

Electron Transfer Reactions between Copper(II) Porphyrin Complexes and Various Oxidizing Reagents in Acetonitrile

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Summary

Homogeneous electron transfer reactions of the Cu(II) complexes of 5,10,15,20-tetraphenylporphyrin (TPP) and 2,3,7,8,12,13,17,18-octaethylporphyrin (OEP) with various oxidizing reagents were spectrophotometrically investigated in acetonitrile. The reaction products were confirmed to be the π -cation radicals of the corresponding Cu(II)-porphyrin complexes on the basis of the electronic spectra and the redox potentials of the complexes. The rate of the electron transfer reaction between the Cu(II)-porphyrin complex and solvated Cu^{2+} was determined as a function of the water concentration under the pseudo first-order conditions where Cu^{2+} is in large excess over the Cu(II)-porphyrin complex. The decrease in the pseudo first-order rate constant with increasing the water concentration was attributed to the stepwise displacement of acetonitrile in $[\text{Cu}(\text{AN})_6]^{2+}$ (AN = acetonitrile) by water, and it was concluded that only the Cu^{2+} species fully solvated by acetonitrile, $[\text{Cu}(\text{AN})_6]^{2+}$, possesses sufficiently high redox potential for the oxidation of Cu(II)-OEP and Cu(II)-TPP. The reactions of the Cu(II)-porphyrin complexes with other oxidizing reagents such as $[\text{Ni}(\text{tacn})_2]^{3+}$ (tacn = 1,4,7-triazacyclononane) and $[\text{Ru}(\text{bpy})_3]^{3+}$ (bpy = 2,2'-bipyridine) were too fast to be followed by a conventional stopped-flow technique. Marcus cross relation for the outer-sphere electron transfer reaction was used to estimate the rate constants of the electron self-exchange reaction between Cu(II)-porphyrin and its π -cation radical: $\log(k / \text{M}^{-1} \text{s}^{-1}) = 9.5 \pm 0.5$ for TPP and $\log(k / \text{M}^{-1} \text{s}^{-1}) = 11.1 \pm 0.5$ for OEP at 25.0°C. Such large electron self-exchange rate constants are typical for the porphyrin-centered redox reactions for which very small inner- and outer-sphere reorganization energies are required.

Introduction

Electron transfer reactions of metalloporphyrins play essential roles in various biological processes.^{1,2} Highly conjugated π systems of the porphyrin molecules are suitable for efficient electron transfer processes, since the release or uptake of an electron

causes minimal structural change of these molecules. In the case of the metalloporphyrins that have redox-active metal ions, additional metal-centered electron transfer reactions are also important. As a result, the reactivity of metalloporphyrins towards electron transfer depends on the nature of the porphyrin ligands and the nature of the metal ions as well as the axial ligands that may control the redox properties of metalloporphyrins through coordination to the central metal ions. Electron transfer reactions of metalloporphyrins have been studied extensively in order to clarify the factors that affect the electron transfer processes involved in the biological systems, such as photosynthesis and the electron transport system in the respiratory chain.³

According to the Marcus theory,^{4,5} 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 a 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 κ_{el} value is unity for adiabatic reactions where the electronic coupling as a result of the orbital overlap between the two reactants is sufficiently large. The reorganization energy for the self-exchange reaction involving metalloporphyrins can be estimated from the cross reactions of metalloporphyrins with the outer-sphere oxidizing or reducing reagents using the Marcus cross-relation: λ in eq 1 is assumed to be the algebraic mean of the reorganization parameters for each redox couple involved in the cross reaction. Self-exchange rate constants for many redox reactions of metalloporphyrins have been determined in this manner, especially for the metal-centered redox couples.³ For example, electron self-exchange rate constants for tetraarylporphyrin complexes fall in the range 10^7 to $10^8 \text{ M}^{-1} \text{ s}^{-1}$ for the $\text{Fe}^{2+/3+}$ complexes,⁶⁻⁹ and 10^{-3} to $10^4 \text{ M}^{-1} \text{ s}^{-1}$ for the $\text{Co}^{2+/3+}$ complexes.^{10,11} On the contrary, the porphyrin-centered redox reactions have been scarcely studied,¹² partly because of the highly reactive nature of this type of reactions: smaller inner-sphere

reorganization energies are required for this type of reactions compared with the metal-centered redox reactions, as the latter type of reactions generally involves large change in the metal-nitrogen bond lengths that pushes up the inner-sphere activation barrier.

In this article, we report the kinetics of the oxidation reactions of Cu(II)-porphyrin complexes, Cu(II)-OEP and Cu(II)-TPP (OEP = 2,3,7,8,12,13,17,18-octaethylporphyrin and TPP = 5,10,15,20-tetraphenylporphyrin) by various oxidizing reagents in acetonitrile. Oxidation reactions of the Cu(II)-porphyrin complexes take place at the porphyrin ligand while the central copper ion remains in the oxidation state of +II.¹³ The rate constants for the electron self-exchange reactions between the Cu(II)-porphyrins 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 rates are extremely slow. The very rapid self-exchange rate for the porphyrin-centered electron transfer reactions and probable structures of the transition states were discussed on the basis of the Marcus theory and the reported crystal structures of mixed-valent $[M(\text{porphyrin})]/[M(\text{porphyrin})]^+$ species.

