Metal-mediated transport of electrons across molecular films†

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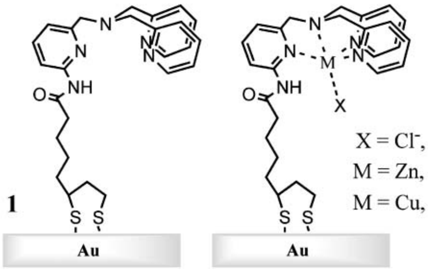
Electron transfer (ET) to a redox probe in solution across the self-assembled monolayers (SAMs) of a tris-(2-pyridylmethyl) amine-based ligand on gold electrodes is greatly enhanced by Cu-binding.

Recent studies have shown that the incorporation of metal-binding units and metals with desired electrical, magnetic, optical, molecular recognition and catalytic properties into SAMs of thiols on gold can be exploited for the development of sensors,[1] catalysts[2] and molecular electronics.[3] The incorporation of redox active units is important because it allows electrochemistry to be applied to regulate the properties of the SAM.[4] Fundamental to this diverse chemistry is the ability to regulate the transport of electrons through the molecular film. Ferrocene-terminated SAMs have received considerable attention while studying the kinetics of ET across SAMs, showing that ET depends on both the thickness and aliphatic *vs.* aromatic nature of the film.[5,6] Although recent reports have suggested that metal(s) can facilitate ET,[1d,7] the extent to which this occurs and the mechanism(s) involved are unclear.

Metal complexes of the tripodal ligand tris-(2-pyridylmethyl) amine (TPA) and related ligands exhibit interesting redox-induced changes in molecular geometry,[8] and excellent properties for catalysis[9] and molecular recognition.[10] Recently, it has been shown that copper containing SAMs of a related ligand, bis(6-methyl-2-pyridylmethyl)amine ethyl sulfide, can catalyze the reduction of NO_2^- to NO.[2a] However, it is known that for catalysis and molecular recognition, the incorporation of H-bonding groups in the proximity of metal binding sites provides a powerful approach to improve the properties of the complexes formed.[11–13] Thus, the attachment of TPA-based ligands with H-bonding groups to gold colloids and electrodes should provide metal complexes with interesting sensing, electronic and catalytic properties.

Here, films of a TPA dithiol derivative, **1**, with an amide H-bonding group close to the metal binding site, and its complexes Cu-**1** and Zn-**1** on gold have been prepared (Scheme 1).† The ET to a solution containing the redox probe $[Fe(CN)_6]^{3-/4-}$ through these molecular films has been studied by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).



Scheme 1

Films of **1** were prepared by placing a clean gold film electrode into a methanol solution of disulfide **1** (10 mM) and $NaBH_4$, as the disulfide reducing agent, for 16 h under a N_2 atmosphere.† Films of the metal complexes were prepared in the same way, following the reaction of equimolar amounts of MCl_2 (M = Cu, Zn) with **1** in methanol (10 mM) for 1 h to yield $[M^{II}(\mathbf{1})Cl]^+$, as shown by EIS-MS studies.† The SAMs were characterized by X-ray photoelectron spectroscopy (XPS).

The XPS spectra of the film formed by **1** showed peaks due to S, N and O, whereas the metal complexes showed, in addition, peaks due to the metal and Cl.† The S 2p peak at 162.2 eV is indicative of Au–thiolate linkages, whereas the feature at 288.5 eV (C 1s) is characteristic of C=O bonds. For the Cu-**1** film, the peaks at 932.5 eV (Cu 2p3/2) and 952.3 eV (Cu 2p1/2), and the absence of shake-up lines characteristic of Cu^{II} ions, are indicative of the presence of Cu^I centres.[14]

The formation and barrier properties of the SAMs on the $[Fe(CN)_6]^{3-/4-}$ redox couple ($E_{1/2}$ = 0.20 V *vs.* SCE) were evaluated by CV and EIS. The CVs were carried out in water in presence of 1 mM $[Fe(CN)_6]^{4-}$, with 0.1 M NaCl as the supporting electrolyte. The CV of the film of **1** shows the complete absence of redox current for the $[Fe(CN)_6]^{3-/4-}$ redox couple, revealing that a densely packed molecular film is formed on the gold electrode (Fig. 1). This is supported by oxide formation/stripping studies,

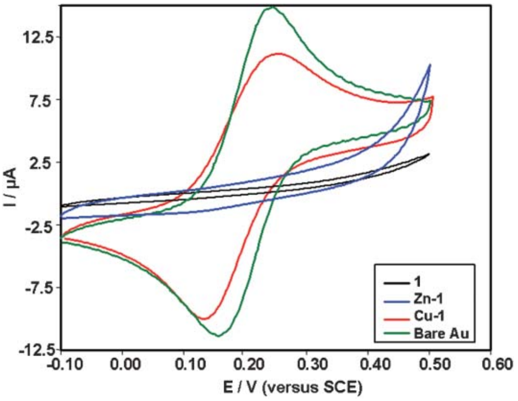


Fig. 1 CVs of 1 mM $[Fe(CN)_6]^{4-}$ in 0.1 M NaCl at a bare gold (green) or monolayer-modified gold electrode with **1** (black), Zn-**1** (blue) and Cu-**1** (red). Scan rate 0.1 V s^{-1}. T = 293 K.

