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

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Supporting Information

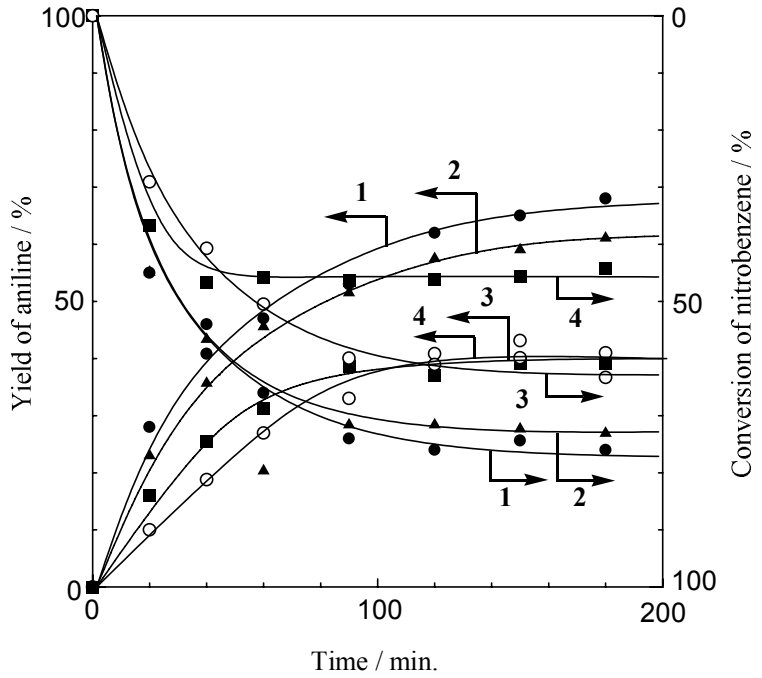

Figure S1. Time-courses of reduction of nitrobenzene catalyzed by *m*-MV-FeCl(TPP) **1**, *p*-MV-FeCl(TPP) **2**, FeCl(TPP) with MV^{2+} **3**, and FeCl(TPP) **4** in diglyme/MeOH, at 25°C. [Iron poprhyrin] = $[MV^{2+}]$ = 3.75×10^{-2} mmol dm^{-3}. Iron porphyrin/nitrobenzene/$NaBH_4$ = 1/400/400 in mole ratio.

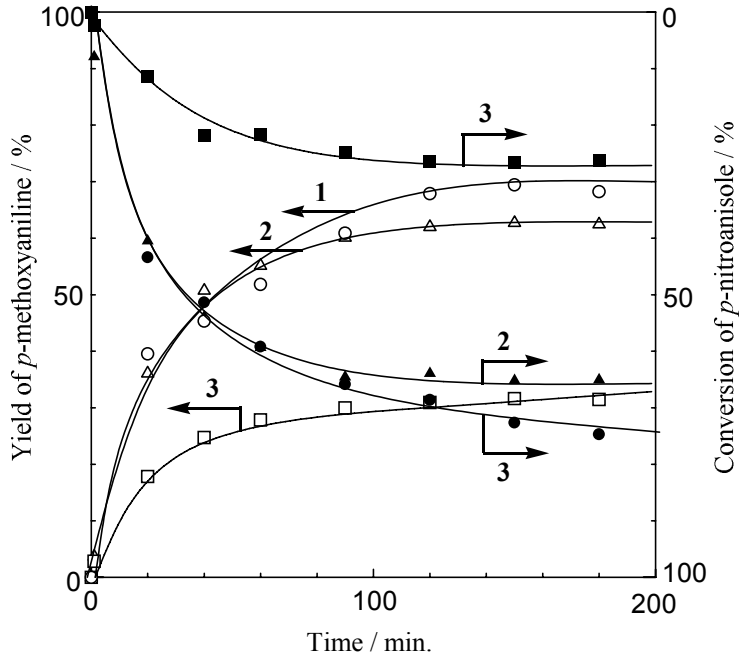

Figure S2. Time-courses of reduction of *p*-nitroanisole catalyzed by *m*-MV-FeCl(TPP) **1**, *p*-MV-FeCl(TPP) **2**, and FeCl(TPP) **3** in diglyme/MeOH, at 25°C. [Iron poprhyrin] = 3.75×10^{-2} mmol dm^{-3}. Iron porphyrin/*p*-nitroanisole/$NaBH_4$ = 1/400/400 in mole ratio.

