Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supplementary Information

Chemical Modification of Gold Electrodes via Non-Covalent Interactions

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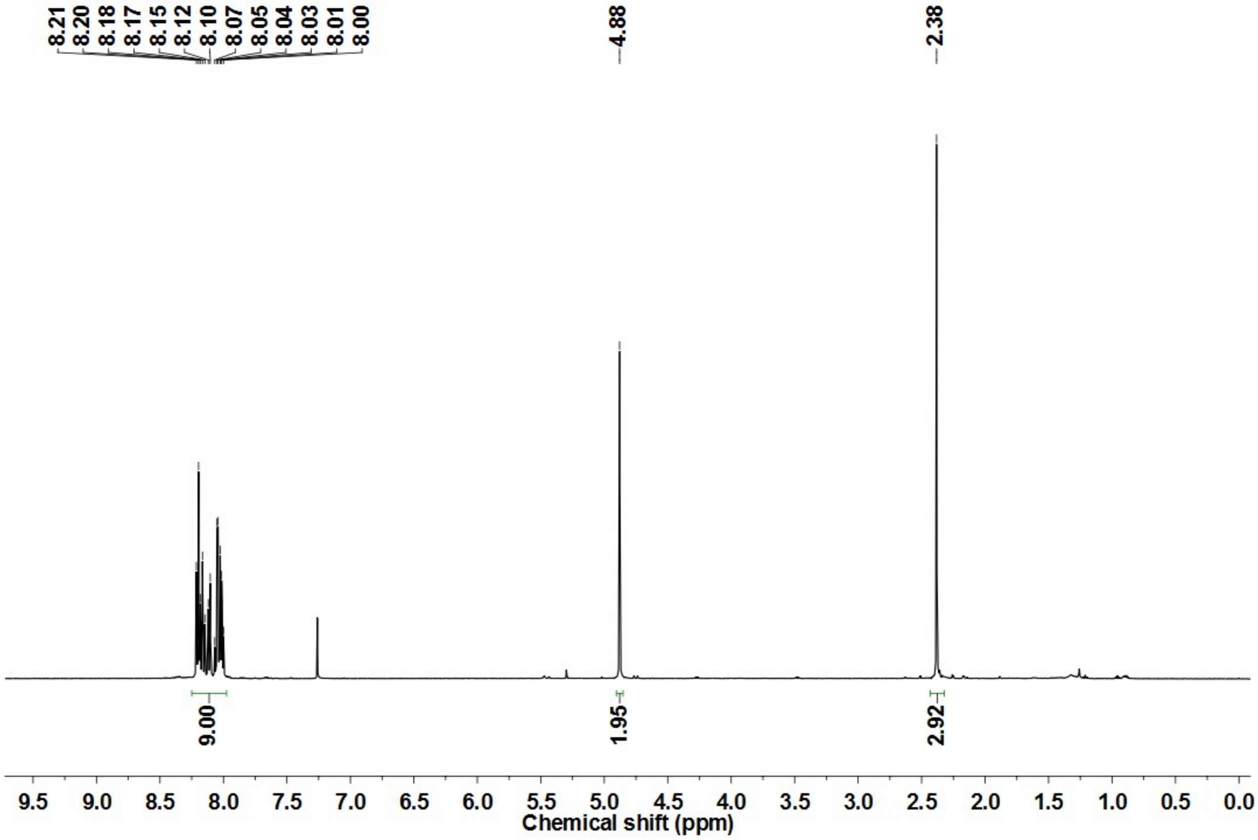

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Figure S1. ^{1}H NMR spectrum of **1** in $CDCl_3$.

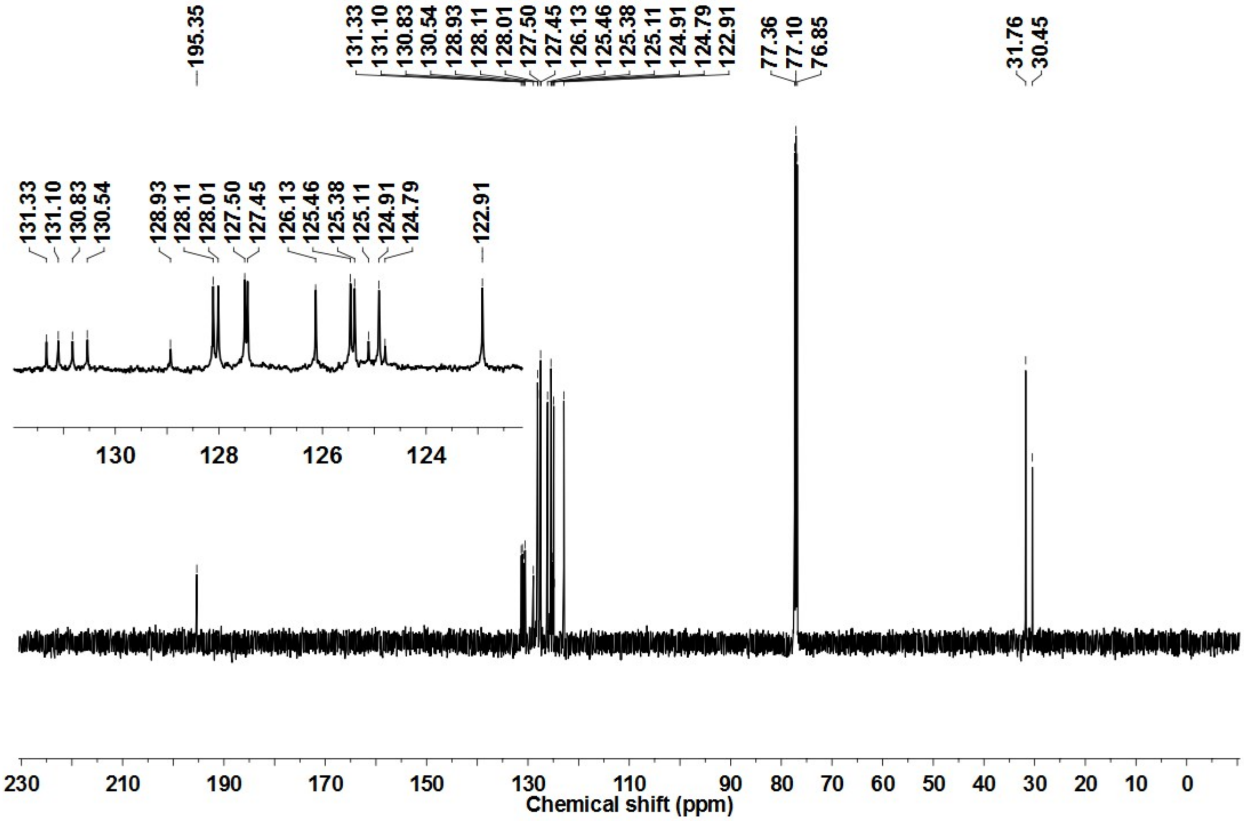

Figure S2. ^{13}C NMR spectrum of **1** in $CDCl_3$.

