

### Bottom-up Fabrication of Bis(terpyridine)metal Polymer Chains and Their Electrochemical Properties

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The ability of molecular chain for assisting the long-range electron transfer is nowadays one of the most important issues to understand the fundamental quantum physics of electron transfer and also to design molecular electronic devices. In the present study, we developed a facile interfacial bottom-up method to fabricate rigid redox polymer chain with the desired number of complex units combined with  $\pi$ -conjugated linkers and with a designed hetero-metal sequence at the surface.

Our method of fabricating redox polymer assembly is a combination of 2,2':6',2''-terpyridine (tpy) ligand SAM formation and stepwise metal-tpy coordination reactions. The polypyridine-metal complexes known for various transition metals show interesting redox, optical, and magnetic properties depending on the metal. Here we fabricated homo-polymer films composed of bis(tpy)iron(II) or bis(tpy)cobalt(III), and hetero-polymer films composed of a designed sequence of bis(tpy)iron(II) and bis(tpy)cobalt(III).

At first, Au-S-AB-tpy SAM was prepared by immersing Au/mica or Au/ITO plate in a chloroform solution of tpy-AB-SS-AB-tpy. Then, in the case of connecting a bis(tpy)iron(II) complex unit, the tpy-terminated surface was immersed in  $\text{Fe}(\text{BF}_4)_2$  aq or  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$  aq, followed by immersion in a chloroform solution of tpy-AB-tpy. These two processes were repeated for the preparation of multi-layered (namely, polymeric) films of the bis(tpy)iron(II) complex. On the other hand, in the case of connecting a bis(tpy)cobalt(III) complex unit, the tpy-terminated substrate was immersed in  $\text{CoCl}_2$  aq and immersed in a chloroform solution of tpy-AB-tpy; the substrate was then held at +0.3 V vs.  $\text{Ag}^+/\text{Ag}$  for a minute to oxidize  $\text{Co}^{\text{II}}$  to  $\text{Co}^{\text{III}}$ . Repeating the three processes afforded a multi-layered film.

Figure 1 shows the CV of one example of such hetero-structured polymer films made of polymer chains composed of 10 bis(tpy)cobalt units plus 5 bis(tpy)iron units, [**10Co5Fe**]. The peak current for  $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$  is larger than that of  $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$  due to the difference in electron self-exchange rate constant values, as noted above, and also the redox wave of  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  is smaller than two-thirds of the  $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$  redox wave because of the existence of a cobalt complex sequence between the electrodes, which acts as a barrier to electron transfer of

the Fe complex, even though  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  is a fast electron-exchange couple. However, it is surprising that the retardation is very small with considering that the barrier layer thickness is large, 20 nm. We will report details of mono and hetero polymer preparation methods and their electrochemical properties.

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Scheme 1. Bottom-up fabrication of bis(terpyridine)metal polymer chain.

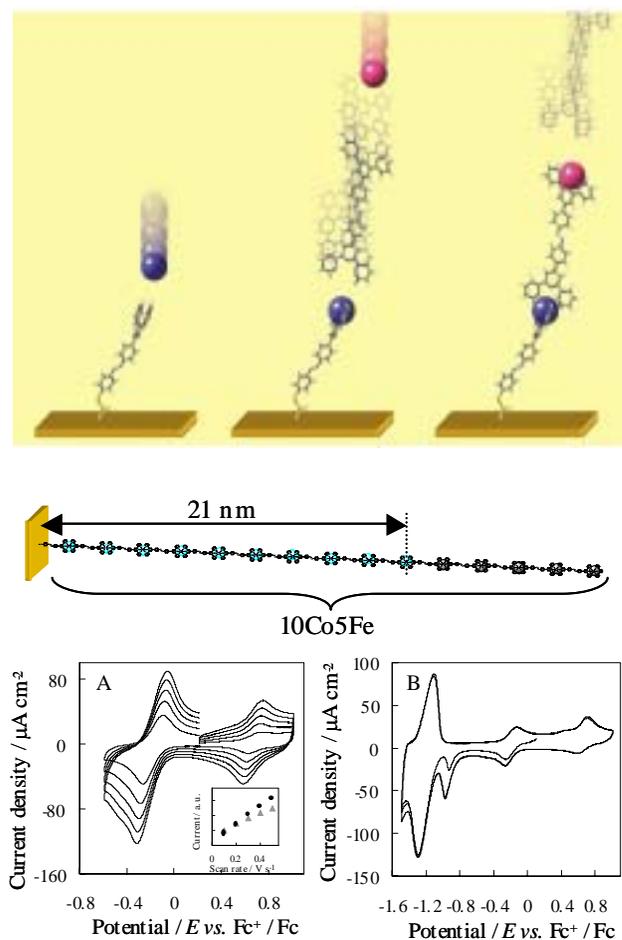


Figure 1. Cyclic voltammograms of **10Co5Fe** in 0.1 M  $\text{Bu}_4\text{NClO}_4\text{-CH}_2\text{Cl}_2$ . A) Scan rates were 0.1-0.5  $\text{Vs}^{-1}$ . The inset shows plots for the peak current vs. the scan rate for  $[\text{Fe}(\text{tpy})_2]^{\text{n}+}$  (black dot), and  $[\text{Co}(\text{tpy})_2]^{\text{n}+}$  (gray triangle). B) The scan rate was 0.1  $\text{Vs}^{-1}$ .