Electronic Supplementary Information

Electrodeposition of ferrocenoyl peptide disulfides

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Table S1. Electrochemical parameters calculated from CV experiments using the electrochemical deposition and incubation methods.

	Incubation			**Electrodeposition**		
	ΔE_p / **mV**	E_{fwhm} / **mV**	I_a/I_c	ΔE_p / **mV**	E_{fwhm} / **mV**	I_a/I_c
1-c	90(8)	200(15)	1.00(9)	90(9)	190(10)	0.92(5)
1-a	120(6)	240(15)	1.00(9)	120 (10)	220(10)	1.00(5)
2-c	60(8)	180(10)	0.90(9)	60(7)	170(8)	1.00(5)
2-a	65(5)	195(10)	1.00(9)	140(10)	175(8)	0.92(5)
3-c	85(7)	190(15)	0.90(9)	55(7)	160(8)	0.94(5)
3-a	90(5)	200(15)	1.00(9)	111(10)	190(10)	0.90(5)
4-c	80(7)	210(8)	0.90(5)	55(7)	170(8)	0.98(5)
4-a	85(5)	230(15)	0.90(5)	120(10)	190(10)	1.00(5)
5-c	70(5)	200(10)	0.90(5)	62(7)	157(10)	0.90(3)
5-a	95(7)	210(10)	0.90(5)	110(10)	190(10)	0.90(3)

Table S2. Electrochemical parameters calculated from CV for the *incubation* method. This is complementary data to Table 1 of the paper.

	$E^{0'}$ / **mV**	$k_{ET} \times 10^3$ / s^{-1}	***Specific Area*** / $Å^2$·**molecule**$^{-1}$
1-c	660(9)	8.0	120(9)
1-a	473(6)	7.0	50(3)
2-c	682(8)	13.0	150(20)
2-a	445(9)	12.0	78(8)
3-c	624(8)	11.0	141(20)
3-a	468(8)	6.9	53(9)
4-c	665(9)	11.0	130(25)
4-a	484(7)	10.0	70(10)
5-c	680(7)	14.0	220(10)
5-a	476(9)	11.0	101(9)

* Error for k_{ET} calculation was 2 x 10^3 s^{-1}

Background (non-Faradaic current) correction for all CVs was made in custom written software by fitting a polynomial curve. Pinholes in the film were analyzed by taking the difference between the gold oxide reduction peak in sulfuric acid CVs of a bare Au electrode and a Fc-peptide film protected electrode. Only 5-7% of the surface was oxidized to gold oxide if the film was prepared by electro-deposition compared to 15-20% of Au was oxidized to gold oxide in films prepared by the incubation method. The electron transfer kinetics were evaluated according to methods described in reference 18.

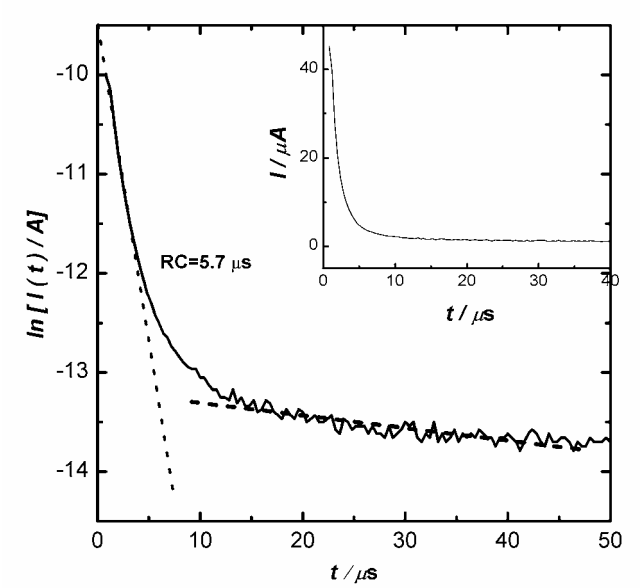

Figure S1. A representative semilog chronoamperometric response from a 400 mV potential jump on an electrodeposited cyclic 1,1'-Fc[GlyCSA]$_2$. 12.5 μm radius Au electrode, 2 M $NaClO_4$ supporting electrolyte and a Ag/AgCl/(3.5 M KCl) reference electrode. The *RC* of 5.7 μs (dotted line) is the time constant of the double layer charging and the linear region (dashed line) is the electron transfer rate at 400 mV overpotential. The inset shows the untransformed data.

k_{et} values that comes from CA are similar to those obtained from CV.

Table S3. Chronoamperometric results from monolayers that were electrodeposited.

