Synthesis and Characterization of Porphyrin-Dimanganese Composite Molecules

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The first porphyrin-dimanganese composite molecules were synthesized. Fluorescense of the porphyrin moiety was effectively quenched by the dimanganese moiety. The oxidation potentials of porphyrins showed no significant change, whereas the oxidation potentials of dimanganese moiety showed about +0.1 V shift from the porphyrin-free reference compound.

Interaction of porphyrins and transition metal complexes has become an important issue in the field of biomimetic chemistry. The hemes (iron porphyrins) covalently linked with other metal centers are the most often studied as models of various redox enzymes.[1,2] On the other hand, photochemical behavior of fluorescent porphyrins (free-base, zinc, magnesium, etc.) in the presence of other metal complexes is important in relation to natural photosynthesis and artificial photochemical energy conversion, as well as other photochemical applications.[3]

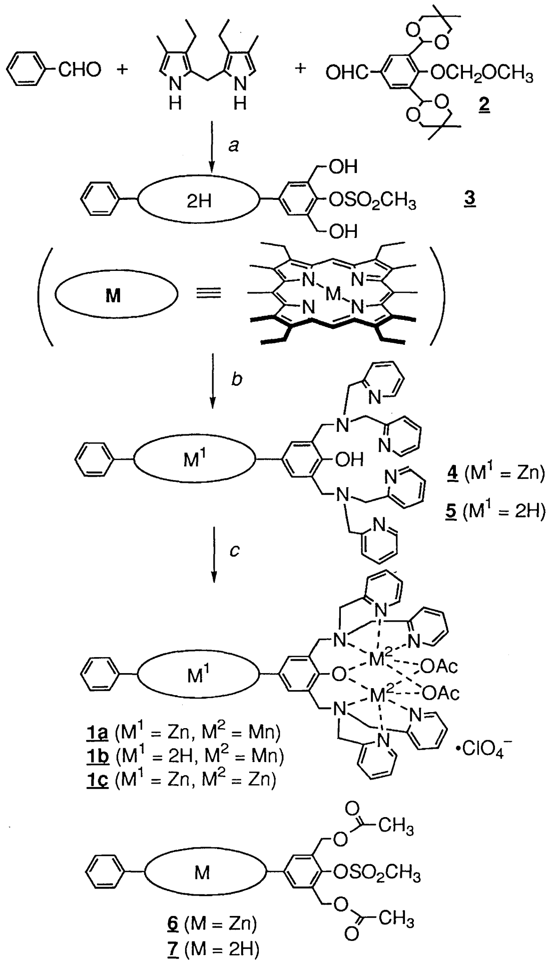
In this letter we wish to report the first synthesis of porphyrin-dimanganese composite molecules, as a potential model of the oxygen evolving system (Photosystem II) of plant photosynthesis.[4] Although the molecular design of our compound is still too crude and ineffective in mimicking the oxygen evolving *function*, these complexes are still useful for evaluating interaction between the photoexcited porphyrins and dimanganese complexes, which has not been studied to date.

The target compounds, **1a** and **1b**, are shown in Scheme 1, together with the synthetic scheme. The 2,6-bis((bis(2-pyridylmethyl)amino)methyl)phenolato(2–) unit[5] was utilized as the metal-chelating component. The dizinc version, **1c**, was prepared as a redox-inactive reference compound.

Syntheses of **1a-c** were carried out as follows. Compound **2** and benzaldehyde were condensed with 2,2'-methylenebis(3-ethyl-4-methylpyrrole) to give a mixture of three porphyrins.[6] The cross-condensation product was separated by column chromatography and converted to a mesylate-diol (**3**, step *a*). This diol was converted to a dibromide and reacted with bis(2-pyridylmethyl)amine; insertion of zinc to the porphyrin ring and subsequent hydrolysis of mesylate protection gave **4** (step *b*). Reaction of **4** (10 μmol) with $Mn(OAc)_2 \cdot 4H_2O$ (24 μmol) in MeOH under Ar, followed by addition of $NaClO_4$ (50 μmol), gave microcrystals of **1a** (55% yield, step *c*). Similar reaction using $Zn(OAc)_2 \cdot 2H_2O$ in place of $Mn(OAc)_2$ gave the trizinc compound **1c** (69% yield). On the other hand, the compound **5**, the metal-free version of **4**, was synthesized in a similar procedure, except that zinc was not inserted before hydrolysis of the mesylate. Reaction of **5** (10 μmol) with $Mn(OAc)_2 \cdot 4H_2O$ (20 μmol), followed by addition of $NaClO_4$ gave **1b** (35% yield).

FAB-MS spectrum of **1a-c** in acetonitrile/3-nitrobenzyl alcohol showed major peaks at 1357, 1296, and 1379, respectively, together with smaller, unassigned peaks. The major peaks correspond to [M – ClO_4^-] and are consistent with the formulation shown in Scheme 1 for all three compounds.

