Stepwise Preparation of Linear π-Conjugated Bis(terpyridine)metal Polymer Chains at Gold Surface

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Defect-free structures of a film composed of linear redox polymer chains were prepared using stepwise complexation of Fe(II) and/or Co(II/III) ions with azobenzene-bridged bis(tpy) (tpy = 2,2′:6′,2″-terpyridine) ligands, tpy–AB–tpy, on tpy-terminated SAM on gold. This method realizes a formation of desired number of polymer units (for example, 47-mer of $Co(tpy)_2$) and a desired sequence of Co–Fe heterometal structures in the polymer chain (for example, 10-mer of $Co(tpy)_2$ plus 5-mer of $Fe(tpy)_2$).

The "redox polymer" is one of the representative electron-conducting substances,[1] which can be useful for the creation of the electronic devices.[2] Redox polymer films on electrodes have been fabricated using chemical modification, electrochemical polymerization, polymer coating, and so on.[3] Recently, a stepwise complexation method has been employed to fabricate multiple complex layers.[4] In the present study, we have succeeded in the stepwise preparation of bis(tpy)cobalt polymer chains for the first time by combining tpy ligand SAM formation and metal–tpy coordination reactions with a redox change between Co(II) and Co(III). Heterometal-polymer films composed of a designed sequence of bis(tpy)iron and bis(tpy)cobalt complex moieties linked by π-conjugated azobenzene spacers[5] could be also fabricated using the stepwise complexation method and their redox behavior reflecting the heterostructure was observed.

A typical fabrication method of multiple complex layers is as follows. First, Au–S–AB–tpy SAM was prepared by immersing an Au/mica or Au/ITO plate in a chloroform solution of 0.1 mmol dm^{-3} tpy–AB–SS–AB–tpy for 5 min (Figure 1). Then, the plate was rinsed with chloroform and dried with a nitrogen blow. In the case of connecting Fe(II) ion, the tpy-terminated surface was immersed in 0.1 mol dm^{-3} $Fe(BF_4)_2$ aq or $(NH_4)_2Fe(SO_4)_2$ aq for 3 h, rinsed with water, and dried with a nitrogen blow. The bis(tpy)iron structure was prepared by immersing the film with the metal-terminated surface in a chloroform solution of 0.1 mmol dm^{-3} tpy–AB–tpy for 3 h, followed by rinsing with chloroform and dried. The latter two processes were repeated for the preparation of multilayered (namely, polymeric) bis(tpy)iron(II) complex films.

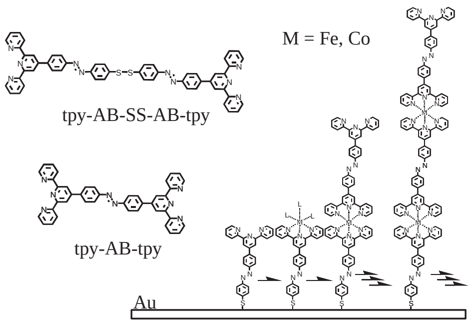

Figure 1. Stepwise fabrication of bis(tpy)metal complex layers on Au.

In contrast, only a combination of immersion in $CoCl_2$ aq and immersion in a chloroform solution of tpy–AB–tpy on the Au–S–AB–tpy SAM was not sufficient for accumulating bis(tpy)cobalt complex units. Similar results have been reported by Abruña et al.,[4b] while the formation constant, k_f of Co(II) ion and tpy in an aqueous solution is high.[6] We then added a process of electrochemical oxidation from Co(II) to Co(III) because the k_f of the d^6 Co(III) ion should be higher than that of the d^7 Co(II) ion (that is, a combination of (a) immersion in $CoCl_2$ aq for 0.5 h, (b) immersion in a chloroform solution of tpy–AB–tpy for 0.5 h, and (c) the plate was held at 0.3 V (vs Ag/Ag$^+$) for 1 min), and succeeded in the construction of multilayered bis(tpy)cobalt complex films.

