

Electron Transfer Reaction of Porphyrin and Porphycene Complexes of Cu(II) and Zn(II) in Acetonitrile

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Summary

The outer-sphere one-electron oxidation reaction of the Cu(II) and Zn(II) complexes of nonplanar 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin and planar porphycenes as well as those of 2,3,7,8,12,13,17,18-octaethylporphyrin and 5,10,15,20-tetraphenylporphyrin by Cu^{2+} giving corresponding π -cation radicals was investigated spectrophotometrically in acetonitrile. The electron self-exchange rate constants between the parent porphyrin and porphycene complexes and their π -cation radicals were determined using the Marcus cross relation for the electron transfer reaction. The obtained rate constants are in the order of 10^9 to $10^{11} \text{ M}^{-1} \text{ s}^{-1}$ for the planar porphyrin and porphycene complexes and 10^4 to $10^6 \text{ M}^{-1} \text{ s}^{-1}$ for the nonplanar OETPP complexes at $T = 25.0^\circ\text{C}$. The relatively slow self-exchange reaction of the distorted porphyrin complexes, as compared with those for the planar porphyrin and porphycene complexes, was ascribed to the significant deformation of the complex associated with the oxidation reaction from the parent complex to the corresponding π -cation radical.

Introduction

Porphyrins and related macrocyclic tetrapyrroles exist in many biological systems, and the electron transfer reactions of these species play essential roles there.¹⁻⁴ The electron transfer reaction of metalloporphyrins has been extensively studied in order to clarify the factors that control the redox processes in the biological systems, such as the electron transport system in the respiratory chain and photosynthesis. Highly conjugated π systems of the porphyrin molecules are suitable for efficient electron transfer processes because the release or uptake of an electron causes minimal structural change of these molecules. Metal-centred electron transfer reactions are also important in the case where a redox-active metal ion is included. In these porphyrin-type cofactors, their reactivity to an electron-transfer depends on the nature of porphyrin ligand and

central metal ion, the axial ligation of metalloporphyrins, and non-planar distortion of the porphyrin skeleton. The latter factor is believed to affect the reactivity of their cofactors as a result of the structural deformation and the axial ligand affinities.

The electron transfer reactions of synthetic metalloporphyrins have been widely investigated to gain an insight into biological functions of this type of species in nature. According to the Marcus theory,^{5,6} rate constant for an electron transfer reaction can be expressed by eq 1

$$k_{\text{et}} = \kappa_{\text{el}} Z \exp[-\lambda(1 + \Delta G_{\text{et}}^0/\lambda)^2/4RT] \quad (1)$$

where κ_{el} is the probability with that the system passes from the precursor to the successor state along the adiabatic potential energy surface, Z is an effective frequency which determines the rate of transmission along the reaction coordinate, and λ is the reorganization parameter associated with the electron transfer reaction. The Marcus cross relation is used to estimate the reorganization energy for the self-exchange reaction of metalloporphyrins from the cross reactions of metalloporphyrins with the outer-sphere oxidizing or reducing reagents. The rate constant of the electron self-exchange reaction of metalloporphyrins has been determined in this manner for the metal-centred redox couples as well as the ligand-centred reactions.⁴ Relatively slow electron self-exchange reactions of metalloporphyrins were observed for the metal-centred $\text{Fe}^{2+/3+}$ and $\text{Co}^{2+/3+}$ couples whose rate constants fall in the range of 10^7 to $10^8 \text{ M}^{-1} \text{ s}^{-1}$ and 10^{-3} to $10^4 \text{ M}^{-1} \text{ s}^{-1}$, respectively.⁷⁻¹² These slow self-exchange rate can be ascribed to a relatively large inner-sphere reorganization energy that originates from the change in the bond length between the metal and pyrrole nitrogen atoms. On the other hand, the porphyrin-centred redox reactions are highly reactive because smaller inner-sphere reorganization energies are required compared with the metal-centred redox reactions. We have recently determined the rate constants of the electron self-exchange reaction between the metalloporphyrin and its π -cation radical. The rate constants are in the range 10^9 to $10^{11} \text{ M}^{-1} \text{ s}^{-1}$ for the Cu(II) complexes of

5,10,15,20-tetraphenylporphyrin (TPP) and 2,3,7,8,12,13,17,18-octaethylporphyrin (OEP).¹³ The EPR line-broadening technique has also been applied to the Zn(II) porphyrins, and high reactivity of this self-exchange was reported.¹⁴ However, the porphyrin-centred redox reactions have been scarcely studied due to the highly reactive nature of this type of reaction.

In the present study, we focused on elucidation of the factors influencing the electron transfer reactivity in the aspects of the distortion of the molecular structure of porphyrins as well as the structural perturbation of the porphyrin skeleton. The structural deformation was introduced by using a porphyrin ligand that has bulky peripheral substituents, 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin (OETPP), and the structure of the Cu(II) and Zn(II) complexes of OETPP is highly distorted in an S_4 saddle conformation due to the steric crowding of the multiple peripheral substituents.^{15,16} The oxidation of the complex results in additional ruffling imposed on the original saddle shape conformation in the case of [Cu(OETPP)].¹⁷ We previously reported on the effect of the deformation of the porphyrin skeleton on the electron transfer reaction for [Cu(OETPP)] as a preliminary report.¹⁸ The structural perturbation of the porphyrin skeleton was derived by using porphycenes, which are structural isomers of porphyrin. We investigated the kinetics of the electron transfer reaction of the Cu(II) and Zn(II) complexes of various porphyrins and porphycenes with Cu(II) ion as an oxidizing reagent in acetonitrile. All the one-electron oxidation reactions of these complexes by Cu(II) are ligand-centred oxidations, and the oxidation state of the central metal ions in the complexes remains unchanged. The rate constants for the electron self-exchange reactions between the porphyrin or porphycene complexes and the corresponding π -cation radicals were estimated using the Marcus cross-relation from the kinetics of the cross reaction with Cu(II) ion whose self exchange reactions are extremely slow. The effect of the structural deformation and

perturbation accompanying the oxidation on the electron self-exchange reactivity will be discussed on the basis of the self-exchange rate constant.

