

# Building Photosynthesis by Artificial Molecules

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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.

## 1. Synthesis of Porphyrin-Cyclopentadienylcobalt(III) Linked Molecules

The light reactions of oxygenic photosynthesis produce dioxygen and NADPH by the aid of photon energy. Although the actual mechanism is very complicated, the net reaction can be conceptually outlined into three unit reactions; the initial photoinduced electron transfer, and the oxidizing and reducing reactions at the both ends of the charge separated state. In this context, the combination of photoinduced electron transfer and a redox reaction mediated by metal complexes is an interesting subject. One interesting target is the redox chemistry of cyclopentadienylcobalt(III) (CpCo) complexes,<sup>1)</sup> which are known to catalyze various redox reactions, including production of hydrogen. However, photoinduced electron transfer from organic pigments like porphyrins to CpCo complexes is not so easy to achieve.

In this work, we report the synthesis of new dyad molecules, **1** and **2**, which contain porphyrin and cyclopentadienyl cobalt(III) (CpCo) moieties within one molecule. The fluorescence emission spectra showed that the singlet excited state of the porphyrin was quenched via intramolecular electron transfer to the CpCo moiety.

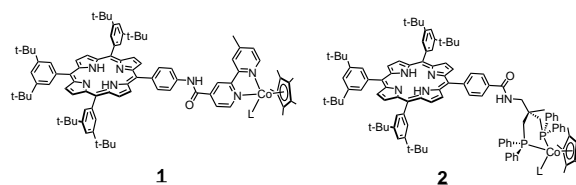


Figure 1. The porphyrin-CpCo linked compounds.

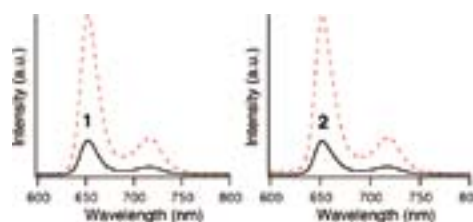


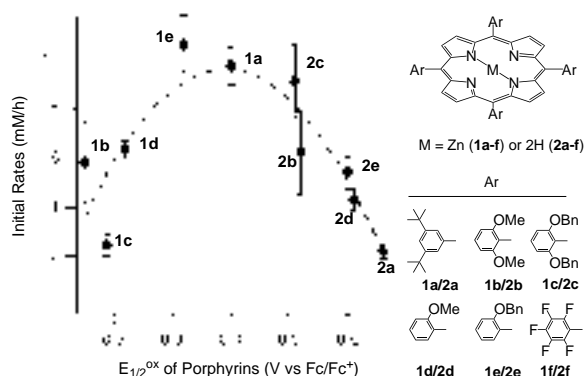
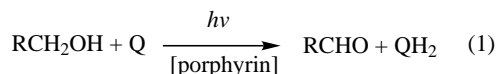
Figure 2. The steady-state emission spectra of compounds **1** and **2** in CH<sub>2</sub>Cl<sub>2</sub>. The red dotted lines indicate the emission spectra of the reference compound without the CpCo moiety.

## 2. An Approach towards Artificial Quinone Pools: Alcohols as the Terminal Reductant<sup>2)</sup>

Quinones are one of the most important cofactors in biological photosynthesis. In the “Type-II” photosynthetic reaction centers, quinones are the terminal electron acceptors, which receive electrons from the photoexcited chlorophylls and are converted into quinols. The quinols are released from the reaction center into the quinone pool, and are eventually reoxidized with concurrent translocation of protons through the membrane. Such a characteristic of natural quinone pools is worth mimicking in artificial systems, because it will provide a key to realize the “Z-scheme” in artificial photosynthesis.

The ultimate goal in mimicking the quinone pools is to convert quinones to quinols with concurrent oxidation of water. However, this is a difficult objective, so we are looking for other oxidation reactions that can be easily realized and can be combined with conversion of quinones to quinols.