Experimental

Materials. 5,10,15,20-Tetraphenylporphyrin (H_2 TPP) was prepared by the literature method.^{14,15} 2,3,7,8,12,13,17,18-Octaethylporphyrin (H_2 OEP) was purchased from Tokyo Kasei Organic Chemicals. Cu(II)-porphyrin complexes were obtained by the Cu(II) acetate method,¹⁶ purified by a column chromatography, and recrystallized from dichloromethane / methanol or dichloromethane / heptane. Anal. Calcd for $C_{44}H_{28}N_4Cu$ ([Cu(TPP)]): C, 78.15; H, 4.17; N, 8.28. Found: C, 77.87; H, 4.46; N, 8.30%. Anal. Calcd for $C_{36}H_{44}N_4Cu$ ([Cu(OEP)]): C, 72.51; H, 7.44; N, 9.40. Found: C, 72.31; H, 7.26; N, 9.19%. Cu(II) triflate, $Cu(CF_3SO_3)_2$, was prepared according to the literature method.¹⁷ Bis(1,4,7-triazacyclononane)nickel(III) perchlorate, $[Ni(\text{tacn})_2](ClO_4)_3$, was synthesized according to the literature method.^{18,19} Anal. Calcd for $C_{12}H_{30}N_6Cl_3NiO_{12}$: C, 23.42; H, 4.91; N, 13.66. Found: C, 23.24; H, 4.74; N, 13.94%. Tris(2,2'-

bipyridine)ruthenium(III) hexafluorophosphate, $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_3$, was prepared by the literature method.^{20,21} Anal. Calcd for $\text{C}_{30}\text{H}_{24}\text{N}_6\text{RuP}_3\text{F}_{18}\cdot 3\text{H}_2\text{O}$: C, 34.04; H, 2.86; N, 7.94. Found: C, 34.02; H, 2.49; N, 7.91%. Preparation of tetra-*n*-butylammonium tris(hexafluoroacetylacetonato)ruthenate(II), $(n\text{-Bu}_4\text{N})[\text{Ru}(\text{hfac})_3]$, was reported previously.²² *CAUTION! Although we have experienced no problems in handling perchlorate compounds, these salts combined with organic ligands are potentially explosive and should be handled in small quantities and with adequate precautions.*^{23,24}

Acetonitrile (AN, Wako Pure Chemical Industries) was dried over activated 4Å molecular sieves for several days and distilled under nitrogen atmosphere. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Fulka, 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.

Measurements. Redox potentials of the metal complexes were determined by cyclic voltammetry using a BAS 100B electrochemical analyzer and a three-electrode system under deaerated conditions at $T = 25.0^\circ\text{C}$. The working and counter electrodes were glassy carbon and platinum wire, respectively, and the reference electrode was Ag/AgNO₃ (0.01M) in acetonitrile. Each solution contains 0.1 M TBAP as a supporting electrolyte.

UV-visible absorption spectra were recorded on a Hitachi U-3000 spectrophotometer. The spectral change corresponding to the reactions of the Cu(II)-porphyrin complexes with solvated Cu²⁺ in acetonitrile was measured by a stopped-flow rapid detection system (RSP-801, Unisoku, Japan). The absorbance, A , was followed after mixing acetonitrile solutions containing each of the metalloporphyrin and a large excess of Cu(II) triflate to determine the conditional 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 values of k_{obsd} are the average of several runs. Reproducibility of the k_{obsd} value was within $\pm 3\%$. The temperature for all measurements

was maintained at $T = 25.0 \pm 0.1$ °C by circulation of thermostated water. 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 has been well documented that two consecutive one-electron oxidation steps are observed for the Cu(II)-porphyrin complex in non-aqueous media,¹³ and these oxidation processes have been assigned to the removal of electrons from the porphyrin macrocycle giving a porphyrin π -cation radical and π -dication, respectively, on the basis of the optical and EPR spectra.²⁵⁻²⁹ Redox potentials of the metal complexes used in this study are listed in Table 1. Due to the poor solubility of the Cu(II)-porphyrin complexes,

// Table 1 //

[Cu(TPP)] and [Cu(OEP)], it was hardly possible to determine the redox potentials for these complexes in acetonitrile. Instead, the acetonitrile solution containing 10% chloroform (v/v) was used as a solvent in order to estimate the redox potentials. As shown in Table 1, the redox potentials are hardly affected by the solvent composition under the present experimental conditions. Therefore, the values obtained in acetonitrile with 10% chloroform will be used in the following discussions. All redox voltammograms other than that for the [Ru(bpy)₃]^{3+/2+} couple are either reversible or quasi-reversible as judged from the separation between the anodic and cathodic peaks. The solvated Cu²⁺ species in acetonitrile exhibited redox waves at 0.66 V vs. the ferricinium/ferrocene couple that was used as the standard throughout this study, and this redox potential is higher than that of the Cu(II)-porphyrin complexes as shown in Table 1. The average potential differences between the first and second ring-centered oxidations of the Cu(II)-porphyrin complexes are ca. 0.28 ± 0.05 V for TPP and ca. 0.45 ± 0.05 V for OEP.¹³ Although the second oxidation

