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Supporting Information

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Self-Assembled Monolayers of Isocyanides on Nickel Electrodes**

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All solvents were HPLC grade. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under an argon atmosphere prior to use. Absolute ethyl alcohol (200 proof) was purchased from Aaper Alcohol and Chemical Co. Flash chromatography was carried using EM science Kieselgel 60 (230-400) mesh. All reagents were purchased from Aldrich and Acros and used as received. ^{1}H NMR spectra were obtained using Bruker DRX-400 and DRX-500 spectrometers.

Syntheses

The (6-Bromohexyl)ferrocene[1] (**1**) and 6-ferrocenylhexane thiol[2] (**10**) were synthesized and purified using literature method.

6-Azidohexyl ferrocene (**2**): (6-Bromohexyl)ferrocene (1.25 g, 3.60 mmol) was dissolved in dimethylformamide (50 ml). Sodium azide (0.26 g, 4.00 mmol) was added to the solution, and the mixture was stirred for 12 h at room temperature. The reaction mixture was quenched with of H_2O (100 ml). The solution was extracted with ethyl acetate (3 x 50 ml). The organic layer was washed with brine and dried over anhydrous Na_2SO_4. The resulting solution was filtered, concentrated under reduced pressure and chromatographed on silica gel. Yield 92.4%.

^{1}H NMR ($CDCl_3$): d 1.32-1.62 (m, 8H, CH_2), 2.32 (t, *J* = 7.6 Hz, 2H,), 3.26 (t, *J* = 6.9 Hz, 2H, CH_2), 4.09 (s, 4H, Fc), 4.13 (s, 5H, Fc). MS (EI) (M^+) calcd. for $C_{16}H_{21}FeN_3$: 311.11 *m/z*. found: 311.0 *m/z*.

6-Aminohexyl ferrocene (**3**): 6-Azidohexyl ferrocene (1.00 g, 3.20 mmol) was dissolved in dry diethylether (50 ml), $LiAlH_4$ (0.18 g, 4.8 mmol) was added to a separate flask and suspended in dry diethylether (30 ml). The solution containing 6-azidohexylferrocene was transferred to the suspension of $LiAlH_4$ dropwise under N_2 for 2 h and quenched with 1mM aqueous NaOH (20 ml). The solution was extracted with ethyl acetate (3 x 50 ml). The organic layer was dried over anhydrous Na_2SO_4. The resulting solution was filtered, concentrated under reduced pressure. Yield 80.0%.

^{1}H NMR ($CDCl_3$): d 1.08-1.53 (m, 10H, CH_2 and NH_2), 2.33 (t, *J* = 7.6 Hz, 2H, CH_2), 2.68 (t, *J* = 6.8 Hz, 2H, CH_2), 4.04 (4H, s), 4.08 (5H, s). MS (EI) (M^+) calcd. for $C_{16}H_{23}FeN$: 285.12 *m/z*. found: 285.1 *m/z.*

6-Ferrocenylhexyl formamide (**4**): 6-Aminohexyl ferrocene (0.50 g, 1.75 mmol) was dissolved in ethyl formate (5 ml). This solution was refluxed for 12 h and the excess ethyl formate was removed under reduced pressure. The resulting mixture was chromatographed on silica gel. Yield: 93.4%.

^{1}H NMR ($CDCl_3$): d 1.24-1.68 (m, 8H, CH_2), 2.31 (t, *J* = 7.5 Hz, CH_2), 3.28 (q, 2H, CH_2), 4.08 (s, 4H, Fc), 4.10 (s, 5H, Fc), 5.50 (bs, 1H), 8.16 (s, 1H). MS (EI) (M^+) calcd. for $C_{17}H_{23}FeNO$: 313.11 *m/z*. found: 313.0 *m/z.*

6-Ferrocenylhexyl isocyanide (**5**): A solution of 6-ferrocenylhexyl formamide (0.77 g, 2.46 mmol) and triethylamine (1.71 ml, 12.3 mmol) in THF (10 ml) was cooled to 0°C. Phosphorous oxychloride (0.252 ml, 2.70 mmol) in THF (1 ml) was added dropwise over 10 min. The reaction mixture was stirred for 2 h at 0°C and was poured into H_2O (20 ml). The solution was extracted with ethyl acetate (3 x 20 ml). The organic layer was dried over anhydrous Na_2SO_4. The resulting solution was filtered and concentrated under reduced pressure. The resulting mixture was chromatographed on silica gel. Yield 60.3%.

