

# 論文内容の要旨

論文題目 Preparation of  $\pi$ -Conjugated Metal Complex Wires

by Stepwise Coordination Method on Gold Surface

and Their Electron Conduction Phenomena

(金表面上での逐次的錯形成反応を用いた  $\pi$  共役金属錯体ワイヤーの作製と  
電子伝導現象)

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## Introduction

Fabrication of molecular wire and the electron transfer property through the molecular wire are important in chemical and biological processes and future application for molecular electronics. We have reported redox active bis(terpyridine)metal complex wires prepared by the stepwise coordination method with a surface-attaching ligand containing thiol and terpyridine moieties and an azobenzene-bridged bisterpyridine ligand and iron or cobalt ion as metal center of the terpyridine complex. In this thesis, general utility of the stepwise coordination method and electrochemical properties of the complex wires prepared by this method are described.

## Procedure of the stepwise coordination method

The preparation of bis(terpyridine)iron,  $\text{Fe}(\text{tpy})_2$ , complex wires was carried out as follows (Figure 1). Flame-annealed Au(111)/mica electrode was immersed in a chloroform solution of a surface-attaching ligand ( $(\text{A})_2$ ,  $(\text{A}_\text{H})_2$  or  $(\text{A}_\text{F})_2$ ). The electrode was subsequently immersed in  $\text{Fe}(\text{BF}_4)_2$  aq, followed by immersion in a chloroform solution of bridging ligand ( $\text{L}_1$ ,  $\text{L}_2$  or  $\text{L}_\text{F}$ ) to make a film with a length of a single complexation cycle. These two processes were repeated stepwisely to grow films of multi-complexation cycles (described in Chapter 2). Preparation of  $\text{Fe}(\text{tpy})_2$  complex wires with redox active terminal was accomplished by further immersion process. The gold electrode modified with desired number of complex cycles was soaked in  $\text{Fe}(\text{BF}_4)_2$  aq and then in a solution of terminal ligand ( $\text{T}_\text{Fc}$ ,  $\text{T}_\text{HRu}$  or  $\text{T}_\text{FRu}$ ) to fix a redox active terminal of the molecular wire (described in Chapters 3 and 4).  $\text{Co}(\text{tpy})_2$  complex wires with  $\text{Fe}(\text{tpy})_2$  as the terminal redox active moiety with  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$  and  $\text{L}_1$  were also prepared in the manner similar to that of ferrocene-terminated  $\text{Fe}(\text{tpy})_2$  complex wires noted above (described in Chapter 3).