step was not observed due to the poor solubility of the Cu(II)-porphyrin complexes in acetonitrile, it is probable that the second oxidation potentials of these porphyrin complexes are significantly higher than the redox potential of the solvated Cu(II)/(I) couple, $E^0 = 0.66$ V vs. $\text{Fc}^{+/0}$. Therefore, it is concluded that the products of the oxidation reactions of these porphyrin complexes with solvated Cu^{2+} are the π -cation radicals of the Cu(II)-porphyrin complexes and $[\text{Cu}(\text{AN})_4]^+$, the latter of which is known as one of the most stable Cu(I) species.^{30,31} As discussed in the later section, stepwise replacements of coordinated acetonitrile in the solvated Cu^{2+} ($[\text{Cu}(\text{AN})_6]^{2+}$) by the water molecule take place when the water is added to the acetonitrile solution of Cu^{2+} . As only a pair of the redox waves corresponding to the $[\text{Cu}(\text{AN})_6]^{2+/+}$ couple was observed in the potential window, it is clear that the aquated Cu^{2+} species, $[\text{Cu}(\text{AN})_{6-n}(\text{H}_2\text{O})_n]^{2+/+}$ ($n \geq 1$), can neither oxidize nor reduce the Cu(II)-porphyrin complexes.

Spectral Changes. The products of the reactions of the Cu(II)-porphyrin complexes with various oxidizing reagents were spectrophotometrically analyzed in acetonitrile. The spectral change in the UV-visible region for the reaction of $[\text{Cu}(\text{TPP})]$ with Cu(II) triflate is shown in Figure 1, and the results for the reactions of OEP complexes

// Figure 1 //

are given in Figure S1 in the electronic supplementary information. A drastic intensity lowering and the blue shift of the Soret band was observed for the oxidation reactions of both porphyrin complexes by $[\text{Cu}(\text{AN})_6]^{2+}$. Such spectral features of the products indicate that the oxidation of the Cu(II)-porphyrin complexes is certainly ring centered rather than metal centered, and the observed spectral changes associated with the oxidation reactions of these porphyrin complexes are typical for the formation of porphyrin π -cation radical complexes.^{25,26} The formation of this type of π -cation radical has also been evidenced by IR, X-ray, and NMR methods.³²⁻³⁶

The stoichiometry of the reaction was studied by the spectrophotometric titration experiments for the reactions of the Cu(II)-porphyrin complexes with solvated Cu(II) triflate in acetonitrile. A known amount of the solution of Cu(II) triflate was added to a solution containing a known amount of Cu(II)-porphyrin, and the resulting spectrum was measured after completion of the reaction. The absorbance at the given wavelength was plotted against the ratio of the concentration of Cu(II) triflate over that of the Cu(II)-porphyrin complex in Figure S2 for the OEP complex. The ratio of moles of Cu(II) triflate consumed per mole of the Cu(II)-porphyrin complex was determined to be 1.00 ± 0.03 for each porphyrin complex, supporting the general overall reaction 2.



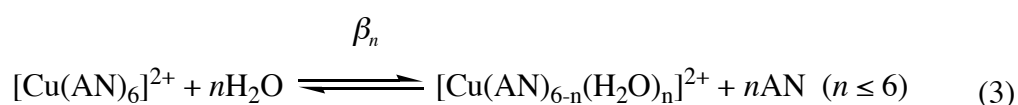
It was evidenced spectrophotometrically that identical Cu(II)-porphyrin complexes bearing π -cation radicals were also formed by the reactions with other oxidants, *i.e.*, $[\text{Ni}(\text{tacn})_2]^{3+}$, and $[\text{Ru}(\text{bpy})_3]^{3+}$. Therefore, it was confirmed that the present electron transfer reactions produce the π -cation radical of the Cu(II)-porphyrin complex and the reduced form of each oxidizing reagent, $[\text{Cu}(\text{AN})_4]^+$, $[\text{Ni}(\text{tacn})_2]^{2+}$, or $[\text{Ru}(\text{bpy})_3]^{2+}$.

Kinetics Studies. A stopped-flow technique was used to determine the rates of the electron transfer reactions in acetonitrile. Ionic strength of the solution was adjusted to 0.1 M by TBAP. The electron transfer reactions between $[\text{Cu}(\text{porphyrin})]$ and various oxidizing reagents were followed under the pseudo-first-order conditions where the oxidizing reagent existed in large excess over the Cu(II)-porphyrin complex. The change in absorbance at a wavelength around the Soret band of the Cu(II)-porphyrin complex was first-order with respect to the metalloporphyrins in the case of the reaction with Cu(II) triflate. 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 solvated Cu^{2+} is shown in Figure 2 for the

// Figure 2 //

reaction of the Cu(II)-TPP complex as an example. The pseudo-first-order rate constant, k_{obsd} , was proportional to the concentration of Cu^{2+} under the constant concentration of water. The second-order rate constant, k_f , was then determined using the relationship, $k_f = k_{\text{obsd}}/[\text{Cu}^{2+}]$. Similar results were obtained for the Cu(II)-OEP complex.

