

## 論文の内容の要旨

# Electrochemical Syntheses of Redox Complex Networks and Ultra-long Wires Covalently Bound to Carbon

(炭素電極に共有結合したレドックス錯体ネットワーク・極長ワイヤの電気化学合成)

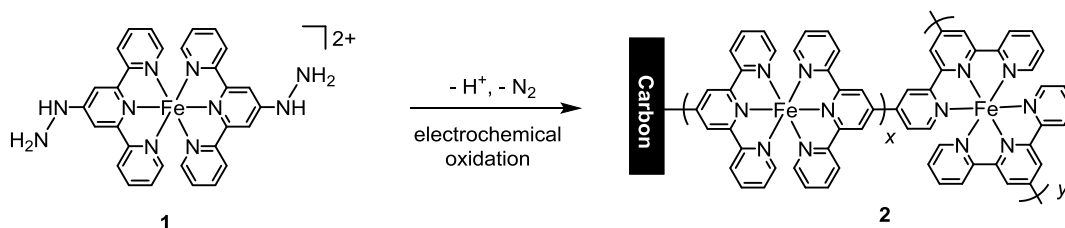
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### Introduction

Efficient synthesis and control of nano-structures of metal complex polymers, such as networks and wires, is highly desirable for molecular engineering and many other applications. Metal complex polymers attract much attention not only because of their resulting unique properties, but also due to advantages in their ease of synthesis and modification. They can be readily prepared under moderate coordination reaction conditions by mixing bridging ligands and metallic species together. These polymers can also be synthesized through organic coupling reactions or condensation reactions of metal complex monomers with active functional groups. In this way, by simply modifying the ligands or changing the metal species or their valences, the structures and properties of such complex polymers can be drastically altered. In my research, efficient construction methods and applications of bis(terpyridine)metal complex networks and extremely long wires are focused on.

### Results and Discussion

#### Bis(terpyridine)iron complex networks



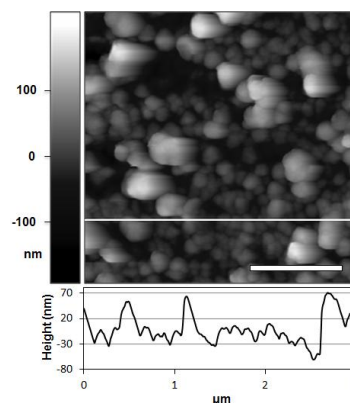
**Scheme 1.** A synthetic route of bis(terpyridine)iron networks

Bis(terpyridine)iron complex network **2** is fabricated from bis(4'-hydrazinyl-2,2':6',2''-terpyridine)iron complexes, **1** (**Scheme 1**). When this complex is subjected to an oxidation potential or reacted with a superoxide anion, one of the aryl hydrazine groups will convert to an aryl free-radical through a diazonium intermediate. The aryl free-radical will attack the carbon electrode and complex **1** to start the immobilizing process and form the network complex **2** respectively.

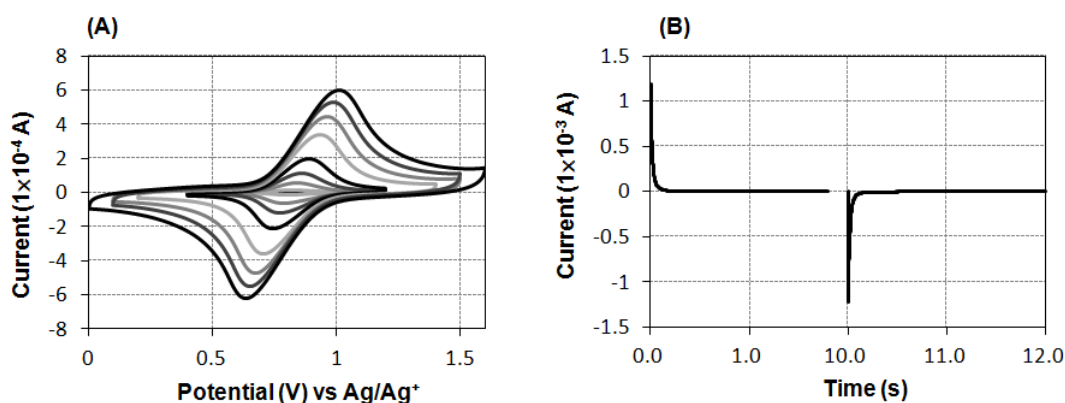
The chemical structure of the complex network **2** is complicated because of the free radical reaction. According to the reaction mechanism, the complex monomer can undergo a free radical coupling reaction to form a linear elongation connection and also free radical addition reactions to generate branch and cross-link structures. Therefore, the resulting complex polymer is a random network complex with C-C bond connections between terpyridine ligand. This random structure also can be proved by AFM measurement (**Figure 1**). In the image, the surface of the modified electrode shows irregular spherical polymer particle structures.