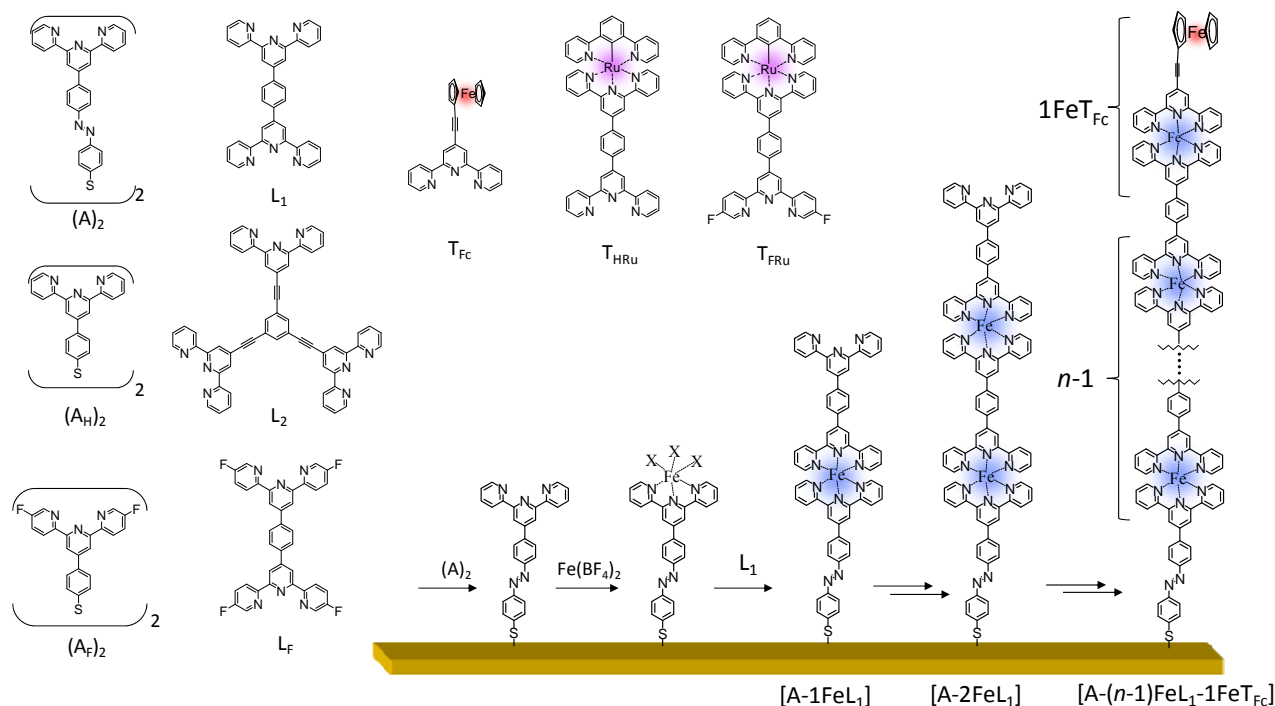


Figure 1 Procedure of stepwise coordination method and chemical structures of ligands used in this thesis.

## Synthesis of linear and dendritic bis(terpyridine)iron complex wires by the surface bottom-up method and the electron transfer mechanism (Chapter 2)

Establishment of the fabrication techniques of desired molecular architectures is one of the important topics for the molecular device. Accomplishment of the structure control of the wire is very significant to realize elaborate molecular interconnection such as a multiarmed wire which is needed for future application of complex wires.

Stepwise preparation of linear (with  $L_1$ ) and dendritic (with  $L_2$ ) metal complex wires on gold electrode has been succeeded by the bottom-up method as shown in Figure 1, according to the contact angle measurement, STM measurement, and estimation of surface coverage from the redox peak area of cyclic voltammogram (Figure 2). Owing to the highly organized structures, we observed unique  $i-t$  characteristics by potential step chronoamperometry (PSCA). Such structures have not been reported previously for redox polymers with a low ordering of molecular wires. These  $i-t$  characteristics of both linear and branched redox-oligomer wires could be interpreted by a mechanism for through-bond electron transport by using two kinetic factors:  $k_1$  ( $s^{-1}$ ), for the electron transfer between the nearest redox site and the electrode, and  $k_2$  ( $cm^2 mol^{-1} s^{-1}$ ), for the electron transfer between neighboring redox sites in a molecular wire (Figure 3).

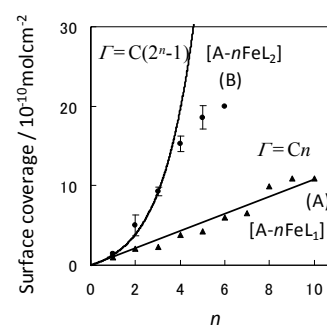


Figure 2 Plots of the surface coverage of redox-active sites,  $\Gamma$ , versus  $n$ , for  $[A-nFeL_1]$  (A),  $[A-nFeL_2]$  (B). The lines denote the relationships  $\Gamma = C \times n$  for A,  $\Gamma = C \times (2^n - 1)$  for B.

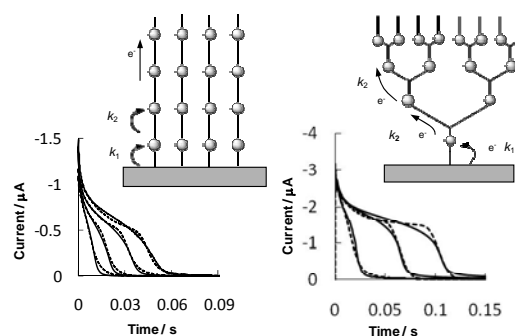


Figure 3 Schematic illustration of the electron transfer mechanism and the analyses of chronoamperograms.

### Long-range electron transfer through a $\pi$ -conjugated bis(terpyridine)metal complex wire (Chapter 3)

Recently, many studies have been carried out regarding the electron transport ability of molecular wires such as alkyl chain,  $\pi$ -conjugated polymers, DNA, and polypeptide. The long-range electron transfer is important for many future applications in solar energy harvesting and molecular electronic devices. Electron portability of a molecular wire can be evaluated with the attenuation factor,  $\beta$ , which is expressed in eq. 1,

$$k = k^0 \exp\{-\beta(d-d_0)\} \quad (1)$$

where  $k$  denotes the electron transfer rate constant when the distance between donor and acceptor units is  $d$  (Å), and  $k^0$  ( $s^{-1}$ ) is the rate constant when the donor and acceptor units are in the closest distance  $d_0$ . The value of  $\beta$  can be obtained for many kinds of molecular chains, but little has been known about redox metal complex polymer chains.

