Supporting Information

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I. Preparation of molecules

The molecules used in this study were prepared by published methods. The bisoxazole was prepared by method of Klare and coworkers, (S1) and the terpyridyls were prepared according to a published procedure, (S2) The thiols were protected as their acetate esters and deprotected using the method of Tour and coworkers, (S3)

II. Monolayer characterization

A. Monolayer formation. The monolayers and the imine-forming surface chemistry of the bisoxazole was previously described, (S1) The formation of the terpyridyl monolayers and their subsequent reaction with cobalt ions is described below.

A few drops of ammonium hydroxide were added into a 1 mM solution of acetate protected terpyridyl thiol in THF (5 mL). Into this solution was placed three fresh Pt substrates for 24 hrs. Then the Pt substrates were taken out and rinsed with THF, CH₂Cl₂, acetone and isopropanol thoroughly and dried under a stream of Argon. One of the three was used for characterization experiments, and the other two were placed into 10mM aqueous solution of
Co(OAc)$_2$ for 72 hrs. After that these two were rinsed with H$_2$O, acetone and isopropanol and dried under a stream of Argon. One of the two samples was used for characterization experiments, and the last one was placed into 10mM aqueous solution of EDTA (tetra sodium salts form) for 24 hrs. Then the sample was rinsed with H$_2$O, acetone and isopropanol and dried under a stream of Argon.

**B. XPS.** XPS experiments were performed with a Perkin Elmer x-ray photoelectron spectrometer equipped with a Al K$_{\alpha}$ X-ray source (1486.6 eV) and a hemispherical analyzer. The pass energy was set to 20.00 eV for high resolution scans. The typical operating pressure was below 5 x 10$^{-9}$ torr. All intensities were determined after subtraction of a linear background and calculated by numerical integration with standard software.

**C. Reflection-Absorption Infrared Spectroscopy.** Reflection-absorption infrared spectroscopy was performed using a N$_2$ purged Nicolet Infrared spectrometer with a MCT detector. Spectra were obtained using a GATR (Harrick Inc.) total reflectance accessory equipped with a hemispherical germanium crystal. All spectra reported were the average of 512 scans obtained at a resolution of 4 cm$^{-1}$ and reference to a blank substrate.

To quantify the amount of cobalt incorporated, we ratio the intensity at 1724 cm$^{-1}$ relative to the pyridyl ring stretching at 1596 cm$^{-1}$. For the monolayer 3 this ratio is 0.03 before reaction and increase by two orders of magnitude to 3 after reaction with cobalt diacetate. The ratio becomes 0.17 after treatment with an EDTA solution.

**III. Junction fabrication**

The electron beam lithography is performed with an FEI Sirion scanning electron microscope equipped with a pattern generator and control system (J. C. Nabity, Inc). First a p-doped silicon wafer with 20nm high quality thermal oxide is placed into an atomic layer
deposition (ALD) system (Cambridge NanoTech Inc.). The deposition process is performed at 250 °C with 50 cycles of H₂O and tetrakis(dimethylamido)zirconium(IV) pulses. After the ALD deposition, a set of alignment marks (30 nm Au on 5 nm Cr) is patterned on the wafer using standard electron beam lithography. A 150 nm of PMMA (25K) is spun onto the wafer and pre-baked on a hot plate at 180°C for 2 hours. Then the first electrode is patterned onto the wafer relative to the align marks. To ensure a near vertical resist profile, we use low temperature water:isopropyl alcohol (< 5 °C) developer and ultrasonication (1 min.) to assist in the development. After being rinsed with water and blow dried with nitrogen, the wafer is transferred into an e-beam evaporation system (Semicore Inc.), where 3nm Pt and 7nm Al are deposited at pressure ≤ 1x10⁻⁶ torr at a rate of ~0.1 Å/s without breaking the vacuum. After lift-off (9:1 methylene chloride:acetone) at 75 °C, second electrode is patterned to overlap the first electrode using the alignment marks. 2.5 nm Pt is deposited by e-beam evaporation and following standard lift-off, the devices are immersed in an tetramethyl ammonium hydroxide solution (Rohm and Haas LDD-26W) solution for 5 min with mild ultrasonic agitation to remove the aluminum.

**IV. Electrical testing**

All electrical measurements were performed using a Karl Suss PM5 probe station connected with HP 4155C semiconductor parameter analyzer. The noise is lower than 10 pA under middle sweep speed. All devices were tested and showed current at the noise level of the instrument. After each reaction step, the devices were rinsed (THF, acetone, and then isopropanol) and dried under a stream of nitrogen gas. They were immediately mounted onto the probestation and tested.
V. Current-Voltage Curves for Control Experiments

**Figure S1.** Control experiment where the order of the steps was reversed (i.e., when the junction was “reacted” with the bridging molecule first and then the monolayer-forming molecule). Representative IV curves shown. The 60 other devices measured were equivalent.

**Figure S2.** Control experiment where 8 nm gaps were utilized, which are too large for the terpyridyl/Co$^{2+}$ complex to bridge. Representative IV curves shown. The 120 other devices measured were equivalent.

**Figure S3.** Control experiment where we first used the monolayer that has terpyridyl termination and then added the diamine bridge. Representative IV curves shown. The 60 other devices measured were equivalent.
Figure S4. Control experiment where we use the aldehyde-terminated monolayer and introduce cobalt ions. Representative IV curves shown. The 60 other devices measured were equivalent.
References

