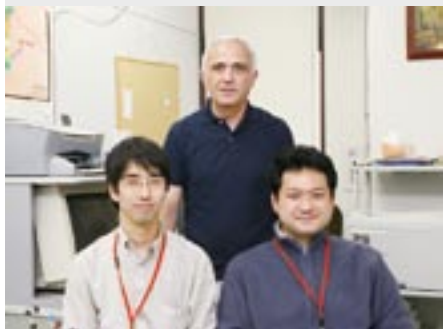


Building Photosynthesis by Artificial Molecules

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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. An Approach towards Artificial Quinone Pools by Use of Photo- and Redox-Active Dendritic Molecules¹⁾

Mimicking individual processes of photosynthesis by use of artificial molecules is an interesting approach for chemists to build up new systems for light-to-chemical energy conversion. In this respect, particular success has been, and is being, achieved by studies on photoinduced electron transfer, models of antenna systems and oxygen evolving complexes. However, many other features of photosynthesis are still unexplored by model chemists. The quinone pool is one of such disregarded features.

We built a “single-molecular” quinone pool by use of synthetic molecules (Figure 1). The molecules are based on dendrimers with well-defined size and shape. A porphyrin (photoactive group) is attached at the center, and multiple quinones are attached at internal positions of the dendrimer.

When these molecules were irradiated with visible light ($\lambda > 500$ nm) in the presence of 4-*tert*-butylthiophenol, the quinones were gradually converted to the corresponding quinols. Figure 2 shows the time-dependent change of ^1H NMR under these conditions. This reaction is triggered by photoexcitation of the porphyrin. A particularly interesting observation in

Figure 2 is that the quinones of all layers in G3Q₁₄P were converted to quinols at similar apparent rates. We attribute this apparent layer independence of the conversion rate to the photoinduced exchange of quinone/quinol.

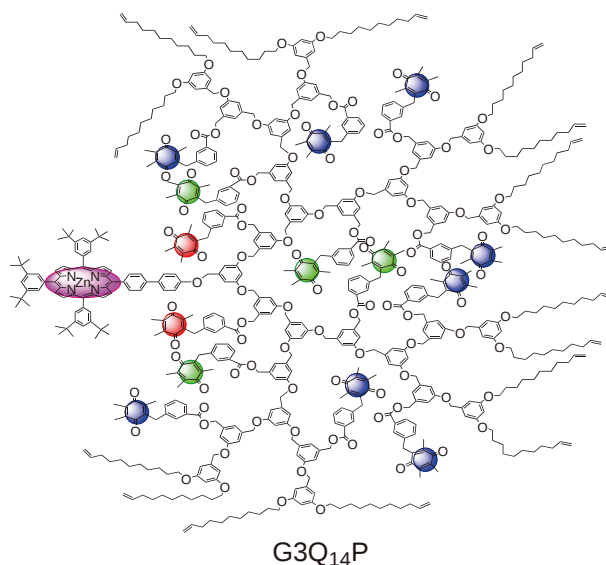


Figure 1. The artificial quinone pool compound.

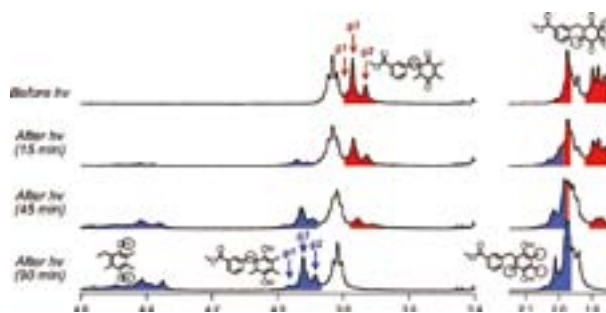


Figure 2. Time-dependent change of the ^1H NMR of G3Q₁₄P during photoreaction with 4-*tert*-butylthiophenol.

2. Rigid Tricarboxylate Ligands Derived from Triarylmesitylenes and Their Metal Complexes

Carboxylate ligands are widely found in active sites of metalloenzymes. From the synthetic point of view, however, there is one long-standing problem about metal-carboxylate clusters; carboxylate ligands can exist in various coordination modes (monodentate, η^1 -bridging, η^2 -bridging with *syn/anti* variations, *etc.*), hence it is very difficult to predict what structure(s) will result under particular reaction conditions. Even preformed clusters can easily rearrange to give products with very different structures.