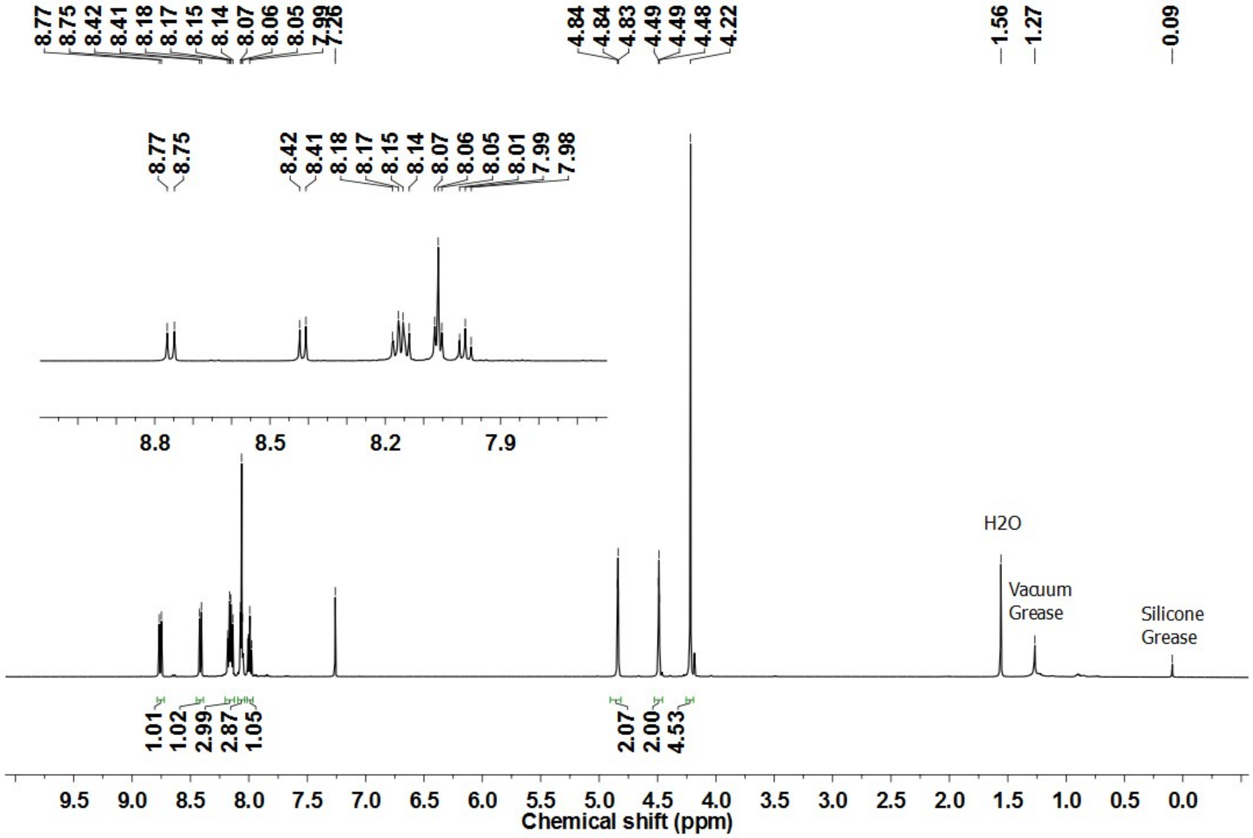

Figure S3. ^{1}H NMR spectrum of **2** in $CDCl_3$.

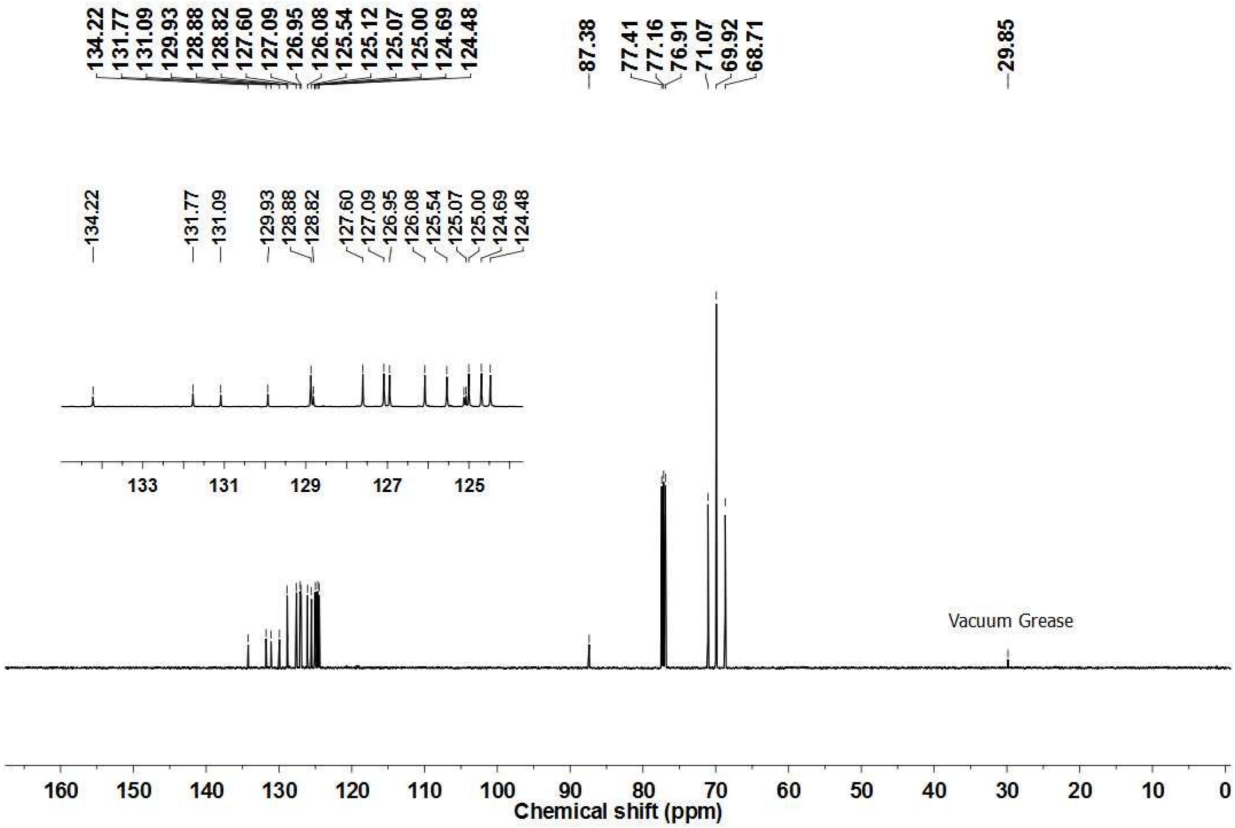

Figure S4. ^{13}C NMR spectrum of **2** in $CDCl_3$.