^{1}H NMR ($CDCl_3$): d 1.34-1.67 (m, 8H, CH_2), 2.33 (t, *J* = 7.5 Hz, 2H, CH_2), 3.38 (t, *J* = 4.7 Hz, 2H, CH_2), 4.04 (s, 4H, Fc), 4.12(s, 5H, Fc). MS (EI) (M^+) calcd. for $C_{17}H_{21}FeN$: 295.10 *m/z*. found: 295.0 *m/z.*

6-ferrocenylhexyl cyanide (**6**): (6-Bromohexyl)ferrocene (0.84 g, 2.41 mmol) was dissolved in dimethylformamide (25 ml). Sodium cyanide (0.13 g, 2.65 mmol) was added to the solution, and the mixture was stirred for 12 h at room temperature. The reaction mixture was quenched with of H_2O (100 ml). The solution was extracted with ethyl acetate (3 x 100 ml). The organic layer was washed with brine and dried over anhydrous Na_2SO_4. The resulting solution was filtered, concentrated under reduced pressure and chromatographed on silica gel. Yield 95.8%.

^1H NMR ($CDCl_3$): d 1.34-1.69 (m, 8H, CH_2), 2.31-2.50 (m, 4H, CH_2), 4.08 (s, 4H, Fc), 4.10 (s, 5H, Fc). MS: *m/z* 295.0 (M^+). MS (EI) (M^+) calcd. for $C_{17}H_{21}FeN$: 295.10 *m/z.* found: 295.0 *m/z.*

6-ferrocenylhexyl isothiocyanate (**7**): 6-Aminohexyl ferrocene (0.58 g, 2.03 mmol) was dissolved in anhydrous methylene chloride (25 ml). Di-2-pyridyl thionocarnonate (0.47 g, 2.03 mmol) was added to the solution, and the mixture was stirred for 1 h at room temperature. The reaction mixture was quenched with of H_2O (50 ml). The solution was extracted with ethyl acetate (3 x 50 ml). The organic layer was washed with brine and dried over anhydrous Na_2SO_4. The resulting solution was filtered, concentrated under reduced pressure and chromatographed on silica gel. Yield 81.2%.

^1H NMR ($CDCl_3$): d 1.36-1.69 (m, 8H, CH_2), 2.31 (t, $J = 7.5$ Hz, 2H, CH_2), 3.51 (t, $J = 7.5$ Hz, 2H, CH_2), 4.07 (s, 4H, Fc), 4.12 (s, 5H, Fc). MS (EI) (M^+) calcd. for $C_{17}H_{21}FeNS$: 327.07 *m/z.* found: 327.0 *m/z.*

6-ferrocenylhexyl selenocyanate (**8**): (6-Bromohexyl)ferrocene (1.15 g, 3.29 mmol) was dissolved in anhydrous CH_3CN (20 ml) at 0°C. Potassium selenocyanate (0.48 g, 3.29 mmol) was added to the solution in one portion. After 15 min at 0°C, The precipitation of salt occurred and the reaction mixture was allowed to stir at room temperature for an additional 15 min. The reaction mixture was poured into cold H_2O (100 ml). The solution was extracted with ethyl acetate (3 x 50 ml). The organic layer was washed with brine and dried over anhydrous Na_2SO_4. The resulting solution was filtered, concentrated under reduced pressure and chromatographed on silica gel. Yield 92.7%.

^{1}H NMR ($CDCl_3$): d 1.34-1.53 (m, 6H, CH_2), 1.87-1.93 (q, 2H, CH_2), 2.33 (t, *J* =7.6Hz, 2H, CH_2), 3.05 (t, *J* = 7.4Hz, 2H, CH_2), 4.04 (s, 4H, Fc), 4.09 (s, 5H, Fc). MS (EI) (M^+) calcd. for $C_{17}H_{21}FeNSe$: 375.02 *m/z*. found: 374.9 *m/z.*

Di-6-ferrocenylhexyl diselenide (**9**): 6-Ferrocenylhexyl selenocyanate (1.14 g, 3.05 mmol) was dissolved in anhydrous dimethylformamide (25 ml). Sodium hydride (0.073 g, 3.05 mmol) was added to the solution, and the mixture was stirred for 24 h at room temperature. The reaction mixture was quenched with of H_2O (50 ml). The solution was extracted with ethyl acetate (3 x 50 ml). The organic layer was washed with brine and dried over anhydrous Na_2SO_4. The resulting solution was filtered, concentrated under reduced pressure and chromatographed on silica gel. Yield 66.0%.

