

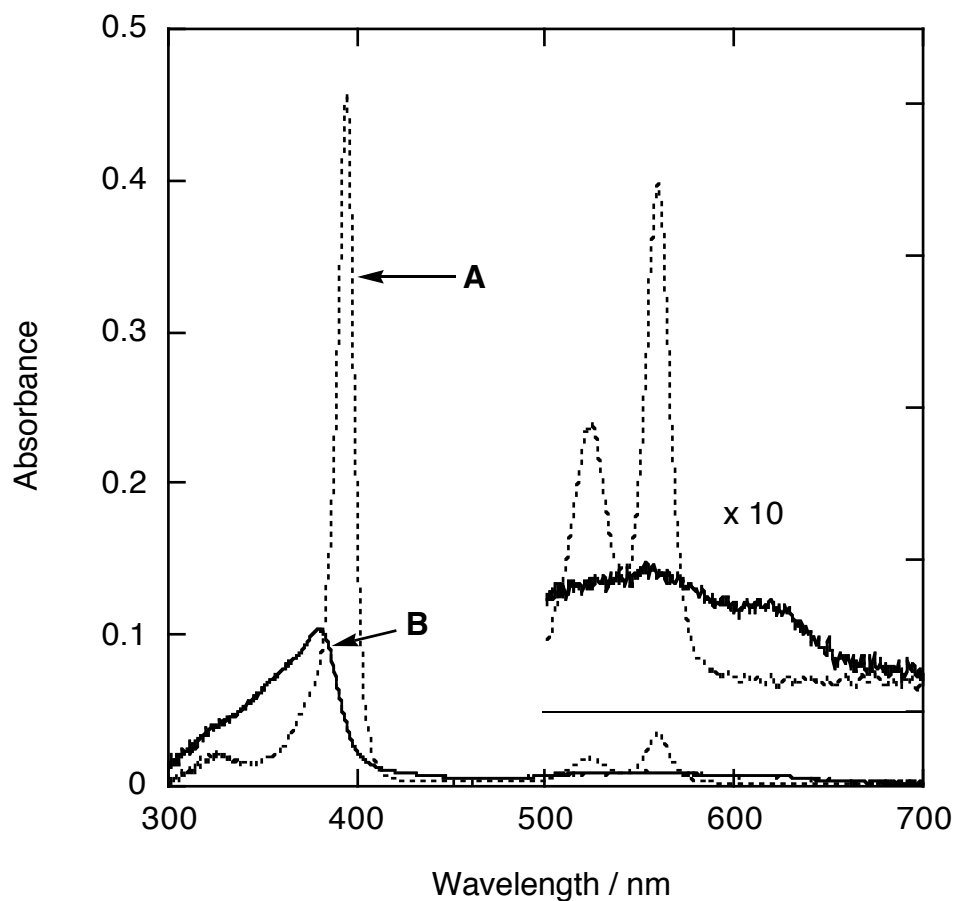
# Supplementary Information

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

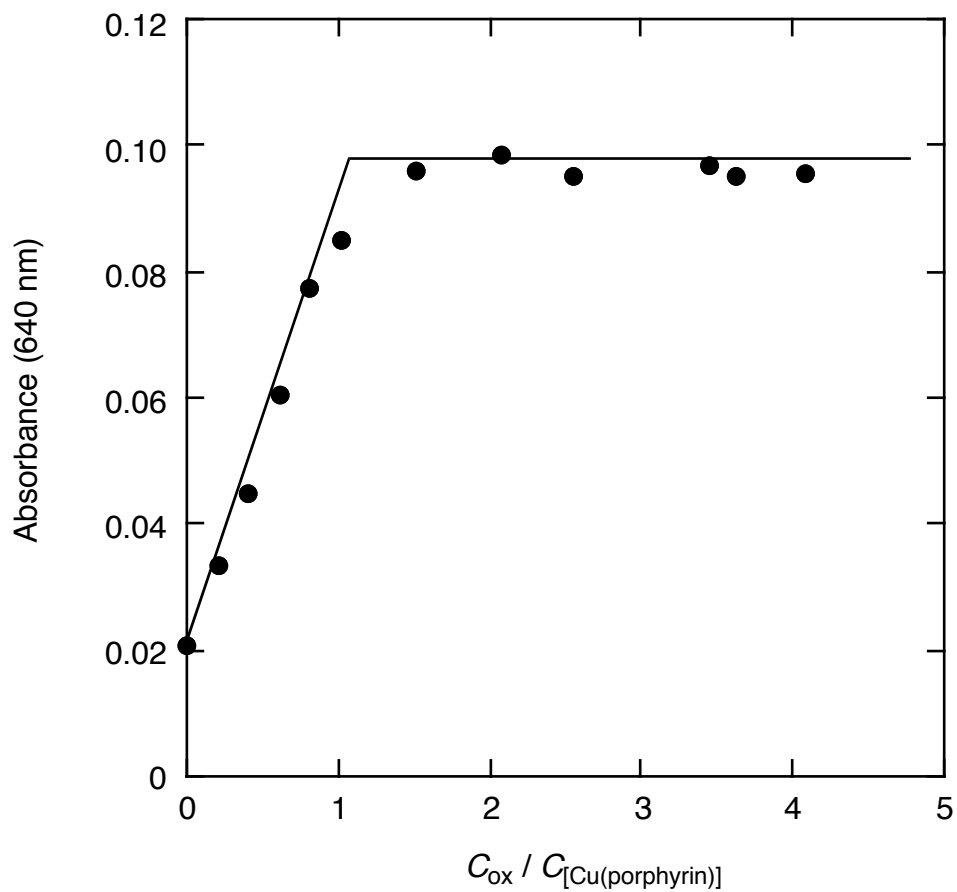
Masahiko Inamo,\* Hideto Kumagai, Ushio Harada, Sumitaka Itoh,  
Satoshi Iwatsuki, Koji Ishihara, and Hideo D. Takagi

*Contribution from the Department of Chemistry, Aichi University of Education, Kariya  
