Electron Transfer Process of lonically Dimeric Cobalt Porphyrin Accompanied with Dissociation Equilibrium

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The ionically dimeric cobalt porphyrin with a II-II valence state undergoes a stepwise two-electron transfer accompanied with dissociation equilibrium (Kd = 1.3×10^{-6} M) with redox potentials at -0.37 and -0.17 V vs. Fc/Fc^{+}.

Investigation of the self-assembling or multi-nuclear porphyrins has attracted significant attention in inorganic chemistry because biologically active porphyrins usually occur as dimers in solution[1] and protein matrices, e.g. the “special pair” of chlorophylls in solution and photosynthetic reaction centers, diamagnetic dimers of metalloporphyrin cation radicals in solution.[2] In our continuous effort to construct a direct 4-electron reduction system of dioxygen, like the breath enzyme,[3,4] a dimeric cobalt porphyrin acts as an efficient multi-electron transfer catalyst on an electrode.[5-7]

Therefore, numerous studies have been developed for the spectroscopic analysis of the ionically assembling metallo-porphyrin or metal free porphyrins,[8-11] however, very few papers of the multi-electron transfer processes have been reported because of their insolubility and complicated dissociation equilibrium in solution. We found that the ionically dimeric cobalt porphyrin is soluble in dimethylsulfoxide, which allowed us to perform the electrochemical measurements. This paper is the first to report the electron transfer process of the ionically dimeric cobalt porphyrin accompanied by a dissociation process.

In this system, it is also very interesting as to whether or not the two metal centers electrochemically interact with each other in the mixed valence state.[12-16] The ionically dimeric cobalt porphyrin is a good model for elucidating the interaction via a through-space, or π-π stacking orbital between each porphyrin ring because the cobalt porphyrins are strongly fixed to each other by the 4 ionic groups, which prevents dissociation by a charge change during the electron transfer.

The spectroscopic measurements of the Soret and Q bands afford very useful information about the assembling structure of the porphyrin. The UV-vis spectra of Co^{II}TPPS and Co^{II}TMPyP show the typical Soret and Q bands at λmax= 416,533 nm and 428,536 nm, respectively. The absorption bands of the mixture containing the equimolar Co^{II}TPPS and Co^{II}TMTpy (10 μM) were shifted to 420 and 534 nm. It is assumed that this shift is caused by the formation of the ionically stack porphyrin. The titration of Co^{II}TPPS to Co^{II}TMPyP (10 μM) in DMSO solution[17] reveals an increase at 420 nm with a decrease at 428 nm along with an isobestic point, which enables one to prepare Job plot. The Job plot (Figure 1) indicates a 1 : 1 complex formation, i.e. the Co^{II}TPPS -Co^{II}TMPyP dimeric porphyrin, in DMSO. On the basisof fitting to the calculated curve, the dissociation constant (Kd) was determined to be 1.3×10^{-6} M. The formation of the dimeric porphyrin obeys a pseudo-second order kinetic in the earlier stage of the reaction. The formation rate constant is estimated to be about 4×10^{3} $M^{-1}s^{-1}$.[18] These results indicate that the dissociation and association of the dimeric porphyrin slowly take place within several minutes. The formation of the dimeric porphyrin is promoted in the aqueous solution. Co^{II}TPPS and Co^{II}TMPyP immediately aggregate to precipitate a powder after mixing due to the hydrophobicity of the diimeric porphyrin, which is the same phenomenon as the previously reported behavior of the metal-free ionic porphyrin. The precipitate is soluble in DMSO below a 0.1 mM concentration. The formation of the dimeric porphyrin in DMSO is supported by the agreement of the UV-vis spectra with the dimeric porphyrin prepared from DMSO. An EXAFS analysis of the dimeric porphyrin reveals that the cobalt centers are located at distance of 3.37 Å, which coincides with the previously reported π-π stack porphyrin complex.

