Bottom-up Fabrication of Polymer-coated Electrodes and Through-bond Redox Conduction

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This article reviews recent studies on preparation of layer-by-layer assembled multilayers by stepwise chemical bond formation on the surface. Coordination reactions are useful to synthesize oligomeric and polymeric molecular wires with the desired number of complex units and with the desired physical structures. Regarding the electrode films of redox molecular wires of bis(terpyridine)metal complex oligomers we have prepared, its electrochemical analysis reveals that these redox films with ordered molecular wire structures showed through-bond redox conduction behaviors.

Key Words: Coordination, Self-assembled Monolayer, Molecular Wire, Redox Conduction, Oligomer

1 Introduction

“Modified electrode” is one of the most epoch-making topics in electrochemistry in three decades. Several methods have been developed to modify the electrode surface; for example, Langmuir-Blodgett films, polymer film deposition, electropolymerization, and self-assembled monolayers (SAMs). Especially, SAMs on metal or oxide substrates have attracted the attention of many scientists for their ability to form ordered organic films with well-defined compositions and thicknesses in recent years, because they are potentially adaptable building blocks for the development of advanced materials such as molecular electronic devices and sensors. SAMs can be prepared simply by immersing a substrate into a solution of the surface-active material, where the driving force of the spontaneous formation of the 2D assembly consists of chemical bond formation of molecules with the surfaces and intermolecular interactions. In particular, the self-assembly of organosulfur compounds on gold surface has been extensively studied because thiol molecules are linked to a gold electrode surface by a strong S-Au bond (167 kJ mol⁻¹).

Most of the SAMs that have previously been studied are in fact “monolayers”. Recently, methods to use SAMs as the starting material for construction of multiple layers have been developed. Coordination chemistry providing a flexible method for creating organic-inorganic assemblies by incorporating metal ions with desirable electrical, magnetic, or optoelectric properties and organic ligands is useful for this purpose. Monolayer films with a reactive terminal group have been extended into coordination polymers or supramolecular structures through covalent chemical reactions using layer-by-layer nanostructural growth. If the films thus prepared are redox polymer films, with the redox sites being aligned along the polymer chain, it may be possible to see unidirectional electron transfer phenomena along the polymer chain; in conventional polymer-coated electrodes, however, redox sites are randomly distributed in most of the films (Fig. 1). Therefore, such ordered structures are a new type of modified electrode and they would be of great interest in the investigation of fundamental aspects of charge-transfer processes. This article describes recent progress in such bottom-up fabrication of multi-layer films on solid surface, and the structures and electrochemical properties of the films.

2 Methods to Construct Multi-layer Films

The concept of a fabrication method to construct multi-layer films utilizing combining of the preparation of self-assembled monolayers and stepwise polymerization reactions of molecular wires on the surface is shown in Fig. 2. Three molecular elements are employed; one is a molecule to anchor a molecular linker at the surface (Fig. 2, A) and the others are two types of bridging molecular linkers which can connect each other (Fig. 2, B and C). When we use the coordination reaction, first, the molecular linker, i.e., ligand, is attached to the surface using a regular SAM preparation technique, after which a metal ion is connected to the ligand. Then, using a bridging...
ligand with more than one coordinating moieties, metal complex wires terminated with coordination moieties are constructed. By repeating the connection of metal ions and bridging ligands, polymer wires with a desired number of metal complex units can be synthesized. One important advantage of this method is an easy preparation of hetero-metal and hetero-ligand complex polymer wires by putting different kinds of metal ions and different kinds of bridging ligands at the desired positions, which can lead to an accumulation of multiple molecular functionalities.

Abe et al. have reported the layer-by-layer deposition of triangular ruthenium cluster complex multilayers on gold controlled by an electrochemical method (Fig. 3). In the triruthenium cluster complex, I, a CO group is eliminated to be smoothly replaced by H2O when the complex in the Ru11Ru11Ru11 state is oxidized to Ru11Ru11Ru111, to which 4,4’-bipyridine-attached triruthenium complex in the Ru11Ru11Ru11 state is newly bound. Cyclic voltammetry (CV) of the redox reaction for CO-bound triruthenium complex moiety and the H2O-bound triruthenium complex moiety are apparently different (0.7 V gap), and the stepwise and almost quantitative deposition could be monitored by estimation of the amount of redox active species on the surface from the charge passed through the redox reaction. Multiple layers up to pentamer have been constructed by this method.

