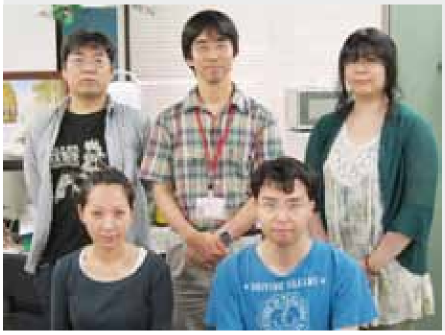
Building Photosynthesis by Artificial Molecules

Research Center for Molecular Scale Nanoscience
Division of Molecular Nanoscience



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The purpose of this project is to build nanomolecular machinery for photosynthesis by use of artificial molecules. The world's most successful molecular machinery for photosynthesis is that of green plants—the two photosystems and related protein complexes. These are composed almost exclusively from organic molecules, plus a small amount of metal elements playing important roles. Inspired by these natural systems, we are trying to build up multimolecular systems that are capable of light-to-chemical energy conversion. At present, our interest is mainly focused on constructing necessary molecular parts and examining their redox and photochemical behavior.

1. Photoreduction of Quinones Sensitized by Soluble Phthalocyanines

Organic pigments are useful molecular parts for photosynthesis because of their ease of modification and high tunability. In particular, pigments for utilizing visible lights with long wavelength (>650 nm) are useful because they can complement the existing series of sensitizers for more efficient use of solar light. Phthalocyanines are good candidates as they have very strong absorption bands around 700 nm. However, studies on photochemistry of phthalocyanines are often hampered by the low solubility. To address this problem, we chose phthalocyanines (Pc) having 2,4-di-*t*-butylphenoxy substituents in the periphery. These phthalocyanines are so soluble in many organic solvents (even in hexanes!) that study of photoreactions in solutions can be easily carried out.

The target photoreaction is shown in Figure 1. The rate of reaction was dependent on the redox potentials of quinones, namely the reaction was faster for quinones with higher potential (*i.e.* more easily reduced). This indicates the reaction proceeds *via* photoinduced electron transfer from Pc to quinones. In particular, 2-*t*-butylanthraquinone and 2,6-dibutoxyanthraquinone did not react at all; these results suggest that the reaction proceeds *via* the triplet state of Pc (^{3}Pc) rather than the excited singlet state (^{1}Pc*), because ΔG's for the photoinduced electron transfer to these quinones were positive for ^{3}Pc but negative for ^{1}Pc*.

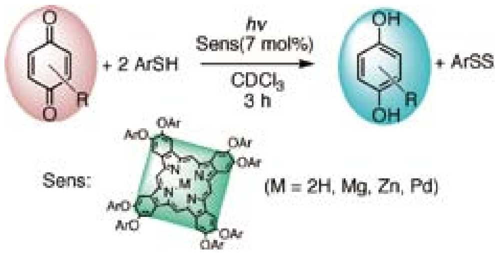

Figure 1. Photoreduction of quinones sensitized by soluble phthalocyanines with various central metals.

On the other hand, when different thiols were used as reductant, the rate of reaction was dependent on the acidity of thiols rather than the redox potential. Therefore, it is likely that the thiol works first as the proton donor to the anion radical of quinone, and then gives an electron to the cation radical of Pc (or to the neutral semiquinone radical).

When phthalocyanines with different central metal ions were employed, the rates of photoreaction were in the order Zn > Mg > Pd > 2H. Although the triplet quantum yield is higher for Pd than Zn, the photoreaction was very slow with Pd phthalocyanine. This is attributed to the high redox potential of PdPc, causing the photoinduced electron transfer unfavorable (ΔG = +0.17 eV for 2,5-di-*t*-butylbenzoquinone).

On the basis of these results, a plausible mechanism of this reaction is proposed as shown in Figure 2. Kinetic studies for important steps are currently underway. This study will lay an important cornerstone in utilization of low-energy photons for direct chemical conversions.

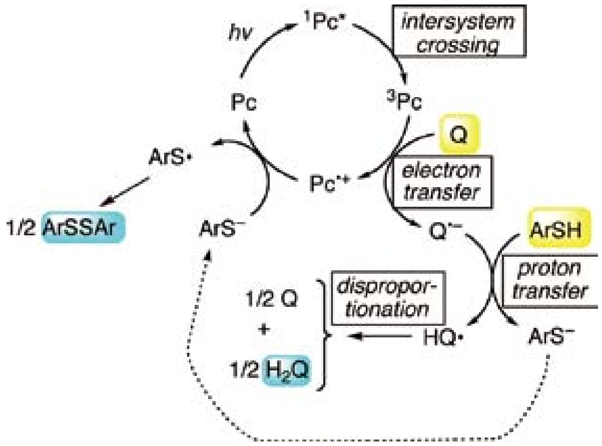

Figure 2. A plausible mechanism of photoreduction of quinones. Pc: phthalocyanine.