The stepwise quantitative film formation was confirmed by UV–vis spectra and cyclic voltammetry (CV). In the UV–vis spectrum of the bis(tpy)iron complex film, absorbance of the peak at 592 nm ascribed to the MLCT transition increased line-

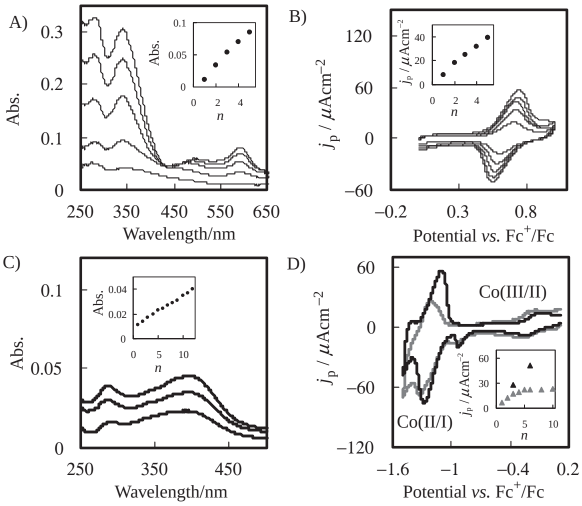

Figure 2. A) Absorption spectra of [***n*Fe**] (n = 1–5), and the plots of absorbance at 592 nm vs the number of complex layers, n (inset). B) CVs of [***n*Fe**] (n = 2, 4, 6, 8, and 10) at 0.1 Vs^{-1}, and the plots of the peak current density, j_p vs n (inset). C) Absorption spectra of [***n*Co**] (n = 5, 10, and 15), and the plots of absorbance at 394 nm vs n (inset). D) CVs of [**3Co**] (gray) and [**6Co**] (black) at 0.1 Vs^{-1}, and inset shows the plots of j_p vs n (gray triangle is Co^{III}/Co^{II}, and black triangle is Co^{II}/Co^{I}).

arly with the number of stepwise complexations, *n* (Figure 2A). In CV, a reversible peak of the Fe^{III}/Fe^{II} couple appeared at 0.67 V vs ferrocenium/ferrocene (Fc^+/Fc) in Bu_4NClO_4–CH_2Cl_2. The peak current density, j_p, was proportional to the scan rate, indicative of a surface-confined species. The anodic charge integration under the voltammetric wave at the sweep rate of $0.1\,Vs^{-1}$ yields $\Gamma_{Fe1,CV} = 1.4 \times 10^{-10}\,mol\,cm^{-2}$, approximately coincident with the maximum surface coverage based on the complex cation size ($1.0\,nm^2$ per a molecule). The peak current density, j_p, increases proportionally with *n*, indicating a linear increase of the coverage of electroactive species (Figure 2B). It should be emphasized that the linear increase of the coverage with *n* confirmed by UV and CV measurements indicates a perfect complexation on the terminal bridging ligands in every step.

UV–vis spectra of the bis(tpy)cobalt(III) complex film also exhibited a linear increase in absorbance of the bands with increase in *n* (Figure 2C). In CV, j_p for the Co^{II}/Co^{I} couple (−1.18 V vs Fc^+/Fc) increases linearly with increased in *n* (and $\Gamma_{Co1,CV} = 1.4 \times 10^{-10}\,mol\,cm^{-2}$), but j_p for the Co^{III}/Co^{II} couple (−0.17 V vs Fc^+/Fc) becomes much clearly bent over at the higher numbers (see Figure 2D), which deformation can be principally attributed to the greatly slower electron self-exchange rate for Co^{III}/Co^{II} relative to that for Co^{II}/Co^{I}.[7] The cathodic peak appearing at −1.0 V can be ascribed to charge trapping.[8]

