VIII-H 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. Our ultimate goal is to design artificial molecular systems that effect multiple chemical reactions triggered by light on the basis of molecular rationale.

VIII-H-1 Photoinduced Oxidation of Alcohols Catalyzed by Porphyrins and TEMPO

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Photoinduced electron transfers involving porphyrins are widely studied, but utilizing the high-energy radical ion pairs for driving chemical reactions remains to be a great challenge. Herein we report the TEMPO-mediated oxidation of alcohols catalyzed by porphyrins under irradiation with visible light. Although there have been many reports on TEMPO-mediated oxidation of alcohols, our system is the first to utilize photoinduced electron transfer including porphyrins.

When a solution of benzyl alcohol (**1**, 0.1 mmol), duroquinone (**2**, 0.1 mmol), TEMPO (**3**, 2,2,6,6-tetramethylpiperidine N-oxide, 0.1 mmol), diisopropyl-ethylamine (0.2 mmol) and 5,10,15,20-tetrakis(3,5-*di-t*-butylphenyl)porphinatozinc(II) (**4**, 0.001 mmol) in THF/DMF (1/1, 0.5 ml) was irradiated with visible light ($\lambda > 500$ nm, halogen lamp with a Toshiba Y-52 filter) for 10 hours, benzaldehyde (**5**) was formed in 23% yield. On addition of tetrabutylammonium perchlorate (0.1 mmol), the yield was improved to 42%. When either TEMPO, duroquinone, diisopropylethylamine or porphyrin was omitted, or in the absence of light, no benzaldehyde was detected.

As the reaction proceeded, 2,2,6,6-tetramethyl-N-hydroxypiperidine (TEMPO-H, **9**) was detected together with benzaldehyde, indicating that the oxidant was TEMPO rather than duroquinone. It is noteworthy, however, that in the absence of duroquinone the reaction did not proceed. The role of duroquinone is rationally understood by assuming photoinduced electron transfer from the porphyrin to the quinone. The tentative reaction mechanism is shown in Scheme 1; (i) the photoexcited porphyrin transfers an electron to the quinone, (ii) the cation radical of the porphyrin (**7**) oxidizes TEMPO to give the oxoammonium intermediate (**8**), (iii) the oxoammonium cation oxidizes the alcohol (**1**) with the aid of the base. The quinone anion radical (**6**) should be oxidized to regenerate the quinone either (iv) by the porphyrin cation radical, (v) by the oxoammonium cation, or (vi) by TEMPO. As the paths (iv) and (v) are non-productive, they result in the lower efficiency. Indeed, the reaction was too slow to be synthetically useful, so that we looked into the way to improve the reaction efficiency.

A moderate success was achived by changing the electron acceptor. When 2,6-*di-t*-butyl-1,4-benzo-quinone was used in place of duroquinone, benzalde-hyde was obtained in 86% yield by use of 0.2 equivalents of TEMPO instead of the stoichiometric amount (solvent = base = pyridine, 27 hours irradiation). In this system, 2,5-*di-t*-butyl-1,4-hydroquinone accumulated instead of TEMPO-H. We assume that direct oxidation of the quinone anion radical was suppressed by the introduction of the bulky *t*-buyl groups.
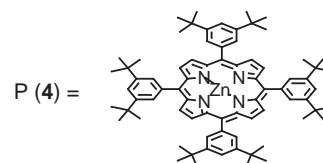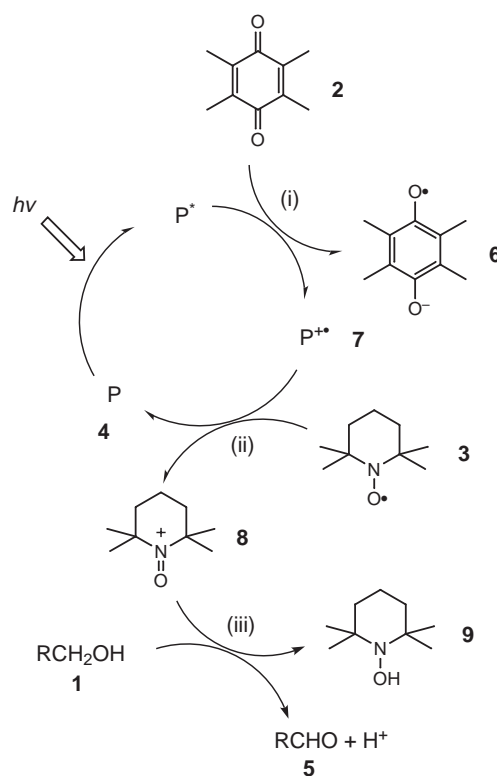
Scheme 1.

