Supporting Information of

Small Reorganization Energy for Ligand-Centered Electron-Transfer Reduction of Compound I to Compound II in Heme Model Study

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Experimental Section.

**Instrumentation.** UV-visible absorption spectra were recorded on an Agilent 8453 spectrometer (Agilent Technologies) equipped with a USP-203 low-temperature chamber (UNISOKU). $^1$H NMR spectra were measured on a Lambda-400 spectrometer (JEOL). Chemical shifts were referenced to the residual peak of dichloromethane (5.32 ppm). The concentrations of NMR samples were about 1 mM. The kinetic analyses were performed on a stopped-flow rapid mixing system USP-R100 (UNISOKU) with a low-temperature double mixer USP-SFM-CRD10 (UNISOKU). The cyclic voltammograms and differential pulse voltammograms were measured with an ALS612A electrochemical analyzer (BAS) in degassed dichloromethane containing 0.1M tetra-n-butylammonium perchlorate (TBAP) as a supporting electrolyte. A platinum electrode was used as the working electrode and a platinum-wire electrode was employed as the counter-electrode. The potentials were recorded with respect to a saturated calomel electrode (SCE) as the reference electrode.

**Materials.** Anhydrous dichloromethane was obtained commercially and stored in the presence of 4 Å molecular sieves. 4-Bromo-4',4''-dimethoxytriphenylamine, tris-p-tolylamine, 4-methyltriphenylamine, triphenylamine, tris-4-bromophenylamine were purchased from TCI (Tokyo). 4-methoxytriphenylamine and 4-bromo-4’,4”-dimethyltriphenylamine was purchased from Aldrich. 4,4’-dibromo-4”-methoxytriphenylamine was prepared by the published method.¹ Other chemicals were purchased commercially and used without further purification. 5,10,15,20-tetramesitylporphyrin (1) was prepared from pyrrole and 2,4,6-trimethylbenzaldehyde according to a previously published procedure.² 2,7,12,17-Tetramesityl-3,8,13,18-tetramethylporphyrin (2) was synthesized by published method.³ Ferric chloride complexes of 1 and 2 were prepared by insertion of iron into porphyrins with FeCl₂ and sodium acetate in acetic acid, and purified with a
silica gel column using CH$_2$Cl$_2$/CH$_3$OH as an eluent.$^4$ Ferric nitrate complexes of 1 and 2 were prepared by the reaction of iron(III) porphyrin chloride complexes with silver(I) nitrate in tetrahydrofuran, and purified by re-crystallization from dichloromethane/$n$-hexane.$^5$

**Computational Details.** All of density functional theory (DFT) calculations were carried out using the Gaussian 09 package with B3LYP functional method employing the unrestricted formalism, denoted as UB3LYP.$^6$ Geometry optimizations were carried out using the Stuttgart-Dresden relativistic effective core potential (SDD)$^7$ associated with its adapted basis set on iron atom and the 6-31G** basis set$^8$ on the rest of atoms (including C, H, O and N) without any symmetry restrictions. Frequency analysis was performed at the same level as the geometry optimization to verify the nature of the minima. Single-point calculations on the optimized structures were done with 6-311G** basis set. Reorganization energy ($\lambda$) of the external sphere electron transfer process was calculated using the following equation:

$$\lambda = \lambda_{\text{int}} + \lambda_{\text{ext}}$$

Therein, $\lambda_{\text{int}}$ is the bond-reorganization energy (i.e., internal reorganization energy), which was calculated in the gas-phase; while $\lambda_{\text{ext}}$ is the solvent-reorganization energy (i.e., external reorganization energy), which was evaluated using Polarizable Continuum Model (PCM) with UFF cavity, per Gaussian 09 default (dichloromethane which was used by the experiment was chosen). Both components were calculated separately using the strategy shown in Scheme S1. In addition, the structural change before and after the ET reaction was evaluated by root-mean square deviation (RMSD) of reactant and product using VMD software.$^9$
**Scheme S1.** A Schematic Diagram about the Calculation for the Bond-/Solvent-Reorganization Energies of the One-Electron Self-Exchange Reaction

\[ \lambda^{(i)} = E_3 - E_1 \]
\[ \lambda^{(ii)} = E_2 - E_4 \]
\[ \lambda_{\text{int/ext}} = \lambda^{(i)} + \lambda^{(ii)} \]

References


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Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D.
J. Gaussian, Inc.: Wallingford CT, Gaussian 09, Revision D.01, 2013.