448-8542, Japan, Department of Chemistry, Graduate School of Science, Nagoya  
University, Nagoya 464-8602, Japan, and Department of Chemistry, Waseda University,  
Tokyo 169-8555, Japan.*

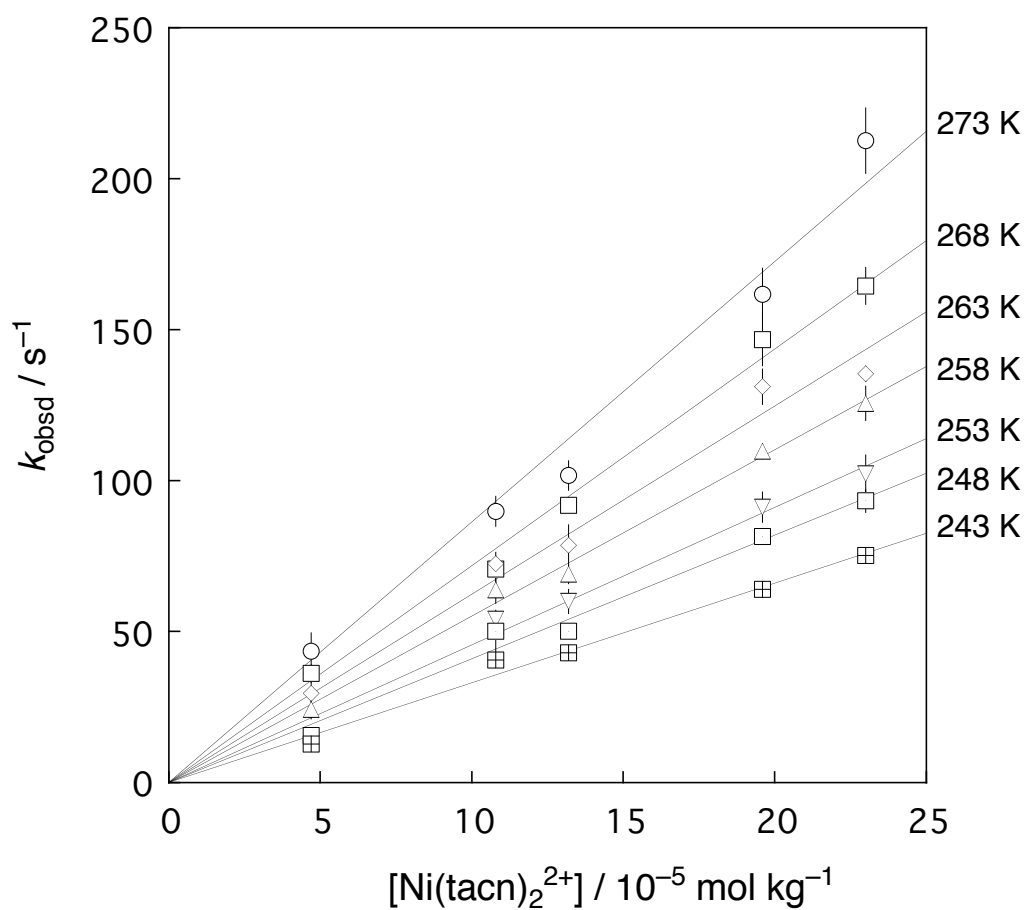
\* To whom correspondence should be addressed. E-mail: minamo@aecc.aichi-edu.ac.jp