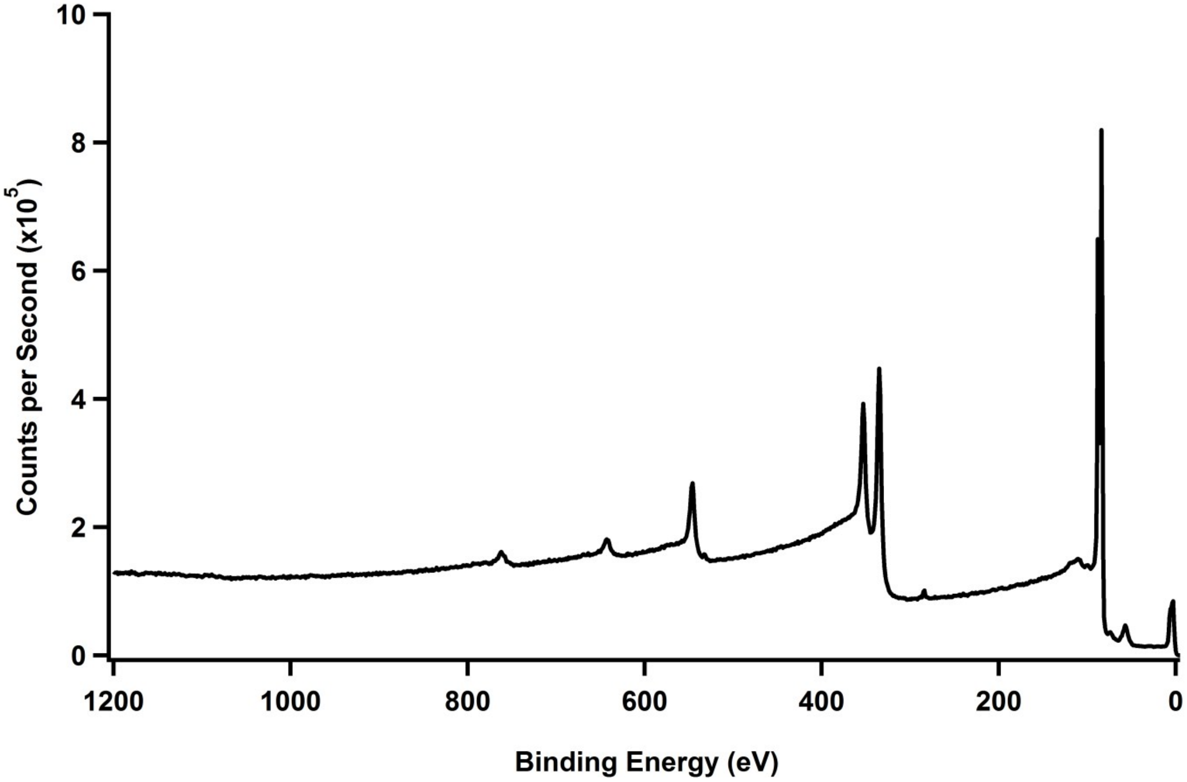

Figure S5. Survey XP spectrum of clean gold.

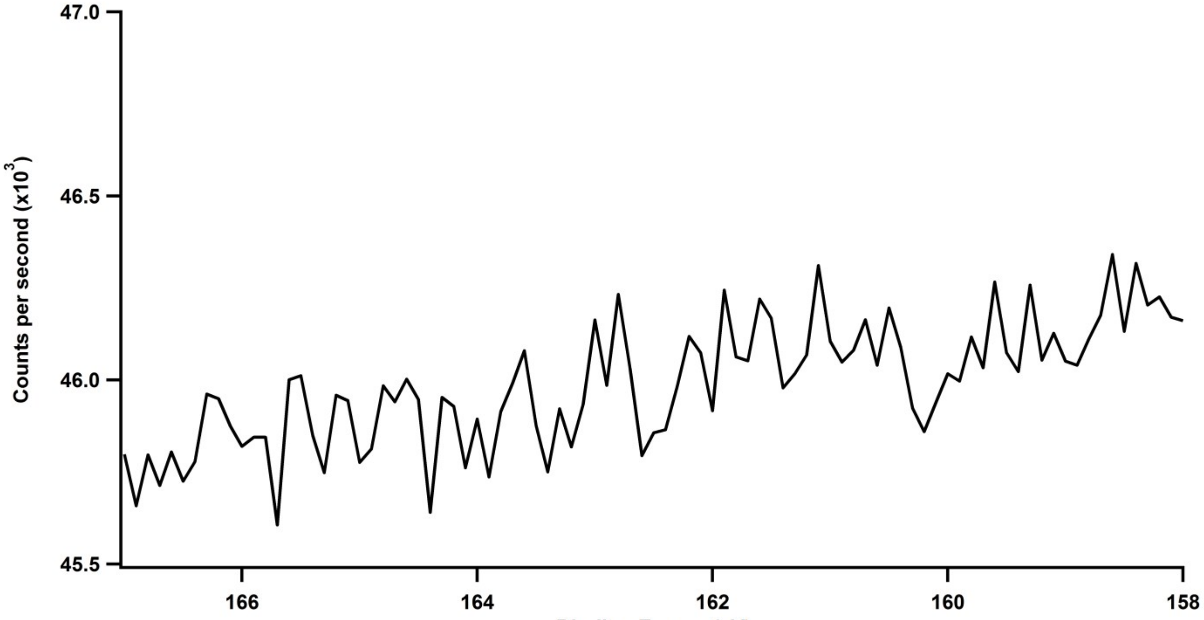

Figure S6. S 2p XP spectrum of clean gold.

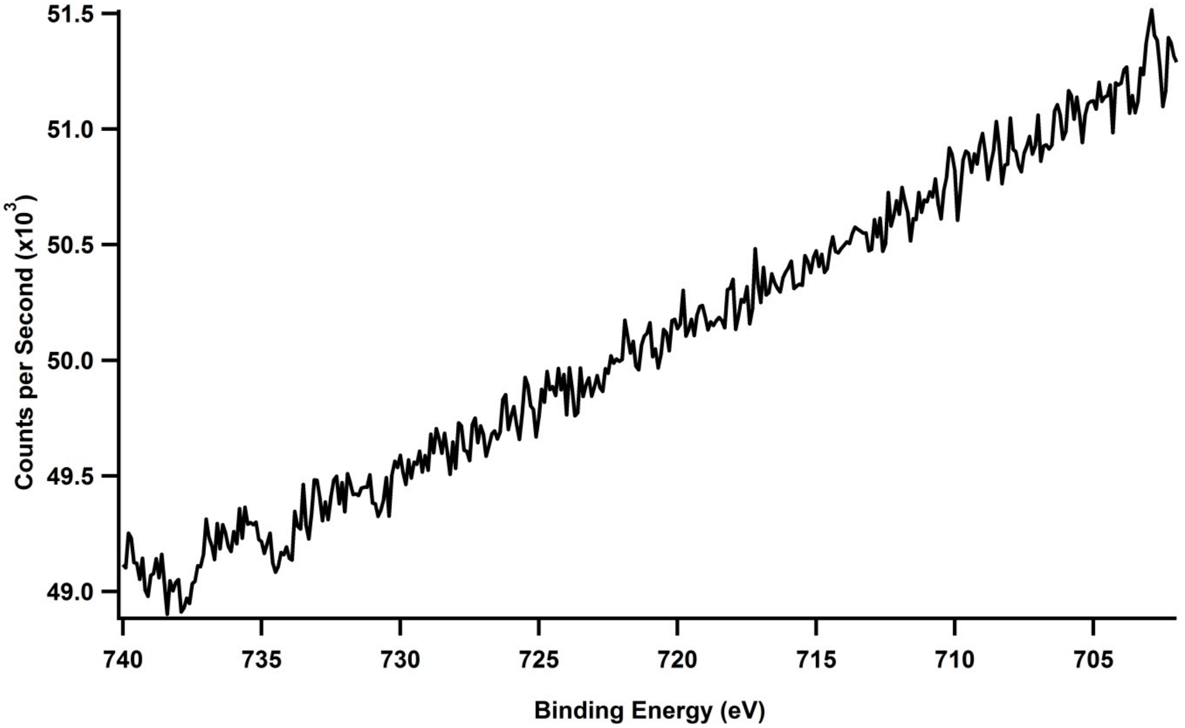

Figure S7. Fe 2p XP spectrum of clean gold.

