Electronic supplementary information

Electron transfer and binding affinities in an
electrochemically controlled ligand transfer system
containing zinc porphyrin and a meso-phenylenediamine
substituent

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Supporting information
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Electrochemical and spectral results

Fig S1 Cyclic voltammograms of 1.0×10^{-3} M ZnTMP-Ph2-PD in CH2Cl2 containing 0.1 M TBAP in the presence of (A) 0.0–1.0 equiv. and (B) 1.0–2.0 equiv. of HIm. Working electrode: glassy carbon. Scan rate: 0.1 Vs^{-1}. 
Fig S2 Spectral changes of $2.0 \times 10^{-4}$ M PD in CH$_2$Cl$_2$ containing 0.1 M TBAP at various applied potentials (0.00V~1.26V).
Fig S3 Spectral changes of 2.0×10^{-4} M ZnTMP in CH2Cl2 containing 0.1 M TBAP at various applied potentials (0.00V–1.21V).
Fig S4 The absorption spectra of $4.0 \times 10^{-5}$ M ZnTMP-Ph-PD in presence of 0.75 equiv. in $\text{CH}_2\text{Cl}_2$ containing 0.1 M TBAP.
Fig S5 The absorption spectra of 4.0×10^{-5} M ZnTMP-PD in presence of 0.75 equiv. in CH₂Cl₂ containing 0.1 M TBAP.
Fig S6 Spectral changes of 4.0×10^{-5} M ZnTMP-Ph2-PD in CH2Cl2 containing 0.1 M TBAP at $E_{\text{appl.}} = +0.00V \sim +0.83V$
Fig S7 Spectral changes of $4.0 \times 10^{-5}$ M ZnTMP-Ph$_2$-PD in presence of 0.75 equiv. in CH$_2$Cl$_2$ containing 0.1 M TBAP at $E_{\text{appl.}} = +0.00\text{V} \sim +0.83\text{V}$
Fig. S8 Absorption spectral change of ZnTMP-Ph-PD in the presence of various concentrations of imidazole.

Fig. S9 Absorption spectral change of ZnTMP-Ph\textsubscript{2}-PD in the presence of various concentrations of imidazole.
Fig S10 EPR spectra of N2** and PD** at 298K.
Spectral titration methods

According to the following equation, the binding constants would be estimated by photometric titration.\textsuperscript{19}

\[
\text{ZnP} + qL \rightleftharpoons \text{ZnP}(L)q \\
K_f = \frac{[\text{ZnP}(L)q]}{[\text{ZnP}][L]^q}
\]

\[
\log \left[ \frac{(A_x - A_i)}{(A_\infty - A_x)} \right] = q \log[L] + \log K_f
\] \hspace{1cm} (1)

where \([L]\) is concentration of the free-ligand, \(A_x\) is absorbance of zinc porphyrin at various imidazole concentration, \(A_i\) is absorption band in absence of imidazole, \(A_\infty\) is the absorption band in the presence of saturated imidazole, \(q\) is the number of binding ligands, and \(K_f\) is a binding constant.

As for the binding constants between HIm and oxidized zinc porphyrins were calculated from the potential shift of CVs as described in the following method.\textsuperscript{20}

\[
\text{ZnP} \quad \text{--} \text{ne}^- \quad \text{ZnP}^{z+} \quad + \quad pL \rightleftharpoons \text{ZnP}^{z+}(L)p \quad K_{f^+} = \frac{[\text{ZnP}^{z+}(L)p]}{[\text{ZnP}][L]^p}
\]

\[
(E_{1/2})_u = (E_{1/2})_c - (0.059/n) \left[ \log \left( \frac{K_f}{K_{f^+}} \right) - \log [L]^{n-q} \right]
\] \hspace{1cm} (2)

where \((E_{1/2})_u\) and \((E_{1/2})_c\) are the half potential of uncomplexed and complexed species, \([L]\) is the ligand concentration, \(p\) and \(q\) are the number of ligation for the neutral and cation radical species, \(K_f\) and \(K_{f^+}\) are the binding constant of \(\text{ZnP}(L)q\) and \(\text{ZnP}^{z+}(L)p\), and \(n\) is the number of electron transfer in the electrochemical reaction.
Figure S11. $^1$H NMR spectra for 4′-bromo-4-triphenylbenzaldehyde.
Figure S12. $^{13}$C NMR spectra for 4′-bromo-4-triphenylbenzaldehyde.
Figure S13. $^1$H NMR spectra for Zn(Ph$_2$-Br)(mesityl)$_3$P.
Figure S14. $\mathrm{C^{13}}$ NMR spectra for $\text{Zn(Ph}_2\text{-Br)(mesityl)}_3\text{P}$.
Figure S15. $^1H$ NMR spectra for Zn(Ph$_3$-Br)(mesityl)$_3$P.
Figure S16. C^{13} NMR spectra for Zn(Ph_{3-Br})(mesityl)_{3}P.
Figure S17. $^1$H NMR spectra for ZnTMP-Ph-PD.
Figure S18. $^{13}$C NMR spectra for ZnTMP-Ph-PD.
Figure S19. $^1$H NMR spectra for ZnTMP-Ph$_2$-PD.
Figure S20. C$^{13}$ NMR spectra for ZnTMP-Ph$_2$-PD.