**Figure S1.** UV-visible absorption spectra of [Cu(OEP)] (**A**) and the product of the reaction with Cu(II) triflate (**B**) in acetonitrile at  $T = 25.0^{\circ}\text{C}$ .  $C_{\text{Cu-OEP}} = 1.26 \times 10^{-6} \text{ M}$ . The absorbance caused by the excess amount of the Cu(II) ion was subtracted from the original spectrum for the latter case.



**Figure S2.** Dependence of the absorbance on the ratio of the total concentrations of Cu(II) ion ( $C_{\text{ox}}$ ) and [Cu(OEP)] ( $C_{[\text{Cu}(\text{porphyrin})]}$ ) for the reaction of [Cu(OEP)] and Cu(II) triflate at  $T = 25.0$  °C. Total concentration of the porphyrin complex is  $3.23 \times 10^{-5}$  M. The mixture of acetonitrile and dichloromethane (1:1 v/v) was used as a solvent instead of pure acetonitrile for the sake of higher solubility of the porphyrin complex.



**Figure S3.** Dependence of the pseudo-first-order rate constant  $k_{\text{obsd}}$  of the reaction of  $[\text{Fe}(\text{phen})_3]^{3+}$  with  $[\text{Ni}(\text{tacn})_2]^{2+}$  on the concentration of the Ni(II) complex in acetonitrile. The concentration of the Fe(III) complex is  $(4.43 \sim 15.8) \times 10^{-6} \text{ mol kg}^{-1}$ .  $I = 0.1 \text{ mol kg}^{-1}$  (TBAP).

**Table S1.** Second-order rate constant  $k_{12}$  for the oxidation reaction of  $[\text{Ni}(\text{tacn})_2]^{2+}$  by  $[\text{Fe}(\text{phen})_3]^{3+}$  in acetonitrile solution.<sup>a</sup>

$T / \text{K}^b$	$k_{12} / 10^5 \text{ mol}^{-1} \text{ kg s}^{-1}$
243	$3.30 \pm 0.04$
248	$4.09 \pm 0.17$
253	$4.58 \pm 0.07$
258	$5.53 \pm 0.06$
263	$6.25 \pm 0.10$
268	$7.13 \pm 0.09$
273	$8.72 \pm 0.15$
298	$16^c$

