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Orthogonal bis(terpyridine)–Fe(II) metal complex oligomer wires on a tripodal scaffold: rapid electron transport[†]

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The present work reports a tripodal scaffold for bis(terpyridine)–Fe(n) oligomer wires on an Au(111) surface: the tripodal scaffold realised both orthogonality of the oligomer wires, and fast interfacial electron transfer through the oligomer wires.

The gold-thiol protocol is the most widely and frequently used procedure for the preparation of self-assembled monolayers (SAMs). It produces dense and ordered monolayers of adsorbates in a short time without a laborious process.1 The Au-S bond forms a good molecular junction between adsorbates and gold electrodes, providing high electrical conductivity² and rapid interfacial electron transfer.3 Taking advantage of the virtues of the gold-thiol protocol, we fabricated bis(terpyridine)-M [M = Fe(n)]and Co(III)] complex oligomer wires on terpyridine-terminated gold-thiol SAMs, and observed excellent long-range intrawire electron transport (Scheme 1a).⁴ One of the drawbacks of the gold-thiol protocol is that the adsorbates possess inclined configurations. For example, the tilt angle of benzenethiol was reported to range from 30° to 76° .⁵ Several efforts have been made to compensate for this weakness. Tripodal surface attaching molecules possessing three thiol, thioacetate, or sulfide groups have been synthesized and chemisorbed on gold surfaces.⁶ This series of tripodal ligands highlights the firm and perpendicular chemisorption of adsorbates, however, no attention has been paid to functionality, including the pursuit of good junctions with a gold electrode for fast interfacial electron transfer phenomena.

The purpose of this work was to realise a tripodal scaffold for bis(terpyridine)–Fe(π) complex oligomer wires that would afford both vertical configuration and fast interfacial electron transfer. To achieve this, we designed a tripodal terpyridine anchor ligand A_T (obtained as the form of thioacetate-protected A_T –Ac, Scheme 1b)

with two distinctive concepts. One is the employment of an sp³ Si atom as the origin of the tripodal architecture. The sp³ Si is known to show σ - π conjugation with aromatic substituents.⁷ We expected that this feature of Si could accelerate interfacial electron transfer. The other concept involves the attaching entity; a π -conjugated benzenethiol group is employed. We note that all tripodal adsorbates reported thus far adopted non- π -conjugated aliphatic thiol groups,⁶ such as benzenemethanethiol^{6a,b,d} and adamantylthiol.^{6e} The π -conjugated benzenethiol group was also expected to increase the interfacial electron transfer rate.

Scheme 2 shows the synthetic procedure for Ar-Ac; see the ESI for details.[†] Then we considered the optimal conditions for the formation of SAMs of A_T on a gold electrode surface using X-ray photoelectron spectroscopy (XPS). Solid AT-Ac showed a doublet at 163.5 eV (doublet a, Fig 1a). This is typical of the S 2p1/2/S 2p3/2 couple with the 1:2 area ratio for an acetyl-protected thiol group.⁸ On the other hand, a gold substrate immersed into a chloroform solution of Ar-Ac for 3 hours showed that two additional doublets emerged at 162.9 eV and 161.7 eV (doublets b and c, respectively; Fig. 1b). An increase in immersion time to 3 days showed the disappearance of doublet a, but doublets b and c were persistent. The area ratio between doublets b and c was 1:2 (Fig. 1c). IR-ATR spectroscopy for an Au substrate immersed in a chloroform solution of Ar-Ac for 3 days (Fig. S1b, ESI⁺) showed neither C=O stretching of the thioacetate group (1704 cm⁻¹ for A_T-Ac; Fig. S1a, ESI⁺) nor S-H stretching (ca. 2580 cm⁻¹).⁹ The IR-ATR spectroscopy result helped us assign the two new peaks in XPS as follows. Doublet c was attributable to a tightly bound Au-S species, because its binding energy was comparable to the reported values for a SAM of benzenethiol (162.0 eV).¹⁰ On the other hand, we attributed doublet b to a weakly bound Au-S species. The immobilisation of A_T on the Au(111) surface with the three sulphur atoms was reflected in the orthogonality of the bis(terpyridine)–Fe(π) oligomer wires constructed on A_T (vide infra).