The UV-visible absorption spectra of **1a-c** in CH_3CN showed no significant changes from the reference compounds, **6** and **7**, indicating that there is no significant interaction between the porphyrin and dimetal moieties in the ground state, and that the dimanganese moiety has the (Mn^{II}, Mn^{II}) oxidation state.[7] The fluorescence emission spectra of **1a** and **1b** (at room temperature, in CH_3CN) revealed that the fluorescence of the porphyrin moiety was effectively quenched; the relative emission intensity (in reference to **6** or **7**) was about 0.1 and 0.03 for **1a** and **1b**, respectively. If we assume the typical lifetime of porphyrin fluorescence (about 10^{-9} s for **6** and 10^{-8} s for **7**),[8] the estimated rate constants of intramolecular quenching are in the order of 10^{10} s^{-1} for both compounds.[9] It is likely that intersystem crossing from S_1 to T_1 of porphyrin is greatly accelerated by the presence of dimanganese component.[10] Interestingly, the compound **1c** showed no decrease of fluorescence, which suggests the presence of the unpaired electrons in **1a** and **1b** is significant in fluorescence quenching.



Scheme 1. Synthesis of porphyrin-dimanganese composite molecules.

Differential pulse voltammograms of compounds **1a-c**, **6** and **7** are shown in Figure 1 ("ZnP", "H_2P" denote zinc- and freebase-porphyrin, respectively). The voltammogram of **1a** showed two prominent peaks at 0.13 V and 0.23 V and two smaller peaks at 0.45 V and 0.66 V (all potentials are reported here in

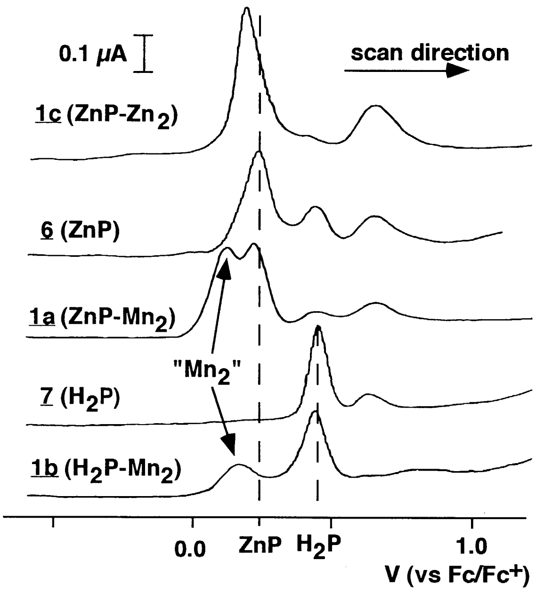


Figure 1. Differential pulse voltammograms of porphyrin-dimanganese composites and related compounds (in CH_3CN, 0.1 mol dm^{-3} Et_4NBF_4, Pt working electrode; scan rate 50 mV/s, modulation amplitude 10 mV, sampling time 10 ms; Fc = ferrocene).

reference to ferrocene/ferrocenium couple), whereas **6** showed the first oxidation peak at 0.23 V. It is therefore reasonable to assign the 0.23 V peak in **1a** to the oxidation of the porphyrin ring and the 0.13 V peak to the oxidation of the Mn_2 moiety. Similarly, the voltammogram of **1b** showed two prominent peaks at 0.16 V and 0.45 V, whereas **7** showed the first oxidation peak at 0.46 V; we can assign the 0.45 V peak in **1b** to the oxidation of the porphyrin ring and the 0.16 V peak to the oxidation of the Mn_2 moiety. Compared with the dimanganese complex of 2,6-bis((bis(2-pyridyl-methylamino)-methyl)-4-methylphenol[7b] (E_{ox} = 0.03 V vs ferrocene/ferrocenium couple) the oxidation peaks of the Mn_2 moiety in **1a** and **1b** show anodic shifts (ΔE = +0.10 V and +0.13 V for **1a** and **1b**, respectively), presumably due to the electron-withdrawing inductive effect of the porphyrin ring.[11] On the other hand, the porphyrin-oxidation peaks in these compounds appear at approximately the same potentials as in the reference compounds **6** and **7**. Interestingly, the voltammogram of **1c** showed a porphyrin-oxidation peak at 0.18 V,[12] which is cathodically shifted (ΔE = −0.05 V) from **6**. These contrasting results in Mn_2 and Zn_2 compounds indicate that the electronic effects of metal complexes on attached organic moieties depend not only on the ionic charge but also on the number of *d* electrons on the metals.

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References and Notes

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7 (a) The (Mn^{II}, Mn^{III}) complex has a characteristic absorption in 400-700 nm range,[7b] which was absent in **1a** and **1b**. (b) M. Suzuki, M. Mikuriya, S. Murata, A. Uehara, H. Oshio, S. Kida, and K. Saito, *Bull. Chem. Soc. Jpn.*, **60**, 4305 (1987).

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9 The rate of intramolecular quenching (k_q) was calculated by the equation $k_q = \tau_0^{-1}(I_0/I - 1)$, where τ_0 is the fluorescence lifetime in the absence of the quencher, I_0 and I are the fluorescence intensities in the absence and presence of the quencher, respectively.

10 (a) The "internal heavy atom effect" (*i.e.* the presence of a "heavy atom" causes rapid intersystem crossing from S_1 to T_1 due to the large spin-orbit coupling) is well known. See: N. Turro, "Modem Molecular Photochemistry," Benjamin/Cummings Publishing (1978), p. 192. (b) Photoinduced electron transfer from the dimanganese complex to the porphyrin is another possibility, although ΔG is not very favorable (about −0.1 eV and −0.3 eV for **1a** and **1b**, respectively, as estimated from the oxidation potentials of the Mn_2 moiety. See electrochemical results).

11 Resonance effect should be small, because the porphyrin and the phenyl rings are not coplanar due to the steric hindrance by the methyl groups.

12 The Zn_2 moiety is redox-inactive in this range of potential.