<chart 1 here>

Experimental

Materials. TPP and OETPP were prepared by the literature method.^{15,19-20} OEP was purchased from Tokyo Kasei Organic Chemicals. Cu(II) and Zn(II) complexes of these porphyrins were obtained by a metal(II) acetate method,²¹ purified by column chromatography, and recrystallized from dichloromethane/methanol or dichloromethane/heptane. 2,7,12,17-Tetra-*n*-propylporphycene (TPrPc), 2,3,6,7,12,13,16,17-octaethylporphycene (OEPc), and their Cu(II) and Zn(II) complexes were synthesized according to the published procedures.²²⁻²⁴ The purity of the obtained compounds was tested by elemental analysis. Cu(II) triflate, $\text{Cu}(\text{CF}_3\text{SO}_3)_2$, was prepared according to the method in the literature.²⁵ Acetonitrile (AN, Wako Pure Chemical Industries) was dried over activated 3A molecular sieves for several days and distilled under a nitrogen atmosphere. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Tokyo Kasei Organic Chemicals, recrystallized from ethyl acetate, and dried under vacuum at room temperature for several days prior to use. Doubly distilled water was used for the preparation of the aqueous acetonitrile solutions. *CAUTION!* *Although we have experienced no problems in handling perchlorate compounds, these salts are potentially explosive and should be handled in small quantities and with adequate precautions.*²⁶⁻²⁷

Measurements. Redox potentials of the metal complexes were determined by cyclic voltammetry using a BAS 100B electrochemical analyzer under deaerated conditions at $T = 25.0^\circ\text{C}$. A three-electrode electrochemical cell was used consisting of a 3 mm

glassy carbon or a Pt working electrode, a Pt wire auxiliary electrode, and an Ag/AgCl reference electrode. Each solution contained 0.1 M TBAP as a supporting electrolyte. Redox potentials in acetonitrile were referenced to the ferrocinium/ferrocene couple ($\text{Fc}^{+/0}$) as an external standard.

UV-visible absorption spectra were recorded on a Hitachi U-3000 spectrophotometer. Kinetic measurements were made using a stopped-flow spectrophotometer (RSP- 801, Unisoku, Japan). The temperature of all solutions was maintained at 25.0 ± 0.1 °C using a circulating water bath. The spectral change for the reactions of the metal complexes of porphyrin or porphycene with Cu^{2+} in acetonitrile was measured by a multi-channel detection system. The absorbance, A , was followed after mixing acetonitrile solutions containing each of the metal complexes of porphyrin or porphycene with that of a large excess of Cu(II) triflate to determine the pseudo-first-order rate constant, k_{obsd} . The k_{obsd} value was evaluated by fitting the absorbance-time traces with a non-linear least-squares fitting program. The reported k_{obsd} value is the average of several runs. Reproducibility of the k_{obsd} value was within ± 3 %. A Karl Fischer apparatus (Mitsubishi Chemicals CA-06) was used to determine the concentration of water in the acetonitrile solution.

Results and Discussion

Redox Potentials. It is well known that free base of porphyrins and their metal complexes show two reversible one-electron oxidations, as well as two one-electron reductions all centred on the tetrapyrrolic ring system.²⁸⁻²⁹ Additionally, the metal-centred oxidation or reduction can be observed for some metal complexes, e.g., those of Co(II) and Fe(III). In the case of Cu(II) and Zn(II) complexes, the central metal undergoes no oxidation or reduction, and all electron transfers are tetrapyrrole ligand centred. In the present study, the oxidation potentials of the metal complexes were

determined by cyclic voltammetry in acetonitrile, and it is difficult to determine the second oxidation potential accurately for most porphyrin and porphycene complexes used here due to poor solubility in acetonitrile. The first oxidation potentials of the porphyrin and porphycene complexes are listed in Table 1 and correspond to the tetrapyrrole ligand centred oxidation reaction of complexes, giving π -cation radicals.³⁰⁻³⁷ The oxidation potential of the porphycene complexes is comparable to those of the corresponding porphyrin complexes. On the other hand, the first oxidation potentials of distorted OETPP complexes are significantly lower than those for the planar porphyrin complexes. [Zn(OETPP)] is easier to oxidize ($E_{1/2}^0 = -0.093$ V vs. $\text{Fc}^{+/0}$ in acetonitrile) than either [Zn(TPP)] (0.390 V vs. $\text{Fc}^{+/0}$) or [Zn(OEP)] (0.314 V vs. $\text{Fc}^{+/0}$). Similarly, the first oxidation potential of [Cu(OETPP)] is -0.011 V vs. $\text{Fc}^{+/0}$, which is significantly lower than the corresponding value of [Cu(TPP)] (0.600 V vs. $\text{Fc}^{+/0}$) and [Cu(OEP)] (0.480 V vs. $\text{Fc}^{+/0}$). These phenomena were observed for the redox reaction in other solvents such as dichloromethane, i.e., the first oxidation potential of [Cu(OETPP)] and [Zn(OETPP)] is lower than those of TPP and OEP complexes by ca. 0.2 – 0.6 V, which can be attributed to the destabilization of the porphyrin π system and/or the stabilization of the π -cation radical caused by the saddle conformation of the sterically constrained nonplanar porphyrin skeleton.^{15,17} In agreement with these observations, the theoretical calculations indicate that the deformation of the porphyrin skeleton destabilizes the π system of the porphyrin and raises the HOMO level with a smaller perturbation of the LUMO level.³⁷