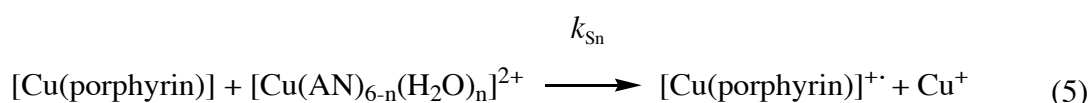
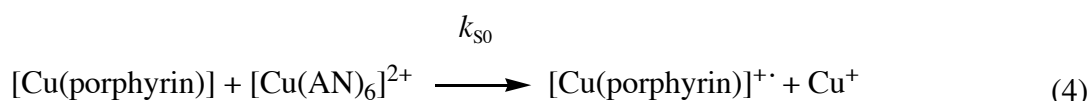
The effect of water on the rate of the oxidation reactions of the Cu(II)-porphyrin complexes by Cu^{2+} was also examined, as it has been known that some of the acetonitrile molecules on $[\text{Cu}(\text{AN})_6]^{2+}$ are replaced by water (eq 3).³⁷



The overall formation constant β_n for the $[\text{Cu}(\text{AN})_{6-n}(\text{H}_2\text{O})_n]^{2+}$ complex is defined as $\beta_n = [\text{Cu}(\text{AN})_{6-n}(\text{H}_2\text{O})_n]^{2+}[\text{Cu}(\text{AN})_6]^{2+}^{-1}[\text{H}_2\text{O}]^{-n}$. The equilibria of the solvation of the Cu(II) ion in the aqueous acetonitrile solution were 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 $\log(\beta_3/\text{M}^{-3}) = 2.12 \pm 0.57$.³⁷ As shown in Figure 3, the reaction was retarded by added water in the acetonitrile solution.

// Figure 3 //

Such a dependence of k_f on the H_2O concentration may be explained by the combination of the following two effects: (1) retardation of the reaction caused by the reduced concentration of reactive $[\text{Cu}(\text{AN})_6]^{2+}$ through reaction 3 (eq 4), and (2) retardation of the oxidation reaction as the oxidation power of $[\text{Cu}(\text{AN})_{6-n}(\text{H}_2\text{O})_n]^{2+}$ ($n \geq 1$) species is small (eq 5).



The concentrations of $[\text{Cu}(\text{AN})_{6-n}(\text{H}_2\text{O})_n]^{2+}$ species were estimated by using the reported values of β_n ,³⁷ and the kinetic results shown in Figure 3 were analyzed by a least-squares calculation to determine the values of k_{s0} and k_{sn} ($n \geq 1$). However, it was not necessary to take into account the contribution of $[\text{Cu}(\text{AN})_{6-n}(\text{H}_2\text{O})_n]^{2+}$ ($n \geq 1$) to the rate of the present electron transfer reaction for the explanation of the results shown in Figure 3, indicating that the aquated Cu^{2+} species, $[\text{Cu}(\text{AN})_{6-n}(\text{H}_2\text{O})_n]^{2+}$ ($n \geq 1$), have oxidation potentials not high enough to oxidize the Cu(II)-porphyrin complexes. Therefore, the second-order rate constant k_f can be expressed by eq 6.

$$k_f = k_{s0} (1 + \beta_1[\text{H}_2\text{O}] + \beta_2[\text{H}_2\text{O}]^2 + \beta_3[\text{H}_2\text{O}]^3)^{-1} \quad (6)$$

In this treatment, it is assumed that the substitution reaction of the coordinated acetonitrile and water molecules around the Cu(II) ion is faster than the present electron transfer reaction. The best-fit values of k_{s0} are $(5.81 \pm 0.12) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for [Cu(TPP)] and $(2.01 \pm 0.03) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for [Cu(OEP)]. As shown in Figure 3, the calculated curves of k_f using thus obtained k_{s0} value reproduced the observed data very well.

Oxidation reactions of the Cu(II)-porphyrin complexes by the other oxidizing reagents, $[\text{Ni}(\text{tacn})_2]^{3+}$ and $[\text{Ru}(\text{bpy})_3]^{3+}$, were also investigated, and the reactions were revealed to be too fast to be followed by a stopped-flow spectrophotometer under the conditions of $C_{\text{oxidant}} = 4 \times 10^{-5} \text{ M}$ and $C_{\text{Cu(II) porphyrin}} < 2 \times 10^{-6} \text{ M}$. These findings indicate that the second-order rate constant of the electron transfer reactions between the Cu(II)-porphyrin complex and these oxidizing reagents are larger than $5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at 25.0°C, judging from the dead time (ca. 5 ms) of the rapid-mixing instrument used in this study.

