

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 present efforts focus on chemistry of manganese complexes (which are known to play a key role in oxygenic photosynthesis), and photochemistry of porphyrin/transition metal complex dyads. 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 Synthesis and Characterization of Manganese Complexes

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In search for rationally designed dimanganese complexes that catalyze four-electron oxidation of water to dioxygen, we developed two xanthene-based dinucleating ligands, XT-btpa and XT-bterpy (Figure 1).

The XT-btpa (xanthene-bis(tris(2-pyridylmethyl)amine) ligand has two metal-binding sites that are located in a well-defined geometry determined by the rigid xanthene spacer. The manganese complex was found to have an $[\text{Mn}_2(\mu\text{-O})_2]$ core.

The XT-bterpy ligand also has two metal-binding sites with a well-defined geometry, and has two terpyridine units which provide more rigid and less decomposition-prone organic environment. Three manganese complexes, $[(\text{XT-bterpy})\text{Mn}_2\text{Cl}_4]$, $[(\text{XT-bterpy})\text{Mn}_2(\text{tropolonato})_2](\text{ClO}_4)_2$, and $[(\text{XT-bterpy})\text{Mn}_2(2\text{-picolinato})_2](\text{ClO}_4)_2$, were prepared; the X-ray structure of $[(\text{XT-bterpy})\text{Mn}_2\text{Cl}_4]$ is shown in Figure 2. Either of these three complexes catalyzed disproportionation of H_2O_2 to water and dioxygen, with much higher activity than the related mononuclear complex $[(\text{terpyridine})\text{MnCl}_2]$.

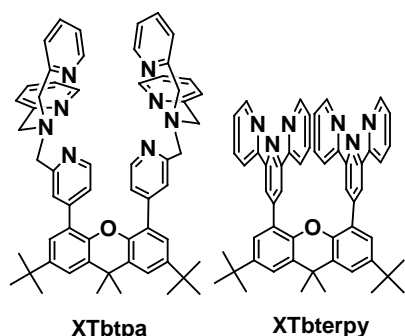


Figure 1. Two xanthene-based binucleating ligands.

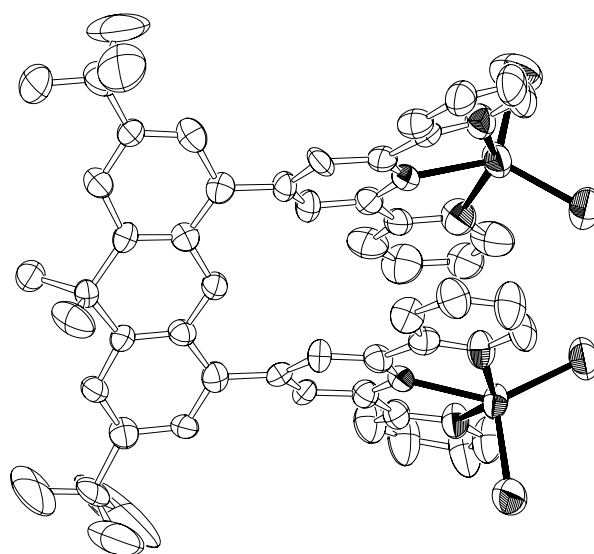


Figure 2. X-ray structure of $[(\text{XT-bterpy})\text{Mn}_2\text{Cl}_4]$.

VIII-H-2 Synthesis and Photochemical Reaction of Porphyrin/Cobalt-complex Dyad Molecules

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One of the essential features in natural photosynthetic reaction centers is ejection of the quinone acceptor from the protein to the "quinone pool," which takes place after photoinduced electron transfer. To mimic this function, we prepared a porphyrin/Co(III)-complex dyad molecule (Figure 1), where the Co(III) moiety is expected to depart from the porphyrin moiety after photoreduction, due to the relative instability of six-coordinate Co(II) complex. The steady-state fluorescence spectrum of this dyad molecule revealed that the excited singlet state of the porphyrin is effectively quenched by the presence of the Co(III) moiety. Electrochemical estimation of the reduction/oxidation potentials suggested photoinduced electron transfer from the excited porphyrin to Co(III) can take place. Irradiation of this dyad molecule in $\text{CD}_3\text{COCD}_3/\text{CD}_3\text{-CN}$ solution led to formation of the Co(III)- CD_3CN complex (80% yield by ^1H NMR) together with the imidazolyl porphyrin without the cobalt moiety. Since this ligand-exchange reaction proceeds only slowly in the absence of light, it is likely that the reaction is

catalyzed by intramolecular photoinduced electron transfer.