The reduction potential of the solvated Cu^{2+} ion to Cu^+ in acetonitrile is 0.660 V vs. $\text{Fc}^{+/0}$, and this redox potential is higher than those of the complexes used in the present study. As has been reported previously, the reaction of the Cu(II)-TPP and Cu(II)-OEP complexes with Cu^{2+} in acetonitrile leads to the formation of the corresponding π -cation radicals.¹³ The average potential differences between the first and second ring-centred oxidations of the Cu(II)- and Zn(II)-porphyrin complexes are

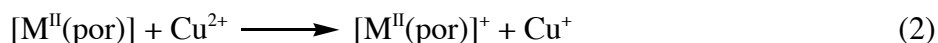
0.28 ± 0.05 V for Cu(II)-TPP, 0.45 ± 0.05 V for Cu(II)-OEP, 0.31 ± 0.03 V for Zn(II)-TPP, and 0.34 ± 0.04 V for Zn(II)-OEP in dichloromethane.³⁸ Although the second oxidation step was not clearly observed in the CV measurements due to poor solubility of these complexes in acetonitrile, it is probable that the second oxidation potentials of [Cu(TPP)] and [Cu(OEP)] are higher than the redox potential of the solvated Cu(II)/(I) couple. Therefore, it is concluded that the products of the oxidation reactions of these porphyrin complexes with solvated Cu²⁺ are the π -cation radicals of the Cu(II)-porphyrin complexes and [Cu(AN)₄]⁺, the latter of which is known as one of the most stable Cu(I) species.^{39,40} Meanwhile, other complexes used in the present study have oxidation potential lower than those of [Cu(TPP)] and [Cu(OEP)], indicating that the obtained π -cation radicals may be further oxidized by Cu²⁺ to give dication of the corresponding porphyrin and porphycene complexes under the conditions where Cu²⁺ exists in large excess over the porphyrin or porphycene complex. A consecutive reaction was observed spectrophotometrically for these reaction systems as described later.

Spectral Change. The oxidation of porphyrin and porphycene complexes by Cu(II) ion was followed spectrophotometrically in acetonitrile. The spectral change in the UV-visible region for the reaction of [Cu(TPrPc)] is shown in Figure 1, and the results for the reactions of other complexes are given in Figures S1-S4. In the case of [Cu(TPrPc)], the spectral change exhibits bleaching of the porphycene peaks and the formation of broad absorptions, followed by an additional small spectral change, as shown in Figure 1, which is consistent with the results of pulse radiolysis of [Cu(TPrPc)] in CH₂Cl₂.³⁶ Similar spectral changes were observed for [Zn(OEPc)], as shown in Figure S1. The spectral change for [Zn(TPP)], [Zn(OEP)], and [Zn(OETPP)] shown in Figures S2-S4 closely resemble with those for the corresponding Cu(II) porphyrin complexes reported previously.^{13,18} Such spectral features of the products

indicate that the observed spectral changes associated with the first oxidation reaction of these complexes is typical for the formation of π -cation radical of the porphyrin and porphycene complexes.^{30,31,35,36}

The stoichiometry of the reaction was determined by spectrophotometric titration experiments for the first oxidation reaction of the complexes with Cu(II). The solution of the porphyrin or porphycene complex was titrated with a Cu(II) triflate solution, and the resulting spectrum was measured. The absorbance at a given wavelength was plotted as a function of the ratio of the concentration of Cu(II) triflate over that of the porphyrin or porphycene complex. The results for [Cu(TPrPc)] are shown in Figure S5 as an example. The ratio of Cu(II) triflate consumed for the oxidation of the complex was confirmed to be 1:1 for each complex.

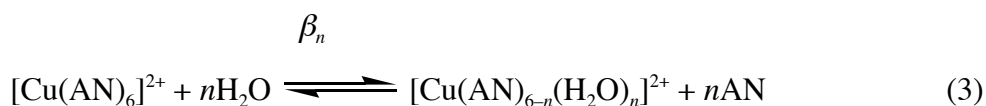
Kinetics Studies. The kinetics of the oxidation reaction of the porphyrin and porphycene complexes by Cu(II) triflate in acetonitrile was studied by a stopped-flow technique with a multi-channel photodiode array detection system. Ionic strength of the solution was adjusted to 0.1 M by TBAP. The reaction was followed spectrophotometrically under the pseudo-first-order conditions in which the Cu(II) triflate exists in large excess over the Cu(II) and Zn(II) complexes. The oxidation of these porphyrin and porphycene complexes by Cu^{2+} is a first-order reaction with respect to the complex in all reaction systems studied here. In the present report, we will describe the kinetics of the first stage of the reaction, which gives π -cation radical of the corresponding porphyrin or porphycene complex (eq 2).