The morphologies of the films were observed with STM and SEM measurements. A nearly closed packing of 6 nm-o.d. circular domains, indicating the stacking of molecular chains, and a formation of fairly smooth surface (apparent roughness of the film is within 1 nm, which is less than the length of one complex unit, 2 nm) are observed in the STM image of the bis(tpy)iron complex film with 2 iron complex layers, which is abbreviated as [**2Fe**], as shown in Figure 3A. The SEM photograph of [**47Co**], shown in Figure 3B, indicates the growth of the film to a thickness of 100 nm on Au in the side-view image. The thickness is nicely consistent with the product of the number of layers, 47, times the molecular unit length, 2 nm.

One merit of this polymer preparation method is that it allows creation of heterometal polymer chains with an intended sequence.[9] A stepwise formation of a heterometal double layer film [**1Co1Fe**] was monitored by CV during film construction (Figure 4a). When the bis(tpy)iron complex units were connected to the initially prepared bis(tpy)cobalt complex layer, the redox activity of the Fe^{III}/Fe^{II} couple appeared without changing of the redox activity of the Co^{III}/Co^{II} couple. The result that the surface coverage of the bis(tpy)iron complex units estimated from the CV, $\Gamma_{Fe} = 1.4 \times 10^{-10}\,mol\,cm^{-2}$, was equal to that of bis(tpy)cobalt complex units ($\Gamma_{Co} = 1.4 \times 10^{-10}\,mol\,cm^{-2}$) indicates that each bis(tpy)cobalt unit is connected to one bis(tpy)iron complex unit and that there is no other sequences of the units in the film. The CV of heterostructured polymer films made of polymer chains composed of [**10Co5Fe**] is shown in Figure 4B. The peak current for Co^{II}/Co^{I} was larger than that of Co^{III}/Co^{II} because of the difference in electron self- exchange rate constant values, as noted above. Also, the redox wave of Fe^{III}/Fe^{II} was less than two-thirds the size of the Co^{II}/Co^{I} redox wave owing to the existence of a cobalt complex sequence between the electrodes, which acts as a barrier to electron transfer of the Fe complex even though Fe^{III}/Fe^{II} is a fast electron-exchange couple. However, the retardation is very small, given that the barrier layer thickness is large (21 nm). This should be due to the fast electron transport ability of inner π-conjugated Co(tpy) polymer chain.

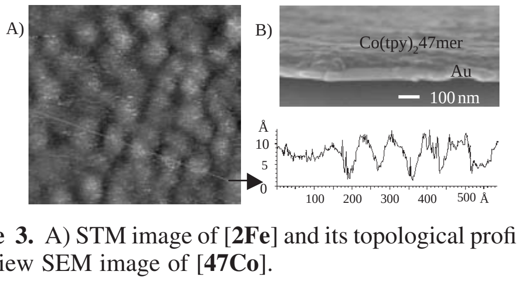

Figure 3. A) STM image of [**2Fe**] and its topological profile. B) Side view SEM image of [**47Co**].

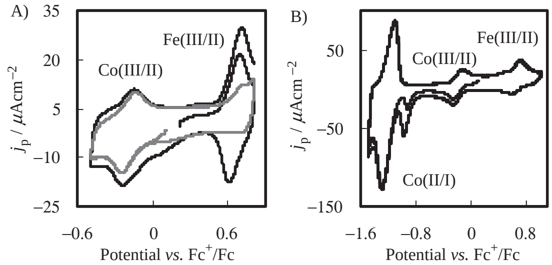

Figure 4. CVs of [**1Co**] (gray) and [**1Co1Fe**] (black) (A), and [**10Co5Fe**] (B) on gold at $0.1\,Vs^{-1}$.

The results obtained indicate that the quantitative formation of heterostructured film can be achieved at the surface by selecting the conditions of stepwise complexation reactions. The surface bottom-up method will give a new strategy for the molecular design of electronically functional molecular chains suitable for development of "molecular electronic devices".

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