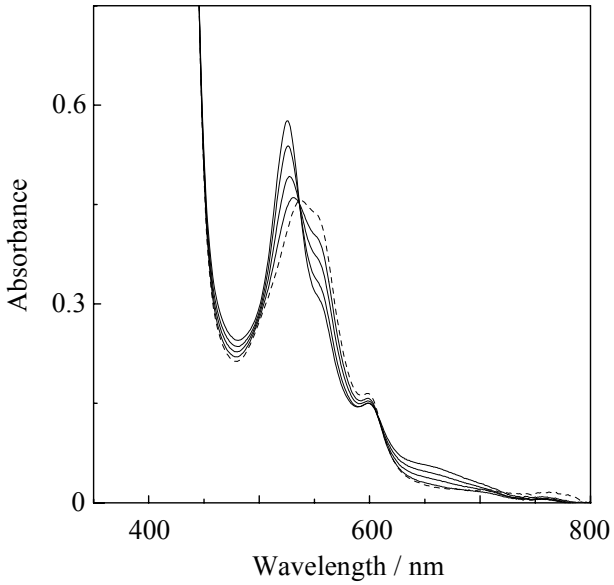

Figure S3. UV-VIS spectral changes of FeCl(TPP) by addition of aniline in the presence of $NaBH_4$.

In diglyme/MeOH (1/1 v/v) at 25°C. [FeCl(TPP)] = 3.75×10^{-2} mmol dm^{-3}. FeCl(TPP)/$NaBH_4$/aniline = 1/400/400 in mole ratio. Broken line represents the spectra of *p*-MV-FeCl(TPP) in the presence of $NaBH_4$. Solid lines represent spectra of *p*-MV-FeCl(TPP) in the addition of aniline.

