

VIII-D Designing Artificial Photosynthesis at Molecular Dimensions

Photosynthesis is one of the finest piece of molecular machinery that Nature has ever created. Its ultrafast electron transfer and following well-organized sequence of chemical transformation have been, and will continue to be, challenging goals for molecular scientists. We are trying to mimic the function of photosynthesis by assembling molecular units that perform individual physical/chemical action. The molecular units include porphyrins, redox active organic molecules, and transition metal complexes. Our ultimate goal is to design artificial molecular systems that effect multiple chemical reactions triggered by light on the basis of molecular rationale.

Last year we focused our attention on combining "redox pool" with photoinduced electron transfer.

VIII-D-1 Synthesis and Photochemical Reactions of Multistep Redox Polymer Containing Porphyrin and Metallocenes

HINO, Takami¹; ITO, Hajime; NAGATA, Toshi
(¹Kyoto Univ.)

Photoinduced electron transfers involving porphyrins are widely studied, but utilizing the high-energy radical ion pairs for driving chemical reactions remains to be a great challenge. One of the missing features in artificial photosynthetic models based on organic molecules is the function of redox pool—that receives the oxidizing and/or reducing equivalents from the photogenerated ion pairs and retains them sufficiently long until the substrates for chemical reactions are ready. This feature is essential for photosynthetic processes to be successful, because the photogenerated high-energy states are otherwise too short-lived to cooperate with (comparatively slow) chemical reactions. In biological systems various electron-carrying substances (proteins like soluble cytochromes, or cofactors like quinones) play the role, whereas in many artificial systems solid particles with electronic band structure (metal or semiconductor nanoparticles) do that. It should be an important research topic to develop redox pools with organic and organometallic substances and utilize in molecule-based artificial photosynthetic systems.

With this goal in mind, we prepared polysiloxanes containing ferrocene and porphyrin moieties (Figure 1). The ferrocenes are present in 20-fold excess of porphyrins, so that they can serve as 'electron pool' that retains photogenerated holes on porphyrin moieties.

The desired polymer **1** was prepared by hydrosilylation of a mixture of vinylferrocene and (4-pentenyl-oxy)phenyl substituted porphyrin with poly(methylhydro)siloxane catalyzed by hexachloroplatinic acid (Figure 2). Purification by reprecipitation from tetrahydrofuran/methanol followed by gel permeation chromatography yielded the product with reasonably narrow size distribution ($M_w/M_n = 1.4$). The cyclic voltammogram of **1** is shown in Figure 3; a large peak of ferrocenes and two small peaks of porphyrins are observed as expected.

The photoreaction of **1** with quinones were examined. We previously reported the reductive silylation of quinones photocatalyzed by porphyrins (H. Ito, T. Hino, T. Nagata, submitted; see also Annual Review 2000). As the photoreduced product of quinones

are trapped by silylating reagents, this reaction can be used to continuously pick up electrons from donor molecules. Indeed, irradiation with visible light of a mixture of the polymer **1**, 2,3,5,6-tetramethyl-1,4-benzoquinone, Me_3SiCl and pyridine in tetrahydrofuran/*N,N*-dimethylformamide gave the oxidized form of **1** (*i.e.* the ferrocene moieties were converted to ferrocenium) together with the reduced product, 2,3,5,6-tetramethyl-1,4-bis(trimethylsiloxy)benzene (Figure 4). The full identification, as well as the follow-up chemistry (*i.e.* reducing back to the original form) of the oxidized form of **1** is currently under way.

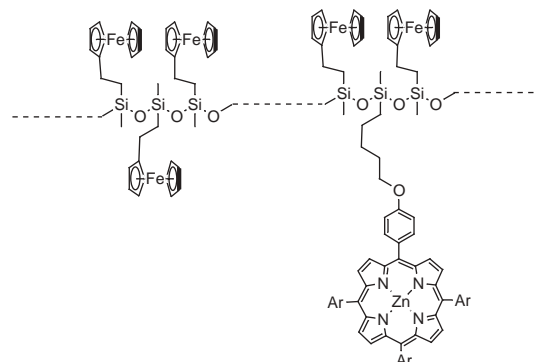


Figure 1. A redox polymer with a photoactive moiety.

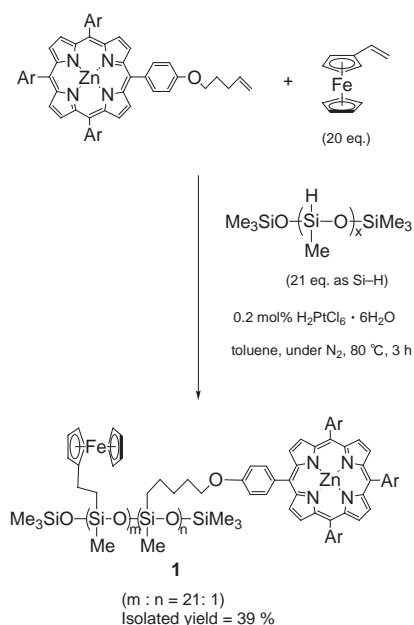


Figure 2. The synthesis of polymer **1**.

