In situ UV-visible Spectral Detection of a Molybdenum Dioxygen Porphyrin Complex Formed in the Solid State Process

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Reversible dioxygenation reaction of a molybdenum(IV) porphyrin, $Mo^{IV}O(tmp)$, in the solid state with dioxygen, was confirmed directly by in-situ UV-vis spectral measurements.

Functionality of dioxygen complexes is of great interest in relation to oxygen atom or dioxygen transfers,[1] catalytic oxygenation reactions of organic substrates,[2] and biochemical reactions in vivo.[3] There are many reports on the metalloporphyrin dioxygen complexes.[4] Some of them are isolated and characterized in the solid state. However, the study of dioxygen complex formation in the solid state is rare. Almost all these dioxygenation reactions proceed in solution except a few reaction systems such as a chromium(II) porphyrin, Cr(tpp) (tpp = 5,10,15,20-tetraphenylporphyrinato dianion),[5] and molybdenum(IV) porphyrins having bulky substuents on the porphyrin rings.[6] Cr(tpp) in the solid state absorbs dioxygen from air to form a superoxo dioxygen complex,[5] though the reversiblity of the dioxygenation in the solid state is not clear. Molybdenum(IV) porphyrins such as $Mo^{IV}O(tmp)$ (tmp = 5,10,15,20-tetramesitylporphyrinato dianion) in solution uptakes dioxygen reversibly.[6] Photoirradiation of the toluene solution of the dioxygen complex, $Mo^{VI}O(tmp)(O_2)$ (Figure 1), with visible light generates MoO(tmp). MoO(tmp) thus formed reacts again with dioxygen to give $MoO(tmp)(O_2)$ in the dark. The powder of MoO(tmp) in the solid state, when it was exposed to air, also gave $MoO(tmp)(O_2)$ as studied by IR measurements.[6] However, the reaction process and reversiblity in the solid state has not been clarified. It is of great significance to study the dioxygenation reaction of metalloporphyrins in the solid state quantitatively.

In the present communication, we report the first UV-vis spectral detection of reversible dioxygenation reactions, i.e., the formation of MoO(tmp) by the photoirradiation of the solid sample of $MoO(tmp)(O_2)$ and its reverse process in the presence of dioxygen in the dark.

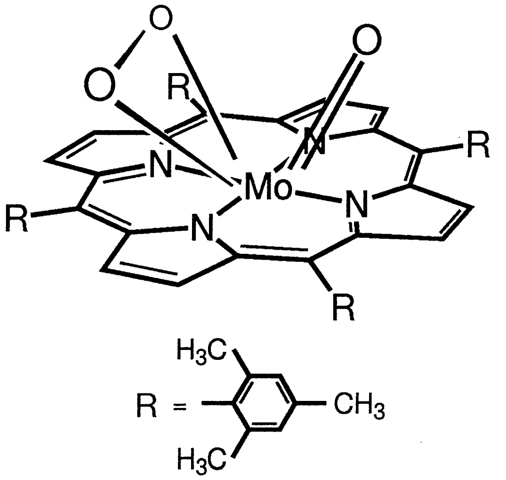
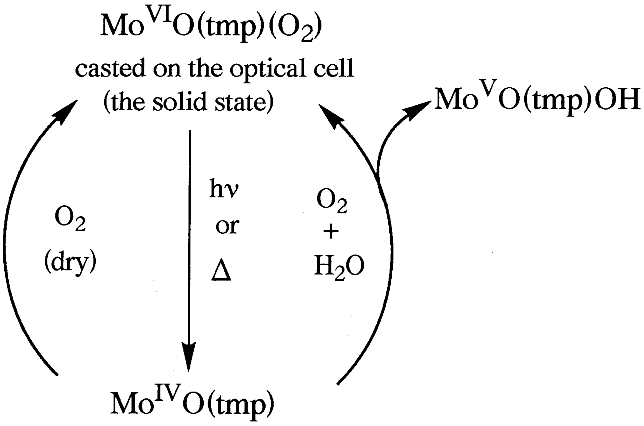


Figure 1. Structure of $Mo^{VI}O(tmp)(O_2)$.

Scheme 1.