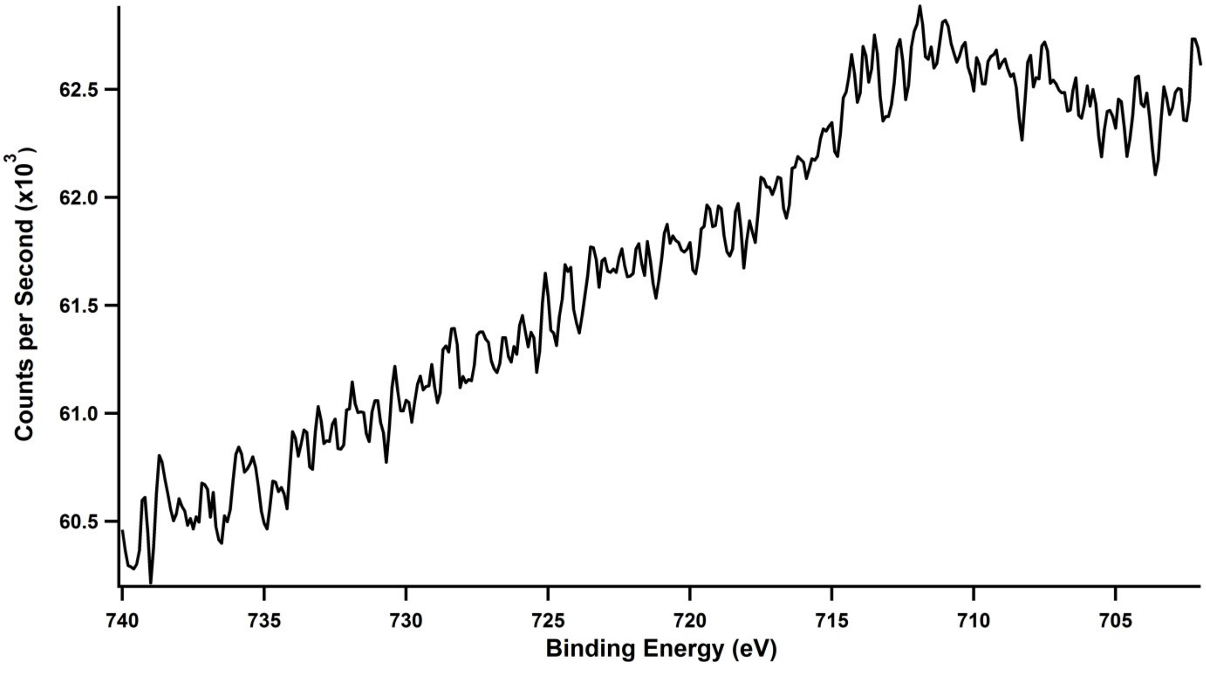

Figure S8. Fe 2p XP spectrum of gold upon covalent attachment of thiol-functionalized pyrene.

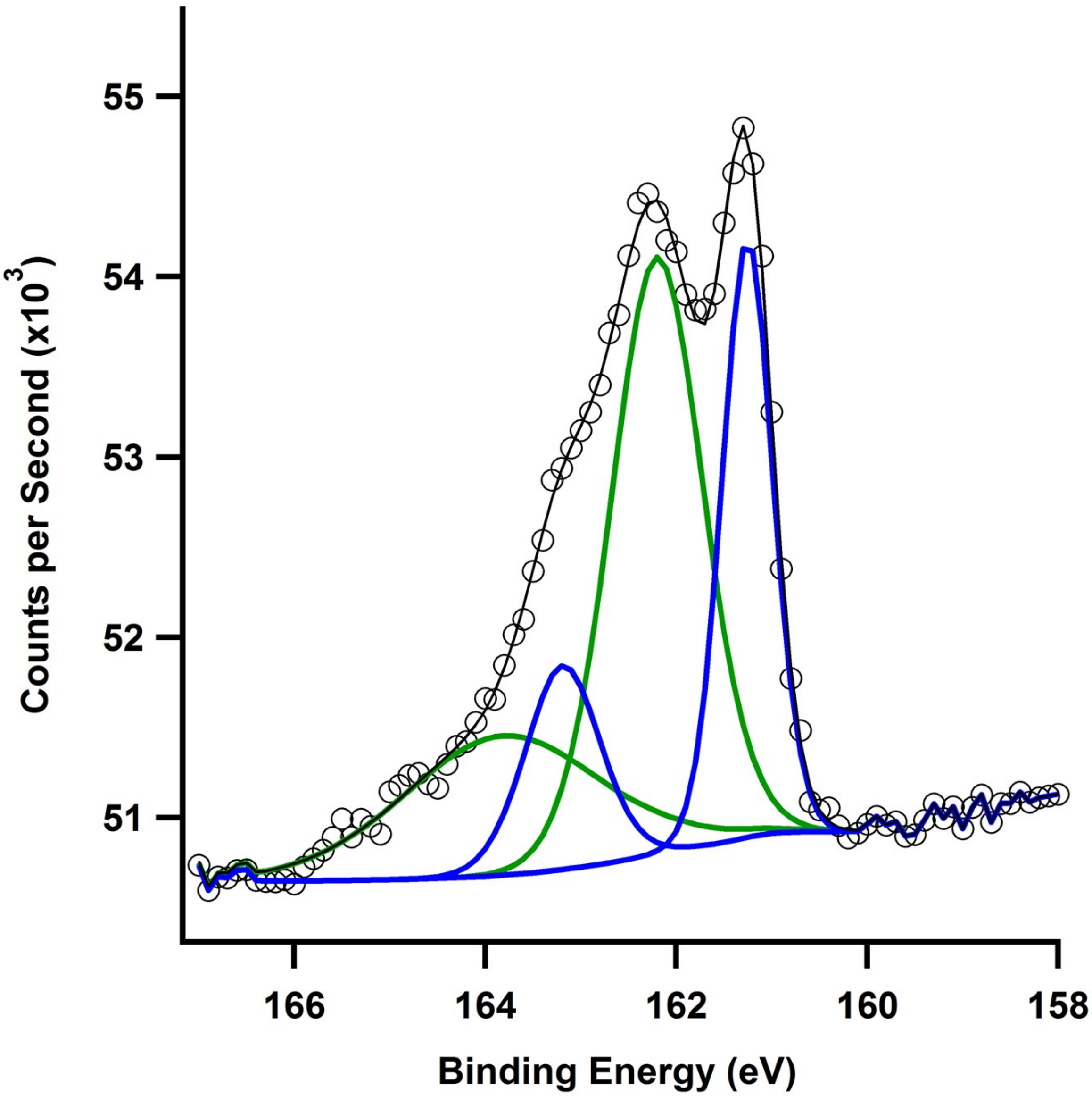

Figure S9. S 2p XP spectrum of gold upon covalent attachment of thiol-functionalized pyrene.

