

Supporting Information for:

Covalently-Anchored Carboxyphenyl Monolayer via Aryldiazonium Ion Grafting: a Well-Defined Reactive Tether Layer for On-Surface Chemistry

Lita Lee,^{¶,‡} Haifeng Ma,^{¶,†} Paula A. Brooksby,^{¶,‡}, Simon A. Brown,^{¶,†} Yann R. Leroux,[¥]
Philippe Hapiot,[¥] Alison J. Downard^{*,¶,‡}

[¶]MacDiarmid Institute for Advanced Materials and Nanotechnology

[‡]Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch, New Zealand 8140

[†]Department of Physics and Astronomy, University of Canterbury, Private Bag 4800, Christchurch, New Zealand 8140

[¥]Université de Rennes 1, Institut des Sciences Chimiques de Rennes (Equipe MaCSE), CNRS, UMR 6226, Campus de Beaulieu, Bat 10C, 35042 Rennes Cedex, France

*To whom correspondence should be addressed. Tel: +64 3 364 2501; fax: +64 3 364 2110;

E-mail address: alison.downard@canterbury.ac.nz

Table S1. Optimized geometry of Ar-COO-Fm (Figure 7)

Optimized Geometry at the B3LYP/6-31G*level

x,y,z coordinates (Standard orientation)

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

1	6	0	6.054323	0.459277	0.582644
2	6	0	5.936721	-0.393367	-0.518273
3	6	0	4.688152	-0.889421	-0.884081
4	6	0	3.547325	-0.532208	-0.152272
5	6	0	3.668342	0.321649	0.953013
6	6	0	4.920467	0.814046	1.317476
7	1	0	7.029018	0.845699	0.868721
8	1	0	6.818288	-0.670730	-1.089532
9	1	0	4.572646	-1.554394	-1.733632
10	1	0	2.786052	0.587743	1.524432
11	1	0	5.012166	1.473897	2.175804
12	6	0	2.238914	-1.095916	-0.591260
13	8	0	2.103909	-1.896823	-1.495193
14	8	0	1.197244	-0.617677	0.132019
15	6	0	-0.102897	-1.132832	-0.226987
16	1	0	-0.116482	-2.210354	-0.034327
17	1	0	-0.274536	-0.977581	-1.295521
18	6	0	-1.147164	-0.404758	0.623530
19	6	0	-2.534665	-1.008062	0.454661
20	1	0	-0.823813	-0.476187	1.672625

21	6	0	-1.377607	1.049105	0.233319
22	6	0	-2.955586	-2.315748	0.668969
23	6	0	-3.446482	-0.024051	0.022053
24	6	0	-0.473728	2.105343	0.185301
25	6	0	-2.729961	1.251084	-0.113735
26	6	0	-4.298652	-2.641896	0.446646
27	1	0	-2.259073	-3.079450	1.007472
28	6	0	-4.786252	-0.350590	-0.196726
29	6	0	-0.927767	3.368771	-0.211077
30	1	0	0.569554	1.952448	0.442994
31	6	0	-3.180751	2.512872	-0.505869
32	6	0	-5.204106	-1.666026	0.017361
33	1	0	-4.640010	-3.660405	0.610065
34	1	0	-5.495946	0.402697	-0.529051
35	6	0	-2.269409	3.569935	-0.551722
36	1	0	-0.230479	4.201177	-0.254159
37	1	0	-4.222109	2.674372	-0.772685
38	1	0	-6.243920	-1.933916	-0.150303
39	1	0	-2.605875	4.557754	-0.855339

Grafting, deprotection and subsequent coupling reactions of N_2^+ -Ar-COO-Fm at Au electrodes

Experimental

Experiments with redox probes were performed using polycrystalline Au disk electrodes (1 mm diameter). Before use, the electrodes were polished with 1 μ m alumina followed by continuous cycling between 0 and 1.5 V at 50 mV s^{-1} in 0.01 M HClO_4 to obtain stable Au oxide formation and reduction peaks. Ar-COO-Fm groups were electrografted to Au disk electrodes from a solution of 5 mM N_2^+ -Ar-COO-Fm and 0.1 M TBABF₄ in acetonitrile (ACN) using 5 potential cycles between 0.80 and -0.75 V vs Hg/calomel/ LiCl_(aq) (1 M) at a scan rate of 50 mV s^{-1} . The modified electrodes were rinsed with acetone, sonicated in ACN for 5 min, and dried with a stream of $N_2(\text{g})$.