The dichloromethane solution of MoO(tmp) has UV-vis bands at 431, 526, and 562 nm . The dilute solution (10^{-4}-10^{-6} mol dm^{-3}) containing a small amount of $MoO(tmp)(O_2)$ was casted on an inside of an usual 10 mm optical cell or on an optical quartz plate using a syringe and dried.[7] The dioxygen complex coated on the optical cell showed the absorption bands at 442, 533, and 569 nm which were red-shifted by 3-10 nm to the solution system (431.5, 530, and 564 nm), with relatively broad half-width of 36.6 nm for the 442-nm band, in comparison to the half-width of 19.8 nm for the 431-nm band in the solution. Then the cell was connected to a vacuum line (10^{-5} Pa) and photoirradiated with visible light (420-700 nm) for 30 s using a 500-w xenon lamp. This procedure immediately gave a new absorption spectrum with the UV-vis bands at 442 and 560 nm, which corresponds to the formation of molybdenum(IV) porphyrin, MoO(tmp) (Scheme 1). By the introduction of pure dioxygen gas (1 atm) to the cell at room temperature, the bands at 442 and 560 nm decreased in the intensity due to the formation of the parent dioxygen complex as shown in Figure 2. It took a few hours to complete the oxygenation reaction. Thus, the UV- vis spectral measurements confirmed the quantitative reversible formation of the dioxygen complex in the solid state. The dioxygenation reaction does not obey pseudo first order rate law. The reaction proceeds fast in the beginning but slows down with the progress of the dioxygen complex formation. This result may be explained by the slow oxygenation inside of the coated solid sample compared to the outside. Reproducibility of the oxygenation and deoxygenation reaction in the presence of dioxygen was demonstrated with the reversible change in absorbance at 442 nm with the turn-on and -off of the light, as

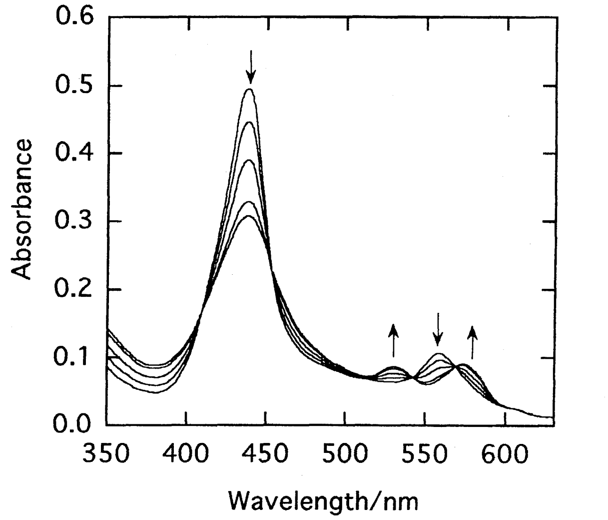


Figure 2. UV-vis spectral change for 75 min on the reaction of the solid sample of Mo^{IV}O(tmp) coated on an optical cell with dry dioxygen at around 20 °C.

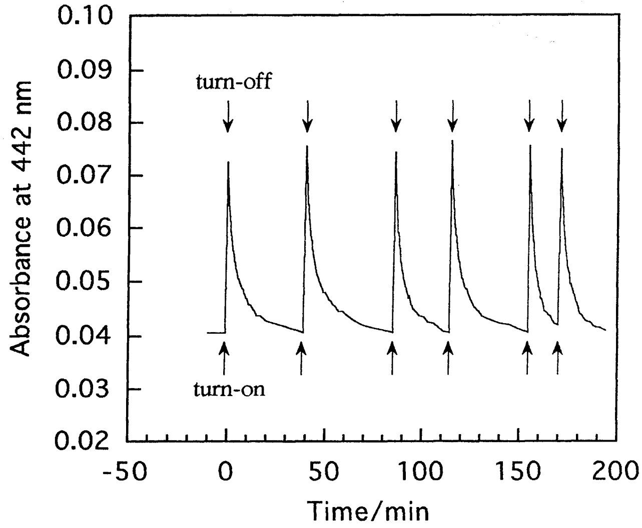


Figure 3. Reversible absorbance change at 442 nm caused by the photoirradiation of Mo^{VI}O(tmp)(O_2) with the 420-700 nm light for 30 s at around 20 °C in the presence of dioxygen.

shown in Figure 3.