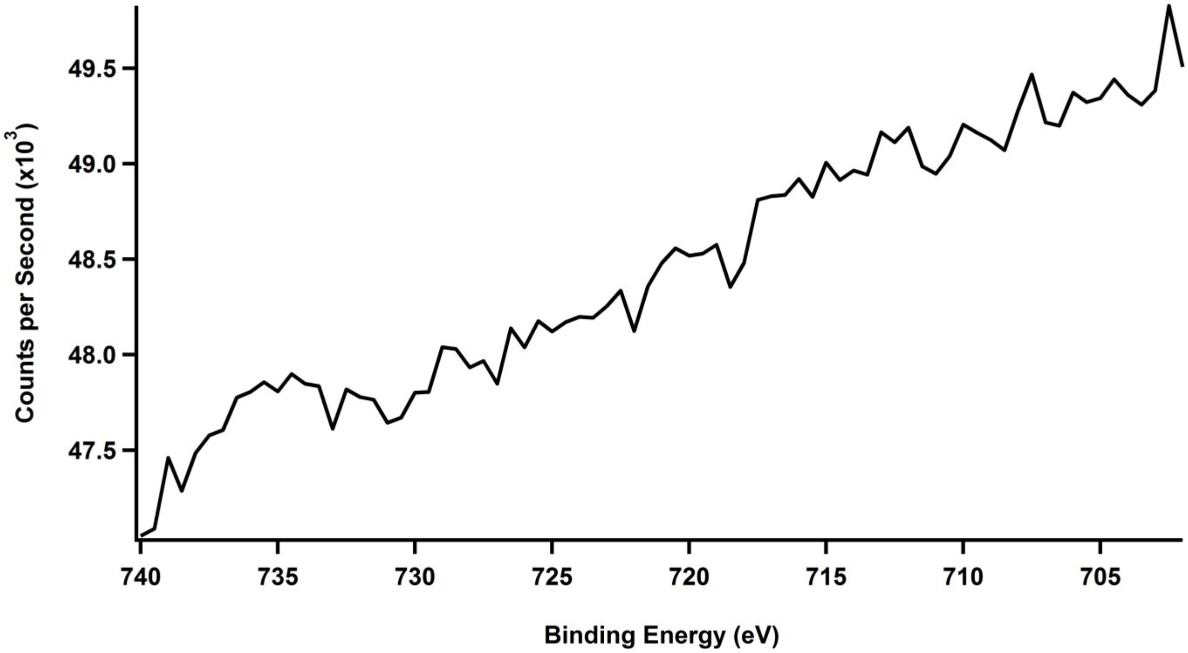

Figure S10. Fe 2p XP spectrum of clean gold treated with **2** and rinsed with CH_3CN. The pyrene modification to the surface is not present in this sample.

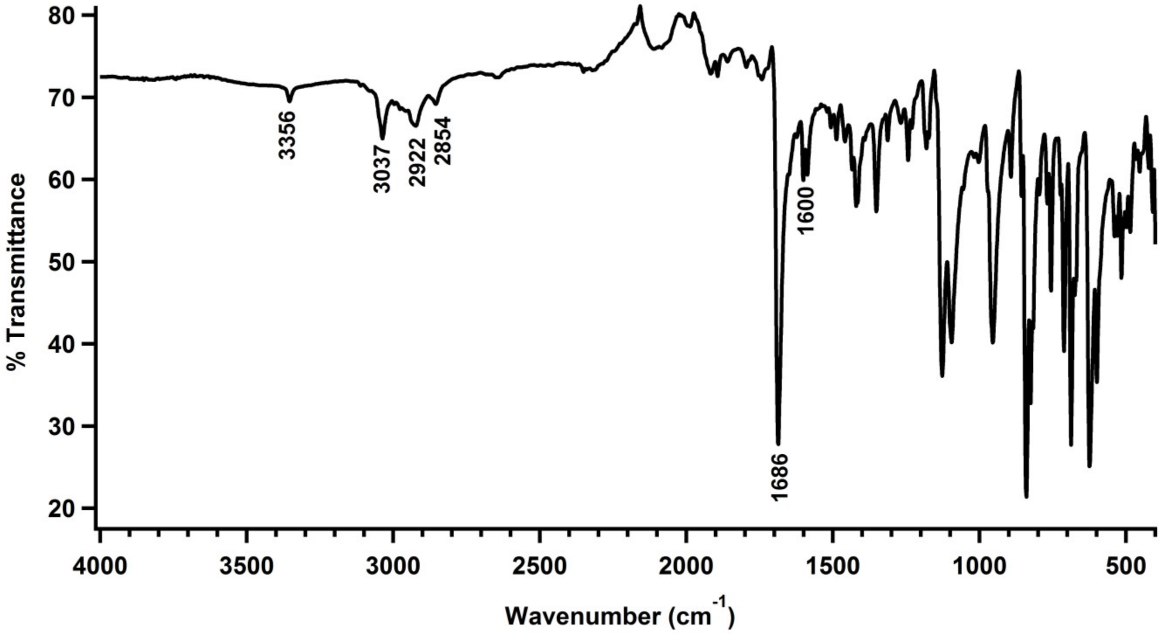

Figure S11. FTIR spectrum of **1**.

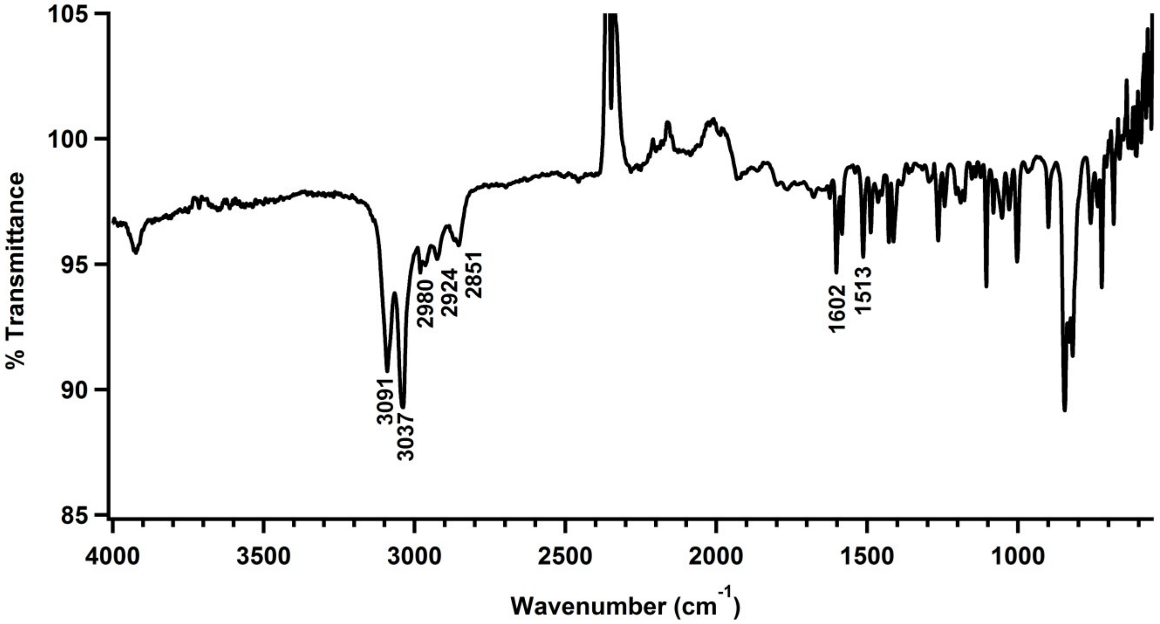

Figure S12. FTIR spectrum of **2**.

