78.0	22.0	17.50	61.6	38.4	4.59	19.30	58.0

[a] Relative intensities of each component are evaluated with respect to the total intensity at two take-off angles.

References

1. N. Nerngchamnong, H. Wu, K. Sotthewes, L. Yuan, L. Cao, M. Roemer, J. Lu, K. P. Loh, C. Troadec, H. J. W. Zandvliet and C. A. Nijhuis, *Langmuir*, 2014, **30**, 13447-13455.
2. N. Nerngchamnong, L. Yuan, D.-C. Qi, J. Li, D. Thompson and C. A. Nijhuis, *Nat. Nano.*, 2013, **8**, 113-118.
3. N. Nerngchamnong, D. Thompson, L. Cao, L. Yuan, L. Jiang, M. Roemer and C. A. Nijhuis, *J. Phys. Chem. C*, 2015, **119**, 21978-21991.
4. L. Yuan, D. Thompson, L. Cao, N. Nerngchangnong and C. A. Nijhuis, *J. Phys. Chem. C*, 2015, **119**, 17910-17919.