

Photopromoted oxidative cyclization of an *o*-phenylene-bridged Schiff base via a manganese(III) complex, leading to a fluorescent compound, 2-(2-hydroxyphenyl)benzimidazole

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Visible light photolysis of [N,N'-*o*-phenylenebis(salicylideneaminato)]diaquamanganese(III) resulted in the fluorescent compound 2-(2-hydroxyphenyl)benzimidazole by a one electron redox reaction between Mn^{III} and the Schiff base ligand, followed by the base-hydrolysis of the oxidized Schiff base, and then the cyclization of the base-hydrolyzed product.

The photoactivation of manganese complexes is an attractive theme both in the modeling of PSII and in the development of a new photoreaction.^{1–4} It has been known that, upon visible light irradiation, in the presence of *p*-quinone, manganese(III) complexes with tetradentate Schiff base ligands having the salen-type skeleton generate molecular oxygen;^{5–7} in the absence of *p*-quinone, rearrangement of the coordinated Schiff base ligand occurs.⁸ Recently, we examined the photolysis of [N,N'-*o*-phenylenebis(salicylideneaminato)]diaquamanganese(III) **1** and observed a photopromoted oxidative cyclization of the coordinated Schiff base ligand, and the effective formation of the fluorescent compound 2-(2-hydroxyphenyl)benzimidazole **2**, which is useful as a laser dye, high-energy radiation detector, molecular energy storage system, and fluorescent probe.^{9–11} **2** is usually prepared from salicylic acid and *o*-phenylenediamine in polyphosphoric acid at 190 °C in 14% yield.¹² This photoreaction thus provides a new and effective synthetic method for the fluorescent compound **2** and its derivatives.[‡]

Cation **1** was prepared by a literature method,¹³ and isolated as its perchlorate salt. § Absence of Mn^{II} was confirmed by EPR spectroscopy. Slow evaporation of methanol solution of the complex produced crystals suitable for single crystal X-ray structure analysis. ¶ An ORTEP drawing of **1** is shown in Fig. 1. The structure of the complex cation comprises a planar tetradentate Schiff base ligand tightly bound to the Mn^{III} center via two Mn–N bonds [1.981(2), 1.978(2) Å] and two Mn–O bonds [1.859(1), 1.875(1) Å], and by axial methanol and water molecules which complete an octahedron around the Mn^{III} ion. Longer Mn–O distances to the apical ligands [2.272(2) Å for Mn–H₂O and 2.291(2) Å for MeOH] may be partly attributed to the Jahn–Teller effect for the d⁴ ion, although it is common for

solvated Mn–O distances to be longer than chelated ones.¹⁴ No hydrogen bond between the phenolic oxygen atoms of the Schiff base ligand and apical water or methanol was observed.⁶

Fig. 2 shows the time courses of UV–VIS (320 nm), fluorescence (432 nm), and EPR spectra of **1** in water at initial pH = 6.4 under irradiation with visible light (150 W tungsten halogen lamp with UV cut filter L-39). The UV–VIS spectral change exhibited an isosbestic point at 223 nm, and the half life (*t*_{1/2}) of **1** was 11–15 h at pH 6.4. || A similar spectral change also occurred in the dark but was very slow (*t*_{1/2} ≈ 55 h). Our preliminary experiments revealed that the photopromotion occurs by the irradiation into the CT band (400 ± 20 nm), but hardly for the π → π* (335 ± 20 nm) and d → d (540 ± 20 nm) bands. Further, the reaction becomes faster with increase of solution pH (*t*_{1/2} ≈ 9 h at pH 7.5, ≈ 5 h at pH 8.6).

On the other hand, the fluorescence and EPR intensities of the photoreaction solution increased with the decay of **1**, indicating that the fluorescent compound, assigned as 2-(2-hydroxyphenyl)benzimidazole **2**, was formed at early stages of the reaction. The EPR spectra show typical six-line Mn^{II} signals (*g* = 2.013), which proves that the Mn^{III} was reduced to Mn^{II} during this reaction. Since neither molecular oxygen nor hydrogen peroxide were detected in the photoreaction solution, it is strongly suggested that intramolecular one electron redox occurred between Mn^{III} and the coordinated Schiff base ligand. A similar photoreaction also occurred under vacuum, however, no EPR signal corresponding to an organic radical was observed.

From the photoreaction solution, **2** and salicylaldehyde **3** could be separated both in about 40% yield by extraction with ethyl acetate, followed by silica-gel column separation using ethyl acetate–*n*-hexane (1 : 2) as eluent (*R*_f = 0.6 for **2**, *R*_f = 0.8 for **3**).** In addition to **2** and **3**, under argon, N,N'-

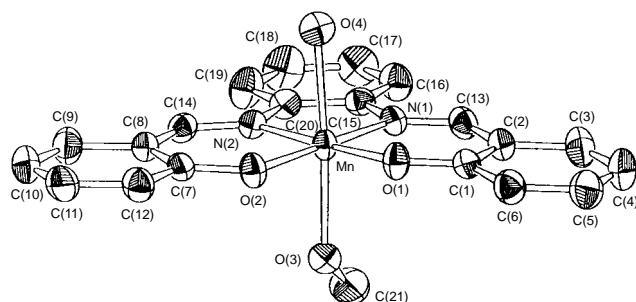


Fig. 1 An ORTEP drawing of cation **1** with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