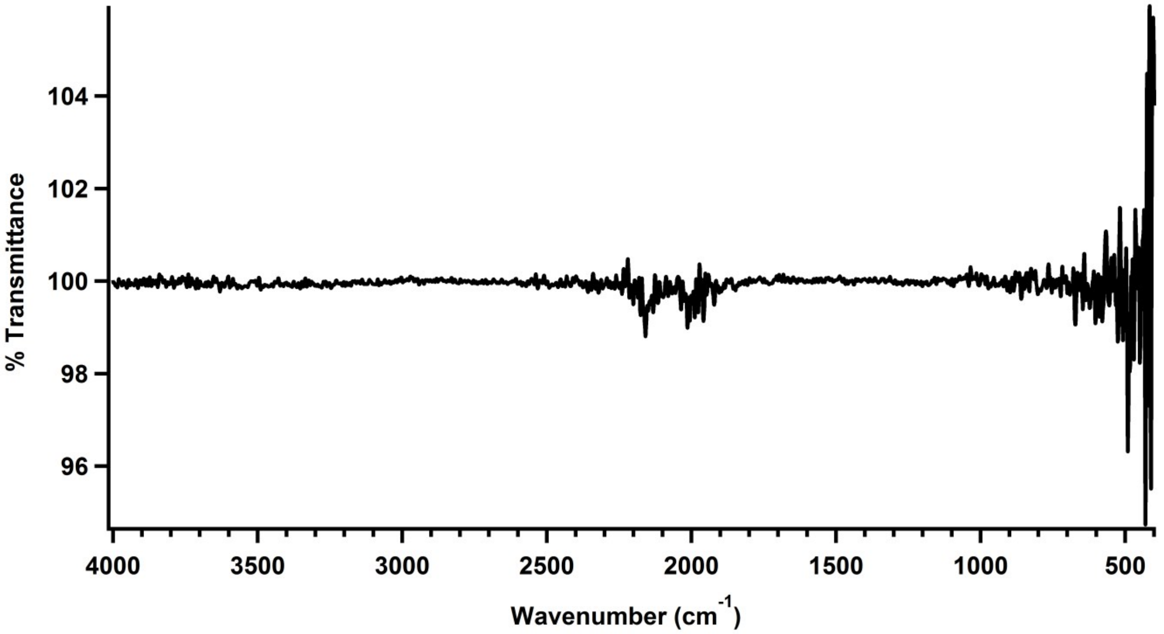

Figure S13. FTIR spectrum of a clean gold substrate using clean gold as a background.

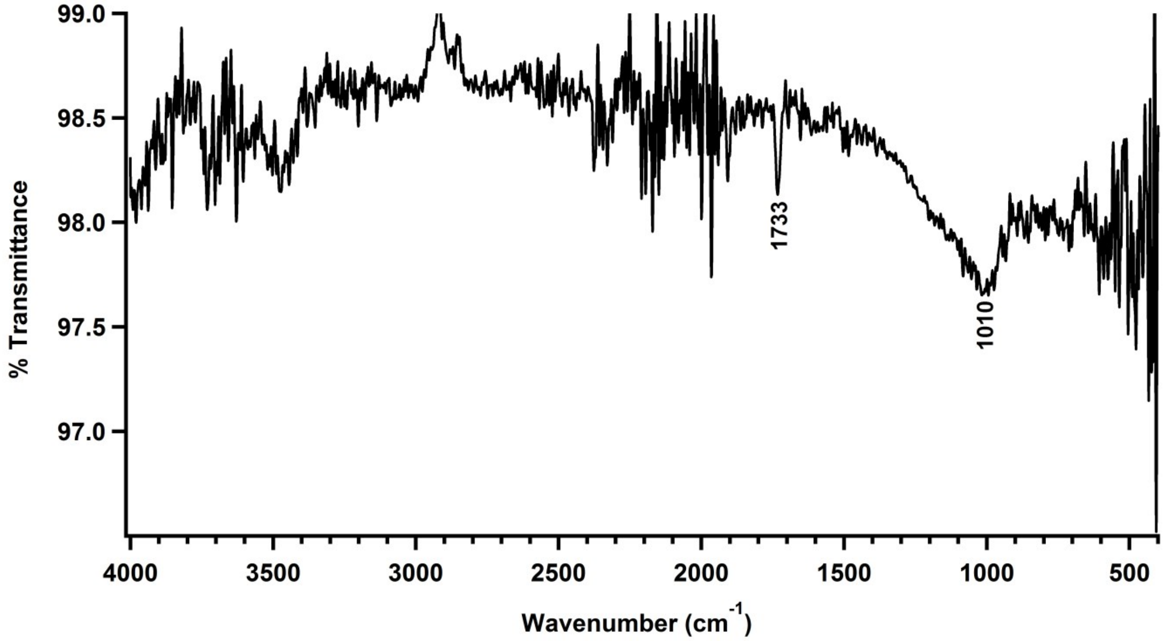

Figure S14. FTIR spectrum of a clean substrate after submersion in a 1 mM solution of **2** and rising with CH_3CN using clean gold as a background.

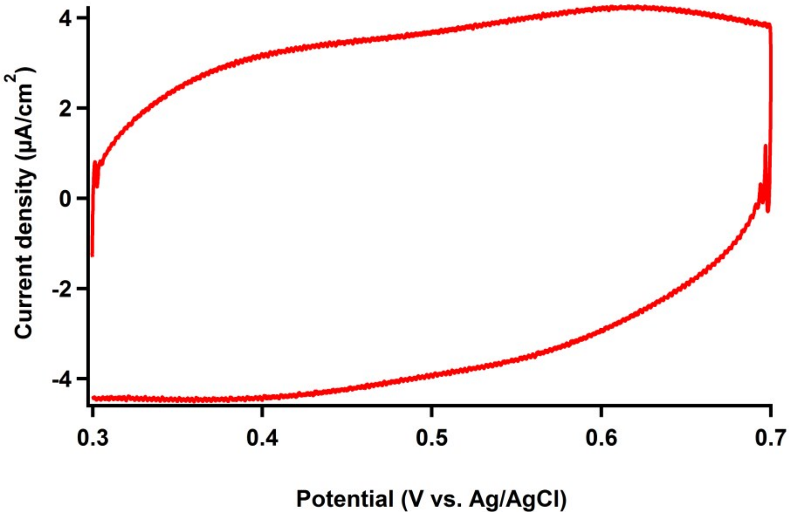

Figure S15. Cyclic voltammogram of a clean Au foil in an aqueous 0.1 M $HClO_4$ solution. Potentials measured versus a Ag/AgCl reference electrode in 1 M KCl. The 1 cm^2 Au substrate was used as the working electrode and glassy carbon as the auxiliary electrode.