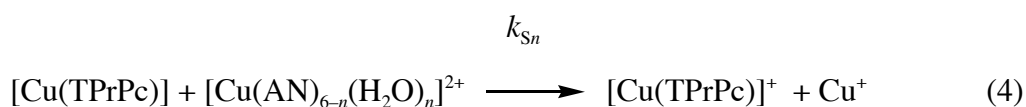
(M = Cu or Zn; por = porphyrin or porphycene)

Because the reaction rate was found to depend on the water concentration in the acetonitrile solution, we studied the kinetics of the electron transfer reaction as a function of the water concentration.

The observed pseudo-first-order rate constant, k_{obsd} , was determined by applying the least squares fitting calculation to the absorbance-time traces of the reactions. The dependence of k_{obsd} on the concentration of the Cu(II) ion is shown in Figure 2 for the reaction of [Cu(TPrPc)] as an example. The pseudo-first-order rate constant, k_{obsd} , is proportional to the concentration of Cu^{2+} under a constant concentration of water. The second-order rate constant, k_f , was then determined using the relationship, $k_{\text{obsd}} = k_f[\text{Cu}^{2+}]$. Similar results were obtained for all reaction systems. The effect of the water concentration on k_f is shown in Figure 3, and the reaction rate decreases as $[\text{H}_2\text{O}]$ increases. The water concentration dependence of k_f can be interpreted by the solvation of the Cu(II) ion in acetonitrile containing a small amount of water. It has been known that some of the acetonitrile molecules on $[\text{Cu}(\text{AN})_6]^{2+}$ are replaced by water molecules (eq 3).⁴¹



The overall formation constant β_n for $[\text{Cu}(\text{AN})_{6-n}(\text{H}_2\text{O})_n]^{2+}$ is defined as $\beta_n = [\text{Cu}(\text{AN})_{6-n}(\text{H}_2\text{O})_n]^{2+} / [\text{Cu}(\text{AN})_6]^{2+} [\text{H}_2\text{O}]^{-n}$. The equilibrium of the solvation of the Cu(II) ion in the aqueous acetonitrile solution was previously studied spectrophotometrically under the conditions of $[\text{H}_2\text{O}] < 0.9 \text{ M}$, and the equilibrium constants were determined to be $\log(\beta_1/\text{M}^{-1}) = 1.19 \pm 0.18$, $\log(\beta_2/\text{M}^{-2}) = 1.86 \pm 0.35$, and $\log(\beta_3/\text{M}^{-3}) = 2.12 \pm 0.57$.⁴¹ The present electron transfer reaction can be expressed by eq 4.



The dependence of k_f on the water concentration can be explained by the retardation of the reaction due to the reduced concentration of reactive Cu(II) species such as $[\text{Cu}(\text{AN})_6]^{2+}$ through reaction 3 because it is expected that the oxidation potential of the solvated Cu(II) species decreases as the coordinated acetonitrile molecules are successively substituted with H_2O molecules. The concentrations of

$[\text{Cu}(\text{AN})_{6-n}(\text{H}_2\text{O})_n]^{2+}$ were estimated by using the reported values of β_n .⁴¹ It is probable that the solvent exchange reaction of $[\text{Cu}(\text{AN})_{6-n}(\text{H}_2\text{O})_n]^{2+}$ is sufficiently fast in this solvent, and then the second-order rate constant, k_f , can be expressed by eq 5.

$$k_f = (k_{s0} + k_{s1}\beta_1[\text{H}_2\text{O}] + k_{s2}\beta_2[\text{H}_2\text{O}]^2 + k_{s3}\beta_3[\text{H}_2\text{O}]^3) \times (1 + \beta_1[\text{H}_2\text{O}] + \beta_2[\text{H}_2\text{O}]^2 + \beta_3[\text{H}_2\text{O}]^3)^{-1} \quad (5)$$

The kinetic results shown in Figure 3 were analyzed by the least-squares fitting calculation to determine the values of k_{s_n} ($n = 0, 1, 2$, and 3). It was revealed that it is not necessary to take into account the contribution of $[\text{Cu}(\text{AN})_{6-n}(\text{H}_2\text{O})_n]^{2+}$ ($n \geq 2$) to the present electron transfer reaction, indicating that only $[\text{Cu}(\text{AN})_6]^{2+}$ and $[\text{Cu}(\text{AN})_5(\text{H}_2\text{O})]^{2+}$ have redox potential high enough to oxidize the porphyrin and porphycene complexes. The values of the rate constants, k_{s0} and k_{s1} , are listed in Table 2. As shown in Figure 3, the calculated curve of k_f using obtained k_{s0} and k_{s1} values reproduces observed rate constants well.