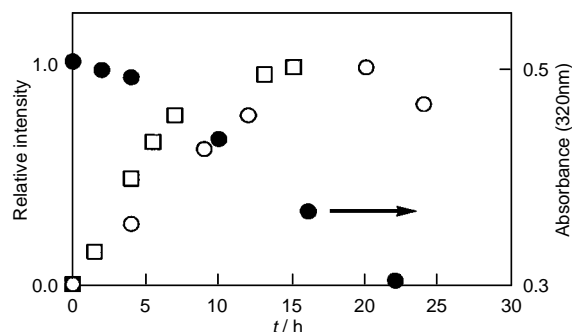
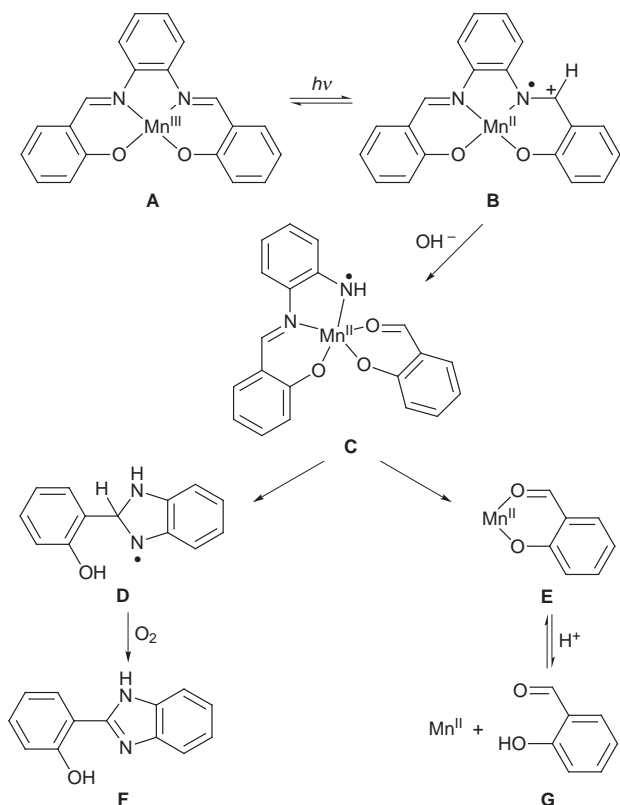


Fig. 2 Time courses of UV–VIS, fluorescence and X-band EPR spectra of the photolysis solution of **1** at pH = 6.4 and 25 °C. The complex concentration is 2.0×10^{-5} mol dm⁻³ for UV–VIS (●) and fluorescence (○) and 1.0×10^{-3} mol dm⁻³ for EPR (□). Fluorescence: λ_{ex} = 325 nm, λ_{em} = 432 nm, EPR: microwave power = 5 mW, microwave frequency = 9.238 GHz, 0.5 mT modulation amplitude, 25 °C.



Scheme 1

o-phenylenebis(salicylideneimine) **4** was isolated in *ca.* 10% yield as a photoreaction product of **1**.

On the basis of these facts, the reaction mechanism (Scheme 1) is suggested as follows: (i) Mn^{III} -Schiff base complex **A** is reduced to Mn^{II} complex **B** with partially oxidized Schiff base ligand, for which visible light promotes the reaction (the reaction has been shown to be enhanced by excitation at the CT band of **1**, probably by LMCT). **B** is thought to be a transient radical and a similar radical has been proposed by Floriani and coworkers.¹⁵ (ii) **B** is base-hydrolyzed to form radical **C**, followed by cyclization of the partially oxidized Schiff base ligand to produce radical **D** and Mn^{II} complex **E**. **D** is oxidized by O_2 to produce **F**. These processes are very fast, since final products **F** and Mn^{II} appear from the start of the reaction with no organic radical being detected in the timescale of EPR measurement. No detection of radical **D** under vacuum may be due to a redox reaction between **A** and **D**, which results in the formation of the corresponding Mn^{II} -Schiff base complex and **F**. This is partly supported by the fact that the Schiff base ligand **4** is detected under argon but not under air. Evidence for base-

hydrolysis of **B** is the formation of salicylaldehyde **G** and rate enhancement with increase of solution pH. A study of the detailed reaction mechanism is under way.

This work was partly supported by a Grant-in-Aid for Science Research (No. 09440224 and No. 97370) from the Ministry of Education, Science and Culture of Japan.

Notes and References

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‡ This method is also applicable for the preparation of the cationic fluorescent compound 2-(2-hydroxy-5-trimethylammoniummethylphenyl)-benzimidazole chloride.

§ This complex contains methanol as apical ligand in the crystal state, however the methanol is thought to be substituted by water in aqueous solution.

¶ Crystal data: $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_8\text{MnCl}$, $M = 518.79$, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 11.804(2)$, $b = 13.435(2)$, $c = 14.358(2)$ Å, $\beta = 109.108(9)^\circ$, $U = 2151.5(5)$ Å³, $D_c = 1.601$ g cm⁻³, Mo-K α radiation ($\lambda = 0.71073$ Å), $R = 0.033$ and $R_w = 0.032$ for 3585 observed reflections with $I > 3\sigma(I)$. CCDC 182/878.

|| Since the reaction occurs with irregular induction time, $t_{1/2}$ is variable.
** 2: ¹H NMR [(CD₃)₂SO, TMS standard], δ 13.18 (br, 1 H), 8.057 (d, 1 H), 7.664 (d, 2 H), 7.400 (t, 1 H), 7.303 (br, 2 H), 7.074–7.019 (m, 2 H). ¹³C NMR [(CD₃)₂SO], δ 158.07, 151.68, 140.93, 133.14, 126.19, 123.27, 122.38, 119.11, 117.93, 112.58, 111.51. EI-MS: m/z 210 (M^+)

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Received in Cambridge, UK, 30th March 1998; 8/02405G