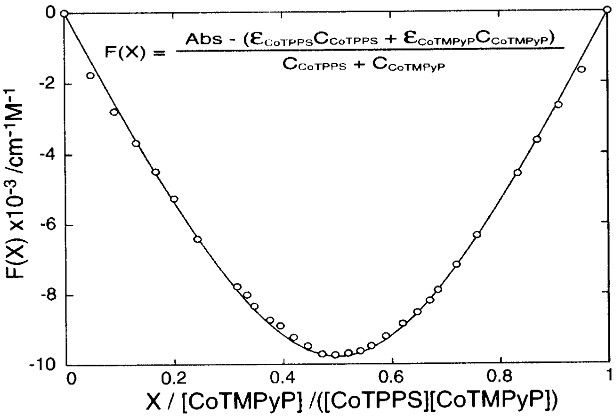


Figure 1. Job plots of the spectroscopic changes against molar ration of Co^{II}TMPyP for the titration of Co^{II}TPPS to Co^{II}TMPyP(0.2 μm) (○) and a theoretical titration curve (Kd = 1.3×10^{-5} M) (solid line).

The equiliblium constant of 1.3×10^{-6} M obtained from the reaction means that more than ca. 90 % of the Co-porphyrin dimer is associated in the initial 0.1 mM solution of dimeric Co-porphyrin. Moreover, the rate of the equilibrium reaction is relatively low so that typical electrochemical measurements provide snapshots of the species present without perturbing this equilibrium distribution. Therfore, cyclic voltammetry was performed in order to obtain the electrochemical response of the dimer (0.1 mM). Two redox waves were observed at -0.37 and -0.17 V vs. Fc/Fc^{+} (Figure 2) in the cyclic voltammogram,[17] which is definitely different from that of the monomeric Co-porphyrins, (Co^{II}TPPS: -0.33 V Co^{II}TMPyP: -0.21 V [vs. Fc/Fc^{+}]). The redox potentials are different from the corresponding monomeric Co-porphyrins. The redox couples were ascribed to Co^{II}–Co^{II} / Co^{II}–Co^{III} and Co^{II}–Co^{III} / Co^{III}–Co^{III}. This result indicates that the dimer possesses a II-III mixed valence state.

The cyclic voltammogram was compared to those of the dimeric porphyrins with only one cobalt center which presents a more accurate electronic structure than the monomeric ones as model compounds. The dimeric Co^{II}TPPS-H_2TMPyP and Co^{II}TMPyP-H_2TPPS show redox potentials at -0.37 and -0.17 V vs. Fc/Fc^+ (Figure 2), respectively. These shifts versus the monomeric porphyrin are caused by the electronic effect due to the π–π stacking. The redox potentials agree with that of the dimeric Co-porphyrins. Each cobalt center in the dimeric porphyrin does not electrochemicaily interact through the electron transfer in spite of the overlapping π–orbitals of the porphyrin rings. Electrospectroscopy of the dimeric Co-porphyrins was carried out at various applied potentials. The Soret and Q bands of the Co^{III}TPPS-Co^{II}TMPyP complex were observed at λmax= 435 and 545 nm, respectively. In the spectroscopic measurements, new absorption bands were not observed in the infrared and near-infrared region. These results suggest that the intervalence transition does not take place in the mixed valence state by the strong interaction in spite of very close distance between the metal centers.

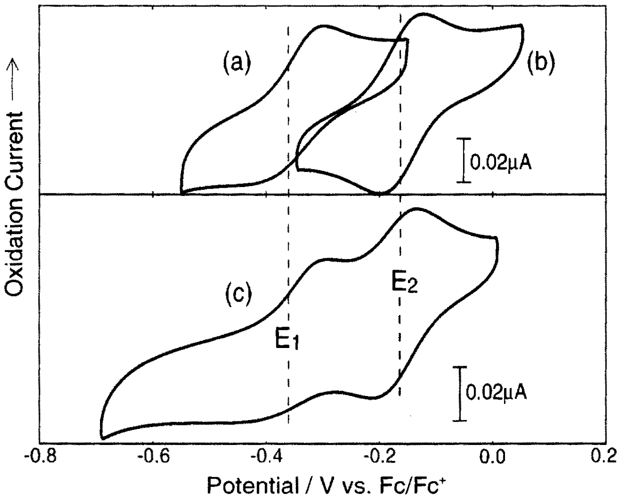
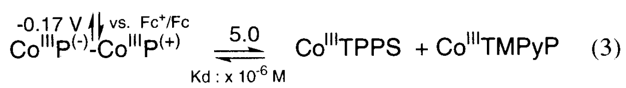


Figure 2. Cyclic voltammograms of CoTPPS-H_2TMPyP(a), H_2TPPS-CoTMPyP(b) and CoTPPS-CoTMPyP(c) in dimethylsulfoxide, scan rate: 20 mV/s.