Electron Self-Exchange Reactions. Rate constant of the electron self-exchange reaction between the parent complex and its π -cation radical for metalloporphyrin and metalloporphycene complexes, k_{11} , was calculated from the cross-reaction rate constant using the Marcus cross relationship in the form^{42,43}

$$k_{12} = (k_{11} k_{22} K_{12} f_{12})^{1/2} W_{12} \quad (6)$$

where

$$\ln f_{12} = [\ln K_{12} + (w_{12} - w_{21})/RT]^2 / 4 [\ln(k_{11} k_{22} / Z^2) + (w_{11} + w_{22})/RT] \quad (7)$$

$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT] \quad (8)$$

$$w_{ij} = 37.9 z_i z_j / \sigma_{ij} (1 + 0.481 \sigma_{ij} I^{1/2}) \quad (9)$$

In the above expressions, w_{ij} is the work required to bring ions i and j (charges z_i and z_j) to the separation distance σ_{ij} (taken as equal to the sum of the radii of the reagents), and Z is the collision frequency ($k_B T/h$). In eq 6, k_{12} represents the rate constant, k_{s0} , for the cross-reaction between each porphyrin or porphycene complex and $[\text{Cu}(\text{AN})_6]^{2+}$; k_{22}

represents the electron self-exchange rate constant for the $\text{Cu}^{2+/+}$ couple in acetonitrile; K_{12} represents the equilibrium constant for reaction 4 ($n = 0$), which can be estimated by using the potential values of the reactants as listed in Table 1; f_{12} represents the nonlinear correction term and W_{12} represents as electrostatic work term correction.^{44,45} This electron transfer reaction is expected to proceed through the ordinary outer-sphere process since no potential bridging ligand exists in the medium. Using the self-exchange rate constant of the $\text{Cu}^{2+/+}$ couple ($k_{22} = 4.2 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$),¹³ we determined the self-exchange rate constant k_{11} listed in Table 3. In the previous paper, the self-exchange rate constant of the Cu(II)-TPP and Cu(II)-OEP complexes were reported to be $3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $1 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ at 25.0°C, respectively.^{13,46} The corresponding values for the $[\text{Zn}(\text{TPP})]^{+/0}$ and $[\text{Zn}(\text{OEP})]^{+/0}$ couples are $1.4 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ and $1.3 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ at 25.0°C, respectively. Fukuzumi et al. determined the self-exchange rate constant for the Zn(II)-TPP complex to be $3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ by using the line-width broadening in the EPR spectra.¹⁴ Although this value is somewhat smaller than that determined in the present study, it could be concluded that these two determinations are consistent with each other, judging from these quite different experimental techniques employed and the errors inherent in the application of the Marcus cross relation.

It has been well documented that the 24-atom core of the porphyrin molecule is readily deformed in a direction perpendicular to the porphyrin skeleton, but to a lesser extent in the radial direction.⁴⁷ In the case of the Cu(II)-TPP complex, the porphyrin core shows a ruffled core conformation in the solid state.⁴⁸ The meso-carbon atoms are displaced alternatively above and below the mean plane of the core. The maximum displacement of the meso-carbon atoms is 0.42 Å for [Cu(TPP)]. The dihedral angle between the peripheral phenyl group and the porphyrin core is larger than 60°. The porphyrin core of the π -cation radical is also deformed. For example, the π -cation radical, $[\text{Cu}(\text{TPP})]^+$, has a saddle-shaped conformation and the pyrrole rings are displaced alternatively above and below the mean plane of the porphyrin core.⁴⁹ The meso-carbon

atoms are nearly in the plane of the core, which is in contrast to the ruffled conformation of the neutral complex, [Cu(TPP)]. The average displacement of the β -pyrrole carbon atoms is 0.65 Å for [Cu(TPP)]⁺. The saddle-shaped conformation of [Cu(TPP)]⁺ should result from the necessity of making the bulky peripheral phenyl groups more nearly coplanar with the porphyrin core, allowing the close contact of the adjacent porphyrin molecules in the solid state to form the dimer species. This is evidenced by the molecular structure of the π -cation radical of the 5,10,15,20-tetramesitylporphyrin complex, [Cu(TMP)]⁺, that has meso-aryl groups with ortho methyl groups on the aryl groups.⁵⁰ The 24-atom core of TMP is almost planar, and the peripheral mesityl groups are nearly perpendicular to the mean plane of the porphyrin core due to these ortho substituents. The peripheral mesityl groups inhibit the approach of a second radical, resulting in a planar conformation of the porphyrin core. These findings indicate that the ruffled and saddle-shaped core conformations for the neutral molecules and π -cation radicals of tetraarylporphyrins are not due to an intrinsic demand but are a consequence of the interaction with adjacent porphyrin molecules in the solid state. In the case of OEP complex in which peripheral substituents are less sterically demanding than those of the tetraarylporphyrin complexes, the inter-ring interactions cause these molecules to form dimers or higher aggregates more easily. The OEP and related complexes have an almost planar core conformation.^{47,51} The π -cation radical of the Zn(II) complex forms a very strongly coupled dimer, and the unpaired electrons on the two porphyrin rings are so strongly coupled that the dimer is diamagnetic.⁵² The porphyrin core is essentially planar, with the largest deviation of an atom from the mean plane of the 24-atom core equal to 0.05 Å.

The porphycene molecule that has no peripheral substituents is centrosymmetric and virtually planar with a maximum distance of the core C and N atoms from the mean plane of ± 0.04 Å,⁵³ as in the case of porphyrins having alkyl substituents at the peripheral positions such as OEP. *n*-Propyl groups in TPrPc little affect the planarity of the

porphycene core due to the lack in the nonbonding interaction between these substituents.²³ On the other hand, the porphycene skeleton of OEPc is twisted to some extent because of the steric repulsion between the peripheral ethyl groups in the 3,6- and 13,16-positions, and the maximum deviation of the core atoms from the mean plane of the porphycene core is $\pm 0.27 \text{ \AA}$.²³ However, the incorporation of a Zn(II) ion into the OEPc core leads to the contraction of the bond angle in the NCCN segment of the porphycene core, resulting in the better alignment of the lone-paired electrons of nitrogen atoms and bonds towards the central metal ion.²³ The metalation of OEPc is, thus, associated with a reduction in the nonbonding interactions between the ethyl substituents and a structural change to a virtually planar core structure. Therefore, both complexes of OEPc and TPrPc studied in the present work show considerably planar core conformations.