Figure 4 shows the cyclic voltammograms of [A-1FeT<sub>Fe</sub>] and [A-2FeL<sub>1</sub>-1FeT<sub>Fe</sub>]. The current peak around 0.1 V (vs. ferrocenium/ferrocene (Fc<sup>+</sup>/Fc)) is assigned to the terminal ferrocene moiety of the wires. The other peak around 0.7 V (vs. Fc<sup>+</sup>/Fc) originates from redox reaction of Fe<sup>III</sup>(tpy)<sub>2</sub>/Fe<sup>II</sup>(tpy)<sub>2</sub>. The ratio of the surface coverage of Fc to Fe(tpy)<sub>2</sub> should be 1:1 for a film with  $n = 1$  and 1:3 for a film with  $n = 3$ . The surface coverage  $\Gamma$  was estimated from the anodic current area of cyclic voltammogram;  $\Gamma_{\text{Fc}}$  and  $\Gamma_{\text{Fe(tpy)}_2}$  were  $1.5 \times 10^{-10}$  and  $1.7 \times 10^{-10}$  molcm<sup>-2</sup>, respectively, for  $n = 1$ , and  $1.4 \times 10^{-10}$  and  $3.9 \times 10^{-10}$  molcm<sup>-2</sup>, respectively, for  $n = 3$ . Surface coverages for the wires with a ruthenium complex terminal were similar to that of ferrocene-terminated wires. Results of IRRAS spectra for [A-1FeT<sub>Fe</sub>], [A-2FeL<sub>1</sub>-1FeT<sub>Fe</sub>], and [A-4FeL<sub>1</sub>-1FeT<sub>Fe</sub>] also indicated that the molecular wires were successfully prepared with the desired conformation on gold surface.

The attenuation factor  $\beta$  was estimated by investigating the rate of electron transfer between gold electrode to the redox active terminal moiety through the complex wires with varying the number of bis(terpyridine)metal complex units within a molecular wire. The electron transfer rate constant was directly measured from the slope of  $\ln i - t$  plots of PSCA. The electron transfer rate constant values of the terminal ferrocene moiety through Fe(tpy)<sub>2</sub> complex wires [A-( $n-1$ )FeL<sub>1</sub>-1FeT<sub>Fe</sub>] are shown in Figure 5(A). From the results, the attenuation factor  $\beta$  was calculated at  $0.015 \pm 0.007$  (Figure 5(B)).

This value is considerably smaller compared with the  $\beta$  values of other molecular wire systems previously reported. Consequently, the above results strongly indicate that the complex wire has a distinguished long range electron portability. In addition, the dependences

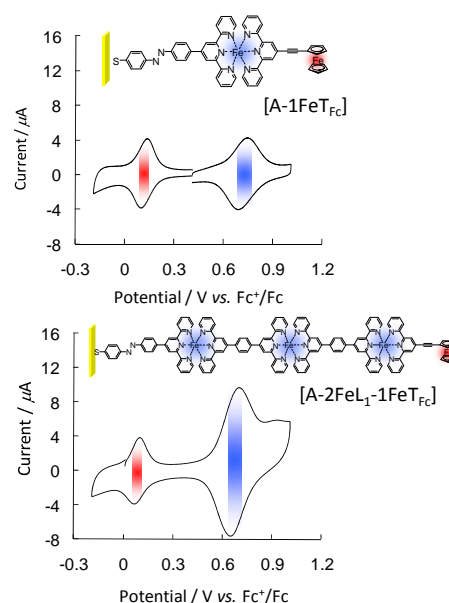


Figure 4 Cyclic voltammograms of [A-1FeT<sub>Fe</sub>] (A) and [A-2FeL<sub>1</sub>-1FeT<sub>Fe</sub>] (B) in 0.1 M Bu<sub>4</sub>N-ClO<sub>4</sub>-CH<sub>2</sub>Cl<sub>2</sub>.