The following systems also utilized coordination reactions for the oligomerization reactions (Table 1), while the electrochemical properties of the films have not been investigated.

Altman et al. has reported layer-by-layer assembly of palladium coordination-based multilayers on silicon and glass substrates. They employed a siloxane-based template layer and rigid-rod chromophores connected by terminal pyridine moieties to palladium centers provided by colloidal palladium and PdCl2(PPh3)2. They have prepared film up to 14 layers in submicron thickness, of which UV-vis absorption maximum has a significant red shift of 23 nm compared with the monolayer film. The films were characterized by UV-vis spectroscopy, spectroscopic ellipsometry, atomic force microscopy (AFM), X-ray reflectivity (XRR), scanning electron microscopy (SEM), and aqueous contact angle (CA) measurements.

Kosbar et al. have reported self-assembled multi-layers of transition-metal-terpyridine complexes on gold surface. They examined 21 different metals and found Ti(IV), Ir(IV), Pt(IV), W(IV), Rh(III), Ti(III), Ir(III), Ru(III), Sn(IV), Zr(IV), and Cu(II), of which the ionic radii are between 66 and 73 pm, as suitable metal ions for construction of multiple layers. Characterization was carried out using UV spectroscopy, variable-angle spectroscopic ellipsometry, and AFM.

Wanunu et al. have reported branched coordination multilayers on gold. They used C9-symmetric tridentate hexahydroxamate ligand and ZrV ions, and the films formed by layer-by-layer growth were characterized by UV-vis spectroscopy, ellipsometry, AFM, and CA. Divergent growth was observed on the surface with a very low density of bis-hydroxamate anchor ligand using octanethiol and anchor ligand mixed SAMs. The heights of variable generations up to 10 are in excellent agreement with the values predicted by molecular models.

Organic reactions have also been used for the construction of organic complex multilayers (Fig. 3).

**Table 1** Systems of surface bottom-up construction of metal complex molecular wires.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Surface anchoring molecule</th>
<th>Metal ion</th>
<th>Bridging ligand</th>
<th>Ref.</th>
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<tr>
<td>glass</td>
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<td>PdII</td>
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</tr>
<tr>
<td>ITO, Si</td>
<td></td>
<td>TiIV, IrIV, PtIV, WIV, RhIV, TiV, IrV, RuV, SnIV, ZrIV, CuIV</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td></td>
<td>TiIV, ZrIV</td>
<td></td>
<td>11</td>
</tr>
</tbody>
</table>

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![Fig. 2 Schematic illustration of the stepwise polymerization. A, B, and C refer to a molecule to anchor a molecular linker at the surface, a bridging molecular linker such as a metal ion, and the other bridging molecular linker such as a two-way bridging ligand, respectively.](image-url)

![Fig. 3 Schematic representation of sequential growth of the layer-by-layer multilayers using two reactions 1) and 2). Reprinted with permission from ref. 8. Copyright: Wiley-VCH Verlag.](image-url)
oligomerization of monomeric species at the surface, as follows (Table 2).

Jiao et al. have investigated the stepwise formation and characterization of covalently linked multiporphyrin-imide architectures on Si(100). A triaryl-porphyrin bearing an amino group serves as the base unit on Si(100), and the altering use of a dianhydride (3,3’-4,4’-biphenyltetraarcboxilic dianhydride) and a porphyrin-diamine for the reaction enables the rapid and simple buildup of oligomers composed of 2-5 porphyrins. Film characterization was carried out using ellipsometry for film thickness, CV for the charge density of redox sites (porphyrin moieties), FT-IR and X-ray photoelectron spectroscopy (XPS) for bond characterization, and AFM for surface morphology. Film thickness estimated by ellipsometry was proportional to the number of porphyrins, but the degree of increase in charge density obtained by cyclic voltammetry with the number of porphyrin layers was not constant and became smaller for higher layer numbers.

Suck et al. have reported assembly of ultrathin polymer multilayer films by click chemistry, i.e., CuI-catalyzed variant of the Huisgen 1,3-dipolar cycloaddition of azides and alkynes to form 1,2,3-triazole. Almost quantitative growth of the films up to eight layers has been characterized by UV-vis and FTIR spectroscopy and AFM analysis. The electrochemical properties of the films have not been reported.