The rate of the electron self-exchange reaction between the porphycene complex and its π -cation radical is extremely fast for both Cu(II) and Zn(II) complexes, as shown in Table 3. These findings are similar to those of the corresponding TPP and OEP complexes. Although the TPP complexes of Cu(II) and Zn(II) and their π -cation radicals have a ruffled or saddle-shaped conformation in the solid state, these deformation from the planar core conformation could be ascribed to the intermolecular interaction between the porphyrin cores in the solid state. In the acetonitrile solution where metalloporphyrin concentration is as quite low, as in the order of 10^{-6} M , it is probable that no aggregation of the porphyrin molecules exists and that the core conformation of the TPP and OEP complexes and their π -cation radicals may be planar, as in the case of $[\text{Cu}(\text{TMP})]^+$. Therefore, the inner-sphere reorganization energy associated with the electron self-exchange reactions between the parent porphyrin complex and its π -cation radical may be small, resulting in a very fast electron self-exchange reaction. Such a fast electron self-exchange rate is consistent with the mechanism of the ligand-centred redox reaction because the structural parameters show little difference between the parent complex and

the π -cation radical species, e.g., the average Cu-N bond distances are 1.981(7) Å and 1.988(4) Å for [Cu(TPP)] and [Cu(TPP)]⁺, respectively.^{48,49}

In contrast to the planar porphyrin and porphycene complexes, the distorted porphyrin complexes show considerable retardation in electron self-exchange rate. According to an X-ray structural study, the Cu(II)-OETPP complex is highly distorted due to the steric interaction between the peripheral phenyl and ethyl groups so as to minimize the steric crowding between the peripheral substituents, and the geminal β -carbons of successive pyrrole rings are displaced alternatively above and below the average nitrogen plane by 1.1 - 1.2 Å.¹⁶ The OETPP complex of Zn(II) is also severely saddle-shaped with the β -carbons of adjacent pyrrole rings displaced by 1.0 - 1.2 Å relative to the plane of the four pyrrole nitrogen atoms.¹⁵ The deformation of the porphyrin core of the OETPP complexes is mainly caused by the intramolecular steric demand, and it is expected that the porphyrin core structure should be deformed not only in the solid state but also in solution. Therefore, the origin of the distorted core conformation of OETPP is different from that of TPP, which can be ascribed to the minimization of the intermolecular distance between the adjacent molecules by rotating the phenyl ring more coplanarly with the porphyrin core for the effective intermolecular interactions in the solid state, as mentioned above. The one-electron oxidation of this distorted metalloporphyrin causes further conformational change to give the π -cation radical, in which the β -pyrrole carbon atoms are further displaced from the mean plane of the porphyrin core about 1.2 - 1.5 Å.¹⁷ Such an additional deformation of the porphyrin skeleton should be associated with a larger inner-sphere reorganization energy, λ , for the one-electron oxidation of the OETPP complex, resulting in the retardation of the electron self-exchange rate by a factor of ca. 10^5 - 10^6 compared with the corresponding TPP complexes. This structural perturbation caused by the steric crowding of the peripheral substituents amounts to an enhancement in the λ value of ca. 110 - 140 kJ mol⁻¹. The schematic representation of the potential energy curves for the

self-exchange reactions is shown in Figure 4. The intrinsic energy barrier, λ , is significantly larger for the reactions of distorted porphyrin complexes because of the very steep slope along the reaction coordinate. The free energy barrier of the reaction is approximated by $\lambda/4$ in the Marcus theory.

The effect of the substituents such as ethyl, phenyl, and propyl groups may contribute to this type of electron transfer reactions through the steric and electronic aspects, where the former was demonstrated clearly in the present study. On the other hand, the electronic effect of the substituents is taken into account in the Marcus cross relation, which was originally derived by assuming that the intrinsic energy barrier for a cross reaction is approximated by the arithmetic mean of the intrinsic energy barriers for two independent self-exchange reactions. It was reported that the identical relation is derived on the purely thermodynamic basis, by assuming (1) the activation process for each reactant is independent of the counter reagent and (2) the activated species are the same for the self-exchange and cross reactions.⁵⁴ With another independent development concerning the electronic work terms between reactants and products, the Marcus cross relation can be utilized to examine the independent activation process and the nature of the activated species involved in outer-sphere electron transfer reactions. Since the difference in the types of the substituents is accounted for as the ground-state (thermodynamic) property of the complexes such as the difference in the redox potentials, discussions in this article is valid as far as the Marcus cross relation holds.

In conclusion, the effect of the deformation of the porphyrin skeleton on the electron self-exchange reaction does not originate from the deformation itself but from the enhancement of the conformational deformation during the oxidation of the OETPP complexes of Cu(II) and Zn(II). These features are in contrast with the planar porphyrin and porphycene complexes that tend to maintain their molecular structures during electron transfer reactions.