Scanning tunnelling microscopy (STM) and atomic force microscopy (AFM) imaging were performed on Au films deposited on mica. Ar-COOH-Fm layers were grafted from a solution of 1 mM N_2^+ -Ar-COO-Fm and 0.1 M TBABF₄ in ACN using 2 potential cycles between 0.6 and -0.2 V vs Hg/calomel/ LiCl_(aq) (1 M) at a scan rate of 100 mV s^{-1} . The modified surfaces were rinsed with acetone and ACN, and dried with a stream of $N_2(\text{g})$.

The protecting Fm group was cleaved from Ar-COOH-Fm layers by immersing the modified electrode in a stirred solution of 20 % piperidine in DMF for 40 min. Electrodes were rinsed with acetone and H_2O after deprotection. For experiments monitoring the response of redox probes at grafted electrodes, cyclic voltammograms were first obtained using the unmodified electrode in the redox probe solution, the electrode was then rinsed with H_2O (or acetone for the ferrocene redox probe) and dried with N_2 gas between each scan.

After deprotection of the grafted electrodes, attempts were made to couple nitrophenyl (NP) groups to the surface. The modified Au electrodes were heated under reflux in anhydrous CH_2Cl_2 (6 mL) with oxalyl chloride (25 μL) and pyridine (8 μL) for 1 h under a N_2 atmosphere. All volatiles were then removed under vacuum followed by the introduction of 4-nitrobenzylamine hydrochloride (NBAHCl) in anhydrous CH_2Cl_2 (6 mL) with excess of triethylamine under a N_2 atmosphere. The reaction was stirred for 5 min in an ice bath and then at room temperature overnight. The electrodes were then washed in clean vigorously stirred CH_2Cl_2 for 10 min followed by sonication in ethanol (EtOH) for 2 min; the modified electrodes were dried with a stream of $\text{N}_2(\text{g})$. To couple ferrocenyl (Fc) groups to the deprotected modified electrodes, the electrodes were stirred overnight in 5 mL of DMF containing 12 μmol 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC, Chem-Impex International), 25 μmol N,N-diisopropylethylamine (DIPEA, Acros Organics), 12 μmol 1-hydroxybenzotriazole hydrate (HOBt) and 10 μmol FcCH_2NH_2 . The treated electrodes were then washed in stirred in DMF for 10 min.

STM and AFM imaging was undertaken in a ultrahigh vacuum (UHV) chamber with a background pressure below 7×10^{-10} mbar using a variable-temperature AFM/STM (Omicron VT-AFM XA). STM scanning parameters were set to 5 pA for the tunnelling current and 1 - 3V for the tunnelling voltage. All AFM/STM images were obtained using Pt-Ir tips.

Results

Figure S1 shows cyclic voltammograms for grafting Ar-COO-Fm to the Au electrode. Figure S2 shows cyclic voltammograms of redox probes at Au electrodes before modification, after grafting an Ar-COO-Fm film and after treatment of the grafted electrode in the deprotection solution. After reaction of the deprotected electrodes with NBAHCl and FcCH_2NH_2 , the cyclic voltammograms shown in Figures S3 and S4, respectively, were obtained.

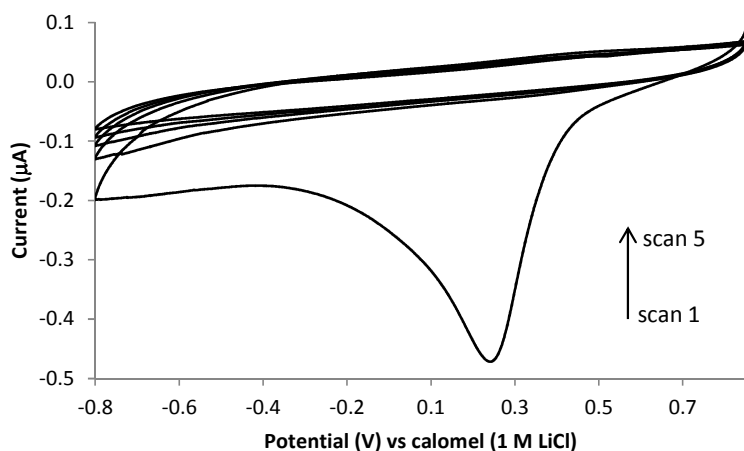


Figure S1. Five consecutive scans at a bare Au disk electrode in a solution of 5 mM N_2^+ -Ar-COO-Fm in 0.1 M TBABF₄-ACN. Scan rate = 50 mV s⁻¹.