Electron Self-Exchange Reaction In order to evaluate the rate constants for the electron self-exchange reactions between each Cu(II)-porphyrin complex and its π -cation radical, it is necessary to determine the electron self-exchange rate constant of the counter reagent, the $\text{Cu}^{2+/+}$ couple. The reduction cross reactions of solvated Cu(II) were examined in acetonitrile by using $[\text{Ru}(\text{hfac})_3]^-$ and $[\text{Ni}(\text{tacn})_2]^{2+}$ as counter reagents. The results are shown in Figure 4.

// Figure 4 //

The second order rate constants of the reduction of Cu^{2+} by $[\text{Ru}(\text{hfac})_3]^-$ and $[\text{Ni}(\text{tacn})_2]^{2+}$ were determined as $1.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $3.5 \text{ M}^{-1} \text{ s}^{-1}$, respectively, at $T = 25.0^\circ\text{C}$. The Marcus cross relation was applied for the estimation of the self-exchange rate constant for the solvated $\text{Cu}^{2+/+}$ couple.^{38,39} The rate constant for a cross reaction, k_{12} , is related to the rate constants of each self-exchange reaction, k_{11} and k_{22} , for the corresponding redox pairs involved in the cross reaction and to the equilibrium constant for the cross reaction K_{12} by

$$k_{12} = (k_{11} k_{22} K_{12} f_{12})^{1/2} W_{12} \quad (7)$$

where

$$\ln f_{12} = [\ln K_{12} + (w_{12} - w_{21})/RT]^2 / 4 [\ln(k_{11} k_{22} / Z^2) + (w_{11} + w_{22})/RT] \quad (8)$$

$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT] \quad (9)$$

$$w_{ij} = 37.9 z_i z_j / \sigma_{ij} (1 + 0.481 \sigma_{ij}^{1/2}) \quad (10)$$

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 equal to the sum of the radii of the reagents) and Z is the collision frequency ($k_B T/h$). Using the one-electron oxidation potentials for each reducing reagent, 0.36 V for $[\text{Ru}(\text{hfac})_3]^-$ and 0.56 V for $[\text{Ni}(\text{tacn})_2]^{2+}$, and the self-exchange rate constant for $[\text{Ru}(\text{hfac})_3]^{0/-}$ ($7.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$)⁴⁰ and $[\text{Ni}(\text{tacn})_2]^{3+/2+}$ ($1.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$) couples,⁴¹ we estimated the self-exchange rate constant for the $\text{Cu}(\text{II})/(\text{I})$ couple as $1.5 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ and $1.2 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ ($T = 25.0^\circ\text{C}$) from these cross reactions, respectively, which may be compared with those estimated for the $\text{Cu}(\text{II})/(\text{I})$ couple in water: $10^{-7} \sim 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$.⁴³⁻⁴⁵ These values are given in Table S2. As these counter reagents, $[\text{Ru}(\text{hfac})_3]^-$ and $[\text{Ni}(\text{tacn})_2]^{2+}$, are typical outer-sphere reagents, the estimated self-exchange rate constant certainly corresponds to the outer-sphere reaction between solvated Cu^{2+} and solvated Cu^+ .

The self-exchange rate constants for the copper porphyrin complexes were then calculated from the rate constants of the cross-reactions with solvated Cu^{2+} . The averaged value of $4.2 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ for the self-exchange rate constant of the solvated $\text{Cu}^{2+/+}$ couple

was used in the following calculation. Although the uncertainty of this self-exchange rate constant for the $\text{Cu}^{2+/+}$ couple introduces somewhat large errors for the estimated self-exchange rate constants for the Cu(II)-porphyrin couples, the difference (the ratio) of the self-exchange rate constants for the Cu(II)-OEP and Cu(II)-TPP couples is unaffected since the activation process of the $\text{Cu}^{2+/+}$ couple is expected to be identical for the two cross reactions. The reactions of Cu(II)-porphyrins with solvated Cu^{2+} are expected to proceed through the ordinary outer-sphere process as no potential bridging ligand exists in the medium. The redox potentials of each complex determined in the acetonitrile solution containing 10% chloroform (v/v) were used to evaluate the K_{12} value. The determined self-exchange rate constants for the Cu(II)-porphyrin / its π -cation radical couples are $\log(k / \text{M}^{-1} \text{s}^{-1}) = 9.5 \pm 0.5$ for TPP and $\log(k / \text{M}^{-1} \text{s}^{-1}) = 11.1 \pm 0.5$ for OEP at 25.0°C .⁴⁶ The reorganization energies for the self-exchange reactions were calculated as ca. 74 kJ mol^{-1} and 39 kJ mol^{-1} for $[\text{Cu}(\text{TPP})]^{+/0}$ and $[\text{Cu}(\text{OEP})]^{+/0}$ couples, respectively, by assuming that the reactions are adiabatic. Such small reorganization parameters may also indicate that the observed oxidation reactions of Cu(II)-porphyrin complexes are ligand-centered. A small inner- and outer-sphere reorganization energies are typical for the electron exchange reactions between large chemical species with highly conjugated π electron systems as little structural change is expected on the occasion of addition or subtraction of an electron to such species. Such a conclusion is supported by the reported structural aspects of the Cu(II)-porphyrin complex and its π -cation radical: the average Cu-N bond distance, $1.988(4) \text{ \AA}$, in the π -cation radical of $[\text{Cu}(\text{TPP})]^{34}$ is comparable to that in the parent complex, $[\text{Cu}(\text{TPP})]$ ($1.981(7) \text{ \AA}$).⁴⁷