^{1}H NMR ($CDCl_3$): d 1.25-1.52 (m, 12H, CH_2), 1.70-1.76 (q, 4H, CH_2), 2.33(t, 4H, CH_2), 2.91 (t, 4H, *J* = 7.5 Hz, CH_2), 4.04 (s, 8H, Fc), 4.09 (s, 10H, Fc). MS (EI) (M^+) calcd. for $C_{32}H_{42}Fe_2Se_2$: 698.03 *m/z.* found: 697.8 *m/z.*

Substrates preparation

Two different Ni substrates were used in this work. The first substrate consisted of polycrystalline Ni disc inserted in a solvent resistant plastic body, while the second substrate was a 100 nm thick Ni film on silicon. The preparation of the first substrate is described in the electrochemistry section.

Nickel on silicon: The Ni electrodes were grown by nickel (99,999%, Puratronic®, Alfa Aesar) evaporation under vacuum (base pressure ~10^{-6} Torr) from a tungsten boat onto fresh etched (South Bay Technology reactive ion etcher) silicon (100) wafer (Silicon Quest International). The typical rate of evaporation was 1-2 Ås^{-1} at an operation pressure of $(1\text{-}3) \times 10^{-6}$ Torr. Since Ni surface is easily oxidized on exposure to atmospheric air, the surface was subjected to an electrochemical pretreatment consisting of a reduction (-1.3 V vs Ag/AgCl, 3M NaCl) in an aqueous solution of $HClO_4$ (1M) for 20 minutes. The electrodes were immediately soaked in nitrogen-saturated water and then immersed in an isocyanide-ethanol solution to minimize the oxidation of the surface. The exposure time of the substrates at ambient atmosphere during this transfer was estimated to be less than 3s. XPS studies of Ni surfaces using this procedure were reported to have very small amount of Ni oxide on polycrystalline Ni surfaces.[3]

Electrochemistry

Cyclic voltammetry (CV) was performed with CV-50W Voltammetric Analyzer (Bioanalytical Systems Inc) in conventional three-electrode cell. A disc of polycrystalline Ni, Ø = 3 mm (Bioanalytical Systems Inc.) was used as the working electrode. Prior to each experiment the electrode was mechanically polished to a mirror finish with diamond (0.5 and 0.1 µm) and then (0.05 µm) alumina polishing solutions, cleaned in an ultrasonic bath and subsequently reduced using the same electrochemical pretreatment described for the Ni on silicon. A platinum wire was used as auxiliary electrode and all potentials were measured against an Ag/AgCl electrode in 3M NaCl (Bioanalytical Systems Inc). Unless stated otherwise, 0.1M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) electrochemical grade (Fluka) in THF was used as supporting electrolyte. The electrolyte solution was degassed prior to the experiment by bubbling argon for 40 minutes. All the measurements were carried out at ambient conditions. The same procedure was used to prepare the samples for RAIR spectroscopy.

Determination of the surface coverage: Surface coverage (Γ) were determined from voltammograms recorded at low scan rate (0.01 Vs^{-1}) according to equation (1).[4]

$$\Gamma = \frac{Q_{Fe}}{nFA} \tag{1}$$

Where Q_{Fe} is the charge consumed for the oxidation-reduction process of the ferrocene groups, n is the number of electrons involved in the electron transfer process (n = 1 for the ferrocene redox couple), A is the geometric surface area of the electrode (0.070686 cm^2) and F is the faraday constant. Values of Q_{Fe} were obtained by the integration of the faradaic current peaks and corrected for charging-currents contributions.[5]

Monolayer Preparation.

The monolayers were formed by soaking the Ni substrates in absolute ethanol solutions of the isocyanide molecules. For electrochemically-reduced Ni substrates, the electrodes were used immediately after the electrochemical pretreatment; the Ni substrates were transferred from the water to the coating solution. After 6-72 h. the electrode was removed from the solution, rinsed several times with ethanol, *n*-hexane, chloroform, and THF to remove any physisorbed molecules. Finally, the samples were dried with a continuous and gentle flow of argon and immediately used for characterization. The formation of SAMs was carried out at room temperature, the solutions were degassed by argon bubbling during 40 min prior to monolayer preparation.

