Building Photosynthesis by Artificial Molecules

Research Center of Integrative Molecular Systems
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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 and examining their redox and photochemical behavior.

1. Synthesis and Dynamic Behavior of Tweezer-Like Molecules with Opposite Electric Charges

The biological photosynthetic devices have mostly static structures that are optimized for efficient energy transfer and charge separation. After the photoinduced charge separation, however, many chemical transformations are necessary to complete the light-to-chemical energy conversion. For this particular purpose, it is rather beneficial to introduce "dynamic" structural features, because chemical transformation is often accompanied by substantial structural change of the substrates.

We aimed at introducing dynamic behavior on photosynthetic model compounds. The ultimate goal should be control of chemical transformation by way of photoinduced electron transfer. Presently, we focus on the synthesis of molecules that potentially respond to local electric field resulting in structural change.

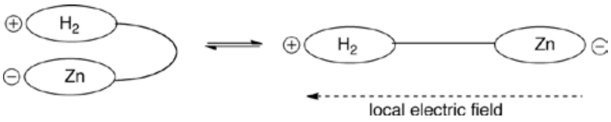

Figure 1. The design of the tweezer molecule.

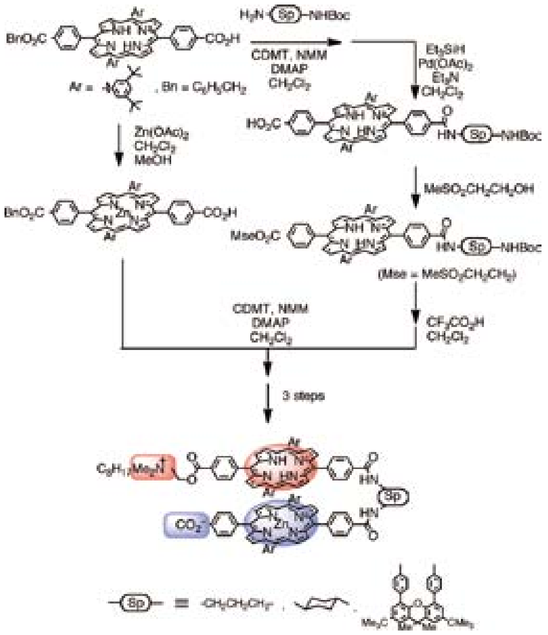

Figure 2. Synthesis of the tweezer molecule.

The design of the target molecule is shown in Figure 1. The molecule has a tweezer-like structure, with a free-base porphyrin and a zinc porphyrin at both ends. The shape of the

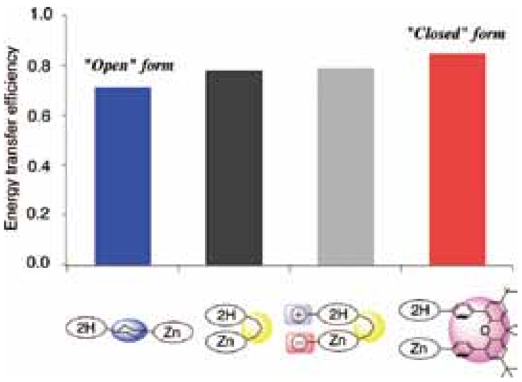

Figure 3. The fluorescence energy transfer efficiencies for the tweezer molecules and reference molecules.

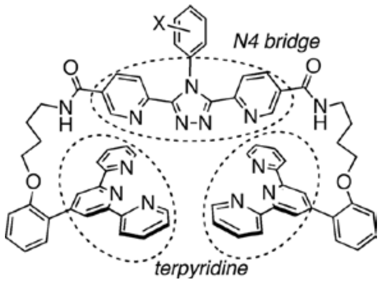

Figure 4. The new ternary binucleating ligand with 1,2,4-triazole bridge.

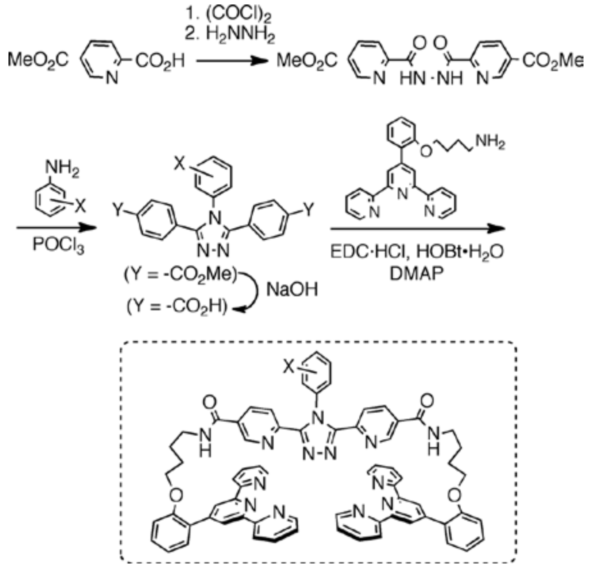

Figure 5. Synthesis of the ternary binucleating ligand.

molecule can be estimated from the degree of the fluorescence energy transfer from the zinc porphyrin to the free-base porphyrin. Moreover, there are introduced two opposite charges on both ends.

The synthesis of the tweezer molecule is shown in Figure 2. Three different spacers were used: Trimethylene (flexible), cyclohexane-1,4-diyl (fixed at "open" conformation), and xanthene-1,8-diyl (fixed at "closed" conformation). The equilibrium conformations of these molecules were estimated by fluorescence energy transfer experiments (Figure 3). The trimethylene-bridged molecules were found to have intermediate conformation between "open" and "closed" forms. Contrary to our expectation, the conformations of the tweezer molecules did not change when two opposite charges were introduced at both ends. In fact, molecular dynamic simulations revealed that the aryl substituents on the porphyrin rings caused substantial steric repulsion that precludes approach of the two charges at the ends. Simulations also revealed that if the charges were introduced at the 10-positions (instead of the 15-position as in the present molecules), the charges can approach each other in spite of the steric repulsion of the aryl substituents.

2. Synthesis of a Ternary Binucleating Ligand with 1,2,4-Triazole Bridge and Its Metal Complexes

Multinuclear transition metal complexes are promising components for artificial photosynthesis, because of their ability to perform multielectron redox reactions. One challenging issue is to use 3d transition metals for this purpose. The 4d and 5d transition metals (Ru and Ir in particular) are frequently used in the area of artificial photosynthesis, however they are expensive and better to be replaced with cheaper 3d metals. Our group have been tackling this problem by use of multidentate organic ligands.[1–3] Herein we report the synthesis of new "ternary" binucleating ligands consisting of two terpyridines and one "N4 bridge," 3,5-bis(2-pyridyl)-1,2,4-triazole (Figure 4).

Synthesis of the ligand is shown in Figure 5. Treatment of the ligand with Co(OAc)$_2$ and Ni(OAc)$_2$ afforded metal complexes with formula [LM$_2$(OAc)]$^{3+}$ (L = ligand, M = Co or Ni). Unlike the ternary binucleating ligands with phthalazine-containing N4 bridges (which we previously reported,[3] complexes with μ_2, η^1-bridging anions (like OH$^-$ or Cl$^-$) were not observed. Such difference can be ascribed to the presence of the 5-membered ring in the present ligand, which causes larger metal-to-metal distances in comparison with the 6-membered ring in the phthalazine system. This reasoning was also supported by the preliminary X-ray results of the [LCo$_2$(OAc)]$^{3+}$ complex.

References

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