Electronic Supporting Information (ESI) for: Effective anion sensing based on the ability of copper to affect electron transport across self-assembled monolayers

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Fig. S1 CVs of the monolayer modified gold electrodes in 1 mM [Fe(CN)₆]⁴⁻, 1 mM [Fe(CN)₆]³⁻, 0.1 M NaCl and 100 mM HEPES (pH 7.3) in the absence and presence of 1 mM CN⁻. Scan rate 0.1 V s⁻¹, T = 293 K.

Fig. S2 CVs in 1 mM [Fe(CN)₆]⁴⁻, 1 mM [Fe(CN)₆]³⁻, 0.1 M NaCl and 100 mM HEPES (pH 7.3) at the monolayer modified gold electrodes in the absence and presence of different anions (1 mM). Scan rate 0.1 V s⁻¹, T = 293 K.

Fig. S3 FTIR spectrum of bulk L¹ (KBr pellet).

Fig. S4 FTIR spectrum of bulk [(L¹)CuCl]Cl (KBr pellet).

Fig. S5 PM-RAIR spectrum of the SAM of L¹ on a gold surface.

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Materials.

Reagents were obtained from commercial sources and used as received unless otherwise stated. Solvents were dried and purified under N₂ by using standard methods and were distilled immediately before use. L¹ and [(L¹)CuCl]⁺ were prepared using the procedure described in our previous paper.¹

Preparation of evaporated gold samples. A gold sample of 99.99% purity was used for the preparation of evaporated thin films of gold having a thickness of ~100 nm on glass with chromium underlayers (~2-5 nm thickness). The substrate was heated to 350 °C during gold evaporation under a vacuum pressure of 2 x 10⁻⁵ mbar, a process that normally yields a very smooth gold substrate with predominantly Au(111) orientation. These gold samples were used as strips for the monolayer preparation and its characterization.

Monolayer preparation. Before SAM formation, the gold strips were chemically cleaned by immersing in a piranha solution (a mixture of H₂O₂ and conc.H₂SO₄ in 1:3 ratio) for 5-10 minutes. Caution: piranha solution reacts violently with organic materials and therefore must be handled with extreme care. Then, the slides were rinsed with water and methanol, dried under N₂ and used immediately. Monolayers of the L¹Cu complex were prepared by immersing the cleaned gold strips into methanol solution (10 mM) in presence of NaBH₄ as disulfide reducing agent for about 15-16 hours under an atmosphere of N₂. After this, the SAM-modified gold surfaces were rinsed with methanol and water and used immediately for the analysis.

Physical Measurements.

Electrochemistry. All electrochemical studies were performed with an Autolab PGSTAT 20 instrument. The electrochemical blocking ability of the monolayers towards electron transfer was studied by cyclic voltammetry and electrochemical impedance spectroscopy using [Fe(CN)₆]³⁻/⁴⁻ redox couple as a probe. The electrolyte solutions used for electrochemical measurements were prepared using millipore water having a resistivity of 17 MΩ. Cyclic voltammetry and impedance measurements were conducted in a three-electrode glass cell at 20 °C. A platinum rod, a saturated
calomel electrode (SCE) and a monolayer-modified gold electrode were used as counter, reference and working electrodes respectively. Cyclic voltammetry was performed in 1mM potassium ferrocyanide aqueous solution containing 0.1 M NaCl as a supporting electrolyte. Impedance measurements were carried out at the formal redox potential (as determined from cyclic voltammetry) in an aqueous solution containing equal concentrations of oxidized and reduced forms of \([\text{Fe(CN)}_6^{3-/4-}]\) (1mM) with 0.1 M NaCl as a supporting electrolyte. The frequency ranging from 10 KHz to 0.1 Hz with an ac amplitude of 10 mV was used for the analysis. Impedance spectroscopy data were analyzed to determine the charge transfer resistance \(R_{\text{CT}}\), a parameter used to quantify the rate of electron transfer across the interface.

**Detection of anions.** The sensitivity of monolayers to various anions such as cyanide (CN\(^-\)), phosphate (H\(_2\)PO\(_4^-\)), nitrate (NO\(_3^-\)), acetate (AcO\(^-\)) and fluoride (F\(^-\)) were analyzed in an aqueous HEPES buffer (100 mM) solution (pH = 7.3) containing 1 mM \([\text{Fe(CN)}_6^{3-/4-}]\) with 0.1 M NaCl as a supporting electrolyte using cyclic voltammetry and electrochemical impedance spectroscopy. The concentration ranging from 1nM to 1mM was analyzed for all the anions studied in this work. The anions were added from a fleshly prepared stock solution of their corresponding sodium salts having concentrations 200 μM, 25 mM and 0.5 M in periodic increments to the aqueous buffer solution (20 mL) and stirred well before carrying out the analysis.

