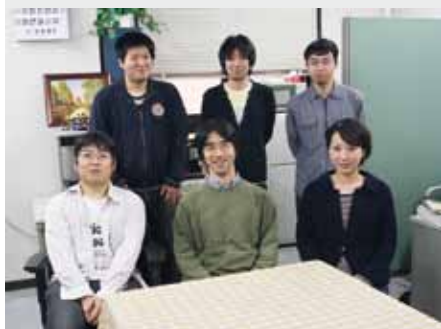


Building Photosynthesis by Artificial Molecules

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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. Photoreaction of Zinc Porphyrin/Co(II) Polypyridine Dyad Molecules with Hydroquinones as Electron Donors

Combination of photoinduced electron transfer and redox chemistry of transition metal complexes is an attractive way to achieve useful photochemical energy and materials conversion. We are particularly interested in systems having organic pigments as photosensitizers and first-row transition metals as catalytic sites.

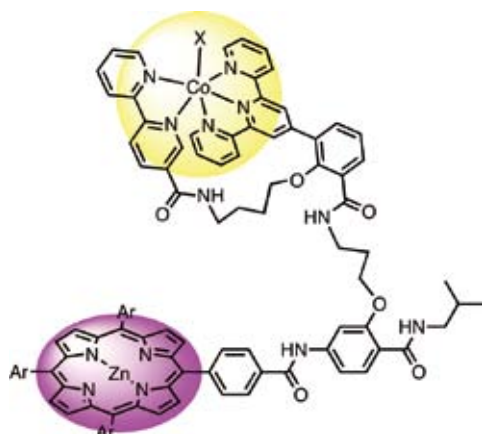


Figure 1. The Zn porphyrin/Co(II) complex dyad molecules.

Along this line, we prepared a series of dyad molecules consisting of zinc porphyrins and cobalt(II) complex (Figure 1). By use of this dyad molecule as a catalyst, we developed a new photoreaction, in which chloroform is reduced to lower chlorinated hydrocarbons with hydroquinone as the electron donor. Hydroquinone is used as the intermediate electron carrier in natural photosynthesis and other biochemical energy conversion systems, and the present system is a novel example of photosynthetic model that utilizes hydroquinone as the electron donor.

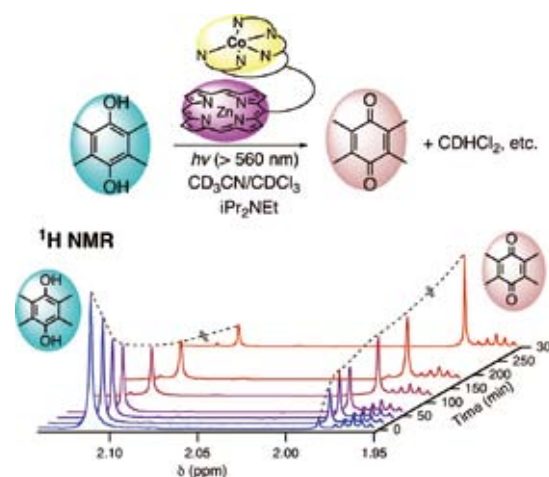


Figure 2. Photoreaction of ZnP/Co dyad with hydroquinone.

Although the detailed reaction mechanism of this photoreaction is still under investigation, one plausible mechanism is shown in Figure 3. The mechanism involves reductive quenching of the excited porphyrin by hydroquinone (or its anionic form), followed by charge shift reaction to generate the Co^{I} intermediate. The Co^{I} species is highly nucleophilic and will easily react with chlorocarbon to produce some active species, which eventually generates the product. This reaction should open the door to utilization of a regenerable electron donor in photochemical materials conversion.

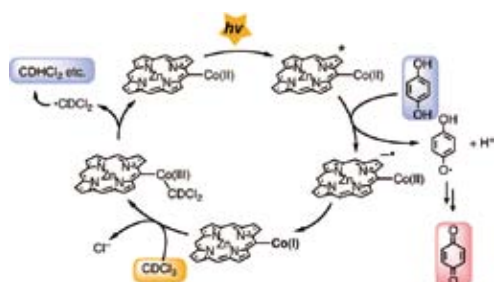


Figure 3. Plausible mechanism of the photoreaction.