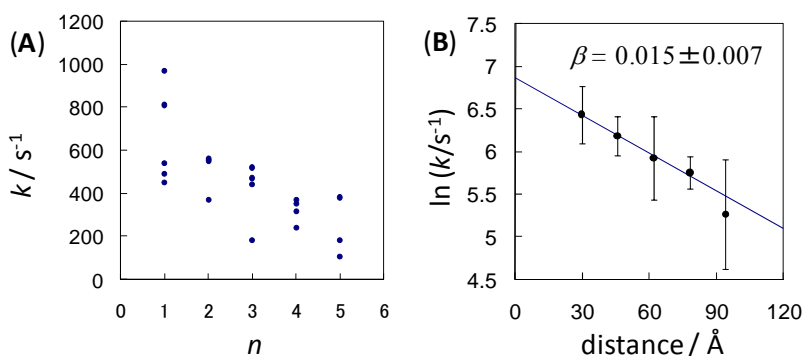


Figure 5 Plots of  $k$  versus  $n$  (A) and  $\ln k$  versus distance (B) for [A-( $n-1$ )FeL<sub>1</sub>-1FeT<sub>Fe</sub>].

of  $\beta$  on the measurement condition, surface-attaching ligand, terminal redox active moiety, bridging moiety of ligand, potential of complex within the wire, and metal center of the metal complex wires were investigated. These results revealed that the value of  $\beta$  was an intrinsic parameter of the composition of the metal complex wire and controllable by bridging moiety and metal center of the complex wire. The  $\beta$  value of  $\text{Fe}(\text{tpy})_2$ -terminated  $\text{Co}(\text{tpy})_2$  complex wire was estimated at  $0.004 \pm 0.002$  which is smaller than that of  $\text{Fe}(\text{tpy})_2$  wire. Therefore, the  $\text{Co}(\text{tpy})_2$  complex wire has a higher long range electron portability compared with the  $\text{Fe}(\text{tpy})_2$  complex wire.

#### **Trials of highly functional metal complex wires (Chapter 4)**

In Chapter 4, I tried to build highly functional systems by exploiting hetero-metals, hetero-ligands, and a three-way ligand to bring out novel functions in the molecular assembly.

Electron transfer behaviors of ferrocene-terminated hetero-metal complex wires,  $[\text{A}-1\text{FeL}_1-1\text{CoL}_1-\text{T}_{\text{Fc}}]$  and  $[\text{A}-1\text{CoL}_1-1\text{FeL}_1-\text{T}_{\text{Fc}}]$  showed that the interesting insight that the long-range electron transfer ability of the complex wires can be controlled with the sequence of the metal ions within the complex wire. The fact indicates that hetero-metal alignment within metal complex wires has a potential to fabricate complex wires with a wide variety of properties by using many kinds of metal ions.

Potential staircase of complexes within the wire was introduced by hetero-ligand fabrication of the complex wires with  $L_1$  and fluorinated ligand  $L_F$  by taking an advantage of electron-withdrawing effect of fluorine. Although the wires with potential staircase are anticipated to exhibit rectification behavior, they did not have any rectification property. However, the wires with the terminal ruthenium moiety have superior long-range electron portability compared with the homo-ligand wires.

The dependence of long-range electron transportability on the structure of the complex wire was investigated. Dendritic complex wires with the terminal ruthenium complex,  $[\text{A}_H-(n-1)\text{FeL}_2-1\text{FeT}_{\text{HRu}}]$  can be prepared on surface by the stepwise coordination method using a branched ligand,  $L_2$ . The electrochemical behavior of the ruthenium complex through the dendritic complex wire was investigated. The results revealed that the dendritic complex wire had a rectification property that can flow electron from the electrode to the complex wire faster compared with the flow in the inverse direction (Figure 6).

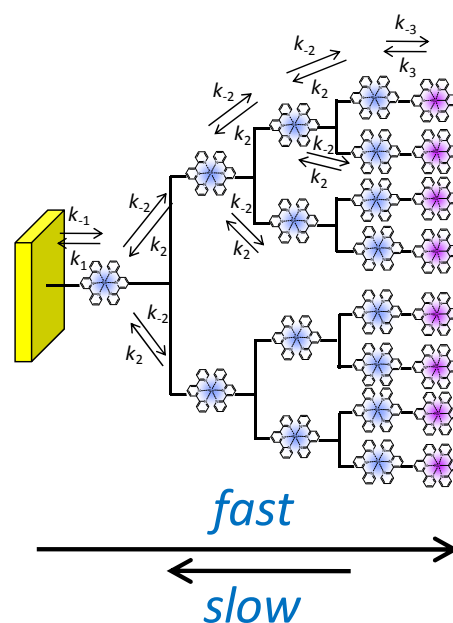


Figure 6 Schematic illustration of rectification property through the dendritic complex.

#### **Conclusion**

The results of the thesis show the excellent properties of  $\pi$ -conjugated metal complex wire, conductivity, intra-system electron transfer, easily controllable length and structure. In addition, the insights into the correlation between electrochemical property and hetero-metal, potential structure within the wire, and structure of wire would serve as a guidance of developing highly functionalized molecular wires.