SUPPORTING INFORMATION

An Ionic Liquid Based Approach for Single Molecule Electronics with Cobalt Contacts

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EXPERIMENTAL DETAILS

Cobalt Electroplating

Cobalt was electrochemically deposited onto a Au (111) textured slide from an aqueous pH 4.5, 0.2 M CoSO4/0.5 M B(OH)3 solution. The gold slides consisted of 200 nm gold evaporated onto ~2 nm chromium (from Arrandee™). Immediately prior to the electroplating the gold slide was rinsed with ethanol and Milli-Q® water, and then flame annealed gently to a slight orange hue in a Bunsen burner. In cases where slides were reused any cobalt remaining from previous experiments was removed by cleaning in fresh piranha solution (3:1 reagent grade H2SO4: 30 wt. % H2O2) for 30 seconds. WARNING: Preparation of piranha solution results in an exothermic reaction which can be dangerous. This reaction can become violent when organic compounds are added. Care should be taken with H2O2 added to H2SO4. Electroplating was carried out by partially immersing the slide in the electroplating solution in an electrochemical cell. One corner of the Au slide was electrically contacted with a flattened crocodile clip, which was wrapped with PTFE tape to keep the plating solution from seeping up. A Pt mesh counter electrode and a saturated calomel reference electrode (SCE) were employed. Electroplating was achieved potentiostatically with an Autolab PGSTAT30 computer-controlled potentiostat, at an electrode potential of -0.9 V. Plating was stopped once a charge of 290 mC/cm2 had been passed and then the slide was rinsed with Milli-Q® water only and dried immediately with nitrogen. Assuming 100 % faradaic efficiency, 290 mC corresponds to a minimum of 500 monolayer equivalents of cobalt on the gold slide. Visual examination confirmed that the deposited film was shiny and cobalt–colored. A photo of the electroplated cobalt surface is shown in Figure S1.
Figure S1  A photo of the electrodeposited cobalt surface (the bottom part of the gold slide has been masked from the deposition to show the contrast). A reflection of a chemical bottle can be seen to highlight the mirror-like finish. Electrodeposition of Co onto Au(111) Arrandee slide was achieved from aqueous 0.2 M CoSO$_4$ /0.5 M B(OH)$_3$ at pH 4.5.

**Electrochemical Studies**

The monolayers were studied by cyclic voltammetry (CV) with a focus on examining the degree to which they passivate the surface (in other words the integrity of the monolayer). Voltammograms were recorded on an Autolab PGSTAT30 computer controlled instrument running GPES. All of these investigations were conducted in a sealed 3-electrode cell, which was prepared in a nitrogen filled glove box. The electrodes employed were the electrodeposited and monolayer coated cobalt sample (working electrode, WE), a 0.5 mm Pt wire quasi reference electrode (QRE) and a Pt wire counter electrode (CE). In order to calibrate the QRE against a known electrode potential scale, ferrocene was added to the cell at the end of the electrochemical experiment and the Fc/Fc$^+$ redox couple was examined to give a known reference potential standard. The ionic liquid for the electrochemical experiments, BMIM-OTf ((1-butyl-3-methylimidazolium trifluoromethanesulfonate), was dried for 18 hours under vacuum and heated to 120 °C. It was subsequently stored in the glovebox.

The effectiveness of the surface passivation by the molecular monolayer was gauged by examining the electrochemistry of redox species in solution; paraquat and ferrocene were employed as well-known redox active species. Paraquat is electrochemically reduced in two one-electron steps as shown in figure S2, while ferrocene exhibits a very well-known single-electron oxidation reaction. A 7.5 mM methylviologen solution (N,N′-dimethyl-4,4′-bipyridinium dichloride or paraquat) in BMIM-OTf solution was made by first dissolving the paraquat in methanol. This solution was then added to BMIM-OTf which was heated to drive the methanol off and promote dissolution of the paraquat in the ionic liquid. This process proceeded for one hour with oxygen-free nitrogen bubbling directly in to the solution. A 5 mM ferrocene in BMIM-OTf solution was made by dissolving the ferrocene directly
into the ionic liquid with gentle heating. Cyclic voltammetry was recorded in ionic liquid electrolytes using the same cell as that employed for oxide reduction and thiol adsorption.

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Figure S2. The electrochemical reduction of paraquat in two one-electron steps: $V^{2+}$ to $V^+$, and then $V^+$ to $V^0$.

Electrochemical impedance spectroscopy (EIS) was performed on an Autolab PGSTAT20 computer controlled potentiostat running FRA. The cobalt samples were prepared as outlined previously. The Au(111) textured working electrodes were prepared by first rising Arrandee™ slides in ethanol, drying in a stream of N$_2$ gas and then flame annealing. The octanethiol monolayer was formed by adsorption on gold by immersion in a 10 mM octanethiol in ethanol solution for 1 hour, followed by rinsing with ethanol and Milli-Q® water and drying in nitrogen. For both the Au and Co systems the electrochemical cell for the EIS measurements was filled with a 5 mM ferrocene in BMIM-OTf solution within a nitrogen atmosphere glove box and sealed. Impedance spectra were taken at the equilibrium potential of the ferrocene redox probe. The impedance spectra were recorded between 1 Hz and 10 kHz.