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Electronic supplementary information (ESI)

Figures reporting the spectral change associated with the oxidations of [Zn(OEPc)], [Zn(TPP)], [Zn(OEP)], and [Zn(OETPP)] by Cu²⁺ in acetonitrile, the spectrophotometric titration for the first oxidation reaction of [Cu(TPrPc)] by Cu(II) triflate.

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of the complexes in pure acetonitrile, and the self-exchange rate constants for Cu(II)-TPP and Cu(II)-OEP were reevaluated.

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Table 1. Redox potentials of the complexes used in the present study^a

Compound	E°/V vs. $Fc^{+/0}$
$[Cu(TPP)]^{+/0}$	0.600
$[Cu(OEP)]^{+/0}$	0.480
$[Cu(OETPP)]^{+/0}$	-0.011
$[Cu(TPrPc)]^{+/0}$	0.418
$[Zn(TPP)]^{+/0}$	0.390
$[Zn(OEP)]^{+/0}$	0.314
$[Zn(OETPP)]^{+/0}$	-0.093
$[Zn(OEPc)]^{+/0}$	0.337

^a Ionic strength of the solution was adjusted to 0.1 M by tetra-*n*-butylammonium perchlorate (TBAP). $T = 25.0^{\circ}C$.

Table 2. Rate constant of electron transfer reaction of porphyrin and porphycene complexes with Cu(II) ion acetonitrile^a

complex	$k_{s0} / \text{M}^{-1} \text{s}^{-1}$	$k_{s1} / \text{M}^{-1} \text{s}^{-1}$
[Cu(TPP)] ^b	$(5.81 \pm 0.12) \times 10^3$	c
[Cu(OEP)] ^b	$(2.01 \pm 0.03) \times 10^5$	c
[Cu(OETPP)] ^d	$(1.46 \pm 0.06) \times 10^5$	$(7.54 \pm 0.42) \times 10^4$
[Cu(TPrPc)]	$(6.54 \pm 0.13) \times 10^4$	$(3.80 \pm 0.65) \times 10^3$
[Zn(TPP)]	$(5.37 \pm 0.03) \times 10^5$	$(7.01 \pm 0.20) \times 10^4$
[Zn(OEP)]	$(1.72 \pm 0.02) \times 10^6$	$(2.95 \pm 0.11) \times 10^5$
[Zn(OETPP)]	$(3.42 \pm 0.11) \times 10^6$	$(2.88 \pm 0.10) \times 10^6$
[Zn(OEPc)]	$(5.77 \pm 0.12) \times 10^6$	$(1.51 \pm 0.07) \times 10^6$

^a Ionic strength of the solution was adjusted to 0.10 M by TBAP. $T = 25.0^\circ\text{C}$.

^b Reference 13

^c The contribution of the k_{s1} term to the second-order rate constant k_f was found to be negligible.

^d Reference 18

Table 3. Self-exchange rate constant between porphyrin and porphycene complexes and their π -cation radicals at $T = 25.0$ °C

complex	$k_{11} / \text{M}^{-1} \text{s}^{-1}$
[Cu(TPP)] ^a	2.7×10^{10}
[Cu(OEP)] ^a	4.3×10^{11}
[Cu(OETPP)] ^b	2.4×10^4
[Cu(TPrPc)]	5.0×10^9
[Zn(TPP)]	1.4×10^{11}
[Zn(OEP)]	1.3×10^{11}
[Zn(OETPP)]	1.9×10^6
[Zn(OEPc)]	3.4×10^{12}

^a Reference 13

^b Reference 18

Figure Captions

Figure 1. Change of the UV-visible absorption spectrum of [Cu(TPrPc)] associated with the reaction with Cu(II) triflate in acetonitrile at $T = 25.0^\circ\text{C}$: [Cu(TPrPc)] (**A**), [Cu(TPrPc)]⁺ (**B**), [Cu(TPrPc)]²⁺ (**C**). $C_{\text{Cu-TPrPc}} = 1.2 \times 10^{-6} \text{ M}$, $C_{\text{Cu(II)}} = 7.40 \times 10^{-4} \text{ M}$. The absorbance of the excess amount of the Cu(II) ion was subtracted from the observed spectrum for each case.

Figure 2. Dependence of the pseudo-first-order rate constant k_{obsd} of the reaction of [Cu(TPrPc)] with Cu(II) triflate on the concentration of the Cu(II) ion in acetonitrile at $T = 25.0^\circ\text{C}$. The concentration of water is 0.094 M (**A**) and 0.20 M (**B**). $I = 0.1 \text{ M}$ (TBAP).

Figure 3. Dependence of the second-order rate constant k_f of the reaction of [Cu(TPrPc)] with Cu(II) triflate on the concentration of water in acetonitrile at $T = 25.0^\circ\text{C}$. Broken (**A**) and dotted (**B**) lines represent the contribution of the k_{S0} and k_{S1} terms, respectively.

Figure 4. Reaction profiles described by diabatic surfaces of the precursor and successor complexes for two different types of the self-exchange reactions, where the diabatic energy surfaces are chiefly made up with the inner-sphere reorganization barrier.