It is also highly probable to consider that the oxidation of metal center is not rapid: a d^8 Cu(III) complex should have a considerably shorter Cu-N bond distance compared to that for the d^9 Cu(II) complex, due to the reduced number of electrons in the antibonding $d_{x^2-y^2}$ orbital and increased Coulombic attraction between Cu(III) and nitrogen donor atoms. Such a speculation may be verified by the fact that the metal-centered oxidation of metalloporphyrins exhibits slower electron transfer rates in comparison to the porphyrin

ring oxidation. Electron self-exchange rate constants estimated for the $\text{Fe}^{3+/2+}$ and $\text{Co}^{2+/3+}$ couples with 5,10,15,20-tetraarylporphyrin are in the range of 10^7 to $10^8 \text{ M}^{-1} \text{ s}^{-1}$ ⁶⁻⁹ and 10^{-3} to $10^4 \text{ M}^{-1} \text{ s}^{-1}$,^{10,11} respectively. On the other hand, the rate of the porphyrin ring-centered oxidation of metalloporphyrins are usually very fast, and recently reported ligand-centered electron self-exchange rate constant for the $[\text{Zn}(\text{TPP})]^{+/0}$ couple ($k_{\text{ex}} = 2.0 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ at 25.0°C)¹² is comparable to those for the $[\text{Cu}(\text{porphyrin})]^{+/0}$ couples estimated in this study.

There exists a difference in the rate constants as well as in the activation free energies of the self-exchange reactions between the $[\text{Cu}(\text{TPP})]^{+/0}$ and $[\text{Cu}(\text{OEP})]^{+/0}$ couples. The difference in the activation free energies for these two rapid self-exchange reactions is 9 kJ mol^{-1} . It is known that neutral metalloporphyrins with peripheral non-aryl substituents and their π -cation radicals tend to form porphyrin-porphyrin dimers in the solid state.⁴⁸ Their structures are characterized as cofacial binuclear complexes with porphyrin ring-ring interactions. Once the metalloporphyrin is oxidized to form a corresponding π -cation radical, then the intermolecular interaction becomes stronger as shown by the decrease in the mean plane separation between two porphyrin rings from $3.42(8)\text{\AA}$ for the neutral porphyrin pair to $3.25(6)\text{\AA}$ for the π -cation radical dimer.⁴⁸ Recently, Scheidt et al. have reported the molecular structure of the mixed-valent π -cation radicals, $[\text{Cu}(\text{OEP}^{7/2})]_2^+$, which can be regarded as the model of the encounter complex for the present electron self-exchange reaction of the $[\text{Cu}(\text{OEP})]^{+/0}$ couple.⁴⁹ This pair of mixed-valent π -cation radicals exhibits unique binuclear structures with cofacial porphyrin rings where the mean plane separation is merely 3.27\AA , which is almost identical to that in the π -cation radical dimer. Therefore, a very strong inter-ring interaction is also expected for the precursor complex for the present reaction, $[\text{Cu}(\text{OEP})]^+ / [\text{Cu}(\text{OEP})]^0$. On the other hand, this type of dimeric structure is hardly observed for the metalloporphyrin complexes with peripheral aryl substituents. Therefore, the stronger cofacial interaction between the π -cation radical and the parent OEP complex seems to be the essential cause of the faster electron self-exchange reaction for the $[\text{Cu}(\text{OEP})]^{+/0}$ couple: the stronger electronic coupling between

two reactants ensures the more efficient electron transfer within the $[\text{Cu}(\text{OEP})]^{+/0}$ couple than in the $[\text{Cu}(\text{TPP})]^{+/0}$ couple due to the effective stacking interaction.

For strongly interacting self-exchange couples, Fukuzumi and co-workers recently reported a very rapid electron self-exchange rate constant with a negative activation enthalpy for the $[\text{Zn}(\text{TPP})]^{+/0}$ and $[\text{Zn}(\text{T}(t\text{-Bu})\text{PP})]^{+/0}$ couples ($\text{T}(t\text{-Bu})\text{PP}^{2-} = 5,10,15,20$ -tetrakis(3,5-di-*tert*-butylphenyl)porphyrin dianion).¹² Their explanation for the very rapid electron self-exchange rate constant observed for the $[\text{Zn}(\text{TPP})]^{+/0}$ couple and for the relatively slow self-exchange reaction of $[\text{Zn}(\text{T}(t\text{-Bu})\text{PP})]^{+/0}$ was based on the formation of the π complex within the encounter complex which may be sensitive to the *t*-Bu substitution on the phenyl group of $[\text{Zn}(\text{TPP})]$. A negative enthalpy for self-exchange reactions is expected as a result of the sum of (1) the negative enthalpy for the formation of the precursor complex with a stacking interaction and (2) the small activation enthalpy for the electron transfer reaction. Although it has been known that the energy for such a stacking interaction is small,⁵⁰ it is still probable that apparent negative activation enthalpies are observed for some very rapid electron transfer reactions as the activation enthalpies for rapid outer-sphere electron transfer reactions are generally small.

