Electronic supplementary information (ESI)

Synthesis of methylviologen-pendent iron porphyrins as functional model of reduction enzyme and its application to six-electron reduction of nitrobenzene to aniline

Hiroaki Koga, Taisuke Hamada, and Shigeyoshi Sakaki*

Supporting Information

Figure S1. Time-courses of reduction of nitrobenzene catalyzed by $m$-MV-FeCl(TPP) 1, $p$-MV-FeCl(TPP) 2, FeCl(TPP) with MV$^{2+}$ 3, and FeCl(TPP) 4 in diglyme/MeOH, at 25°C. [Iron pophrpyrin] = [MV$^{2+}$] = 3.75×10$^{-2}$ mmol dm$^{-3}$. Iron porphyrin/nitrobenzene/NaBH$_4$ = 1/400/400 in mole ratio.
Figure S2. Time-courses of reduction of \( p \)-nitroanisole catalyzed by \( m \)-MV-FeCl(TPP) 1, \( p \)-MV-FeCl(TPP) 2, and FeCl(TPP) 3 in diglyme/MeOH, at 25\(^\circ\)C. [Iron porphyrin] = 3.75x10\(^{-2}\) mmol dm\(^{-3}\). Iron porphyrin/\( p \)-nitroanisole/NaBH\(_4\) = 1/400/400 in mole ratio.
Figure S3. UV-VIS spectral changes of FeCl(TPP) by addition of aniline in the presence of NaBH₄.

In diglyme/MeOH (1/1 v/v) at 25°C.  [FeCl(TPP)] = 3.75×10⁻² mmol dm⁻³.  FeCl(TPP)/NaBH₄/aniline = 1/400/400 in mole ratio.  Broken line represents the spectra of p-MV-FeCl(TPP) in the presence of NaBH₄.  Solid lines represent spectra of p-MV-FeCl(TPP) in the addition of aniline.
Figure S4. Cyclic voltammograms of methylviologen (a), FeCl(TPP) (b), p-MV-FeCl(TPP) (c), and m-MV-FeCl(TPP) (d) in diglyme/MeOH. Supporting electrolyte is n-Bu₄NPF₆ (0.1 mol dm⁻³). Scan rate is 50mV s⁻¹.
Figure S5. Cyclic voltammogram of nitrobenzene in diglyme/MeOH. Open-circle represents first scan and closed-circle represents continuous scan. Supporting electrolyte is \( n\text{-Bu}_4\text{NPF}_6 \) (0.1 mol dm\(^{-3}\)). Scan rate is 50mV s\(^{-1}\).

Figure S6. Cyclic voltammogram of phenylhydroxylamine in diglyme/MeOH. Supporting electrolyte is \( n\text{-Bu}_4\text{NPF}_6 \) (0.1 mol dm\(^{-3}\)). Scan rate is 50mV s\(^{-1}\).
**Figure S7.** Cyclic voltammograms of mixtures of FeCl(TPP) with phenylhydroxylamine in diglyme/MeOH. Supporting electrolyte is \( n\)-BuNPF\(_6\) (0.1 mol dm\(^{-3}\)). Scan rate is 50mV s\(^{-1}\).

**Figure S8.** EPR spectra of \( p\)-MV-FeCl(TPP) with NaBH\(_4\) in THF/MeOH at 77K. Inset is \( p\)-MV-FeCl(TPP) with NaBH\(_4\) in diglyme/methanol.
Table S1. Reduction of $p$-nitroanisole catalyzed by FeCl(TPP) and $p$-MV-FeCl(TPP) with NaBH$_4$ in the presence of dioxygen molecule.

<table>
<thead>
<tr>
<th>Oxygen</th>
<th>FeCl(TPP)</th>
<th>$p$-MV-FeCl(TPP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conversion (%) $^b$</td>
<td>Yield (%) $^b$</td>
</tr>
<tr>
<td>10 eq.</td>
<td>54</td>
<td>50</td>
</tr>
<tr>
<td>50 eq.</td>
<td>56</td>
<td>45</td>
</tr>
<tr>
<td>100 eq.</td>
<td>24</td>
<td>10</td>
</tr>
</tbody>
</table>

$^a$[Iron porphyrin] = 3.75x10$^{-2}$ mmol dm$^{-3}$, [cat.]/NaBH$_4$/substrate = 1/1200/ 400, 3h at 15$^\circ$C. $^b$Based on $p$-nitroanisole.