2. Improved Synthesis of Single-Molecular Quinone Pools with Internal Redox Gradients and ^{19}F -NMR Handles

As demonstrated in the last section, hydroquinone/quinone interconversion is becoming important as a component of photochemical materials conversion. In this context, the “quinone pool” of natural photosynthesis should need much attention. The quinone pool in natural photosynthesis consists of a collection of plastoquinones embedded in thylacoid membranes, and transport electrons (and protons) between different redox enzymes.

Previously we reported our research on building “single-molecular” quinone pools by use of synthetic dendrimer molecules.¹⁾ Our next targets are (1) quinone pools containing two different quinones with different redox potentials, and (2) linearly extended quinone pools with two different photosystems on both ends. We synthesized the molecule shown in Figure 4, which is a third-generation dendrimer molecule with two different quinones in the internal positions. Although we had already published a quinone pool molecule based on a similar amide-dendrimer framework,²⁾ our new synthesis employs introduction of protected quinones in the early stage of dendron synthesis, thus allowing generation-selective incorporation of different quinones.

3. Synthesis and Photoreaction of Soluble Phthalocyanines

Although porphyrins are very useful pigments in photo-synthetic model systems, they are not optimal in terms of utilizing solar light. In particular, they do not absorb light of wavelength longer than 650 nm, which limits usage of red to near-infrared light. Therefore, it is desirable to use pigments

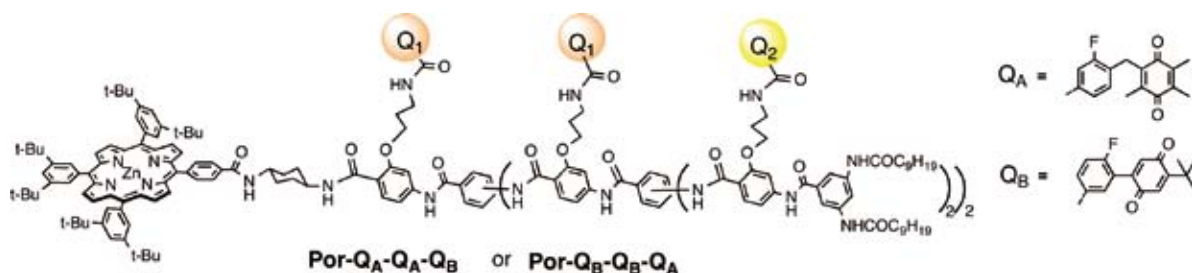


Figure 4. The third-generation quinone pool molecule with internal redox gradient.

that have strong absorption in this region. Phthalocyanines are good candidates as they have very strong absorption bands around 700 nm. However, incorporating phthalocyanines in complex molecular systems often causes difficulty because of the low solubility of phthalocyanine derivatives. To address this problem, we chose phthalocyanines having 2,4-di-tert-butylphenoxy substituents in the periphery. These phthalocyanines are very soluble in many organic solvents (including hexanes), so that the manipulation is easy.



Figure 5. Highly soluble phthalocyanines used in this work.

The high solubility of these phthalocyanines also allowed us to study photoreactions in a solution phase. Thus, the photoreduction of duroquinone by thiophenol was carried out in the presence of phthalocyanine and porphyrin. The results clearly show that phthalocyanine can utilize low-energy light more efficiently than porphyrin.

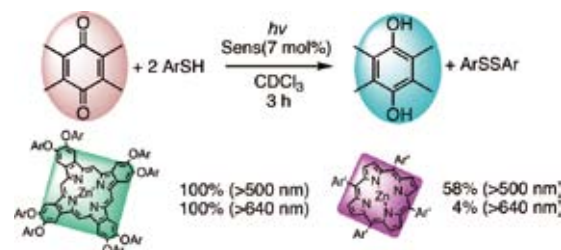


Figure 6. Comparison of photoreaction of phthalocyanine and porphyrin.

References

- 1) T. Nagata and Y. Kikuzawa, *Biochim. Biophys. Acta* **1767**, 648–652 (2007).
- 2) T. Nagata, Y. Kikuzawa, T. Nagasawa and S. I. Allakhverdiev, *Trans. Mater. Res. Soc. Jpn.* **34**, 505–508 (2009).