Single molecules of A_T were identified in an STM image of a sparse SAM of immobilised A_T (Fig. 2).

Next we fabricated bis(terpyridine)–Fe(n) oligomer wires on the SAM of A_T . Scheme 1a illustrates the schematic procedure (see the ESI[†] for details). Hereafter, the bis(terpyridine)–Fe(n) oligomer wire with *n* layers is abbreviated as Au– $[A_T(FeL_H)_n]$. First, we verified

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[†] Electronic supplementary information (ESI) available: Experimental details, IR spectra of solids A_T and A_T on a gold substrate (Fig. S1), estimation of the length of Au-[A_T (FeL_H)_n] (n = 5 and 40, Fig. S2), and current (*i*)-time (*t*) and (b) ln *i*-*t* plots for Au-[A_T (FeL_H)_{*n*-1}FeT¹] and Au-[A^2 (FeL_H)_{*n*-1}FeT¹] (Fig. S3 and S4). See DOI: 10.1039/c3cc42478b



Scheme 1 (a) Bottom-up fabrication of bis(terpyridine)–Fe(II) oligomer wires Au–[A_T(FeL_H)_n] and Au–[A_T(FeL_H)_{n-1}FeT¹]. (b) Anchor (A), bridging (L), and terminal (T) terpyridine ligands.



Scheme 2 Synthesis of A_T -Ac. TsOH = p-toluenesulphonic acid.



Fig. 1 Experimental (black) and simulated (red) XPS focusing of the S2p region. (a) Solid A_T –Ac; (b) SAM of A_T (immersion time: 3 h); (c) SAM of A_T (immersion time: 3 d). The simulated spectra were reproduced by pair(s) of doublets. Orange, green, and blue doublets correspond to doublet a, doublet b, and doublet c, respectively.



Fig. 2 STM topological image of a SAM of A_{T} sparsely immobilised on an Au(111) surface.

the quantitative formation of the bis(terpyridine)–Fe(π) unit by means of cyclic voltammetry. Fig. 3a shows voltammograms of Au–[A_T(FeL_H)_n] (n = 1, 2, 4, 6, 8, and 10). The voltammograms feature a reversible redox wave at 0.64 V vs.



Fig. 3 (a) Cyclic voltammograms of $Au-[A_T(FeL_H)_n]$ (n = 1, 2, 4, 6, 8, and 10) in 1 M Bu₄NClO₄-dichloromethane at a scan rate of 0.1 V s⁻¹. (b) Γ [Fe(tpy)₂]-n plot.

ferrocenium/ferrocene (Fc⁺/Fc), assignable to the Fe(m)/Fe(n) redox couple of the bis(terpyridine)–Fe unit.⁴ Fig. 3b shows surface coverage of the bis(terpyridine)–Fe unit, Γ [Fe(tpy)₂], determined by the quantity of the electricity of the redox wave depicted in Fig. 3a. A linear relationship between Γ and n confirms that the bottom-up fabrication of Au–[A_T(FeL_H)_n] proceeded quantitatively.

We verified the orthogonal configuration of Au–[$A_T(FeL_H)_n$] by means of atomic force microscopy (AFM) and cross-sectional scanning electron microscopy (SEM). Fig. 4 shows AFM topological and phase images of Au–[$A_T(FeL_H)_5$] after scratching using an AFM tip. From the topological image the depth of the tip was found to be 9–10 nm. This value was in good agreement with the height of Au–[$A_T(FeL_H)_5$] estimated by molecular modelling (Fig. S2, ESI†). In addition, Au–[$A_T(FeL_H)_{40}$] was subjected to cross-sectional



Fig. 4 (a) AFM topological and (b) phase images of Au–[A_T(FeL_H)₅] after scratching using an AFM tip. The white dashed squares indicate the scratched area. (c) Cross-sectional analysis of image (a) at the intersecting white line.