We have reported homo- and hetero-metal complex oligomer and polymer wires of bis(terpyridine)metal complexes using rigid π-conjugated bridging ligands. A typical method for fabricating multiple complex layers is as follows. First, Au-S-AB-tpy SAM is prepared by immersing an Au/mica or Au/ITO plate in a chloroform solution of a terpyridine-terminated disulfide, (tpy-C\(_2\)H\(_2\)N = NC\(_6\)H\(_2\)S) (tpy-AB-SS-AB-tpy) (Fig. 4), tpy = 2,2’;6’;2’’-terpyridine). In the case of connecting the Fe(II) ion, the tpy-terminated surface is immersed in 0.1 M Fe(BF\(_4\))\(_2\) aq or (NH\(_4\))\(_2\)Fe(SO\(_4\))\(_2\) aq, and the bis(tpy)iron structure is then prepared by immersing the film in a chloroform solution of an π-conjugated bis-terpyridine ligand (Fig. 4B). Repeating the latter two processes gives multilayer bis(tpy)iron complex films. In contrast, it is not possible to accumulate bis(tpy)cobalt by the mere combination of immersion in CoCl\(_2\) aq and immersion in a chloroform solution of the bridging ligand. But we found that the addition of an electrochemical oxidation process from Co(II) to Co(III) successfully produced multilayer bis(tpy)cobalt complex films.

Azobenzene-bridge- and p-phenylene-bridged bis(terpyridine) ligands, tpy-C\(_6\)H\(_5\)N = NC\(_6\)H\(_2\)-tpy (L\(_1\)) and 1,4-(tpy)-C\(_6\)H\(_4\)-tpy (L\(_2\)), respectively, were employed for preparation of linear complex wires (Fig. 4). The stepwise quantitative film formation could be monitored by UV-vis spectra and CV. For example, UV-vis spectrum of the bis(tpy)iron complex film, [nFeL\(_1\)] (where n refers to the film prepared with n times of iron-complexation cycles), where absorbance of the peak at 592 nm ascribed to the MLCT transition increased almost linearly with the number of stepwise complexations, n (Fig. 5A). The peak current, i\(_p\), for the Fe(III)/Fe(II) couple at 0.67 V vs. ferrocenium/ferrocene (Fc+/Fc) in Bu\(_4\)NClO\(_4\)-CH\(_2\)Cl in CV of [nFeL\(_1\)] and [nFeL\(_2\)] increased almost proportionally with n (Fig. 5B for [nFeL\(_2\)]). The anodic charge integration under the voltammetric wave of the first layer yields \( \Gamma_{CV(nFeL_1)} = 1.4 \times 10^{-10} \) mol cm\(^{-2}\) for an azobenzene-bridged bis-tpy ligand, L\(_1\), and \( \Gamma_{CV(nFeL_2)} = 1.0 \times 10^{-10} \) mol cm\(^{-2}\) for a p-phenylene-bridged bis-tpy ligand, L\(_2\), approximately coincident with the maximum surface coverage based on the complex cation size (1.0 nm\(^2\) per molecule). The UV-vis and CV results of [nCoL\(_1\)] also indicate the quantitative formation of the layers. The side view image of the SEM photograph for [47CoL\(_4\)] indicates the growth of the film to a thickness of ca. 100 nm, which is reasonable, as the value is close to the product of the number of layers, 47, times the molecular unit length, 2 nm.

A similar stepwise coordination method can also afford branched and rigid molecular wires of metal complex oligomers when we use a three-way bridging ligand, 1,3,5-C\(_6\)H\(_3\)(C ≡ C-tpy), L\(_3\) (Fig. 4). In this case, \( \Gamma \) can be expected to increase with the number of complexation cycles, n, having the 2\(^n\) relationship, if the coordination

**Table 2** Systems of surface bottom-up construction of organic molecular wires.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Surface molecule</th>
<th>Bridging molecules and reaction</th>
<th>Ref.</th>
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</thead>
<tbody>
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<td>Si(100)</td>
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<td>12</td>
</tr>
<tr>
<td>quartz</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si, Au</td>
<td></td>
<td></td>
<td>13</td>
</tr>
</tbody>
</table>

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**Fig. 4** Chemical structures of the ligands used in this study (A), and stepwise coordination methods for the preparation of linear wire (B).
reaction at the terminals of the molecular wires occurs perfectly. The experimental results of $\Gamma_{CV}[\text{FeL}]$ values obtained by CV indicate that an increase in $\Gamma$ obeying the $2^n - 1$ relationship was observed up to $n = 4$, while the increase rate of $\Gamma$ slowed when $n$ was more than 4 until the rate was similar to that of linear polymers, $[n\text{FeL}]$. These findings, as suggested from the molecular structures obtained by the MM+ calculation, indicate that the wire can extend in only one dimension at higher generations due to the significant interwire and wire-to-gold surface steric repulsion.