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from which the surface coverage was estimated to be 99.7% for **1**, 93.9% for Cu-**1** and 96.8% for Zn-**1**.[15]† The CVs of the SAMs of the metal complexes show larger currents due to the $[Fe(CN)_6]^{3-/4-}$ redox couple, particularly the Cu-**1** monolayer (Fig. 1).

This result suggests that the metal-containing films facilitate ET to the redox probe and that the magnitude of this effect is greater for those containing the redox-active metal. Similar results were obtained using $M(ClO_4)_2$ as metal precursors with $NaClO_4$ as the supporting electrolyte, suggesting that Cl^- anions are not essential to mediate ET. ET is also facilitated by adding the corresponding metal precursors to films of **1**. However, the magnitude of the effect is smaller, presumably because close packing in the film limits the accessibility of metal ions to the binding sites.[15]

EIS was employed to investigate the extent to which ET is facilitated. The impedance plots (Nyquist) for bare and monolayer-coated gold electrodes are shown in Fig. 2. The charge transfer resistance, R_{CT}, reflects the charge-transfer resistance across the SAMs, and can be used to evaluate the rate of ET to the solution containing the redox probe.[16] The monolayer-modified gold electrode with **1** has a R_{CT} value of $6.75 \times 10^3\ \Omega\ cm^2$, compared to $1.35\ \Omega\ cm^2$ for the bare gold electrode. Thus, the SAM of **1** blocks very effectively ET to the redox probe. For Zn-**1** and Cu-**1** monolayers, R_{CT} is 1.73×10^3 and $9.42\ \Omega\ cm^2$, respectively. For comparison, monolayers of decanethiol and thiophenol give a R_{CT} of 1.70×10^3 and $440\ \Omega\ cm^2$, respectively. Using the R_{CT} values obtained from the impedance plots, we have calculated the apparent rate constant values, k_{app}, of $[Fe(CN)_6]^{3-/4-}$ for the SAM-modified electrodes (or real k_0 for bare gold) using eqn. (1), where R is the gas constant, T is the temperature, F is Faraday's constant and C is the concentration of the redox probe.

$$k_0 \text{ or } k_{app} = RT/[F^2 R_{CT} C] \qquad (1)$$

The k_{app}, k_o and R_{CT} values obtained for different monolayers and bare gold are collected in Table 1. Decanethiol monolayers separate the gold surface from the probe by ten saturated bonds, and **1** by at least eleven bonds (saturated and unsaturated), leading to apparent rate constants of 1.54×10^{-4} and $3.87 \times 10^{-5}\ cm\ s^{-1}$, respectively. Remarkably, for monolayers of Cu-**1**, k_{app} is $2.78 \times 10^{-2}\ cm\ s^{-1}$; much faster than across the shorter, unsaturated bridge provided by thiophenol ($k_{app} = 5.95 \times 10^{-4}\ cm\ s^{-1}$). Thus, although Zn^{II} ions seem to facilitate ET to the probe, redox-active Cu^{II} ions are, remarkably, more effective.[17]

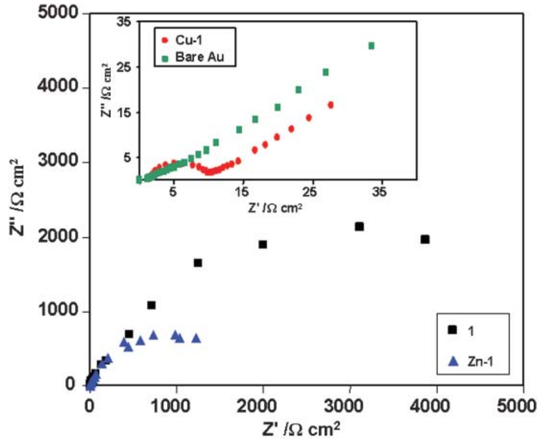


Fig. 2 Impedance (Nyquist) plots in 10 mM $[Fe(CN)_6]^{4-}$, 10 mM $[Fe(CN)_6]^{3-}$ and 1 M NaCl at a bare (green squares) or monolayer-modified gold electrode with **1** (black squares), Zn-**1** (blue triangles) and Cu-**1** (red circles). $T = 293$ K.