Additional Details for the Molecular Conductance Measurements

Cobalt STM tips were prepared by electrochemical etching using an etching method described by Albonetti et al. followed by coating in Apiezon wax.\(^1\,^2\) These Co STM tips were fabricated from 0.25 mm Co wire which was etched in a 1 M KCl aqueous solution. Etching proceeded with 3 V applied between the cobalt anode and a 15 mm diameter Pt ring cathode. A 1 g ball of clay was attached to the bottom of the long cobalt wire. This resulted in the wire being cleaved into two usable tips as etching came to completion. The cobalt wire tip was then coated to all but the very end of the tip with Apiezon wax. This coated tip was then assembled into the electrochemical STM cell containing the ionic liquid. The surface of the cobalt tip was electroreduced in-situ in the STM cell by cycling its electrode potential between -1 V and -2 V versus the Pt quasi-reference electrode used. By cycling the potential any voltammetric changes could be monitored. A Pt wire counter electrode was also used.

Au-octanedithiol-Au junctions were also investigated in control experiments. Gold STM substrates used for these measurements was prepared in the same manner as outlined for electrochemical impedance spectroscopy. Gold STM tips were prepared by cutting 0.25 mm Au wire and coating with
Apiezon wax prior to each experiment. The Au substrate was prepared by rinsing in ethanol, and Milli-Q® water, followed by drying in nitrogen, and flame annealing. The monolayer was prepared from a 10 mM octanethiol in ethanol solution with 1 hour adsorption.

For the single molecule conductance measurements a rational data selection criterion is applied, with the aim of selecting out current-distance retraction traces where there is clear evidence for stable molecular junction formation (and thereby not including simple exponentially decaying traces where no molecular junction is formed or noisy traces where unstable junctions and no plateau results). Stable molecular junctions give current plateaus in the retraction curves such as shown in Figure 6 of the main manuscript. The criterion we use is to select curves giving rise to plateaus greater in length than 0.2 nm.

**Cyclic voltammetry with the ferrocene redox probe**

The surface passivation properties of the octanethiol and octanediithiol covered electroplated cobalt surfaces have also been investigated with the ferrocene redox probe in BMIM-OTf solution. Again it is seen that while the redox properties are clear for the bare cobalt surface, they are blocked for the monolayer coated cobalt surface (see Figure S3). The stability of the OT modified cobalt surface to 1 hour exposure to ambient atmosphere was also assessed. After transferring the sample to atmospheric air for 1 hour it was transferred back to the 5 mM ferrocene in BMIM-OTf solution and a cyclic voltammogram recorded (Figure S4). From this CV it is apparent that the Fc/Fc⁺ redox waves has not returned, which testifies to stability of the OT monolayer to 1 hour air exposure. Figure S5 demonstrates the ability of the octanethiol (ODT) monolayer to passivate the Co surface. Cyclic voltammograms recorded in 5 mM Fc in BMIM-OTf, on ODT covered and bare cobalt surfaces, are shown.

![Figure S3. Cyclic voltammograms of the bare oxide free Co (black) and the octanethiol monolayer passivated Co (red) surfaces in 5 mM ferrocene in BMIM-OTf solution. CVs were recorded at a scan rate of 0.5 V s⁻¹.](image)
Figure S4: The stability of the octanethiol monolayer in ambient conditions was investigated by comparison of the cyclic voltammograms of the bare oxide free Co in 5 mM Fc in BMIM-OTf (black) to that of the octanethiol monolayer protected Co after 1 hour exposure to ambient conditions (red). CVs were recorded at a scan rate of 0.5 V s⁻¹.

Figure S5: The ability of the octanedithiol monolayer to passivate the Co surface was investigated using cyclic voltammetry recorded in 5 mM Fc in BMIM-OTf. Comparison of the bare (black) and octanedithiol monolayer coated Co (red) shows the surface is passivated. Scans were run at 0.5 V s⁻¹.

Surface Infrared Spectroscopy

Surface infrared spectra of the freshly prepared octanethiol monolayers on cobalt were recorded using polarization modulation-infrared reflection-adsorption spectroscopy (PM-IRRAS). A Bruker IFS 66v/S spectrophotometer controlled by OPUS Software was employed together with a PMA 37 PM-IRRAS module. The IR beam, which was modulated by a Hinds Instruments PEM-90 photoelastic modulator, was incident on the sample at close to grazing angles. A liquid nitrogen cooled, mercury cadmium telluride infrared detector from Infrared Associates was employed. Spectra were referenced
against a blank cobalt plated gold slide which had been treated in the same manner as the monolayer coated sample and subjected to oxide removal in BMIM-OTf prior to rinsing, drying and then spectra collection. Figures S6 and S7 show ex-situ surface infrared spectra recorded using PM-IRRAS for the octanethiol monolayer on electrodeposited cobalt, with the thiol monolayer being formed from the ionic liquid. For comparison spectra of the cobalt surface without the thiol monolayer after emersion from the ionic liquid are shown. Spectral assignments are from refs. 3, 4.

Figure S6: Blue curve - an ex-situ surface infrared spectrum of the octanethiol monolayer on electrodeposited cobalt, with the thiol monolayer being formed from the ionic liquid. Green curve – this uses the same procedure for recording the ex-situ spectrum after emersion from the ionic liquid, except in this case no octanethiol monolayer is adsorbed.

Figure S7 A surface infrared spectrum using the same conditions as Figure S6, but magnified in the C-H stretching region. The black spectrum is with octanethiol monolayer and the red one without.