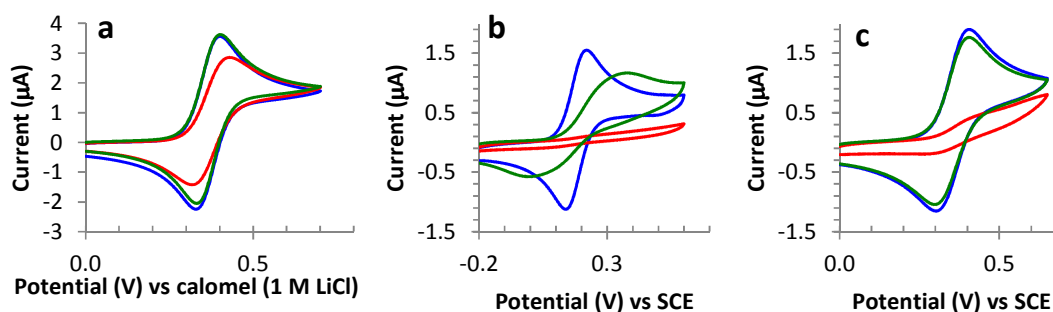


Figure S2. Cyclic voltammograms obtained in a solution of: a) 1 mM ferrocene in 0.1 M TBABF₄-ACN; b) 1 mM ferrocyanide in 0.1 M phosphate buffer (pH 6.9); and c) 1 mM ferrocyanide in 0.1 M H₂SO₄ at scan rate = 100 mV s⁻¹. Bare Au: blue line, Au modified with Ar-COO-Fm before deprotection: red line; and after deprotection in 20% piperidine/DMF for 40 min: green line.

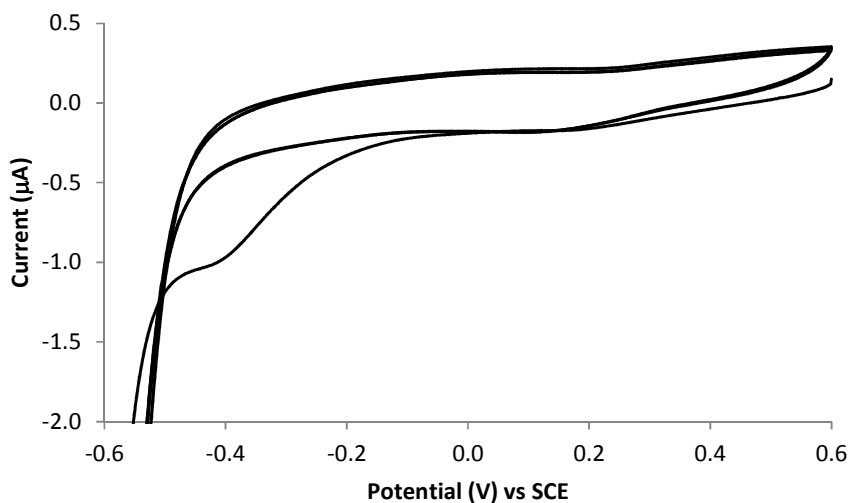


Figure S3. Repeat cyclic voltammograms obtained in 0.1 M H_2SO_4 at scan rate = 100 mV s^{-1} of a Au disk electrode modified with an Ar-COO-Fm layer, deprotected and reacted with NBAHCl.