<sup>a</sup>  $[\text{Fe}(\text{phen})_3]^{3+} = (4.43 \sim 15.8) \times 10^{-6} \text{ mol kg}^{-1}$ ,  $[\text{Ni}(\text{tacn})_2]^{2+} = (4.7 \sim 23.0) \times 10^{-5} \text{ mol kg}^{-1}$ .  $I = 0.1 \text{ mol kg}^{-1}$  (tetra-*n*-butylammonium perchlorate),  $[\text{CF}_3\text{SO}_3\text{H}] = 1 \text{ mmol kg}^{-1}$ . <sup>b</sup> The temperature of all samples was held constant within  $\pm 1 \text{ K}$ . <sup>c</sup> Rate constant at  $T = 298 \text{ K}$  was calculated using the kinetic parameters ( $\Delta H^\ddagger = 15.0 \pm 0.8 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -75.9 \pm 2.8 \text{ J mol}^{-1} \text{ K}^{-1}$ ) determined from the rate constants in the temperature range from 243 K to 273 K. The value of  $k_{12}(298 \text{ K})$  in the molarity unit is  $2.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ .

**Table S2.** Electron Transfer Properties of the Complexes Used in the Present Study: Equilibrium Constant of the Electron Transfer Reaction ( $K$ ), Radii of the Complexes ( $a_1$ ,  $a_2$ ), So-called Work Terms in the Marcus Theory ( $w_{11}$ ,  $w_{22}$ ,  $w_{12}$ ,  $w_{21}$ , and  $W_{12}$ ), Rate Constant for the Self-Exchange Reaction ( $k_{11}$  or  $k_{22}$ ), and the Factor  $f$ .

Oxidant	[Fe( <i>o</i> -phen) <sub>3</sub> ] <sup>3+</sup>	Cu <sup>2+</sup>	Cu <sup>2+</sup>	Cu <sup>2+</sup>	Cu <sup>2+</sup>
Reductant	[Ni(tacn) <sub>2</sub> ] <sup>2+</sup>	[Ni(tacn) <sub>2</sub> ] <sup>2+</sup>	[Ru(hfac) <sub>3</sub> ] <sup>-</sup>	[Cu(TPP)]	[Cu(OEP)]
$K$	9.9 x 10	4.9 x 10	9.7 x 10 <sup>4</sup>	33	1600
$a_1$ / pm	680	340	340	340	340
$a_2$ / pm	380	380	500	1800	1500
$w_{11}$ / kJ mol <sup>-1</sup>	5.5	5.5	5.5	5.5	5.5
$w_{22}$ / kJ mol <sup>-1</sup>	13.9	13.9	0	0	0
$w_{12}$ / kJ mol <sup>-1</sup>	8.2	10.1	-4.0	0	0
$w_{21}$ / kJ mol <sup>-1</sup>	8.2	7.5	0	0.4	0.5
$W_{12}$	1.80	1.43	6.72	2.78	2.71
$k_{12}$ / M <sup>-1</sup> s <sup>-1</sup>	2.0 x 10 <sup>6</sup>	3.50	1.60 x 10 <sup>4</sup>	5.80 x 10 <sup>3</sup>	1.98 x 10 <sup>5</sup>
$k_{11}$ / M <sup>-1</sup> s <sup>-1</sup>	1.4 x 10 <sup>7</sup>	1.2 x 10 <sup>-4</sup> <sup>a</sup>	1.5 x 10 <sup>-5</sup> <sup>a</sup>	4.2 x 10 <sup>-5</sup> <sup>b</sup>	4.2 x 10 <sup>-5</sup> <sup>b</sup>
$k_{22}$ / M <sup>-1</sup> s <sup>-1</sup>	1.2 x 10 <sup>3</sup> <sup>a</sup>	1.2 x 10 <sup>3</sup>	7.0 x 10 <sup>6</sup>	3.4 x 10 <sup>9</sup> <sup>a</sup>	1.2 x 10 <sup>11</sup> <sup>a</sup>
$f$	0.7613	0.8744	0.5727	0.9268	0.6774

<sup>a</sup> Value determined from eq 7. <sup>b</sup> The averaged value of 1.2 x 10<sup>-4</sup> M<sup>-1</sup> s<sup>-1</sup> and 1.5 x 10<sup>-5</sup> M<sup>-1</sup> s<sup>-1</sup>.