Compound	*CA electrodeposition* $k_{ET} \times 10^3$ / s^{-1} *
1-c	7.5
1-a	7.0
2-c	11.0
2-a	12.0
3-c	11.0
3-a	8.0
4-c	10.0
4-a	8.0
5-c	16.0)
5-a	10.5

* Error for k_{ET} calculation was 1.5 x 10^3 s^{-1}

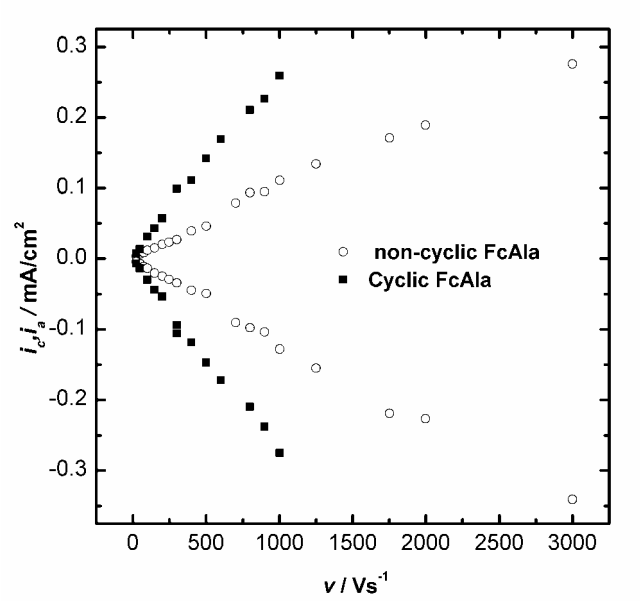

Figure S2. Linear response of anodic and cathodic peak currents for 3-c and 3-a derivatives, indicating successful surface immobilization.

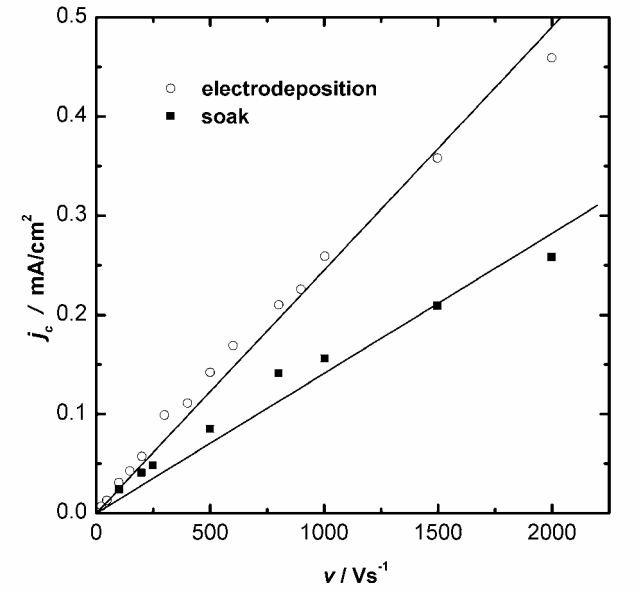

Figure S3. Linear response of anodic peak currents for 3-c using both the incubation and electrodeposition methods, indicating successful surface immobilization.

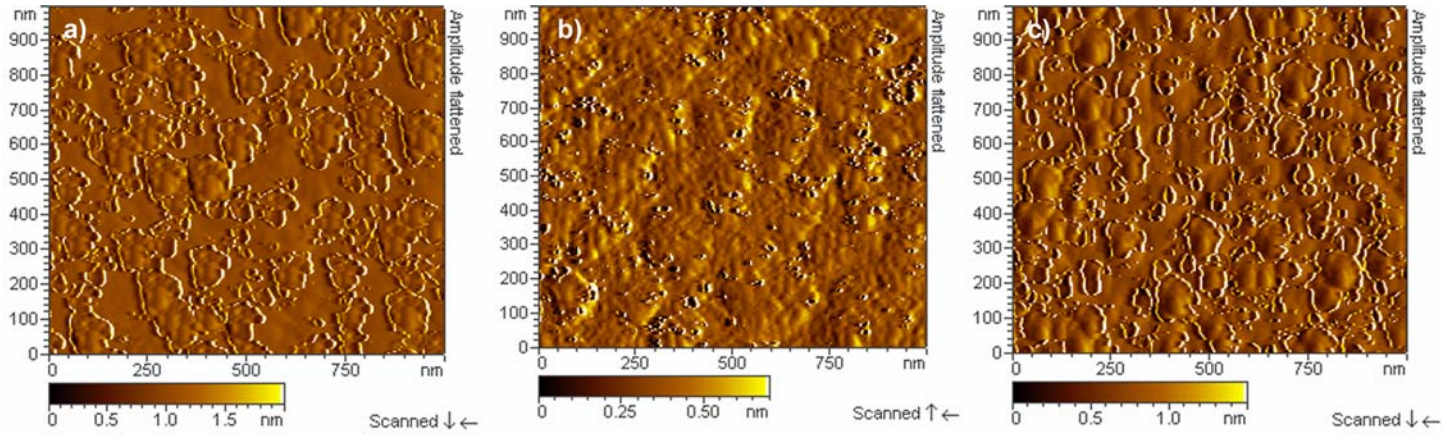

Figure S4. a) AFM image of Au on Si(100); b) AFM image of Au on Si(100) after 400 cycles (0 V to 1.4 V vs. Ag/AgCl (3.5 M KCl)) in 0.5 M H_2SO_4; c) AFM image of Au on Si(100) after electrodeposition of cyclo-1,1'-Fc[AlaCSA]$_2$.