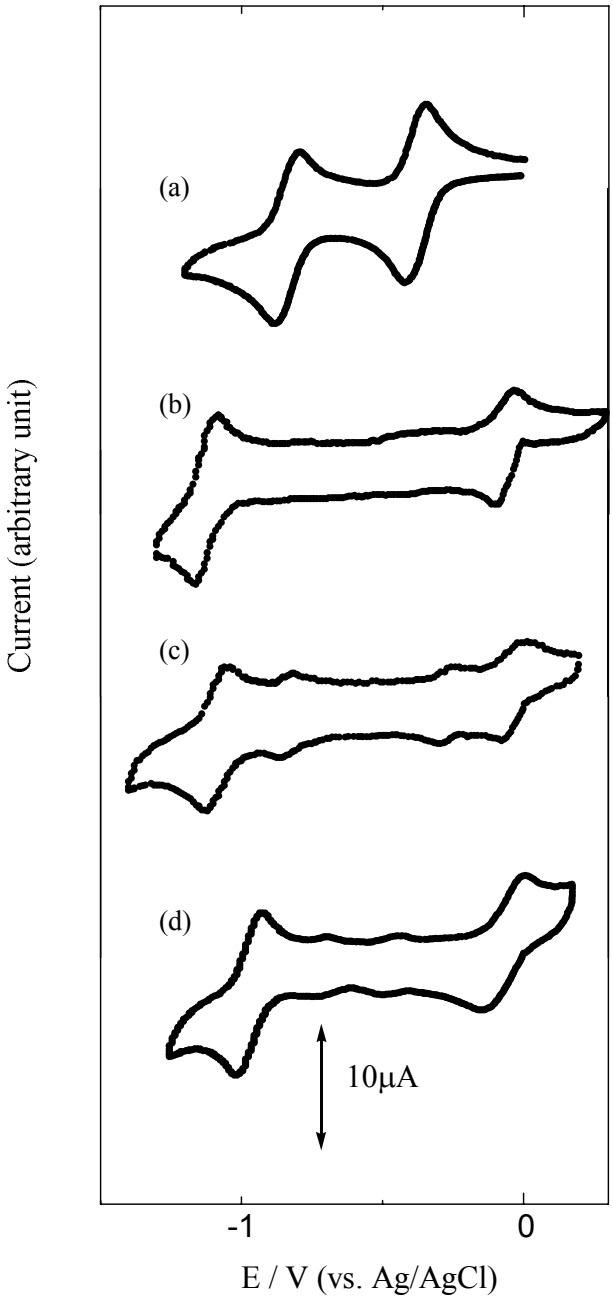

Figure S4. Cyclic voltammograms of methylviologen (a), FeCl(TPP) (b), *p*-MV-FeCl(TPP) (c), and *m*-MV-FeCl(TPP) (d) in diglyme/MeOH. Supporting electrolyte is *n*-Bu_4NPF_6 (0.1 mol dm^{-3}). Scan rate is 50mV s^{-1}.

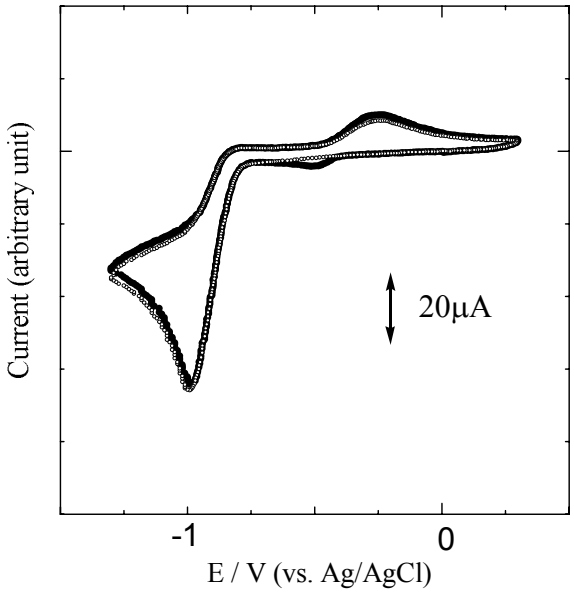

Figure S5. Cyclic voltammogram of nitrobenzene in diglyme/MeOH. Open-circle represents first scan and closed-circle represents continuous scan. Supporting electrolyte is *n*-Bu_4NPF_6 (0.1 mol dm^{-3}). Scan rate is 50mV s^{-1}.

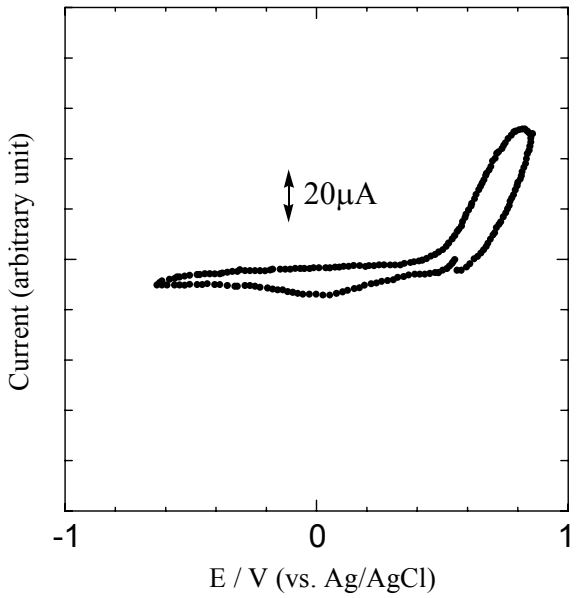

Figure S6. Cyclic voltammogram of phenylhydroxylamine in diglyme/MeOH. Supporting electrolyte is *n*-Bu_4NPF_6 (0.1 mol dm^{-3}). Scan rate is 50mV s^{-1}.

