

# 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.

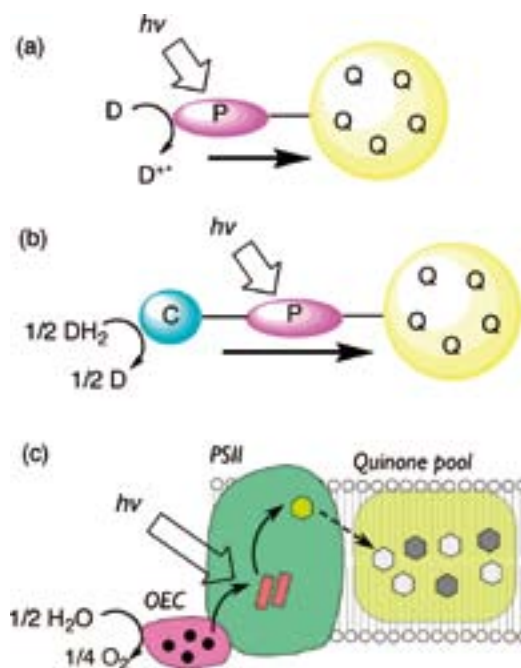
## 1. Synthesis of A New, Ternary TEMPO-Porphyrin-Quinone Pool Molecule<sup>1)</sup>

Plant photosynthesis is one of the most important biological activities on this planet. It is of interest, both academic and industrial, to mimic this process by artificial chemical systems. To achieve this goal, it is useful for chemists to mimic individual processes of photosynthesis by use of artificial molecules. Although many aspects of natural photosynthesis have been modeled by use of artificial molecules, there are still many important features of photosynthesis that are yet unexplored by model chemists.

Among these disregarded features in photosynthesis, we have been focusing on the quinone pools. The quinone pools in biological systems consist of a collection of quinones embedded in special membranes, and they work as buffers between the redox enzymes embedded in the same membranes. Previously we reported our research on building a “single-molecular” quinone pool by use of synthetic dendrimer molecules; in these molecules, the quinones were converted to quinols by irradiation in the presence of reducing agent (thiols).

Our “first-generation” quinone pool, however, lacked one important aspect. After giving an electron to the quinone, the

oxidized porphyrin must receive an electron from the electron donor directly (Figure 1a). This is not always easy, because one-electron oxidation of a closed-shell molecule often requires high overpotential. To overcome this difficulty, it is desirable that the porphyrin has a neighboring catalytic site that oxidizes the substrate (electron donor) with low overpotential and supply electrons to the porphyrin (Figure 1b).



**Figure 1.** Pictorial representation of the quinone pools. P, Q, D, C denote pigment (porphyrin), quinone, electron donor, and catalytic site, respectively. The bold arrows indicate the flow of electrons. (a) A simple quinone-pool molecule, (b) a “ternary” quinone-pool molecule with an electrocatalytic site, (c) a schematic view of the oxidizing end of plant photosynthesis. OEC: oxygen evolving complex, PSII: photosystem II.

In this work, we present the first preparation of “ternary” quinone-pool molecules (Figure 2). As the electrocatalytic site, we featured TEMPO (2,2,6,6-tetramethylpiperidinyloxy free radical), which is known to catalyze oxidation of various organic substrates including alcohols, thiols, and alkenes. The choice of TEMPO was based on our previous finding that the TEMPO/porphyrin/quinone ternary system was effective for photochemical oxidation of alcohol.<sup>2)</sup>

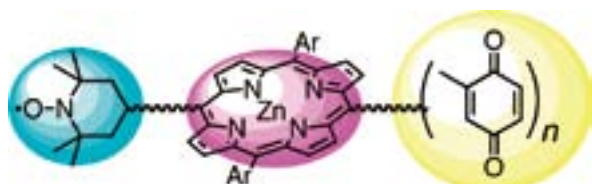


Figure 2. The “ternary” quinone-pool molecule in this work.

