

# Building Photosynthesis by Artificial Molecules

Research Center for Molecular Scale Nanoscience  
Division of Molecular Nanoscience



NAGATA, Toshi  
KAWAO, Masahiro  
KON, Hiroki  
MIURA, Takahiro  
YUSA, Masaaki  
WANATABE, Yoko

Associate Professor  
IMS Fellow  
Post-Doctoral Fellow  
Graduate Student  
Graduate Student  
Secretary

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.

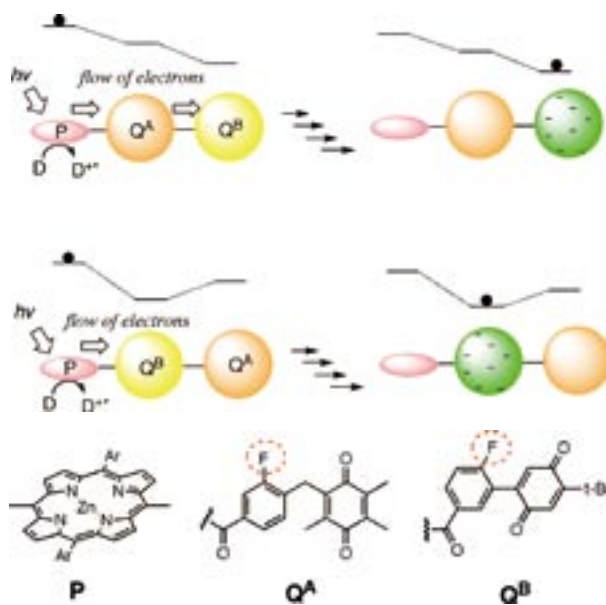
## 1. Synthesis of Single-Molecular Quinone Pools with Internal Redox Gradients and $^{19}\text{F}$ -NMR Handles

Mimicking photosynthesis by artificial molecules is an interesting research subject from both academic and industrial viewpoints. Although many aspects of natural photosynthesis have been successfully modeled by use of artificial molecules, there are still many important features that are yet unexplored by model chemists. One of such disregarded features is the quinone pool, which consists of a collection of quinones embedded in some biomembranes.

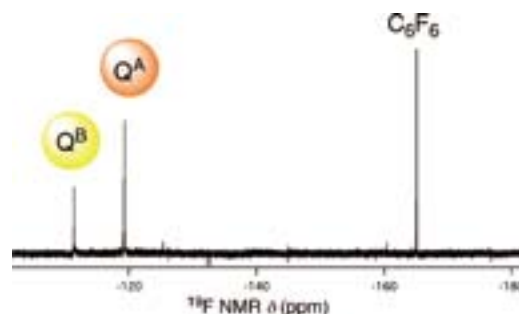
Previously we reported our research on building “single-molecular” quinone pools by use of synthetic dendrimer molecules.<sup>1,2)</sup> In these molecules, the quinones were converted to quinols by irradiation of the attached porphyrin with visible light in the presence of reducing agents (thiols). However, all quinones in these molecules were the same, so that there was no chance to realize vectorial electron transport which is essential for photochemical energy conversion.

In this work, we prepared new quinone pool molecules that contained two different quinones with different redox potentials. By changing the locations of the quinones, we can control the vectorial electron transport within the pool. We also introduced fluorine atoms to the quinones, which enable

selective observation of the changes in the quinone moieties by  $^{19}\text{F}$  NMR spectroscopy.



**Figure 1.** Pictorial representation of the quinone pool molecules in this work. P: Pigment (porphyrin), QA and QB: Quinones, D: Electron donor.