In this work, we study the combination of a photoinduced electron transfer from the porphyrin to the quinone and a TEMPO-catalyzed oxidation of alcohols triggered by one electron oxidation (eq. 1). The dependence of initial rates on the oxidation potentials of the porphyrin showed a characteristic bell shape, which is caused by two competitive factors, the efficiency of photoinduced electron transfer and the equilibrium of electron exchange between the porphyrin cation radical and TEMPO.



**Figure 3.** The initial rates of formation of PhCHO plotted versus the oxidation potentials of the porphyrins.

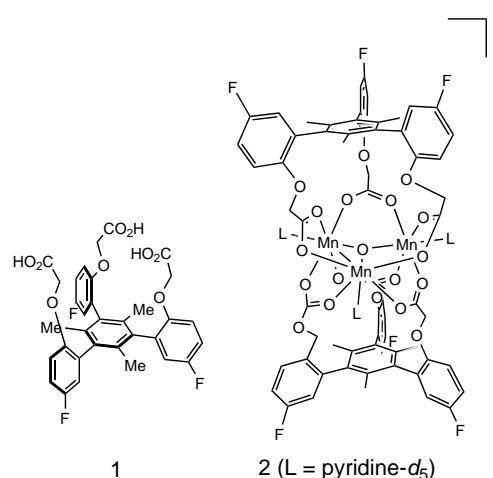
### 3. Reconstitution of the Water-Oxidizing Complex in Photosystem II Using Synthetic Mn Complexes: A Fluorine-19 NMR Study<sup>3)</sup>

Oxygen evolution is one of the most important processes in plant photosynthesis. The function is performed at the oxygen-evolving complex (OEC), which resides at the oxidizing terminal of Photosystem II (PS2) and contains manganese ions as essential cofactors. One interesting approach research on photosynthetic oxygen evolution is the reconstitution of the Mn-depleted PS2 with synthetic Mn complexes. In some cases the reconstituted PS2 shows similar activity as the native one, and in other cases the reconstituted PS2 performs different reaction from the native one.<sup>4)</sup> However, owing to the large size and extreme complexity of the PS2 protein, it is not easy to elucidate the reconstitution process at the molecular level. Specifically, the fate of the synthetic ligands during the reconstitution process remained unclear.

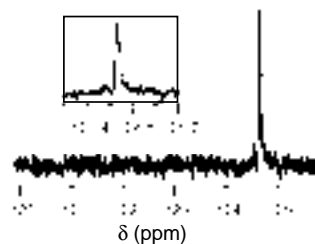
In this work, we developed a new tricarboxylate ligand **1** containing fluorine (Figure 4). The ligand is designed suitably to bind to a trinuclear Mn<sub>3</sub>(μ<sub>3</sub>-O) core, which is an important structural motif in the OEC. When the Mn-depleted PS2 particles were treated with the trinuclear Mn complex **2**, all the photosynthetic activities (including oxygen evolution) were restored. It was particularly notable that the reconstitution was

completed at much lower concentration than the simple salts like MnCl<sub>2</sub>, which suggests the positive role of the ligand in the reconstitution process.

The <sup>19</sup>F NMR of the reconstituted PS2 was examined. In spite of the very low concentration of the Mn complex, the signal was clearly observed after 30000 scans (Figure 5). This signal was assigned to the free ligand **1**, which indicates that the ligand was released from the complex **2** during the reconstitution. On the other hand, in the absence of the PS2 particles the decomposition of the complex **2** was slow. We propose that the primary step in the reconstitution process is the prebinding of the Mn complex to the hydrophobic part of the PS2 particle. This proposal is also consistent with our previous results on the reconstitution of OEC with synthetic Mn complexes.



**Figure 4.** The tricarboxylate ligand **1** and the Mn<sub>3</sub> complex **2**.



**Figure 5.** <sup>19</sup>F NMR spectra of the mixture of the Mn-depleted PSII particles (Chl 100 mg ml<sup>-1</sup>) and **2** (10 μM) in the MES/D<sub>2</sub>O buffer.

#### References

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