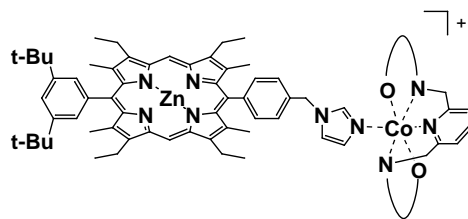


Figure 1. The porphyrin/cobalt(III)-complex dyad molecule.

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. So far we have succeeded in preparing a series of terpyridine-catechol linked ligands; application of these ligands for development of new redox catalysts is currently in progress.

VIII-I-1 Synthesis of Terpyridine-catechol Linked Ligands and Their Cobalt(III) Complexes

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Transition metal catechol complexes are gaining interest because of unique electronic properties of the catechol ligand, specifically the two-electron redox transformation between catechol and quinone forms. Combination with the terpyridine ligand should provide metal complexes with interesting redox properties and well-defined geometry. The chemistry of terpyridine/catechol/metal ternary complexes, however, is often complicated by ligand disproportionation to give stable bis(terpyridine) complexes.

We prepared three terpyridine-catechol linked ligands (Figure 1) and their cobalt(III) complexes. The X-ray structure of two Co(III) complexes are shown in Figure 2. The two complexes have a different number of CH₂ units in the linker between terpyridine and catechol. It was revealed that the C₄ linked complex (part a) has a symmetric structure with the (CH₂)₄ linker running along an approximate mirror plane that contains the catechol ring and bisects the terpyridine ligand, whereas the C₅ linked complex (part b) has no such approximate symmetry. Since the local structures around the Co(III) center are very similar for the two complexes, the structural difference is solely due to the different lengths of the polymethylene linkers; the C₄ linker presents the "just fit" length while the C₅ linker has to go the winding way to accommodate the extra CH₂ unit.

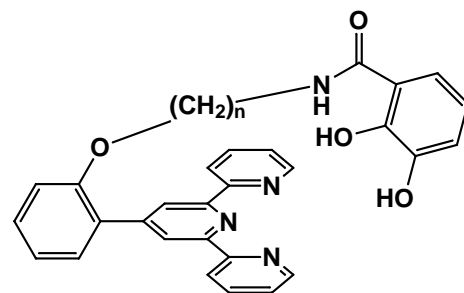


Figure 1. The terpyridine-catechol linked ligands.

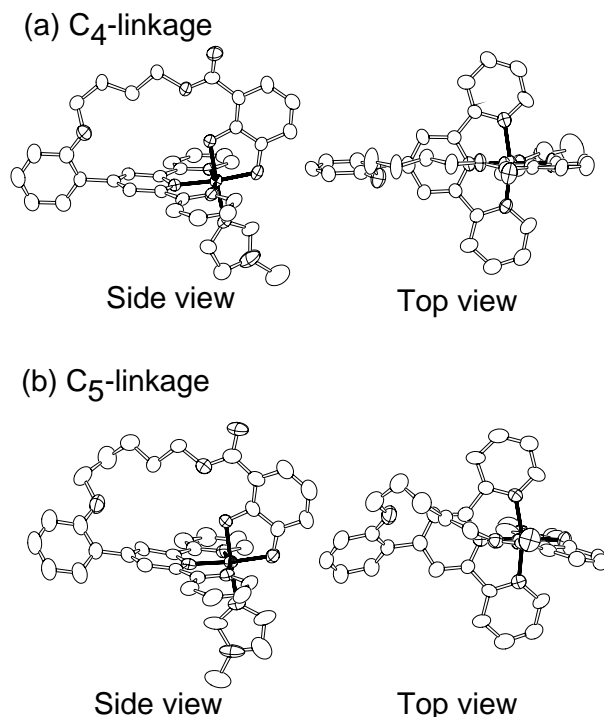


Figure 2. The X-ray structures of cobalt(III) complexes of the C₄- and C₅- linked ligands.