To overcome these general difficulties in metal carboxylate chemistry, we developed a new tricarboxylate ligand **1**, which is designed suitably to bind to a particular trinuclear $M_3(\mu_3-O)$ core (Figure 3). The ligand **1** is a derivative of *syn*-2,4,6-tris(2'-X-aryl)-1,3,5-trimethylbenzene (triarylmesitylene), in which the three side chains (X) of the aryl groups are fixed in the same side of the central mesitylene ring because of the restricted rotation of the aryl-mesityl bonds. In addition, the carboxylate groups at the end of the side chains are located in suitable positions to bind to a $M_3(\mu_3-O)$ core.

We successfully prepared the triiron complex $[Fe_3(\mu_3-O)(1)_2(H_2O)_3]FeCl_4$ and characterized by X-ray crystallography (Figure 4). Interestingly, the similar compound lacking the 1,3,5-methyl groups did not give the similar complex. Such difference was rationalized by the molecular dynamic (MD) simulations (Figure 5). This ligand will serve as useful building blocks for constructing difficult metal clusters as observed in the photosynthetic oxygen-evolving center.

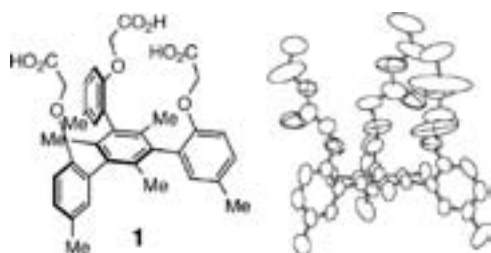


Figure 3. The ligand **1** and the X-ray structure of the triethyl ester.

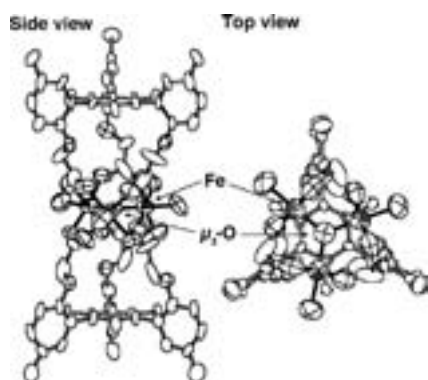


Figure 4. The X-ray structure of $[Fe_3(\mu_3-O)(1)_2(H_2O)_3]^+$.

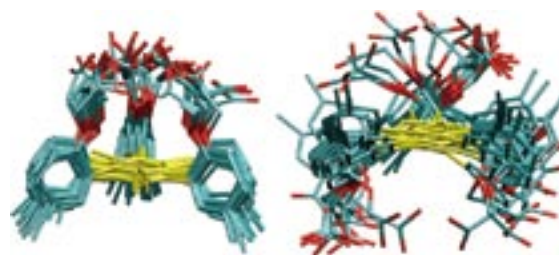


Figure 5. The MD trajectory of **1** (left) and that lacking the 1,3,5-methyl groups (right).

3. Reconstitution of the Water-Oxidizing Complex in Photosystem II Using Synthetic Mn Complexes: Production of Hydrogen Peroxide²⁾

Oxygen evolution is one of the most important, and most enigmatic, processes in plant photosynthesis. The function is performed at the oxygen-evolving complex (OEC), which contains, among others, four manganese ions as essential cofactors. The OEC resides at the oxidizing terminal of Photosystem II (PS2). Since the PS2 is a very efficient biomolecular device for photoinduced charge separation, replacing the OEC with other metal complexes is an interesting approach for developing new functions of photoinduced chemical conversion.

We attempted the reconstitution of the OEC with several dinuclear complexes of Mn(II) and Mn(IV). The reconstituted PS2 samples with these compounds regained the electron-transfer capability, but the oxygen evolution capability was less efficient. More interestingly, it was shown that hydrogen peroxide was produced by these reconstituted PS2 samples. This is the first example of reconstituted PS2 samples that exhibit non-natural photochemical functions.

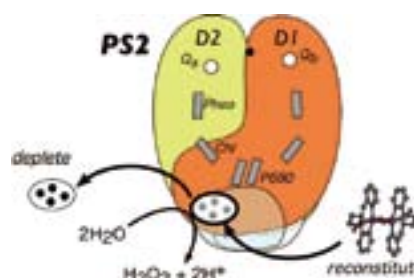


Figure 6. Schematic representation of PS2 reconstituted with an artificial Mn complex.

References

- 1) T. Nagata and Y. Kikuzawa, *Biochim. Biophys. Acta* **1767**, 648–652 (2007).
- 2) T. Nagata, T. Nagasawa, S. K. Zharmukhamedov, V. V. Klimov and S. I. Allakhverdiev, *Photosynth. Res.* **93**, 133–138 (2007).

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