Fig. 5 Cross-sectional SEM image of Au-[A_T(FeL_H)₄₀]



Fig. 6 In k_{et} -*d* plots for Au-[A_T(FeL_H)_{*n*-1}FeT¹] (red) and Au-[A²(FeL_H)_{*n*-1}FeT¹] (green). Dashed lines were obtained by least-squares fitting and solid lines by fitting assuming that both plots had the same slope (-0.018 Å⁻¹).

SEM (Fig. 5), from which the thickness of the $[A_T(FeL_H)_{40}]$ film was found to be 66 nm, also consistent with the molecular modelling (Fig. S2, ESI[†]).

Finally, intrawire electron transport behaviour was investigated. We prepared ferrocene-terminated bis(terpyridine)–Fe(π) oligomer wires, Au–[A_T(FeL_H)_{*n*-1}FeT¹] (*n* = 1–4), and the redox reaction between ferrocene and a gold electrode was monitored by means of potential-step chronoamperometry (PSCA). The electron transfer rate constant for the one-dimensional molecular wire is as follows:¹¹

$$k_{\rm et} = k_{\rm et}^0 \exp(-\beta^{\rm d} d) \tag{1}$$

where $k_{\rm et}$ is the rate constant for the electron transfer between the redox site and the electrode, *d* is the electron transfer distance along the molecular wire, $k_{\rm et}^0$ is the zero-distance rate constant, and $\beta^{\rm d}$ is the distance attenuation factor. Large $k_{\rm et}^0$ and small $\beta^{\rm d}$ indicate that the molecular wire can achieve good electron transport. In this context, PCSA can extract $k_{\rm et}$ experimentally:

$$i = i_0 \exp(-k_{\rm et}t) \tag{2}$$

where i_0 is the current flow at t = 0. Fig. S3 (ESI[†]) shows current-time (i-t) and $\ln i-t$ plots for Au- $[A_T(FeL_H)_{n-1}FeT^1]$ (n = 1-4). The slope of the $\ln i-t$ plot gives k_{et} , and Fig. 6 shows a $\ln k_{et}-d$ plot for Au- $[A_T(FeL_H)_{n-1}FeT^1]$ (n = 1-4). Fig. 6 also includes plots for Fe(tpy)₂ oligomer wires underlain by another anchor ligand, Au- $[A^2(FeL_H)_{n-1}FeT^1]$ (see Fig. S4, ESI[†] for i-t and $\ln i-t$ plots). The slope of the $\ln k_{et}-d$ plot gives β^d , whereas the intercept of the vertical axis corresponds to $\ln k_{et}^0$. We reported previously that β^d was independent of the anchor ligand (A).^{4d} The present results agree with this finding, showing that the two $\ln k_{et}-d$ plots possess the same β^d value, 0.018 Å⁻¹. On the other hand, $\ln k_{et}^0$ of Au- $[A_T(FeL_H)_{n-1}FeT^1]$ is greater than that of Au- $[A^2(FeL_H)_{n-1}FeT^1]$. It is surprising that A_T features rapid electron transport despite lacking manifest π -conjugation.

As indicated in the introductory section, the σ - π conjugation between the Si centre and arenes could account for the fast electron transport. Another possibility is that an electron goes through the three benzenethiol legs in Au-[A_T(FeL_H)_{*n*-1}FeT¹]. We reported previously that doubly-anchored biferrocene on an Au(111) surface through Au–S bonds underwent a faster interfacial electron transfer than in the singly-anchored case.¹²

In conclusion, we designed and synthesised tripodal terpyridine ligand A_T (A_T -Ac). The SAM formation of A_T on a gold electrode surface was optimized to ensure that all S atoms of A_T were chemisorbed. We constructed bis(terpyridine)–Fe(II) oligomer wires on the SAM of A_T , the orthogonality of which was confirmed by means of AFM and cross-sectional SEM. A_T realised fast intrawire electron transfer behaviour, showing a large k_{et}^0 value.

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