Table 1 Charge transfer resistance (R_{CT}) and rate constants (k_0 and k_{app}) for bare and monolayer-modified gold electrodes, obtained from EIS

Sample	$R_{CT}/\Omega\ cm^2$	k_0 or $k_{app}/cm\ s^{-1}$
Bare Au	1.35	0.197
Decanethiol	1.70×10^3	1.54×10^{-4}
Thiophenol	440	5.95×10^{-4}
1	6.75×10^3	3.87×10^{-5}
Zn-**1**	1.73×10^3	1.51×10^{-4}
Cu-**1**	9.42	2.78×10^{-2}

To determine the mechanism by which the Cu-**1** film mediates the transport of electrons to the redox probe in solution, we have studied its redox behaviour in 0.1 M NaCl as the supporting electrolyte without the redox probe. The CV (Fig. 3) shows a non-reversible oxidation at 0.49 V, and reductions at 0.21 and −0.28 V. Presumably, this is because the copper ions are in different coordination environments. It means that there are species capable of both accepting and donating electrons at the potential of the redox probe (0.2 V).[18] The solid-state structures of related $[(L)Cu^{I/II}Cl]^{0/+}$ complexes with pivaloylamido H-bonding groups in the pyridine 6-position have been determined by X-ray crystallography.[19,20] They reveal that the copper centre in the 2+ oxidation state is pentacoordinated to the four ligand-based N atoms and a Cl^- ligand, and in the 1+ state to only two N atoms and a Cl. It is reasonable to suggest that the close packing of molecules on the electrode surface could allow a similar behavior with the involvement of Cl^- anions or solvent molecules. On the basis of the electrochemical and crystallographic studies, a plausible mechanism for mediating ET between the electrode and the redox probe in solution is proposed (Scheme 2). In this mechanism, copper ions in different coordination environments and with different redox potentials are in rapid equilibrium in order to mediate the ET. Based on the crystallographic and electrochemical data, and the coordination chemistry of copper, we propose that the Cu^I ions are predominantly in a lower

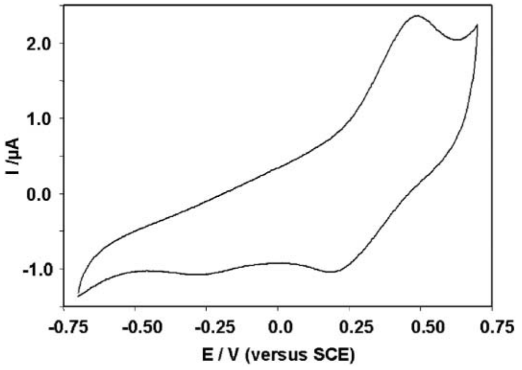
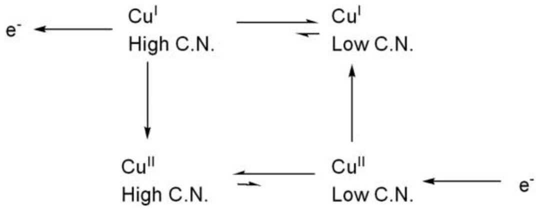


Fig. 3 CV of the monolayer modified gold electrode with Cu-**1** in 0.1 M NaCl. Scan rate 0.1 V s^{-1}. $T = 293$ K.



Scheme 2

coordination number environment, whereas the Cu^{II} ions prefer to be coordinated to additional ligands.

In summary, this work has studied the extent to which SAMs of metal complexes of a versatile ligand facilitate ET to a redox probe in solution, and the mechanism involved. Monolayers containing redox-active $Cu^{II/I}$ ions accelerate ET by *ca.* 700-fold, compared to only 3-fold for those containing Zn^{II} ions. Moreover, ET across films containing redox-active copper centers is considerably faster than across shorter, aromatic interfaces. The electrochemical data, together with crystallographic data available for related $Cu^{I/II}$ complexes, is consistent with the proposed mechanism for ET where these copper ions are in different coordination environments and rapidly undergoing interconversion. Studies related to ET across these and similar SAMs, and their applications in catalysis and molecular recognition, are in progress.

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15 As pointed out by one of the referees, it is also possible that repulsive electrostatic interactions among metallated head groups prevent the complete metallation of the pre-formed SAM of **1**. Repulsive interactions may explain the lower surface coverage of the SAMs of the preformed metal complexes.

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17 The rate enhancement provided by the copper-containing SAM of **1** is greater than with any of the other ligands we have investigated so far. We have also found that, in some cases, the presence of metals in the SAM provides a bigger barrier to ET to the redox probe. These and additional studies will be published elsewhere.

18 There is an apparent lack of oxidation peak for the Cu^{I} complex with the lowest oxidation potential (*i.e.* in the high coordination number (CN) environment). This means that Cu^{I} ions can rapidly change from the less favourable (high CN) coordination environment to the more favourable (low CN) one. The reduction peak at −0.28 V is smaller than that at 0.21 V (1 : 7). This result suggests that the conversion of Cu^{II} in the higher CN to Cu^{II} in the lower CN is slower, and probably not complete at this scan rate.

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