Scanning tunneling microscopy (STM) showed a clear difference in the surface morphology between the films of linear and branched molecular wires. The STM image of $[2\text{FeL}]$ shows a nearly close packing of 6 nm-thick, circular domains, indicating the stacking of molecular chains and the formation of a fairly smooth surface. In contrast, the film of branched oligomers wires, $[2\text{FeL}]$, shows a clearer image of domain structures that are evenly distributed in shape and size all over the surface. Figures 6 shows STM images of the films with a combination of linear and branched oligomer wires, $[1\text{FeL}]_3[3\text{FeL}]$, prepared with a short immersion time ($t_I = 10$ s) of Au/mica in a chloroform solution of tpy-AB-SS-AB-tpy to create a sparse distribution of the oligomer wires. The images show circular dots that increased in diameter with the number of complexation cycles.

The stepwise coordination method allows facile creation of hetero-metal polymer chains with an intended sequence. Electrochemical monitoring of the stepwise formation of a hetero-metal double-layer film $[1\text{CoL}_1\text{FeL}_1]$ indicated that the redox activity of the $\text{Fe}^{III}/\text{Fe}^{II}$ couple appeared without changing the redox activity of the $\text{Co}^{III}/\text{Co}^{II}$ couple when the bis(tpy)iron complex units were connected to the initially prepared bis(tpy)cobalt complex layer, and also that the redox activities of both redox couples are the same (Fig. 7A). Similarly, multilayer heterometal films such as $[10\text{CoL}_1\text{FeL}_1]$ could be prepared. XPS spectra of $[1\text{FeL}_3\text{CoL}_1]$ (the counterion of which is $\text{ClO}_4^-$) and $[3\text{CoL}_3\text{FeL}_3]$ (the counterion of which is $\text{BF}_4^-$) indicated that only Co existed at the surface in the latter, supporting the formation of hetero-layer structures. The CV of $[10\text{CoL}_1\text{FeL}_1]$ shown in Fig. 7B indicated that 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. 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. A Co-Ru hetero-metal complex wire could also be prepared by the

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Fig. 5 Absorption spectra of $[n\text{FeL}_1] (n = 1 - 5)$ and plots of the absorption peak (592 nm) vs. the number of complex layers (inset) (A), and cyclic voltammograms of $[n\text{FeL}_1] (n = 2, 4, 6, 8, 10)$ in 1 M Bu$_4$NClO$_4$/CH$_2$Cl$_2$ at a scan rate of 0.1 V s$^{-1}$. Reprinted with permission from ref. 15. Copyright: Wiley-VCH Verlag.

Fig. 6 Scheme of the film preparation method for STM measurement and an STM image of $[1\text{FeL}_3\text{FeL}_3]$.

Fig. 7 Cyclic voltammograms of $[1\text{CoL}_1]$ (gray) and $[1\text{CoL}_1\text{FeL}_1]$ (black) (A), and $[10\text{CoL}_1\text{FeL}_1]$ (B) on gold at 0.1 V s$^{-1}$. 
stepwise coordination method.\textsuperscript{17}

### 3 Through-bond Redox Conduction Mechanism and Kinetics

In the conventional polymer coated electrode, redox sites are randomly distributed in the film. But the redox sites are aligned along the polymer chain in the film prepared by the stepwise coordination method. This situation has caused a difference in electron transport behavior compared with the conventional polymer-coated electrode as described in this section.

Before focusing on the redox conduction mechanism of the aligned polymer wire-coated electrode, the redox conduction mechanism in the conventional polymer-coated electrode, in which the redox sites are randomly and homogeneously distributed in the polymer film, is described.

The concept of “redox conduction” in film with a homogeneous distribution of redox sites is first theoretically developed by Dahms and Ruff, considering the physical motion of the redox species and the electron exchange between the neighboring redox sites in the film as expressed in equation 1:\textsuperscript{19}

\[ D_{app} = D_0 + (\pi/4)k_c\delta C \]  

where \( D_{app} \), \( D_0 \), \( k_c \), \( \delta \), and \( C \) are the apparent diffusion coefficient for electron transfer, the diffusion coefficient for physical motion of the redox sites in the film, the electron self-exchange rate constant, the center-to-center distance between redox sites at the time of electron transfer, and the concentration of the redox sites in the film, respectively (Fig. 8A).