Electronic supplementary information (ESI) available: Figures reporting the UV-visible absorption spectra of $[\text{Cu}(\text{OEP})]$ and the product of the reaction of $[\text{Cu}(\text{OEP})]$ with $\text{Cu}(\text{II})$ triflate in acetonitrile, the dependence of the absorbance on the ratio of the total concentrations of $\text{Cu}(\text{II})$ ion and $[\text{Cu}(\text{OEP})]$ for the reaction of $[\text{Cu}(\text{OEP})]$ and $\text{Cu}(\text{II})$ triflate, and the dependence of the pseudo-first-order rate constant of the reaction of $[\text{Fe}(\text{phen})_3]^{3+}$ with $[\text{Ni}(\text{tacn})_2]^{2+}$ on the concentration of the $\text{Ni}(\text{II})$ complex are given. Tables of the second-order rate constant of the reaction of $[\text{Fe}(\text{phen})_3]^{3+}$ with $[\text{Ni}(\text{tacn})_2]^{2+}$ and the electron transfer properties of the complexes used in the present study are given.

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- 41) Redox reaction of $[\text{Ni}(\text{tacn})_2]^{2+}$ with $[\text{Fe}(\text{phen})_3]^{3+}$ was examined in acetonitrile. Kinetic results are given in Figure S3 and Table S1. Self-exchange rate constant for $[\text{Ni}(\text{tacn})_2]^{3+/2+}$ couple was estimated from the rate constant of the cross-reaction between $[\text{Fe}(\text{phen})_3]^{3+}$ and $[\text{Ni}(\text{tacn})_2]^{2+}$ ($2.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at $T = 25.0^\circ\text{C}$) and the self-exchange rate constant for $[\text{Fe}(\text{phen})_3]^{3+/2+}$ ($1.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$).⁴²
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Table 1. Redox Potentials of the Complexes Used in the Present Study ^a

Compound	Medium	E^0/V vs. $Fc^{+/0}$
$[Cu(TPP)]^{+/0}$	AN + $CHCl_3$ (9:1 v/v)	0.57
$[Cu(OEP)]^{+/0}$	AN + $CHCl_3$ (9:1 v/v)	0.47
$Cu^{2+/+}$ ^b	AN + $CHCl_3$ (9:1 v/v)	0.66
	AN	0.66
$[Ni(tacn)_2]^{3+/2+}$	AN + $CHCl_3$ (9:1 v/v)	0.57
	AN	0.56
$[Ru(bpy)_3]^{3+/2+}$	AN + $CHCl_3$ (9:1 v/v)	0.78 ^c
	AN	0.70 ^c

^a Ionic strength of the solution was adjusted to 0.1 M by TBAP.

^b Copper(II) triflate was used.

^c Potential at the anodic peak of the cyclic voltammogram. The separation between the anodic and cathodic peaks is 330 mV in AN + $CHCl_3$ (9:1 v/v) and 250 mV in AN.

Figure Captions

Figure 1. UV-visible absorption spectra of [Cu(TPP)] (**A**) and the product of the reaction with Cu(II) triflate (**B**) in acetonitrile at $T = 25.0^\circ\text{C}$. $C_{\text{Cu-TPP}} = 4.0 \times 10^{-7} \text{ M}$. The absorbance caused by the excess amount of the Cu(II) ion was subtracted from the original spectrum for the latter case.

Figure 2. Dependence of the pseudo-first-order rate constant k_{obsd} of the reaction of [Cu(TPP)] 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 $7.95 \times 10^{-3} \text{ M}$ (**A**), $3.19 \times 10^{-2} \text{ M}$ (**B**), $3.77 \times 10^{-2} \text{ M}$ (**C**), $5.53 \times 10^{-2} \text{ M}$ (**D**), and $8.84 \times 10^{-2} \text{ M}$ (**E**). $I = 0.1 \text{ M}$ (TBAP).

Figure 3. Dependence of the second-order rate constant k_f of the reaction of the Cu(II)-porphyrin complexes with Cu(II) triflate on the concentration of water in acetonitrile at $T = 25.0^\circ\text{C}$. $I = 0.1 \text{ M}$ (TBAP).

Figure 4. Dependence of the pseudo-first-order rate constant k_{obsd} of the reaction of [Ru(hfac)₃]⁻ (**A**) or [Ni(tacn)₂]²⁺ (**B**) with Cu(II) triflate on the concentration of the Cu(II) ion in acetonitrile at $T = 25.0^\circ\text{C}$. $I = 0.1 \text{ M}$ (TBAP).