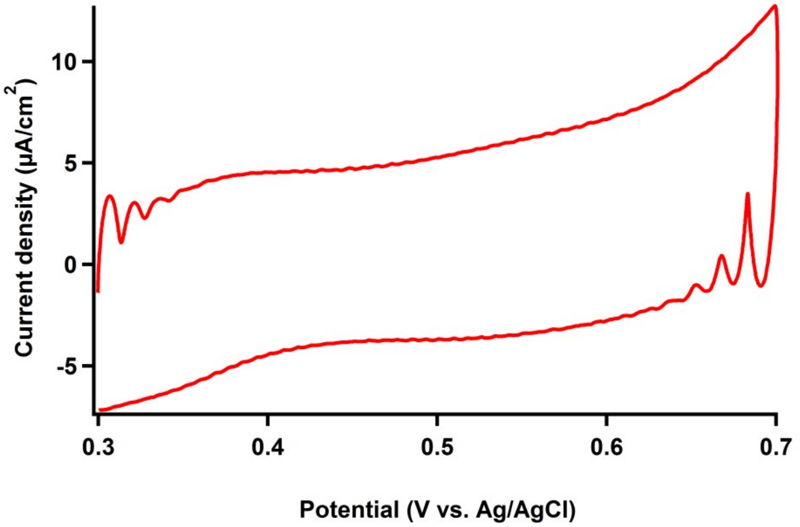

Figure S16. Cyclic voltammogram of a Au foil after pyrene-functionalization in an aqueous 0.1 M $HClO_4$ solution. Potentials measured versus a Ag/AgCl reference electrode in 1 M KCl. The 1 cm^2 Au substrate was used as the working electrode and glassy carbon as the auxiliary electrode.

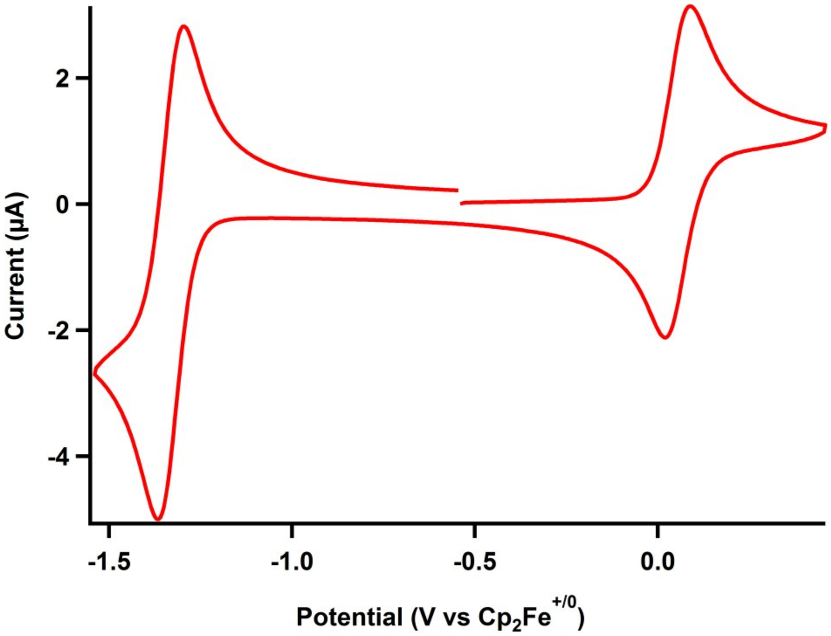

Figure S17. Cyclic voltammogram of 1-pyrenylferrocene (**2**) in CH_3CN. 100 mV/s scan rate. 1 mM analyte in 0.1 M $[Bu_4N][PF_6]$ solution with internal cobaltocene reference. Potentials reported versus the cobaltocene/cobaltocenium redox couple shown at -1.38 V. Glassy carbon working and auxiliary electrodes; Ag/Ag^+ pseudo-reference electrode. $E_{1/2}$ = 1.38 V vs. $Cp_2Co^{+/0}$. $[Cp_2Co][PF_6]$ was used as the internal standard because **2** has an indistinguishable couple to ferrocene when measured together.

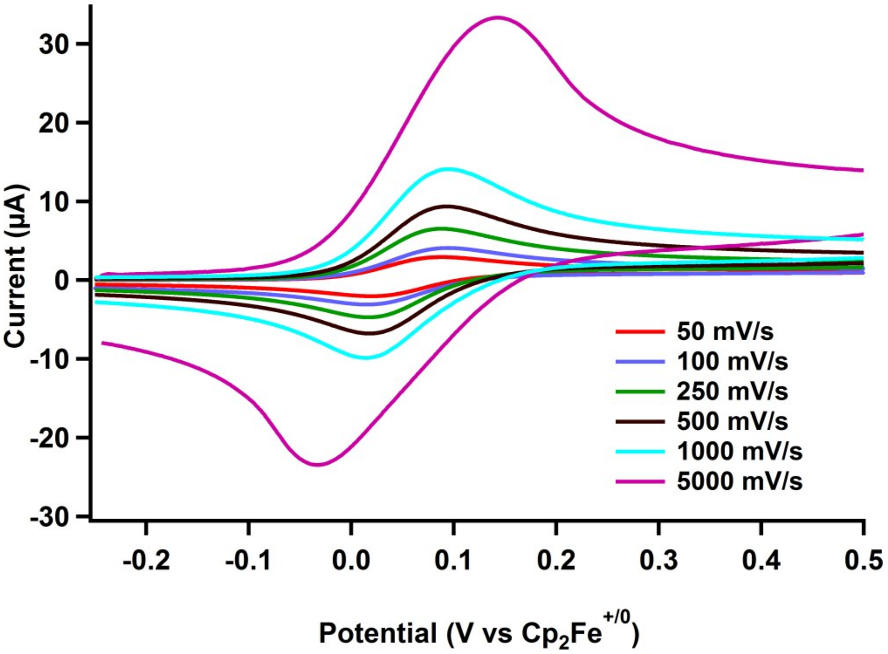

Figure S18. Variable scan rate cyclic voltammogram of 1-pyrenylferrocene (**2**) in CH_3CN ($E_{1/2}$ = 0.055 V vs. $Cp_2Fe^{+/0}$). Scan rates varying from 50 – 5000 mV/s. 1 mM analyte in 0.1 M $[Bu_4N][PF_6]$ solution with an internal cobaltocene reference. Glassy carbon working and auxiliary electrodes; Ag/Ag^+ pseudo-reference electrode. Potentials were measured against the cobatocene/cobaltocenium redox couple and then referenced to the ferrocene/ferrocenium redox couple (-1.33 V vs. $Cp_2Fe^{+/0}$) using previously reported values.[1]