**X-ray photoelectron spectroscopy (XPS).** X-ray photoelectron spectra were obtained with a VG Scientific Sigma Probe (UK) XPS system. The Al K\(\alpha\) anode X-ray source (\(h\nu = 1486.6\) eV) was operated at 200W and the take-off angle for photoelectrons was 37º. Samples were mounted with a spring clip. In a typical experiment, a few survey scans in the -10 to 1100 eV kinetic energy range were collected at a resolution of 1 eV. Then, detailed scans of 20-60 eV over a single feature were collected at a resolution of 0.2 eV. During the measurements the pressure was 10\(^{-9}\) - 10\(^{-10}\) Torr.

**IR spectroscopy.** Infrared spectra of the bulk materials were recorded with a JASCO FTIR-410 spectrometer between 4000 and 400 cm\(^{-1}\) as KBr pellets. A Nicolet Nexus 860 FTIR spectrometer was used to acquire the polarization-modulation reflection-absorption (PM-RAIRS) data of the SAMs on gold using a liquid N\(_2\)-cooled mercury cadmium telluride (MCT) detector.
References:

Fig. S1 CVs of the monolayer modified gold electrodes in 1 mM [Fe(CN)₆]⁴⁻, 1 mM [Fe(CN)₆]³⁻, 0.1 M NaCl and 100 mM HEPES (pH 7.3) in the absence and presence of 1 mM CN⁻. Scan rate 0.1 V s⁻¹, T = 293 K. The redox wave is due to the Fe³+/²⁺ redox couple.
**Fig. S2** CVs in 1 mM [Fe(CN)₆]⁴⁻, 1 mM [Fe(CN)₆]³⁻, 0.1 M NaCl and 100 mM HEPES (pH 7.3) at the monolayer modified gold electrodes in the absence and presence of different anions (1 mM). Scan rate 0.1 V s⁻¹, T = 293 K. The redox wave is due to the Fe³⁺/²⁺ redox couple.
Fig. S3 FTIR spectrum of bulk L¹ (KBr pellet). The bands due to CH and CH₂ stretching appear in the 2800-3100 cm⁻¹ frequency range, whereas those due to pyridine ring stretching (C-C and C-N) appear in the 1300-1600 range. The amide I band, which results from the C=O stretching vibration of the amide group coupled to the bending of the N-H bond and the stretching of the C-N bond is centered around 1600-1700 cm⁻¹.
Fig. S4 FTIR spectrum of bulk [(L¹)CuCl]Cl (KBr pellet). The IR due to CH and CH₂ stretching appear in the 2800-3100 cm⁻¹ frequency range, whereas those due to pyridine ring stretching (C-C and C-N) appear in the 1300-1600 cm⁻¹ range. The amide I band, which results from the C=O stretching vibration of the amide group coupled to the bending of the N-H bond and the stretching of the C-N bond is centered around 1600-1700 cm⁻¹.
Fig. S5 PM-RAIR spectrum of the SAM of L¹ on a gold surface. The IR due to CH and CH₂ stretching appear in the 2800-3100 cm⁻¹ frequency range, whereas those due to pyridine ring stretching (C-C and C-N) appear in the 1300-1600 cm⁻¹ range. The amide I band, which results from the C=O stretching vibration of the amide group coupled to the bending of the N-H bond and the stretching of the C-N bond is centered around 1600-1700 cm⁻¹.
Fig. S6 PM-RAIR spectrum of the SAM of the copper complex of L₁ on a gold surface. The IR due to CH and CH₂ stretching appear in the 2800-3100 cm⁻¹ frequency range, whereas those due to pyridine ring stretching (C-C and C-N) appear in the 1300-1600 cm⁻¹ range. The amide I band, which results from the C=O stretching vibration of the amide group coupled to the bending of the N-H bond and the stretching of the C-N bond is centered around 1600-1700 cm⁻¹.
Fig. S7 PM-RAIR spectrum of the SAM of the copper complex of L\(^1\) on a gold surface after the addition of 100 \(\mu\)M CN\(^-\). The IR due to CH and CH\(_2\) stretching appear in the 2800-3100 cm\(^{-1}\) frequency range, whereas those due to pyridine ring stretching (C-C and C-N) appear in the 1300-1600 cm\(^{-1}\) range. The amide I band, which results from the C=O stretching vibration of the amide group coupled to the bending of the N-H bond and the stretching of the C-N bond is centered around 1600-1700 cm\(^{-1}\).