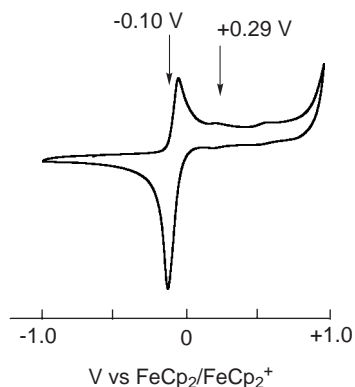


Figure 3. The cyclic voltammogram of polymer **1**. Conditions: CH₂Cl₂ with 0.1 M Bu₄NClO₄, Pt working electrode.

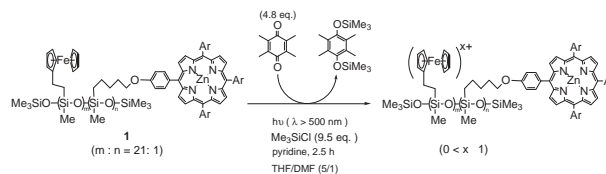


Figure 4. The photoreaction of polymer **1** with quinone and Me₃SiCl.

VIII-E Development of New Metal Complexes as Redox Catalysts

Redox catalysis is an important field of chemistry which translates a flow of electron into chemical transformation. It is also one of the requisites for artificial photosynthesis. This project of ours aims at developing new metal complexes that perform redox catalysis at low overpotential. Last year we focused our attention to developing terdentate ligands with strong donor character. 2,2':6',2''-Terpyridine has been the ligand of choice in this field, but our study has now revealed that 2,2':6',2''-terpyridine-1,1''-dioxide is also a good candidate for developing new catalysts.

VIII-E-1 Synthesis of Terpyridine-based Binary Ligands and Their Metal Complexes

ITO, Kaname; NAGATA, Toshi; TANAKA, Koji

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In recent years, metal complexes of 2,2':6',2''-terpyridine (terpy) and their derivatives are gaining considerable attention as electrochemical catalysts. Derivatives of terpyridine are particularly suitable for electrocatalytic applications because they are chemically robust and form stable complexes with a wide variety of transition metals. On the other hand, the syntheses of terpyridine derivatives are often so troublesome that it is difficult to tune the electrochemical behavior of the metal complexes.

The *N*-oxides of pyridines are promising ligands that are easily derived from pyridine compounds by one-step peracid oxidation. Metal complexes of pyridine *N*-oxide and 2,2'-bipyridine 1,1''-dioxide are numerous, whereas the *N*-oxides of terpyridine have been much less studied. Only a few reports were published on the metal complexes of 2,2':6',2''-terpyridine 1,1',1''-trioxide (terpyO₃).

We prepared a series of first-row transition metal complexes of 2,2':6',2''-terpyridine 1,1''-dioxide (terpyO₂) are reported. Four new bis complexes [M(terpyO₂)]X₂ (M = Mn(II), Fe(II), Co(II) and Ni(II); X = ClO₄⁻ and BF₄⁻) and one mono complex [Cu(terpyO₂)(H₂O)](ClO₄)₂ were isolated and characterized, and

electrochemical properties were examined. The crystal structure of the Fe(II) complex [Fe(terpyO₂)₂](ClO₄)₂ is shown in Figure 1. The ligands have non-planar conformations with an approximate C₂ symmetry, which makes the overall symmetry of the complex cation approximately D₂. The Ni(II) complex [Ni(terpyO₂)₂](ClO₄)₂ was isostructural with the Fe(II) complex. The X-ray structure of the Cu(II) complex was also examined (Figure 2), and it was revealed that the Cu(II) ion was square-planar with the terdentate terpyO₂ ligand whose conformation was similar as in the Fe(II) and Ni(II) complexes.

The cyclic voltammograms of the four bis complexes revealed that the M(III)/M(II) redox potentials of the Mn(II), Fe(II) and Ni(II) complexes showed negative shifts (−0.77 to −0.24 V) compared to the terpyridine complexes, whereas the potential of the Co(II) complex showed a slightly positive shift (+0.03 V). The Fe(II) complex is particularly interesting, because the low *E*_{1/2} value and the ease of ligand exchange (revealed by ESI-MS) make the complex promising for application as a redox catalyst. Also worth noting is the Mn(II) complex, for which another reversible wave corresponding to the Mn(IV)/Mn(III) couple was observed. The electrocatalytic properties of the terpyO₂ complexes is now being investigated.

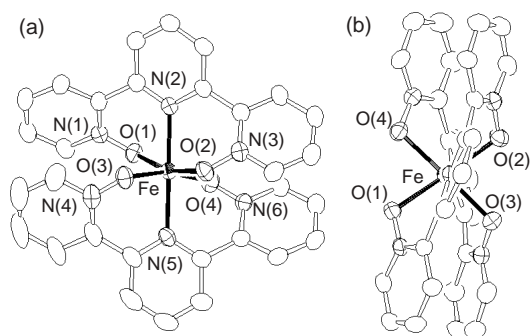


Figure 1. ORTEP view (50% probability ellipsoids) of the complex cation $[\text{Fe}(\text{terpyO}_2)_2]^{2+}$.

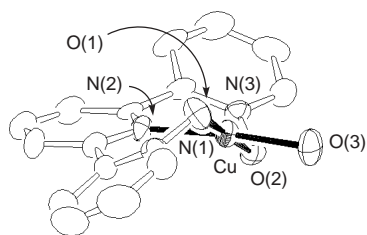


Figure 2. ORTEP view (50% probability ellipsoids) of the complex cation $[\text{Cu}(\text{terpyO}_2)(\text{H}_2\text{O})]^{2+}$.