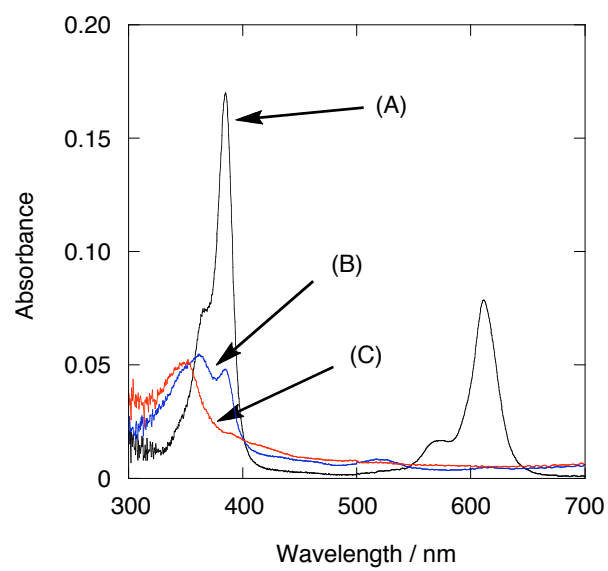


Figure 1. K. Aoki et. al.

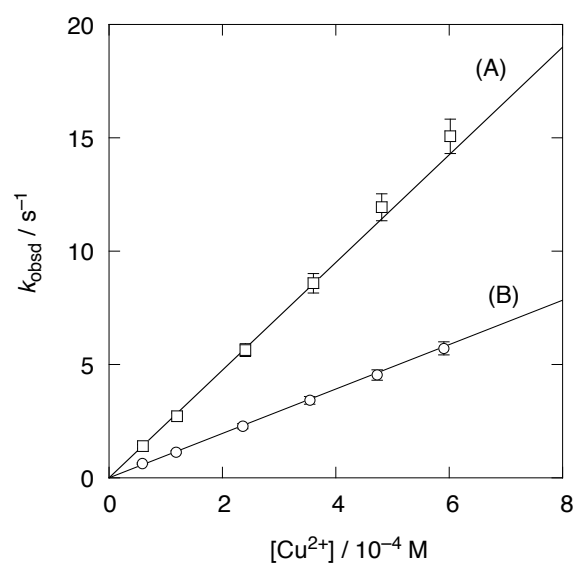


Figure 2. K. Aoki et. al.

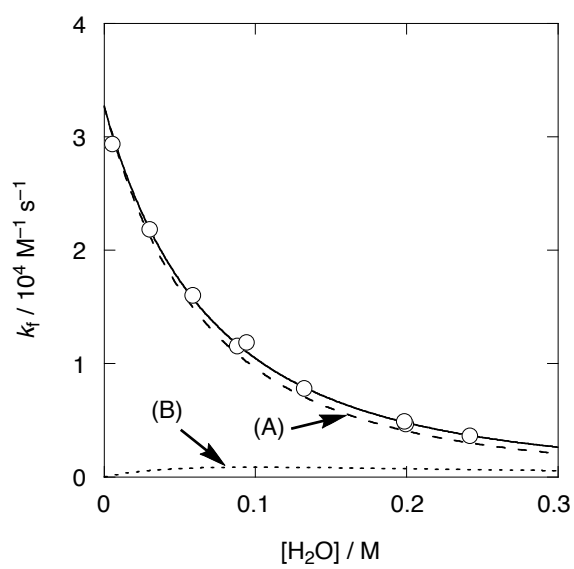


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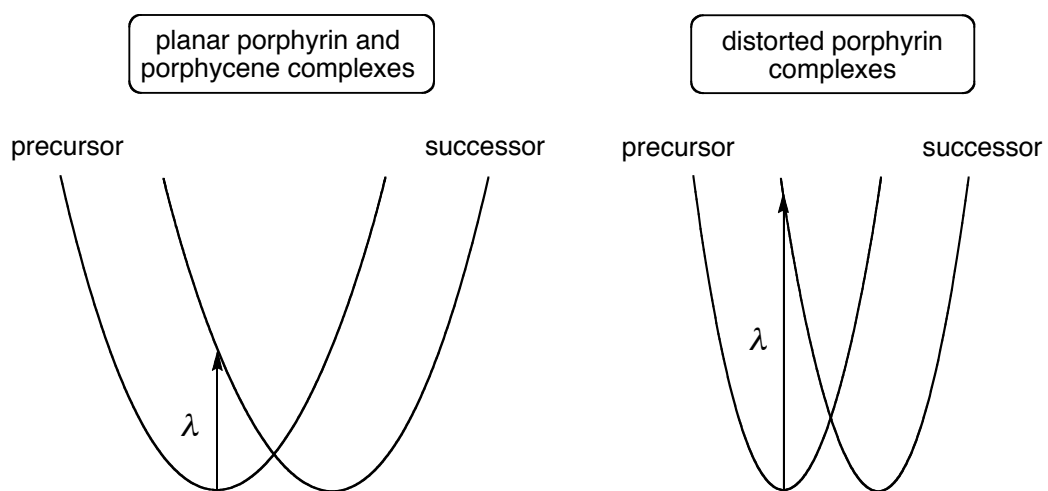
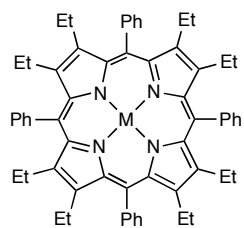
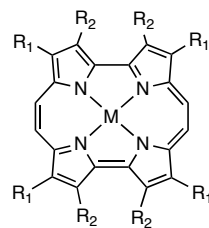


Figure 4. K. Aoki et. al.



[M(OETPP)]
M = Cu(II), Zn(II)



[Cu(TPrPc)] R₁ = C₃H₇, R₂ = H
[Zn(OEPc)] R₁ = R₂ = C₂H₅