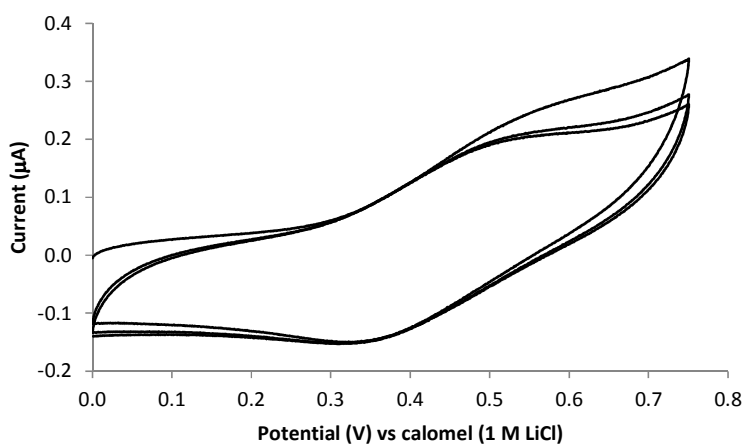


Figure S4. Repeat cyclic voltammograms obtained in 0.1 M $\text{LiClO}_4\text{-EtOH}$ at scan rate = 200 mV s^{-1} of a Au disk electrode modified with an Ar-COO-Fm layer, deprotected and reacted with FcCH_2NH_2 .

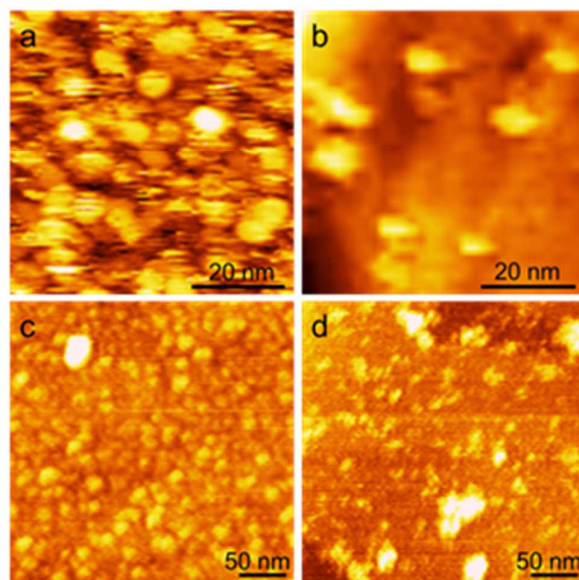


Figure S5. STM a), b) and AFM c),d) images of a Au film electrode modified with an Ar-COO-Fm layer before a), c) and after b), d) deprotection in piperidine solution.

Discussion

The cyclic voltammograms of Figures S1 are typical of those obtained for grafting from diazonium salt solution and are consistent with the formation of a surface film of Ar-COO-Fm, as shown by the STM and AFM images of Figure S5 a) and c). Cyclic voltammograms of redox probes at the Ar-COO-Fm modified surfaces (Figure S2) show that the response of ferricyanide is significantly blocked at the modified surfaces and that the response of ferrocene is partially blocked compared to that at an unmodified Au surface. After treatment of the modified electrodes in the deprotection solution, the responses of ferrocene, and ferricyanide in 0.1 M H₂SO₄, closely match the responses at unmodified electrodes. In contrast, the cyclic voltammogram of ferricyanide in pH 6.9 solution exhibits slow kinetics indicating the presence of a partially blocking surface layer. The contrasting behaviour of ferricyanide at the deprotected surface at pH 6.9 and in 0.1 M H₂SO₄ suggest that the surface is modified with a layer with acid-base properties. This is consistent with the presence of an

Ar-COOH layer which is deprotonated at pH 6.9 (and therefore repels the anionic ferrocyanide redox probe) and protonated in 0.1 M H₂SO₄.

Although the redox probe experiments described above suggest that the deprotection step at Au proceeded analogously to that at glassy carbon (GC), to give an Ar-COOH monolayer, further investigations demonstrated that this is not the case. Attempts to couple redox active NP and Fc groups to the (supposed) Ar-COOH monolayer resulted in only very small amounts of immobilized species (Figures S3 and S4). Both the oxalyl chloride coupling method used successfully at GC and a milder method using EDC and HOBt proved unsuccessful. Consideration of the AFM and STM images of Au surfaces after treatment in the deprotection solution strongly suggest that the surfaces bear only scattered adsorbates which may be largely attributed to adventitious contaminants. We tentatively suggest that the deprotection conditions largely strip the grafted layer from the surface through interactions between piperidine and Au surface atoms.