Infrared spectroscopy

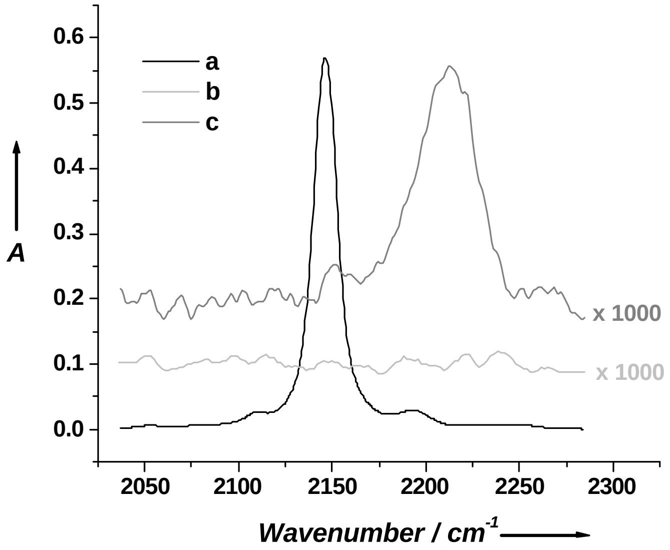

Figure 1: FTIR spectra for *6-Ferrocenylhexyl isocyanide* (**5**) in the region 2000-2300 cm^{-1}: (a) **5** on KBr plate; (b) RAIR spectrum of **5** on a nickel surface; (c) RAIR spectrum of **5** on a gold surface.

The RAIR spectra of the monolayers were obtained using a Nicolet Magna Spectrometer equipped with a FT-85 fixed 85° grazing angle accessory (Thermo Spectra-Tech) and a liquid nitrogen cooled MCT detector, the beam was p polarized. Reference spectrum was recorded on a freshly prepared Ni substrate prior to the collection of the spectra of SAMs on nickel-coated silicon wafers. Before each acquisition, the sample chamber was purged with dry nitrogen until a constant spectrum was obtained during 100 consecutive scans (1-2 h.). Two thousands consecutive scans were averaged for the sample and reference spectra and the spectra resolution was set at 2 cm^{-1}. The baselines of the spectra were corrected over the range of 700-3400 cm^{-1}.

Atomic Force Microscopy

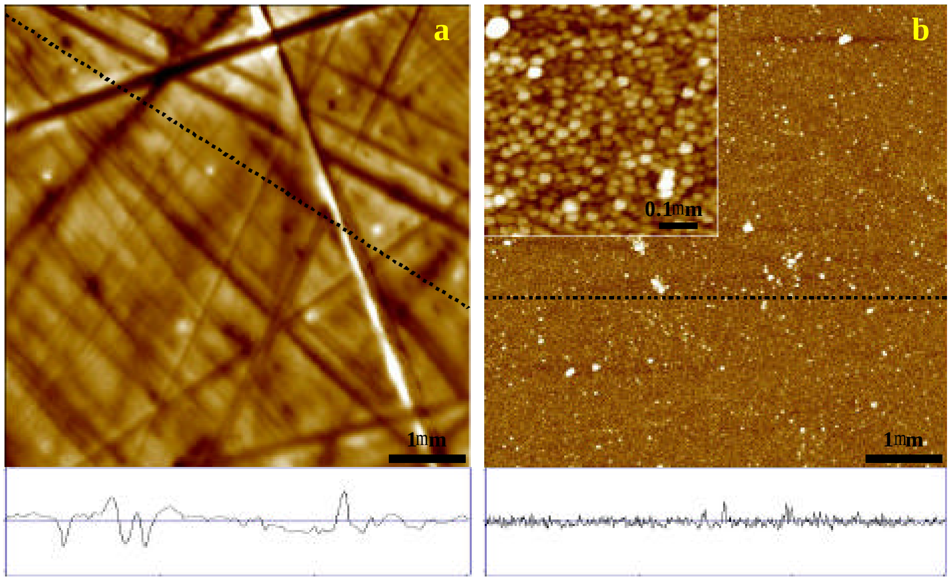

Figure 2. AFM images of surface profiles (vertical scale: 20 nm) of bare electrochemically-reduced nickel a) disk used for electrochemistry experiments and b) 100 nm thick nickel film evaporated on silicon for RAIR spectroscopy (vertical scale: 30 nm). The dashed lines indicate the surface profile.

The tapping mode AFM imaging of the sample was performed under ambient conditions using a Multimode Nanoscope IIIA (Digital Instrument multimode scanning probe microscope). Rectangular silicon cantilevers with a nominal spring constant of 40 Nm^{-1} were used with a J type scanner. The drive frequency was ca. 320 kHz. The images were acquired with typical scan rates of 0.5-1.0 Hz with a frame rate of 512.

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