The pyrolytic formation of MoO(tmp) from MoO(tmp)(O_2) casted on the optical cell was also clarified by the UV-vis spectral measurements. MoO(tmp) formed by heating the casted dioxygen complex at 120 °C in vacuo for 2 h, gave the dioxygen complex on cooling to the room temperature in the presence of dioxygen in the dark. The dioxygen complex was also regenerated in the presence of dry air instead of dioxygen.

Introduction of moist dioxygen or moist air into the cell containing coated MoO(tmp) obtained by the photoirradiation or pyrolysis gave a small amount of byproducts (470 nm) besides MoO(tmp)(O_2). ESR measurements of the byproduct clarified the formation of a molybdenum(V) porphyrin complex such as Mo^{V}O(tmp)OH,[8] i.e., the solution prepared by dissolving the coated solid sample exposed in humid air for 2 days showed an ESR signal having a strong central line ($\bar{g}$ = 1.97) split to nine lines due to nitrogen atoms of porphyrin rings and six weak lines, which is characteristic to molybdenum(V) porphyrins.[9]

In conclusion, the formation of MoO(tmp) from the casted MoO(tmp)(O_2) in the solid state by the photoirradiation or pyrolysis was detected directly by the UV-vis spectral method. The reversible reaction between MoO(tmp) and dioxygen was followed by the in-situ UV-vis spectral method.[10]

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References and Notes

1 R. H. Holm, *Coord. Chem. Rev.,* **100**, 183 (1990); G. Mclendon and A. E. Martell, *Coord. Chem. Rev.*, **19**, 1 (1976).

2 B. Meunier, *Chem. Rev.*, **92**, 1411 (1992); K. A. Jørgensen, *Chem. Rev.,* **89**, 431 (1989).

3 M. J. Gunter and P. Turner, *Coord. Chem. Rev.*, **108**, 115 (1991).

4 T. D. Smith and J. R. Pilbrow, *Coord. Chem. Rev.*, **39**, 295 (1981); M. H, Dickman and M. T. Pope, *Chem. Rev.*, **94**, 569 (1994); E. C. Niederhoffer, J. H. Timmons, and A. E. Martell, *Chem. Rev.*, **84**, 137 (1984); M. Momenteau and C. A. Reed, *Chem. Rev.*, **94**, 659 (1994).

5 S. K. Cheung, C. J. Grimes, J. Wong, C. A. Reed, *J. Am. Chem. Soc.*, **98**, 5028 (1976).

6 J. Tachibana, T. Imamura, and Y. Sasaki, *J. Chem. Soc., Chem Commun.*, **1993**, 1436.

7 The initial and produced compounds on the optical cell were identified UV-vis spectrometrically as Mo^{IV}O(tmp)(O_2) and Mo^{IV}O(tmp) respectively, by dissolving the casted solid samples in degassed dichlorometane in the dark.

8 Both the d^2 and d^0 complexes, Mo^{IV}O(tmp) and Mo^{VI}O(tmp)(O_2), are diamagnetic and ESR silent.

9 Y. Matsuda and Y. Murakami, *Chem. Rev.*, **92**, 157 (1988).

10 The powder of MoO(tmp) uptakes dioxygen as we reported previously.[6] On the basis of the results described in the text, the oxygenation reaction of the powder system of MoO(tmp) was reexamined by the UV-vis spectral method. The powder of MoO(tmp) was left to stand in the dark for long time (2 days) to complete the dioxygenation reaction in the presence of dry dioxygen, dry air, or humid air, and then dissolved in toluene. The solution of each system gave essentially the UV-vis spectrum of MoO(tmp)(O_2) with the yield larger than 98%. The difference in the reaction processes between the casted sample and the powder sample in the presence of humid air suggests the condition of the solid state significantly affects the formation of byproducts. We think the solid sample of MoO(tmp) formed from casting MoO(tmp)(O_2) on the optical cell is in more favorite to afford Mo^{V}O(tmp)OH than the powder sample is.