

VIII-F Designing Artificial Photosynthesis at Molecular Dimensions

Photosynthesis is one of the finest piece of molecular machinery that Nature has ever created. Its ultrafast electron transfer and following well-organized sequence of chemical transformation have been, and will continue to be, challenging goals for molecular scientists. We are trying to mimic the function of photosynthesis by assembling molecular units that perform individual physical/chemical action. The molecular units include porphyrins, redox active organic molecules, and transition metal complexes.

Last year we focused our attention on developing organic reactions that utilize photoinduced electron transfer processes and are useful for synthetic organic chemistry. This is an important step toward our ultimate goal, which is to design artificial molecular systems that effect multiple chemical reactions triggered by light on the basis of molecular rationale.

VIII-F-1 Porphyrin Catalyzed Reductive Silylation and Acylation of Quinones under Irradiation of Visible Light

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Considerable studies were reported for inter- or intramolecular photoinduced electron transfer from porphyrins to quinones, however, the synthetic application of a porphyrin as a photocatalyst for the reduction of quinones is thought to be still difficult. For example, when attempts to obtain the reduced products of a quinone was carried out using a porphyrin catalyst under irradiation of visible light in the presence of a proton source, no reduced products were detected. The reason for this unsuccessful result would be mainly attributed to the reverse electron transfer from a semiquinone anion radical to the porphyrin cation radical generated by the photoinduced electron transfer. If the semiquinone anion radical is chemically trapped by a silyl reagent and the successive silylation occurs, the reductive silylation product of the quinone is obtained. On the basis of this idea, we found both phenylthiotrimethylsilane (PhSTMS) and chlorotrimethylsilane (TMSCl) are a good trapping reagent for the reduced intermediate formed by photoinduced electron transfer from photo-excited porphyrins. In addition, the electrophilic substitution of a silyl sulfide with a phenoxy group releases a thiolate anion which would act as an electron donor. In the presence of a catalytic amount of porphyrin 1 (0.5 mol %), the

reductive silylation of duroquinone was proceeded under the irradiation of yellow light ($\lambda > 500$ nm) using PhSTMS to give 1,4-bis(trimethylsiloxy)-2,3,5,6-tetramethylbenzene (99%) and diphenyl disulfide (97%) in good yields. We also found that chlorotrimethylsilane (TMSCl), a more easily available silyl reagent, was also useful for the porphyrin-catalyzed reductive silylation.

Despite the reductive silylation and acylation of quinones with chlorotrimethylsilane and metal (K, Mg, Zn) were well known procedure, these methods require a stoichiometric amount of metals as a reductant and generate waste metal salt. Our method exhibit the practical advantage in view of this points. Further work on the precise mechanism for these reactions is underway.

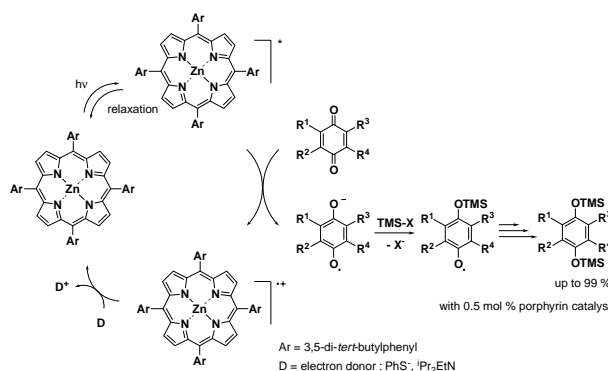


Figure 1. Porphyrin-catalyzed silylation of quinones under visible light.

VIII-G Development of New Metal Complexes as Redox Catalysts

Redox catalysis is an important field of chemistry which translates a flow of electron into chemical transformation. It is also one of the requisites for artificial photosynthesis. This project of ours aims at developing new metal complexes that perform redox catalysis at low overpotential. Our approach is to develop a series of "binary" ligands, which consist of two different types of ligands that are linked together to form metal chelates. Such ligands are particularly useful for utilizing first-row transition metal elements, because fast ligand exchange (which is often a major obstacle in studying first-row transition metal complexes in solution) is suppressed by chelate effects.

VIII-G-1 Synthesis of Terpyridine-Based Binary Ligands and Their Metal Complexes

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2,2':6',2''-Terpyridine is a promising ligand for application in redox catalysis, thanks to its structural

rigidity and chemical stability. Unfortunately, with first-row transition metals it easily forms homoleptic bis(terpyridine) complexes that are too stable to serve as redox catalysts. Such difficulty can be overcome by connecting a bidentate ligand to a terpyridine molecule. The “binary” ligand thus formed is potentially pentadentate and binds an octahedral metal ion leaving one vacant site for catalytic reactions. We already reported synthesis of terpyridine-catechol linked ligands and their cobalt(III) complexes (Figure 1a). Here we report synthesis of a terpyridine-salicylaldehyde linked ligand (Figure 1b) and their metal complexes.

The ligand (tpyC5NHCOsalH) was prepared by condensation of 4-(2-(5-aminopentyloxy)phenyl)-terpyridine and 2-allyloxy-3-diethoxymethyl-5-methylbenzoic acid potassium salt (prepared by 6 steps and 4 steps from commercially available material, respectively), followed by removing the allyl and diethyl acetal protecting groups (60% yield). The metal complexes ($M^{2+} = Mn^{2+}, Fe^{2+}, Co^{2+}$) were prepared by the reaction of the ligand with $[M(CH_3CN)_x](ClO_4)_2$ and 2,6-lutidine (1:1:2 in molar ratio) in CH_3CN . The ESI-MS spectra suggested 5-coordinate complexes, $[M(tpyC5NHCOsal)]^+$, were present in solutions.

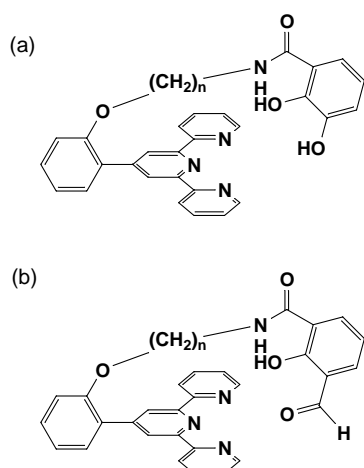


Figure 1. Terpyridine-based binary ligands.