Terminal Redox Moiety Effects on the Long-Range 
Electron Conduction of π-Conjugated Bis(terpyridine)
Metal Complex Oligomer Wires on Electrode
Shunsuke Katagiri, Ryota Sakamoto, Hiroshi Nishihara
Department of Chemistry, Graduate School of Science,
The University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Stepwise coordination reactions to fabricate self-assembled multilayers have recently attracted much attention as a convenient method to connect molecular wires to the surface because these reactions are programmable to connect different units at the desired positions. We previously reported the synthesis of π-conjugated linear and branched M(tpy)2 (M = CoIII, FeII; tpy = 2,2':6,2''-terpyridine) oligomer wires attached to Au and Si(111) surface using the stepwise coordination method.1,2 We have clarified that the redox conduction of the Fe(tpy)2 oligomer wires occurs along the molecular wire, implying that intrawire electron transfer is much faster than interwire transfer.

In addition, these metal complex oligomer wires comprising metal ion, and anchoring (A), bridging (L) and redox-site appended terminal (T) terpyridine ligands show excellent long-range electron-transport abilities.3,4 The electron transfer rate constant through the wires, k0et, could be formulated with eq 1:

$$k_{et} = k_{et}^0 \exp[-\beta(d-d^0)]$$  \hspace{1cm} (1)

where d is the distance between the gold electrode and the terminal redox site, d0 is the shortest wire length, k0et is the k0 value at d = d0, and β is the attenuation factor. The β values were found to be 0.008-0.07 Å-1 and 0.002-0.004 Å-1 for molecular wires composed of Fe(tpy)2 and Co(tpy)2 oligomers, respectively.3 We have disclosed that the bridging ligand L significantly impacts β rather than k0et whereas the surface anchoring ligand A does not affect β, but it alters k0et.4

In this study, we investigated the terminal redox moiety effects on the long-range electron transport ability. For this purpose, we fabricated three kinds of molecular wires containing different T: T1, T2 and T3 has a cyclometallated Ru(II)-terpyridine complex as a redox site.

A schematic illustration about the fabrication process of the Fe(tpy)2 wires A(FeL)nFeTx (x = 1-3) was shown in Figure 1. Primarily, the anchoring ligand A was immobilized on annealed gold surfaces. The growing of the molecular wires was undertaken by the stepwise coordination reaction between FeII ion and bridging ligand L. Lastly, the fabrication was completed by capping with T1.

To investigate the electrochemical properties, cyclic voltammograms of A(FeL)nFeTn+ (x = 1-3) were measured. Two reversible redox peaks assigned to the terminal redox moiety and Fe(tpy)2 were observed among the three kinds of molecular wires. The surface coverages of Fe(tpy)2 units, which were estimated from peak areas of cyclic voltammograms, proportionally increased with n, whereas those of the terminal redox sites were insensitive to n. These data indicate that the almost quantitative development of the Fe(tpy)2 oligomer wires was achieved by the stepwise coordination method.

The k0et values for the electron transfer from the electrode to the oxidized terminal redox site of the molecular wires were measured for A(FeL)nFeTn+ by potential step chronoamperometry (PSCA). Figure 2 shows ln k0et-d plots for A(FeL)nFeTn+. From the relationship between k0et and the wire length d, one can be seen two important relationships involving T: (1) β is independent of T; (2) k0et is much greater in the wires with T than those with T1 and T3.