To evaluate the performance of this network complex for energy storage, an approximately 21-layer-thick network of **2** was used. From the cyclic voltammogram, when the scan rate increased from  $0.01 \text{ Vs}^{-1}$  to  $10 \text{ Vs}^{-1}$ , there was only moderate peak broadening and separation, and the charging and discharging capacity showed a slight 24% decrease (**Figure 2A**). This indicates that the film possesses a well porous structure for electrolyte penetration and the network has excellent electronic conductivity. The specific capacity deduced from chronocoulometry could reach  $55.5 \text{ mAh g}^{-1}$  when a 1 V potential step was used. Moreover, from chronoamperometry, this material could be charged 80% in 0.08 s, 90% in 0.16 s and 95% in 0.35 s; and discharged 80% in 0.08 s, 90% in 0.16 s and 95% in 0.62s (**Figure 2B**). Further analysis showed that 80% of its capacity was retained at a discharge rate of  $280 \text{ A g}^{-1}$ , 90% at  $60 \text{ A g}^{-1}$ , and 95% at  $7.6 \text{ A g}^{-1}$ . In a stability test, after 3000 cycles of charging and discharging, this material showed only 5% capacity decay.

It was also established that this network complex could be immobilized easily on a carbon nanotube electrode, a highly specific surface area electrode, with the same process. The resulting electrode also showed high power density and high durability. This hybridized material could be a promising electrode for supercapacitors.

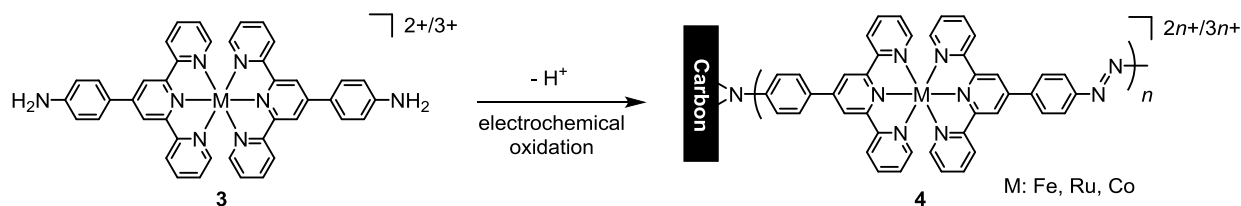


**Figure 1.** An AFM topological image of complex network **3**; scale bar:  $1 \mu\text{m}$ .



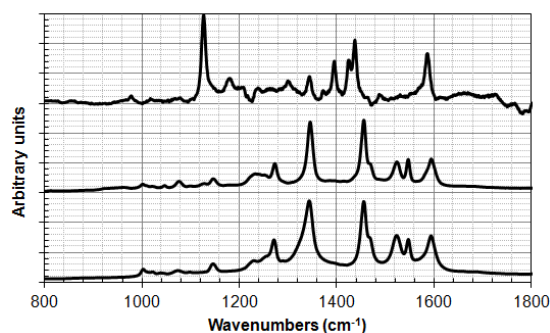
**Figure 2.** Electrochemical measurements: (A) cyclic voltammograms of **4** scanning from  $0.01 \text{ Vs}^{-1}$  to  $10 \text{ Vs}^{-1}$  and (B) a chronoamperogram of **4** at the potential difference of 0.4 V.

## Extremely long molecular wires



**Scheme 2.** A synthetic route of extremely long bis(terpyridine)metal complex wires

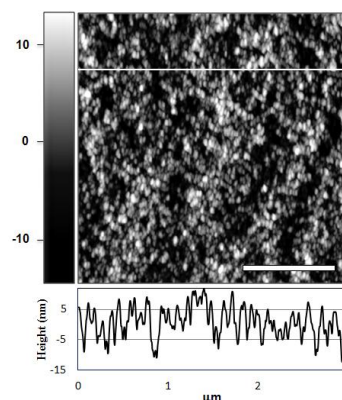
A series of bis(terpyridine) metal complex wires were prepared by an electrochemical coupling reaction (**Scheme 2**). These wires are synthesized from bis(4'-(4-aminophenyl)-2,2':6',2''-terpyridine)metal complexes, **3**. Under oxidation conditions, one of the terminal amino groups of the complex will become an amino free radical. This radical can, in turn, attack the carbon electrode surface to form a covalent linkage and then immobilize the complex on it. After anchoring on the electrode, the other amino group of the same complex will also be oxidized to generate an immobilized amino free radical. It will then react with an amino group of other complexes to form an azobenzene bridge to connect these two complexes and elongate the molecular wire. Finally, a molecular wire array of even length will form on the electrode surface.