Savéant has presented another model in which redox sites are fixed in the polymer chain, thus restricting physical motion. In this case, the redox conduction kinetics is given by equations 2 and 3:\textsuperscript{20}

\[ D_{app} = k_c\lambda \Delta x^2 / 6 \]  

\[ \Delta x^2 = \delta_2 + 3\Delta^2 \] (in the three-dimensional case)  

where \( \Delta x \) and \( \lambda \) are the thickness of a “monolayers” of redox centers and the mean displacement of a redox molecule out of its equilibrium position, respectively (Fig. 8B).

The models of redox conduction noted above are based on the occurrence of the redox conduction in the diffusion process, with electrons taking a random walk according to the concentration gradient of the redox species in the film, and the apparent diffusion constant for redox constant, \( D_{app} \), has been the parameter to be measured. \( D_{app} \) values have been obtained by various electrochemical techniques such as potential step chronomeamperometry (PSCA), CV, normal pulse voltammetry, AC impedance measurements, and four-electrode (sandwich) voltammetry, etc. PSCA is one of the simplest methods, and the current-time relationship gives a one-dimensional diffusion-like behavior obeying the Cottrell equation, equation 4, where the current decays in proportion with \( t^{-1/2} \) in a short period until the diffusion layer reaches the film surface if the charge diffusion process within the film is rate-determining.\textsuperscript{21,22}

\[ i(t) = m\text{FAC} (D_{app}/\pi t)^{1/2} \]  

where \( m \), \( F \), and \( A \) are the number of electrons, the Faraday constant, and the electrode area.

We have recently proposed a mechanism of through-bond redox conduction,\textsuperscript{15} which is totally different from the diffusion-based mechanism, as noted above. The concept of the mechanism is as follows. When the oxidized form in the film of molecular wires, \( O_x \)-s, is reduced to Red and the back electron transfer can be neglected by applying a sufficient overpotential in PSCA, the electron transfer kinetics in the case of the \( n \)-th complex sequence can be written as follows,

\[ O_{x1} + e^{-} \rightarrow \text{Red}_1 \quad \text{rate constant:} \ k_1 \]  

\[ \text{Red}_1 + O_x \rightarrow O_{x1} + \text{Red}_1 \quad \text{rate constant:} \ k_2 \]  

\[ \text{Red}_2 + O_x \rightarrow O_{x2} + \text{Red}_2 \quad \text{rate constant:} \ k_3 \]  

\[ \text{Red}_n+1 + O_x \rightarrow O_{xn+1} + \text{Red}_n \quad \text{rate constant:} \ k_2 \]  

where \( \text{Red}_i \) and \( O_x \) are reduced and oxidized forms, respectively, in the \( i \)-th layer or generation in the film, and

\[ d[O_{x1}] / dt = -k_1[O_{x1}] + k_d([O_{x1}] - [O_{x1}])[O_x] \]  

\[ d[O_x] / dt = -k_d([O_{x1}] - [O_{x1}])[O_x] \]  

\[ + ([O_{x1}]/[O_{x1}])k_d([O_{x1}] - [O_{x1}])[O_{x1}] \]  

\[ d[O_{x2}] / dt = -([O_{x1}]/[O_{x1}])k_d([O_{x1}] - [O_{x1}])[O_x] \]  

\[ + ([O_{x1}]/[O_{x1}])k_d([O_{x1}] - [O_{x1}])[O_{x1}] \]  

\[ d[O_{n+1}] / dt = -([O_{xn+1}]/[O_{xn+1}])k_d([O_{xn+1}] - [O_{xn+1}])[O_x] \]  

\[ + ([O_{xn+1}]/[O_{xn+1}])k_d([O_{xn+1}] - [O_{xn+1}])[O_{xn+1}] \]  

\[ - [O_{xn+1}])[O_x] \]  

where \([O_{x1}]\) and \([O_x]\) are the initial and present two-dimensional concentrations, respectively, of the oxidized form of the redox moiety in the \( i \)-th layer or generation in mol cm\(^{-2} \). The reaction kinetics are controlled by two factors: \( k_1 \) (s\(^{-1} \)), for the electron-transfer between the nearest redox site and the electrode (the electron-trans-
fer model for four complex layers is described), and \( k_2 \) (cm\(^2\) mol\(^{-1}\) s\(^{-1}\)), for the electron transfer between the neighboring redox sites in a molecular wire (in a primary approximation, the neighboring-site electron-transfer rate constant in a polymer wire can be constant).