2. Synthesis of Dinuclear Metal Complexes with Ternary Binucleating Ligands

As we already reported,[1] combination of photochemistry of organic pigments and redox chemistry of transition metal complexes is a promising approach to develop new photoredox chemistry. In particular, use of first transition metals (3d metals) is worth studying, because they can provide crucial bridge between one-electron (photochemical) and two-electron (common organic chemical) processes. Synthesis of 3d metal complexes, however, is not always straightforward, because many 3d metal ions exchange ligands so easily that there are only limited choices of isolable compounds. In this respect, we can learn from biological systems where 3d metal complexes are utilized with a wide structural variation. This is made possible by the surrounding organic ligands (proteins).

Along this context, we prepared two new "ternary" ligands **1** and **2**, which consist of two terpyridines and one "N4 bridge" (1,4-bis(2-pyridyl)phthalazine for **1** and 3,6-bis(2-pyridyl) pyridazine for **2**). They formed stable dinuclear complexes $[(\mathbf{1})Co_2(\mu\text{-}OH)]^{3+}$, $[(\mathbf{1})Ni_2(\mu\text{-}Cl)]^{3+}$ and $[(\mathbf{2})Co_2(\mu\text{-}OH)]^{3+}$. The X-ray structures of the first two complexes revealed subtle but characteristic differences (Figure 4). The steric repulsion between the hydrogen atoms at the *peri*-positions of the phthalazine ring and the 3-positions of the neighboring pyridine rings (indicated by arrows in Figure 4) caused twisting of the pyridine rings resulting in local axial chirality, and the stereochemistry of the axes were different between the Co and Ni complexes. In the Co complex, the two axes have the opposite axial stereochemistry, whereas in the Ni complex, the two axes have the same stereochemistry. Such difference was caused by the different ionic radii of the metal centers and by the different bridging anions (OH^- and Cl^-).

The cyclic voltammogram of $[(\mathbf{1})Co_2(\mu\text{-}OH)]^{3+}$ showed interesting behavior in the presence of acid (Figure 5). When triflic acid was added, the peaks of the Co_2 parts disappeared and new peaks corresponding to a mononuclear Co complex appeared instead. This change was attributed to the (reversible) release of one Co ion upon addition of acid.

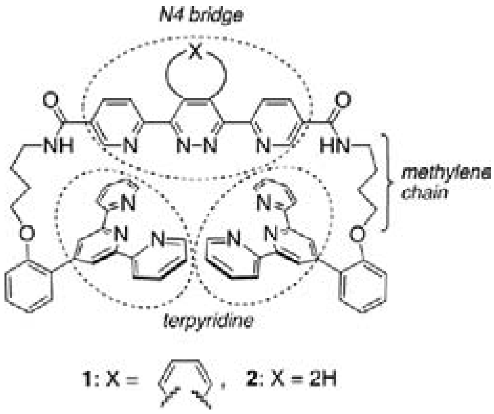

Figure 3. The ternary ligands consisting of two terpyridines and one "N4 bridge."

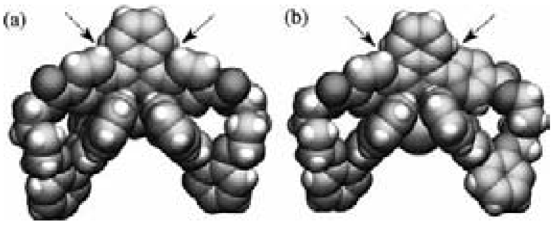

Figure 4. The space-filling drawing of the X-ray structures of (a) $[(\mathbf{1})Co_2(\mu\text{-}OH)]^{3+}$ and (b) $[(\mathbf{1})Ni_2(\mu\text{-}Cl)]^{3+}$.

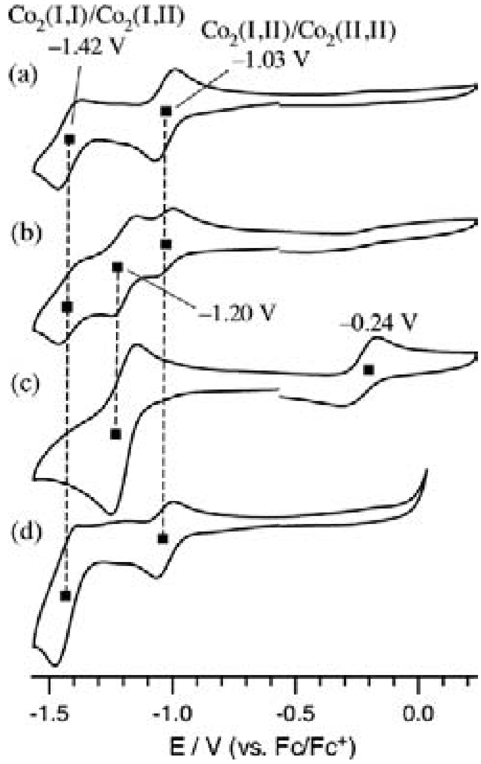

Figure 5. The changes of the CVs of $[(\mathbf{1})Co_2(\mu\text{-}OH)]^{3+}$ with the addition of CF_3SO_3H (a) 0 eq., (b) 1.0 eq., (c) 2.0 eq. and (d) after the addition of 5 eq. *i*$PrNEt_2$.

Reference

1) H. Kon and T. Nagata, *Chem. –Eur. J.* **18**, 1781–1788 (2012).