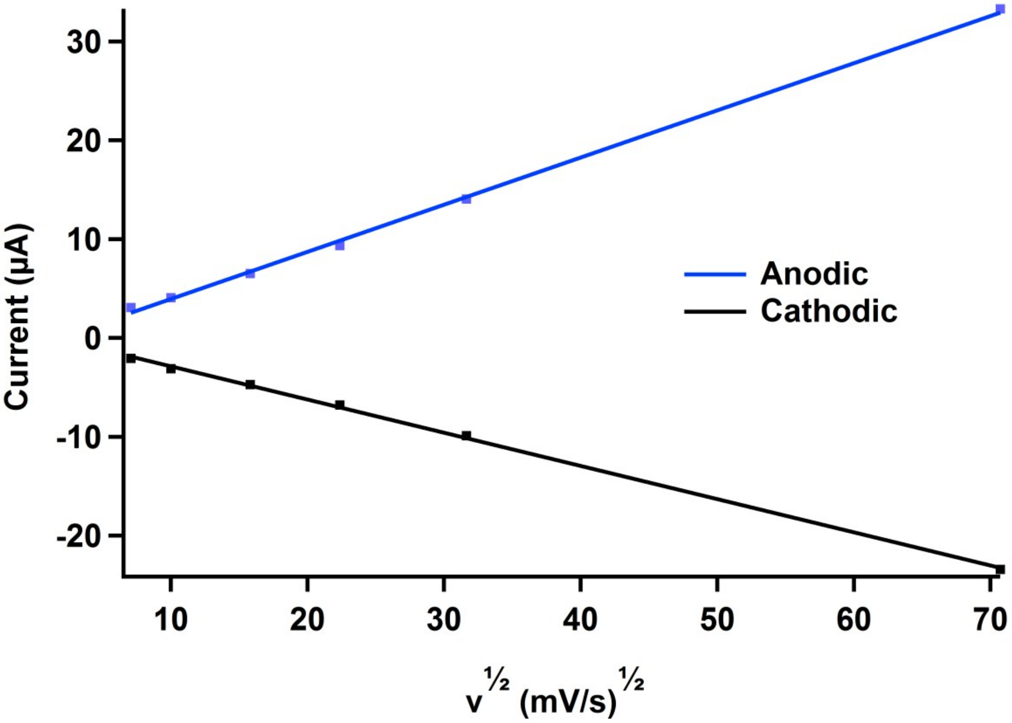

Figure S19. Plot of current vs. the square root of scan rate from cyclic voltammograms in Figure S18**.** The linear trend for both anodic and cathodic waves suggests diffusion control of the analyte, **2**, which is expected for a non-surface bound species.

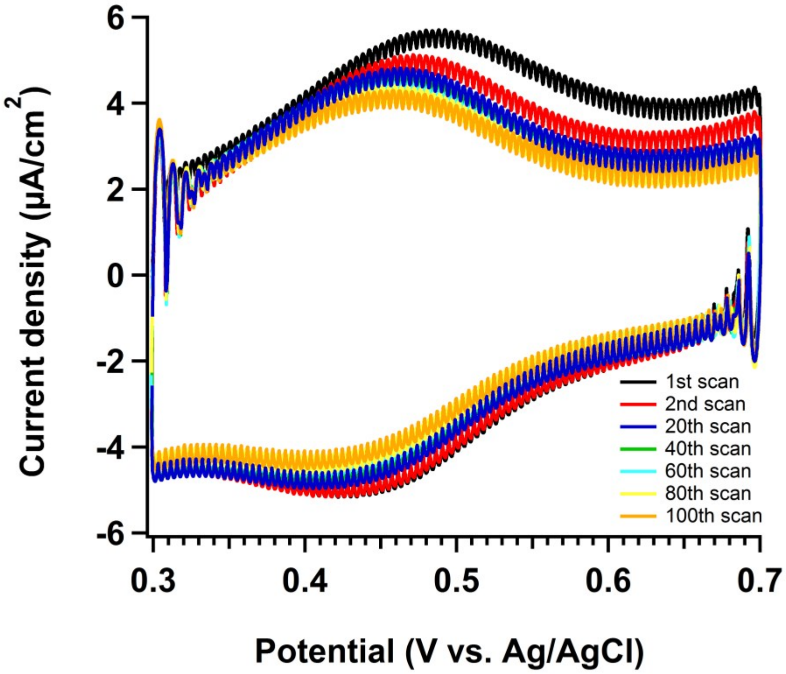

Figure S20. Cyclic voltammogram of a gold substrate functionalized with pyrene followed by exposure to **2**. 100 subsequent oxidation/reduction cycles were performed to probe redox stability of the pi-pi interactions fixing **2** to the surface. The voltammogram was recorded in an aqueous 0.1 M $HClO_4$ solution at 250 mV/s. Potentials were measured versus a Ag/AgCl reference electrode in 1 M KCl. The 1 cm^2 Au substrate was used as the working electrode and glassy carbon as the auxiliary electrode.

Scan #	Γ_O (pmol/cm^2)	Γ_R (pmol/cm^2)
1	17.1	8.8
2	16.8	7.5
20	16.6	9.6
40	19.8	10.4
60	13.9	8.7
80	15	9.1
100	17.5	8.4
Average	16.7	8.9
Standard deviation	1.9	0.9

Table S1. Calculated surface concentrations (Γ) of **2** for oxidative (Γ_O) and reductive waves (Γ_R) for various scans from the voltammogram in Figure S20 assuming a 1 e^- oxidative or reductive process. Surface concentrations were calculated through integration of the faradaic current per cm^2, divided by scan rate and then divided by Faraday's constant.

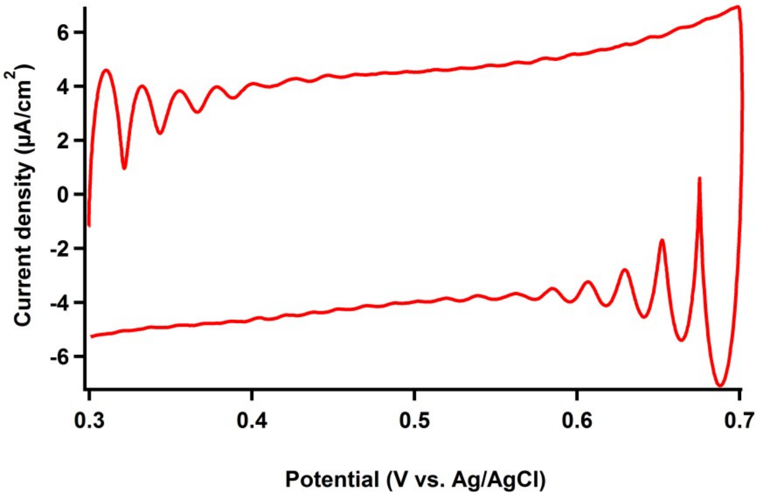

Figure S21**.** Cyclic voltammogram of a Au foil after soaking in a 1 mM CH_2Cl_2 solution of **2** and rinsing with CH_3CN. The pyrene-functionalized monolayer is not present on the sample. The voltammogram was recorded in an aqueous 0.1 M $HClO_4$ solution. Potentials measured versus a Ag/AgCl reference electrode in 1 M KCl. The 1 cm^2 Au substrate was used as the working electrode and glassy carbon as the auxiliary electrode.

References

1. N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877-910.