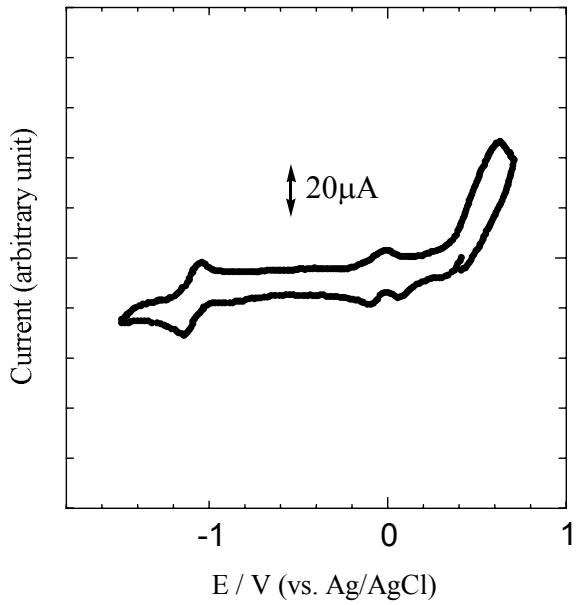

Figure S7. Cyclic voltammograms of mixtures of FeCl(TPP) with phenylhydroxylamine in diglyme/MeOH. Supporting electrolyte is *n*-$BuNPF_6$ (0.1 mol dm^{-3}). Scan rate is 50mV s^{-1}.

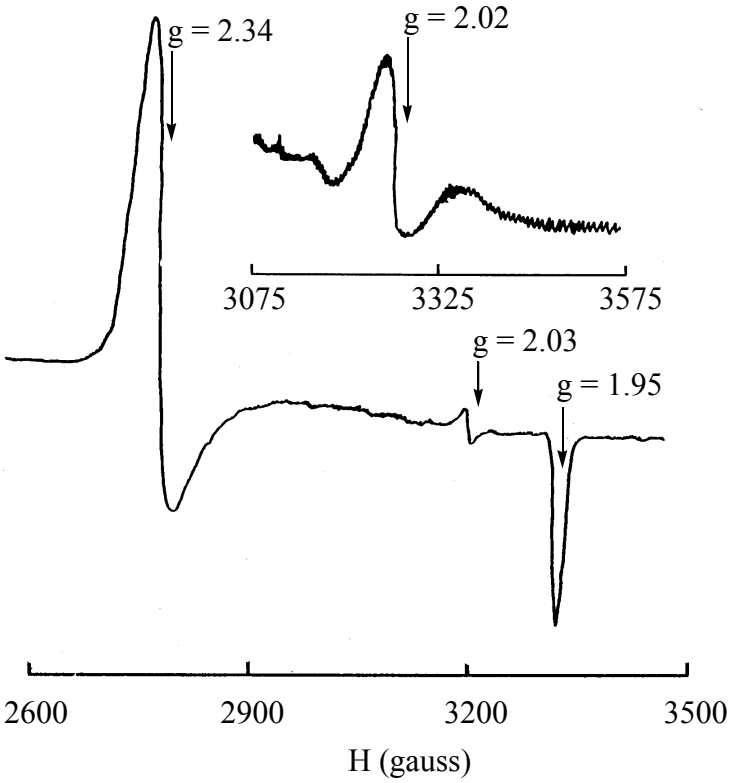

Figure S8. EPR spectra of *p*-MV-FeCl(TPP) with $NaBH_4$ in THF/MeOH at 77K. Inset is *p*-MV-FeCl(TPP) with $NaBH_4$ in diglyme/methanol.

Table S1. Reduction of *p*-nitroanisole catalyzed by FeCl(TPP) and *p*-MV-FeCl(TPP) with $NaBH_4$ in the presence of dioxygen molecule.

	FeCl(TPP)		[*p*-MV-FeCl(TPP)]	
Oxygen	Conversion (%)[b]	Yield (%)[b]	Conversion (%)[b]	Yield (%)[b]
10 eq.	54	50	97	94
50 eq.	56	45	76	58
100 eq.	24	10	56	45

[a][Iron porphyrin] = 3.75×10^{-2} mmol dm^{-3}, [cat.]/$NaBH_4$/substrate = 1/1200/ 400, 3h at 15°C. [b]Based on *p*-nitroanisole.