**Figure 3.** Raman spectra of (A) tpy-Ph-N=N-Ph-tpy, **5**, (B) [(tpy-Ph-N=N-Ph-tpy)Fe(BF<sub>4</sub>)<sub>2</sub>]<sub>n</sub>, **6**, (C) molecular wire **4-Fe**

The chemical structure of the extremely long molecular wire was analyzed by Raman spectroscopy (**Figure 3**). As reference, free bridging ligand tpy-Ph-N=N-Ph-tpy, **5**, and a random length wire, **6**, prepared by mixing **5** directly with Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in acetonitrile, were used. The characteristic signals of azobenzene, the bridging part of the wires, in the Raman spectra are aryl-N stretching, around 1140 cm<sup>-1</sup>, and trans N=N stretching, 1380 to 1460 cm<sup>-1</sup>. In the spectrum of bridging ligand **5**, these two typical stretching can be found as strong scatterings at 1126 and 1437 cm<sup>-1</sup> (**Figure 3A**). In random length wire **6** and electrochemically synthesized **4-Fe**, the aryl-N stretching signals are much weaker at 1145 cm<sup>-1</sup>, which might be because of the restriction of the neighboring units (**Figure 3B&C**). However, the trans N=N stretching signals show strong scattering at 1455 cm<sup>-1</sup>. From these two almost identical spectra, it can be inferred that **4-Fe** also has a linear bis(terpyridine)iron complex wire structure with azobenzene bridge, [(tpy-Ph-N=N-Ph-tpy)FeX<sub>2</sub>]<sub>n</sub>.

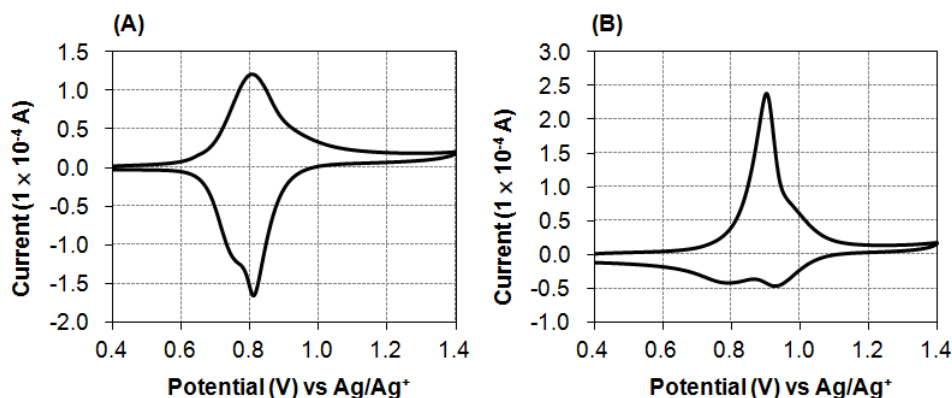
The nano structure of **4-Fe** was investigated by AFM (**Figure 4**). The AFM image shows that the electrode surface is covered by an array of upright standing peaks with only around 5 nm height differences. However, the widths of these peaks are around 30 to 40 nm which are larger than that of a signal wire. One possible reason is that some wires are much closer to each other to form a bundle-like structure. Another reason could be that the width of AFM tip is much wider than the space between wires. Therefore, the real width and also length of the wires cannot be observed directly from this measurement. However, from electrochemical methods, the real length of the molecular wires can be evaluated from the surface coverage of bis(terpyridine)iron complex. The longest wires could reach 7410 units,



**Figure 4.** An AFM topological image of molecular wire **4-Fe**; scale bar: 1 μm.

around 15  $\mu\text{m}$  by this synthetic method.

With this efficient method, complex wires of other metal ions and hetero metal species also can be prepared easily (**Scheme 2**). These hetero metal complex wires showed an interesting diode property, which is very different from single metal species wires (**Figure 5**).



**Figure 5.** Cyclic voltammograms of (A) electrode-(4-Fe)-(4-Ru) (B) electrode-(4-Ru)-(4-Fe)

## Conclusion

In this research, a highly efficient electrochemical method was utilized to fabricate complex networks on carbon electrode surface. This complex network can offer very high power output with minor capacity loss and has very good durability for charging and discharging processes. These results show the potential of this novel material to be a supercapacitor electrode material of high performance. A similar, electrochemical method also was used to synthesize and ultra-long uniform linear molecular wires. This elegant method can not only offer simple single metal species complex wires, but can also provide unique long hetero metal wires. These promising results demonstrate the possibility of applying these electrochemical methods in molecular engineering.