**Figure S1.** Absorption spectra of Cpd II and ferric porphyrin complexes of 1 and 2, and tris-$p$-tolylamine $\pi$-cation radical in dichloromethane. (a) Cpd II (0.1 mM) of 1, (b) Cpd II (0.1 mM) of 2, (c) ferric complex (0.1 mM) of 1, (d) ferric complex (0.1 mM) of 2, (e) tris-$p$-tolylamine $\pi$-cation radical (0.05 mM).
Figure S2. Dependence of the observed first-order rate constant of ET from tris-p-tolylamine to Cpd of 1 on concentration of tris-p-tolylamine in dichloromethane at –20 °C.
Figure S3. Absorption spectral change for ET from tris-\(p\)-tolylamine (250 \(\mu\)M) to Cpd I of 2 (12.5 \(\mu\)M) in dichloromethane at –20 °C. (a) 0 ~ 0.006 s. (b) 0.006 ~ 0.500 s. Green line: immediately after rapid mixing, red line: after 0.006 s, blue line: after 0.500 s. (c) Time course of the absorbance at 567 nm. Red circle: experimental data, black line: simulation line obtained from a least-square curve fit with a double exponential function.
Figure S4. Dependence of the observed first-order rate constant of ET from tris-p-tolylamine to Cpd I of 2 on concentration of tris-p-tolylamine in dichloromethane at –20 °C.
**Figure S5.** Cyclic (left) and differential pulse (right) voltammograms for triphenylamine derivatives (1 ~ 2 mM) in dichloromethane containing 0.10 M tetra-n-butylammonium perchlorate. (a) 4-Bromo-4’,4”-dimethoxytriphenylamine, (b) tris-p-tolylamine, (c) 4-methoxytriphenylamine, (d) 4-bromo-4’,4”-dimethyltriphenylamine, (e) 4,4”- dibromo-4”-methoxytriphenylamine, (f) 4-methyltriphenylamine, (g) tris-4-bromophenylamine, (h) 1,1’-diacetylferrrocene. Scan rate = 100 mV/s
Figure S6. Absorption spectral change for the reaction of Cpt I of 1 (12.5 µM) with 4-methoxytriphenylamine (250 µM) in dichloromethane at −20 °C. (a) 0 ~ 0.228 s. (b) 0.228 ~ 2.000 s. Green line: immediately after rapid mixing, red line: after 0.228 s, blue line: after 2.000 s. (c) Time course of the absorbance at 545 nm. Red circle: experimental data, black line: simulation line obtained from a least-square curve fit with a double exponential function.
Figure S7. Absorption spectral change for the reaction of Cpt I of 2 (12.5 µM) with 4-methoxytriphenylamine (250 µM) in dichloromethane at −20 °C. (a) 0 ~ 0.007 s. (b) 0.007 ~ 1.500 s. Green line: immediately after rapid mixing, red line: after 0.007 s, blue line: after 1.500 s. (c) Time course of the absorbance at 567 nm. Red circle: experimental data, black line: simulation line obtained from a least-square curve fit with a double exponential function.
Figure S8. Dependence of apparent reduction rate constant of Cpts I of 1 and 2 with 4-methoxytriphenylamine in dichloromethane at −20 °C. Red circle: 1, blue circle: 2. The red and blue straight lines are simulation lines, obtained from least-square fitting with a linear function, for 1 and 2, respectively.
Figure S9. Reactions of Cpt I of 1 and 2 with tris-\(p\)-bromophenylamine in dichloromethane at \(-20\) °C. (a) Absorption spectral change for the reaction of Cpt of 1 (12.5 \(\mu\)M) with tris-\(p\)-bromophenylamine (6.24 mM). (b) Time course of the absorbance at 508 nm. Red circle: experimental data, black line: simulation with a single exponential function. (c) Absorption spectral change for the reaction of Cpt of 2 (12.5 \(\mu\)M) with tris-\(p\)-bromophenylamine (2.51 mM). (b) Time course of the absorbance at 725 nm. Red circle: experimental data, black line: simulation with a single exponential function.
Figure S10. Reaction of Cpt I of 1 with tris-phenylamine in dichloromethane at −20 °C. (a) Absorption spectral change for the reaction of Cpt of 1 (12.5 µM) with tris-phenylamine (0.63 mM). (b) Time course of the absorbance at 667 nm. Red circle: experimental data, black line: simulation with a single exponential function.
Figure S11. Reactions of Cpt I of 1 and 2 with 1,1'-diacetylferrrocene in dichloromethane at –20 °C. (a) Absorption spectral change for the reaction of Cpt of 1 (12.5 µM) with 1,1'-diacetylferrrocene (186 µM). (b) Time course of the absorbance at 667 nm. Red circle: experimental data, black line: simulation with a single exponential function. (c) Absorption spectral change for the reaction of Cpt of 2 (12.5 µM) with 1,1'-diacetylferrrocene (194 µM). (d) Time course of the absorbance at 567 nm. Red circle: experimental data, black line: simulation with a single exponential function.
Table S1. The Bond-Reorganization ($\lambda_{\text{int}}$, in eV), Solvent-Reorganization ($\lambda_{\text{ext}}$, in eV) and Reorganization Energies ($\lambda$, in eV) of the One-Electron Reduction of Cpd I for Two Ligand Systems