Thickness of the monolayers were measured by ellipsometry and gave values 9(3) Å which is in good agreement with data obtained from x-ray crystallography [10] and Spartan software molecular simulation.

Table S4. Root-Mean-Square (RMS) roughness of 3 AFM images of Figure S4.

	RMS (nm)	
	Left Scan Direction	**Right Scan Direction**
Au on Si(100)	2.139	2.058
Au on Si(100) after 400 cleaning cycles	1.196	1.240
cyclo-1,1'-Fc[AlaCSA]$_2$.	1.692	1.678

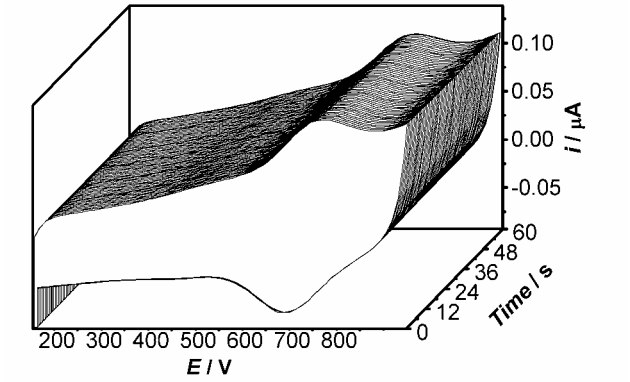

Figure S5. Multiple CVs of cyclo-1,1'-Fc[AlaCSA]$_2$ (3-c) taken every 0.05 seconds for 60 seconds with a 12.5 µm radius Au-modified electrode, 2 M $NaClO_4$ supporting electrolyte and a Ag/AgCl/(3.5 M KCl) reference electrode.

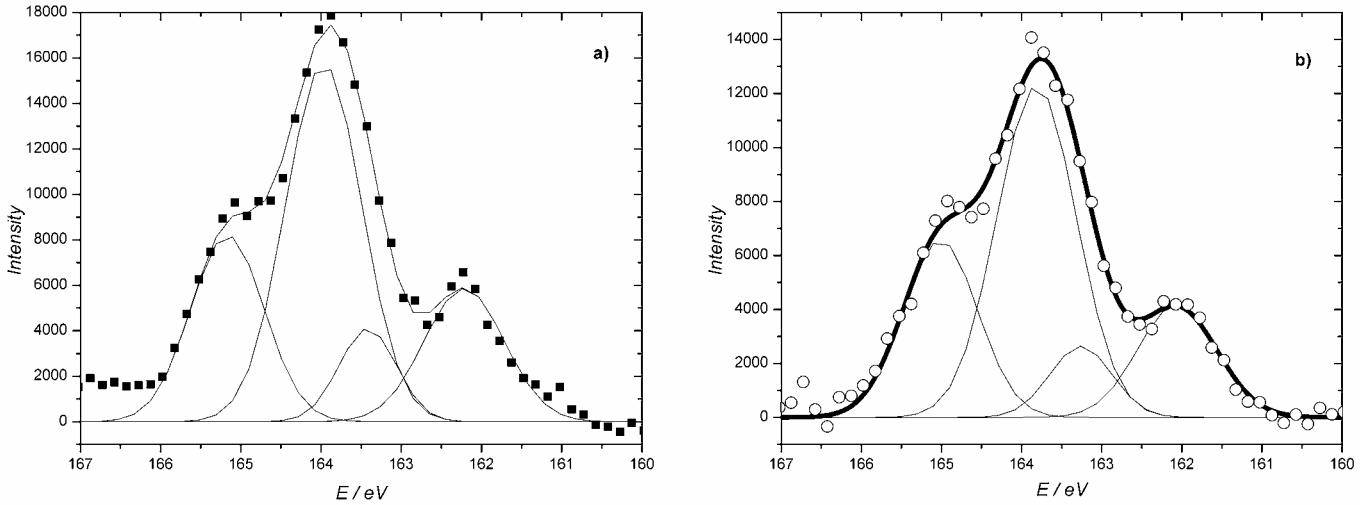

Figure S6. XPS results for sulfur sp^2 for **a)** electrodeposited, **b)** incubated compound **1-c**. Sulfur population in both cases is virtually identical. The similar results was obtained for other cyclic compounds.

Ellipsometry. Au on Si(100) (Platypus Technologies, Inc) wafers were incubated in a 1 mM Fc-peptide ethanolic solution for 5 days and finally rinsed with EtOH and H_2O. A Stokes ellipsometer LSE (Gaertner Scientific Corporation, Skokie, IL, fixed angle (70°), fixed wavelength (632.8 nm)) was used, and the data were collected and analyzed using LGEMP (Gaertner Ellipsometer Measurement Software) on a PC. Ellipsometry constants were as follows: $n_S = 0.25$ and $K_S = 3.46$ for the substrate and 1.40 was used as the refractive index of the monolayer.