The dimer undergoes a 2 step electron transfer accompanied with a dissociation equi]ibrium (Scheme l). The dissociation constants in each valence state were determined to be 2.5×10^{-6} and 5.0×10^{-6} M, respectively, by means of Job plots using the monomeric Co-porphyrin with each valence state. The Kd decreases with an increase in the valence due to charging. The reactions of (2) and (3), which control the equilibriums, were also obeyed by the minute-order kinetics. This means that the 2-electron transfer process of the dimeric porphyrin dominates the chemistry.



Scheme 1.

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References and Note

1 J. -H. Fuhrhop, *Angew. Chem., Int. Ed. Engl.*, **15**, 648 (1976).

2 H. Song. C. A. Reed, and W. R. Scheidt, *J. Am. Chem. Soc.*, **111**, 6865 (1989).

3 S. Iwata, C. Ostermeier, B. Ludwig. and H. Michel, *Nature*, **376**, 660 (1995).

4 T. Tukihara. H. Aoyama, E. Yamashita.T. Tomizuka, H. Yamaguchi, K. Itoh, R. Nakashima, R. Yaono, and S. Yoshikawa, *Science*, **269**, 1069 (1995).

5 K. Yamamoto. K. Oyaizu, und E. Tsuchida, *J. Am. Chem. Soc.*, **118**, 12665 (1996).

6 K. Yamamoto and D. Taneichi, *Chem. Lett.*, **1999** in pres's

7 K. Yamamoto, S. Nakazawa and A. Matsufuji, *Mol. Cry. Liq. Cry.*, (2000) in press

8 C. Endisch. J. -H. Fuhrhop. J. Buschmann, P. Luger, and U. Siggel, *J. Am. Chem. Soc.*, **118**, 6671 (1996).

9 L. Ruhlmann, A. Nakamura. J. G. Vos, and J, -H. Fuhrhop. *Inorg. Chem.*, **37**, 6052 (1998),

10 T. Sawaguchi, T. Matsue, K. Itaya. and I. Uchida, *Electrochim. Acta*, **36**, 703 (1991).

11 T. Fournier, Z. Liu, T. -H. Tran-Thi, D. Houde, N. Brasseur, C. L. Madeleine, R. Langlois. J. E. V. Lier, and D. Lexa, *J. Phys. Chem. A*, **103**, 1179 (1999).

12 G. C. Allen and N. S. Hush, *Prog. Inorg. Chem.*, **8**, 357 (1967).

13 P. Ceroni. F. Paolucci, C. Paradisi, A. Juris, S, Roffia, S. Serroni, S. Campagna. and A. J. Bard. *J. Am. Chem. Soc.*, **120**, 5480 (1998).

14 C. Patoux, J-P. Launay. M. Beley, S. Chodorowski-Kimmes, J-P. Collin, S. James, and J-P. Sauvage. *J. Am. Chem. Soc.*, **120**, 3717 (1998).

15 T-Y. Liu, Y. J. Chen, C-C. Tai. and K. S. Kwan, *Inorg. Chem.*, **38**, 674 (1999).

16 D. O. Cowan, C. LeVanda, J. Park, and F. Kaufman, *Acc. Chem. Res.*, **6**, 1 (1973).

17 C. A-McAdams and K. M. Kadish, *Inorg. Chem.*, **29**, 2749 (1990).

18 CoTPPS-H_2TMTPy: Dissociation equilibrium constant = 8.3×10^{-7} M, Formation rate constant = 8.2×10^3 $M^{-1}s^{-1}$, λmax = 423,518, 546,589 nm; CpTMTPy-H_2TPPS: Dissociation equilibrium constant = 1.0×10^{-6} M, λmax = 420,516, 549,589 nm.

19 Differential puls voltammetry shows 2 broad peaks on the basis of the dissociation equilibrium of the dimer.