**Figure 2.** The  $^{19}\text{F}$  NMR of the synthesized quinone-pool molecule.

## 2. Synthesis of Zinc Porphyrin/Co(II) Polypyridine Dyad Molecules by Use of Terpyridine-Bipyridine Binary Ligands

Combination of photoinduced electron transfer and redox chemistry of transition metal complexes is an attractive way to achieve useful photochemical energy and materials conversion. A number of successful systems have been reported in the literature, however most of them share one potentially disturbing issue: Use of precious metals such as Ru, Rh and Re. In addition to their high cost, they may suffer from availability problems due to the low abundance of these elements. Therefore, it is desirable to substitute them with more common elements.

In the present study, we chose Zn porphyrins as photosensitizers, and a Co(II) polypyridine complex as a redox-active metal center. The redox chemistry of Co(II) is particularly interesting, because it can be converted to a super-nucleophilic Co(I) species by one-electron reduction, which can be easily achieved by photoinduced electron transfer.

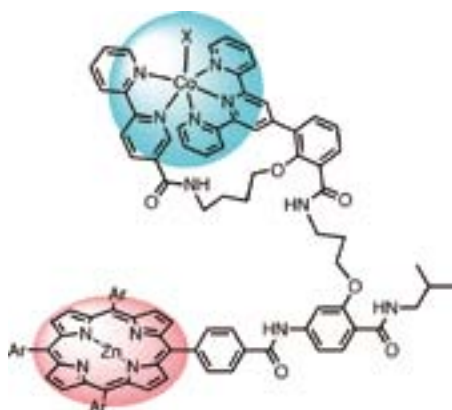


Figure 3. The Zn porphyrin/Co(II) complex dyad molecules.

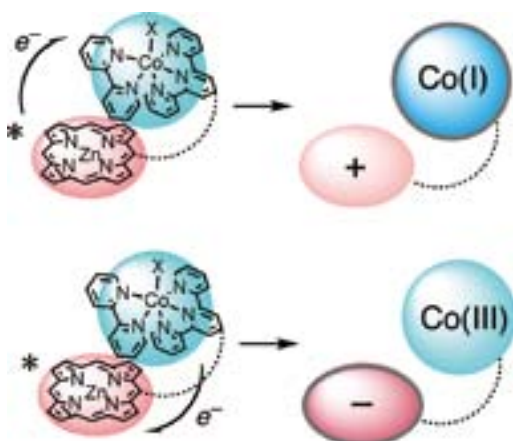


Figure 4. Two different routes for photoinduced electron transfer between the porphyrin and Co(II) complex

We synthesized a series of Zn porphyrin/Co(II) complex dyad molecules with two objectives. One is to utilize our terpyridine-bipyridine binary ligand which enabled predictable formation of Co(II) mononuclear complexes without complication by ligand exchange.<sup>3)</sup> The other is to examine the photochemical interaction between the Zn porphyrin and the Co(II) complex in the intramolecular manner, particularly with porphyrins having various redox potentials.

## 3. Synthesis of Diporphyrin Molecules with Tweezer-Like Bridges

Molecules capable of dynamic conformational change are gaining interest as components of “molecular machines.” Such conformational changes should be also useful in chemical energy conversions, as known in the molecular mechanism of cytochrome bc1 enzyme. Based on this consideration, we have started research on tweezer-like molecules whose photochemistry and redox chemistry can be modulated by conformational changes.

In this study, we synthesized a diporphyrin molecule with a tweezer-like bridge, where one leg of the tweezer has a zinc porphyrin and a positive charge, and the other leg has a free-base porphyrin and a negative charge. The conformation of the molecule was estimated by the intramolecular energy transfer from the zinc porphyrin to the free-base porphyrin. The conformational change in the solution phase was recorded by systematic change of the polarity and ionic strength of the surrounding media.



Figure 5. The diporphyrin tweezer and the conformational change.

## References

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- 2) T. Nagata, Y. Kikuzawa, T. Nagasawa and S. I. Allakhverdiev, *Trans. Mater. Res. Soc. Jpn.* **34**, 505–508 (2009).
- 3) H. Kon and T. Nagata, *Inorg. Chem.* **48**, 8593–8602 (2009).