In the case of linear oligomer wires (Fig. 9A), the concentration balance of the reduced and oxidized sites can be written as

\[
[\text{Red}_i] + [\text{Ox}_i] = [\text{Red}_{i-1}] + [\text{Ox}_{i+1}] = \cdots = [\text{Red}_2] + [\text{Ox}_2] = \text{constant.} \tag{7}
\]

On the other hand, the balance in the case of branched oligomer wires (Fig. 9B) is expressed as

\[
[\text{Ox}_i] + [\text{Red}_i] = ([\text{Ox}_{i+1}] + [\text{Red}_{i+1}])/3 = ([\text{Ox}_{i-1}] + [\text{Red}_{i-1}])/7 = \cdots = [\text{Red}_2] + [\text{Ox}_2]/(2^n - 1) = \text{constant.} \tag{8}
\]

The actual current can be observed as \( \frac{d[\text{Ox}_i]}{dt} \). If the electron transfer between the neighboring redox sites is faster than that between the nearest redox site and the electrode, the reaction kinetics can be regarded as a “zero-order reaction,” which implies that the constant current flows in the initial period.

We expected that the redox polymer films formed by the bottom-up coordination method are suitable to examine the possibility of the through-bond redox conduction mechanism. PSCA results of linear oligomers [nFeL\(_2\)] with \( n = 2, 4, 6 \), and 8 are shown in Fig. 10A. The \( i-t \) characteristics showed a plateau-like region, with the period becoming longer with increase in the number of layers, \( n \). Their Cottrell plots did not have any region of straight line penetrating the origin, indicating that the analysis based on one-dimensional diffusion is inadequate. PSCA results of branched oligomers, [nFeL\(_3\)] with \( n = 2, 3, \) and 4 also showed a plateau-like region, with the peri-

Fig. 9 Schematic illustration of the electron-transfer mechanism in (A) linear and (B) branched molecular wires. \( G \) = generation. Reprinted with permission from ref. 15. Copyright Wiley-VCH Verlag.

Fig. 10 Current-time plots after the potential step from 0.96 to 0.36 V versus Fe\(^{3+}/Fe\) to reduce the Fe\(^{3+}\)-complex moieties in [nFeL\(_2\)] (\( n \) = 2, 4, 6, and 8) (A), and in [nFeL\(_3\)] (\( n \) = 2, 3, and 4) (B) in Bu\(_4\)NClO\(_4\)-CH\(_2\)Cl\(_2\) (1 M). Reprinted with permission from ref. 15. Copyright: Wiley-VCH Verlag.

The concentrations of redox sites in the films of both linear and branched oligomers can be estimated to be \( ca. 1 \text{ mol dm}^{-3} \) from both the experimental data noted above and molecular structure simulation using MM+. As such, low concentration of electrolyte (less than 1 M) would have a large effect on reducing the rate of redox conduction in the film because it is known that electron hopping is limited by the counterion motion. We thus analyzed the effects of electrolyte concentration on the kinetics of redox conduction. All the \( i-t \) characteristics with different \( n \)'s at a given electrolyte concentration
between 0.1 M and 2 M could be simulated using similar $k_1$ and $k_2$ values, and the average values of $k_3$ and $k_2$ values are plotted versus electrolyte concentrations in Fig. 11. Strong dependences of $k_1$ and $k_2$ on the electrolyte concentration are observed at lower concentrations and they become constant above 1 M, as expected. It can be concluded that the $k_1$ and $k_2$ values express an apparent rate constant, including not only the intrinsic electronic exchange kinetics but also the factor of through-bond electronic interaction between the redox sites and counterion motion\textsuperscript{23)}

### 4 Conclusion

In this article, we have shown a new fabrication method of hetero-structured molecular wires using surface coordination reactions. The molecular wires show intra-wire electron transport behaviors, which are essential characteristics for the fabrication of molecular devices. One advantage of this methodology is the possibility of introducing electro- and/or photo-functional chemical structures at desired positions in the molecular wire, which could be a useful approach to the development of molecular devices.

### References