## 2. Syntheses of the Terpyridine-Bipyridine Linked Binary Ligands, and Structural, Redox Properties of Their Cobalt Complexes<sup>3)</sup>

One of the necessary components for photosynthetic chemical conversion is the redox catalysts that generate useful chemicals from abundant source via electrochemical reactions. Transition metal complexes are especially important in this respect, because they are capable of facile single-electron transfer. Among the various transition metals, the 3d metals are particularly important because of their wide availability. However, the 3d metals are generally more substitution labile than the 4d and 5d congeners, so that a certain artifice is necessary in the ligand part to make useful complexes of 3d metals. It is noteworthy that many metalloenzymes use 3d metals in their active centers, where appropriate arrangement of donor atoms are provided by the amino acids embedded in the protein backbone.

We are currently studying “binary” ligands, in which the two different ligands are arranged closely so that the construction of mixed-ligand complexes are made easy and, at the same time, the connection is flexible enough for the complex to accommodate to the change of the chemical environments. We are particularly interested in cobalt complexes among the 3d metals, and previously we synthesized the terpyridine-catechol-Co(III) complexes and discussed their structural and redox properties. However, we would also like to work with Co(II) and Co(I) complexes, because Co(II) and Co(I) complexes exhibit various interesting chemistry, such as hydrogen production and formation of metal-carbon bonds, which should be useful in development of photosynthetic chemical conversion. On the other hand, the Co(II) and Co(I) complexes pose a greater synthetic challenge than the Co(III) complexes, because these ions are more labile towards ligands substitution than Co(III).

In this work, we report the syntheses of new terpyridine-based binary ligands, **1a-d** and their Co(II) complexes, **2a-2d** and **2a'-2d'**. By using the bipyridine and terpyridine, the ligands act as the penta-dentate ligands and, one coordination site will be vacant. We found that the redox properties were greatly affected by ligand exchange at this “vacant” site, as well as by the length of the intervening methylene chains.

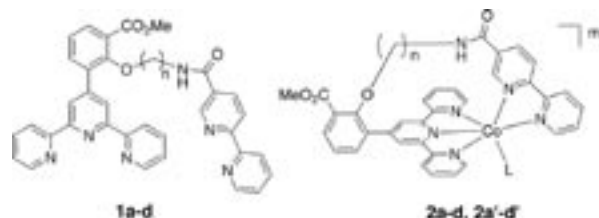


Figure 3. (a) The binary ligands **1a-d** ( $n = 3-6$ ). (b) The cobalt(II) complexes **2a-d** ( $L = \text{Cl}$ ,  $m = 1$ ) and **2a'-d'** ( $L = \text{H}_2\text{O}$ ,  $m = 2$ ).

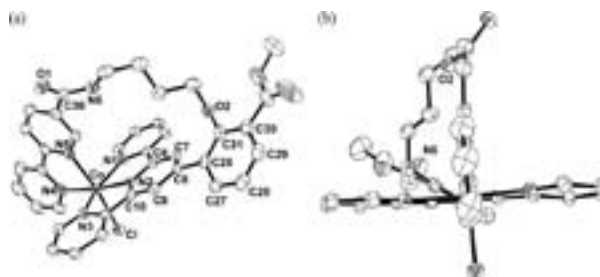


Figure 4. The ORTEP drawing of the complex cation of **2b**. [Reprinted with permission from ref. 3, Copyright (2009) American Chemical Society.]

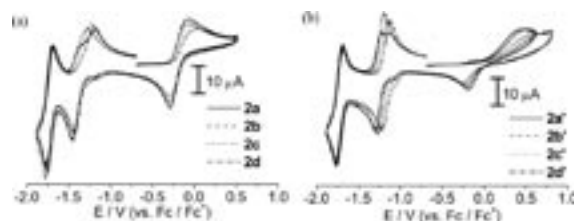


Figure 5. The cyclic voltammograms of the cobalt complexes **2a-d** and **2a'-d'**. [Reprinted with permission from ref. 3, Copyright (2009) American Chemical Society.]

## References

- 1) T. Nagata, Y. Kikuzawa, T. Nagasawa and S. I. Allakhverdiev, *Trans. Mater. Res. Soc. Jpn.* in press.
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