<table>
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<tr>
<th>Reaction</th>
<th>$\lambda_{\text{int}}$, eV</th>
<th>$\lambda_{\text{ext}}$, eV</th>
<th>$\lambda$, eV</th>
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<tr>
<td>$[(\text{TMP}^•+)\text{Fe}^{IV}(O)]^+ \xrightarrow{\delta} [(\text{TMP})\text{Fe}^{IV}(O)]$</td>
<td>0.083</td>
<td>0.131</td>
<td>0.440</td>
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<tr>
<td>$[(\text{TMTMP}^•+)\text{Fe}^{IV}(O)]^+ \xrightarrow{\delta} [(\text{TMTMP})\text{Fe}^{IV}(O)]$</td>
<td>0.053</td>
<td>0.060</td>
<td>0.444</td>
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Table S2. The Optimized Geometric Parameters of Both Cpd I and Cpd II, and the Root-Mean Square Deviation (RMSD) between Them for Two Ligand Systems

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<th>D_{(Fe-O)}</th>
<th>D_{(Fe-N1)}</th>
<th>D_{(Fe-N2)}</th>
<th>D_{(Fe-N3)}</th>
<th>D_{(Fe-N4)}</th>
<th>\theta_{(Fe-N1-N2-N3)}</th>
<th>RMSD</th>
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<tr>
<td>[(TMP^{•+})Fe^{IV}(O)]^+</td>
<td>1.600</td>
<td>2.013</td>
<td>2.013</td>
<td>2.012</td>
<td>2.012</td>
<td>11.369</td>
<td>0.262</td>
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<tr>
<td>[(TMP)Fe^{IV}(O)]</td>
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<td>2.013</td>
<td>2.013</td>
<td>2.013</td>
<td>2.013</td>
<td>12.063</td>
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<tr>
<td>[(TMTMP^{•+})Fe^{IV}(O)]^-</td>
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<td>2.007</td>
<td>2.006</td>
<td>2.006</td>
<td>2.007</td>
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<tr>
<td>[(TMTMP)Fe^{IV}(O)]</td>
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<td>2.017</td>
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<td>2.016</td>
<td>2.017</td>
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