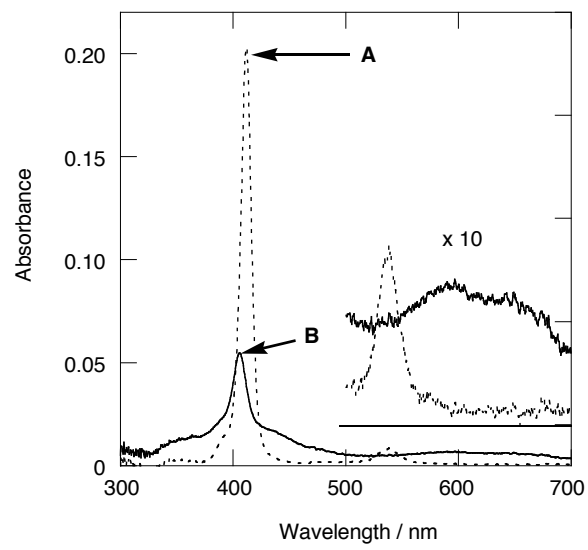


Figure 1. M. Inamo et al.

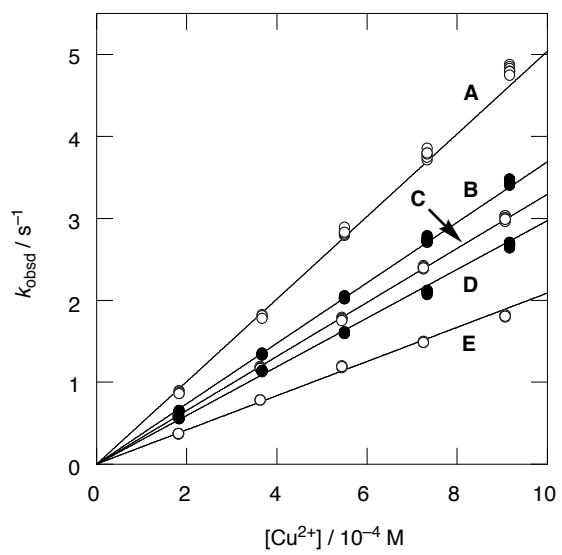


Figure 2. M. Inamo et al.

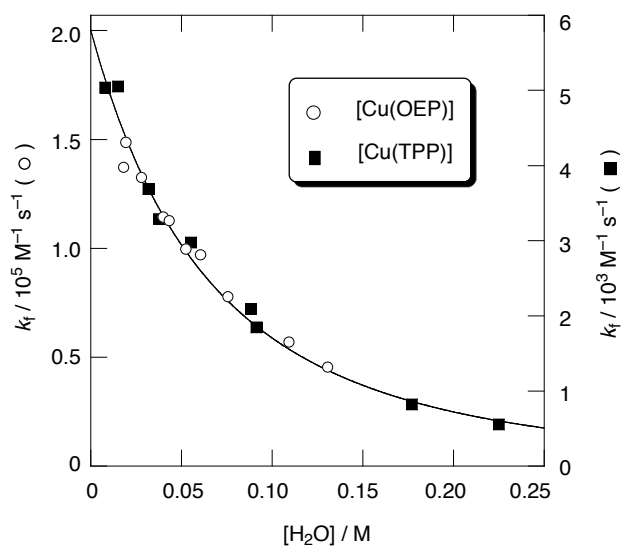


Figure 3. M. Inamo et al.

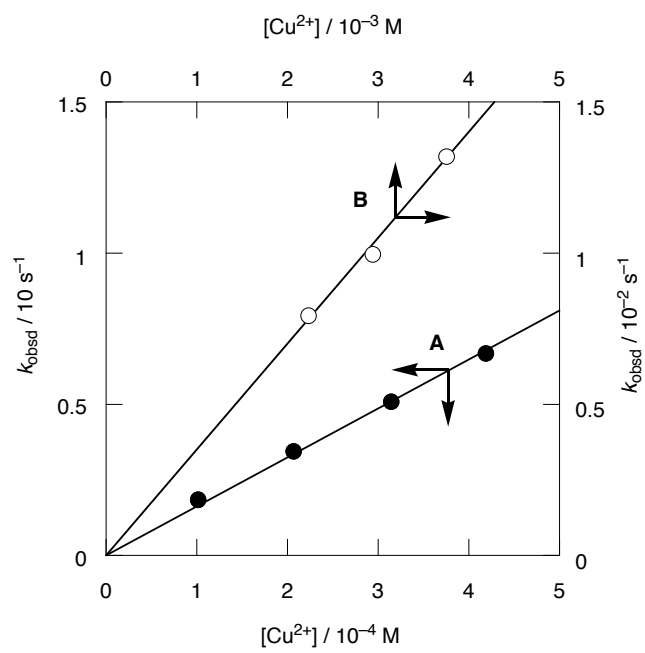


Figure 4. M. Inamo et al.

Graphical contents entry

Homogeneous electron transfer reactions of the Cu(II) porphyrin complexes with various oxidizing reagents were spectrophotometrically investigated in acetonitrile. The very rapid self-exchange rates for the porphyrin-centered electron transfer reactions and probable structures of the transition states were discussed on the basis of the Marcus theory.