VIII-I 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. We have been focusing our attention to developing terdentate ligands with strong donor character, and have found that introducing a pyrrole ligand in place of pyridine leads to useful ligands.

VIII-I-1 Syntheses of a 6-(2-Pyrrolyl)-2,2'-Bipyridine Derivative and Its Ruthenium Complex
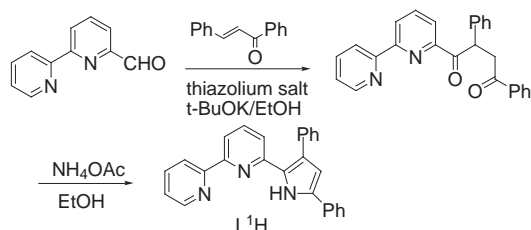
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Metal complexes of pyrroles are gathering interest as an activator of the pyrrole ring, an intermediate for synthesizing pyrrole derivatives, and as a component of conducting polymers. Herein we report the syntheses of 6-(3,5-diphenyl-2-pyrrolyl)-2,2'-bipyridine (L^1H) and its ruthenium complex $[Ru(L^1)_2]$. The compound L^1H is the first example of the "ter-aryl" ligand that has one pyrrole and two pyridine rings in this order, and it will be a useful substitute for 2,2':6',2"-terpyridine (terpy) when more electron-donating character is desirable.

The synthesis of L^1H is shown in Scheme 1. The Stetter condensation of 2,2'-bipyridine-6-carbaldehyde with chalcone was utilized, followed by ring closure of the 1,4-diketone with an ammonium salt (67% yield). By use of pyridine-2,6-dicarbaldehyde as a starting material, the compound L^2H_2, 2,6-bis(3,5-diphenyl-2-pyrrolyl)pyridine, was also obtained (69% yield).

The ORTEP drawing of the complex $[Ru(L^1)_2]$ is shown in Figure 1. The coordination geometry around the Ru(II) center is similar to that of $[Ru(terpy)_2]X_2$, however the six pyridine/pyrrole rings are not exactly coplanar.

The cyclic voltammograms of $[Ru(L^1)_2]$ and $[Ru(terpy)_2](ClO_4)_2$ are shown in Figure 2. The Ru(III)/Ru(II) couple appeared at –0.29 V (*versus* ferrocene/ferrocenium couple) in $[Ru(L^1)_2]$, which was 1.10 V more negative than in $[Ru(terpy)_2](ClO_4)$, consistent with the strong donor character of the L^1 ligand. The first reduction wave (reduction of the ligand) was also negatively shifted by 0.51 V. At higher potential range (+0.5–0.7 V), $[Ru(L^1)_2]$ showed irreversible waves suggesting the oxidative degradation of the complex. Apparently the oxidation of the pyrrole rings led to the degradation of the ligand and/or the decomplexation of the metal ion.
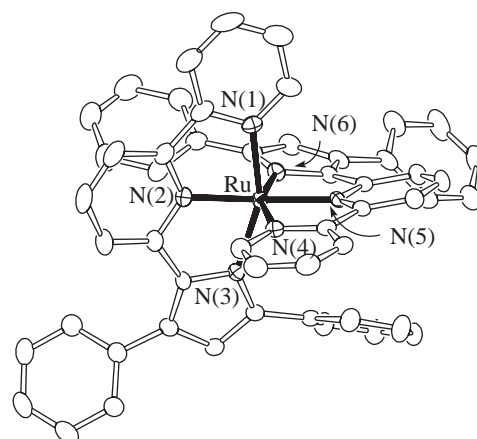

Figure 1. ORTEP view (50% probability ellipsoids) of the complex $[Ru(L^1)_2]$.
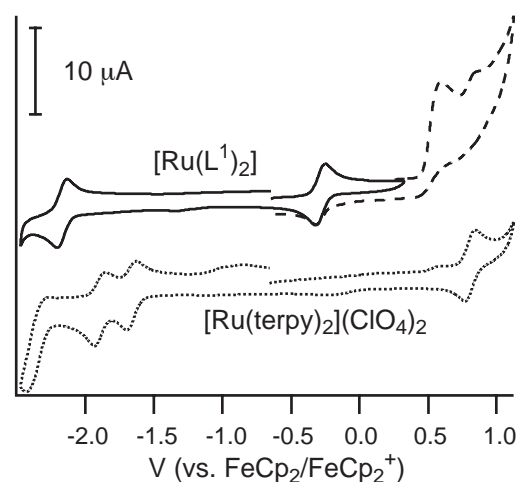

Figure 2. The cyclic voltammograms of $[Ru(L^1)_2]$ and $[Ru(terpy)_2](ClO_4)_2$.

Scheme 1. Synthesis of the ligand L^1H.