Electronic Supplementary Information

Proton-Coupled Electron Transfer Kinetics for the Hydrogen Evolution Reaction of Hangman Porphyrins

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Experimental Section

Materials

Catalysts **1** (Co-HPXCOOH), **2** (Co-HPXBr), and **3** ($Co(C_6F_5)_4$) were prepared following published procedures.[1–3] Benzoic acid (≥99.5%) and tetrabutylammonium hexafluorophosphate ($TBAPF_6$, ≥99.0%) were purchased from Aldrich and used as received.

Electrochemical studies

Electrochemical measurements were performed on a CH Instruments (Austin, Texas) 760D Electrochemical Workstation using CHI Version 10.03 software. Cyclic voltammetry (CV) experiments were conducted in a nitrogen-filled glovebox at 295 K using a CH Instruments glassy carbon button working electrode (area = 0.071 cm^2), BASi $Ag/AgNO_3$ reference electrode, and Pt mesh counter electrode in 0.2 M $TBAPF_6$ acetonitrile solutions 2 or 4 mL total volume. Acetonitrile was previously dried by passage through an alumina column under argon. All CVs were recorded with compensation for solution resistance, and were referenced to the ferrocene/ferrocenium (Fc/Fc^+) couple by recording the CVs of the complexes in the presence of a small amount of ferrocene. Appropriate background scans were subtracted from all CVs. Solutions were stirred between acquisition of individual CVs and the working electrode was polished before each measurement.

The concentration dependence of the $Co^{+/0}$ peak potential of **1** (Fig. S3) was determined by preparing a 1 mM solution of **1** in 0.2 M $TBAPF_6$ and successively diluting this solution with electrolyte to afford solutions of 0.75, 0.5, and 0.25 mM **1**. A CV of each solution was recorded at 0.03, 0.3, and 3 V s^{-1} (Fig. S3).

In the case of the titration experiment shown in Fig. 3a, to a 2 mL of 0.1 mM **3** solution in 0.2 M $TBAPF_6$ was added, 2, 10, and 12 μL of a 50 mM benzoic acid solution in 0.2 M $TBAPF_6$ to afford solutions comprising 0.05, 0.3, and 0.6 mM benzoic acid. The change in the total volume of the sample, and thus, in the concentration of **3**, was negligible.

In the case of the titration experiments shown in Fig. 3c, for the CVs that correspond to 0.1 mM **3** (black and red lines), to a 2 mL of 0.1 mM **3** solution in 0.2 M $TBAPF_6$, 2 μL of a 50 mM benzoic acid solution in 0.2 M $TBAPF_6$ was added to afford a solution comprising 0.05 mM benzoic acid. The change in the total volume of the sample, and thus, in the **3** concentration, was negligible. The CV of the solution was recorded at the beginning for the acid free sample (black line in Fig. 3c) to get the i_0 value, and after the benzoic acid addition (red line in Fig. 3c) to get the i_{cat} value.

For the CVs that correspond to 0.3 mM **3** (blue and green lines in Fig. 3c), to a 2 mL of 0.3 mM **3** solution in 0.2 M $TBAPF_6$, 2 μL of a 150 mM benzoic acid solution in 0.2 M $TBAPF_6$ was added to afford a solution comprising 0.15 mM benzoic acid. The change in the total

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[1] C. H. Lee, D. K. Dogutan and D. G. Nocera, *J. Am. Chem. Soc.*, 2011, **133**, 8775–8777.

[2] D. K. Dogutan, D. K. Bediako, T. S. Teets, M. Schwalbe and D. G. Nocera, *Org. Lett.*, 2010, **12**, 1036–1039.

[3] R. McGuire Jr., D. K. Dogutan, T. S. Teets, J. Suntivich, Y. Shao-Horn and D. G. Nocera, *Chem. Sci.*, 2010, **1**, 411–414.

volume of the sample, and thus, in the concentration of **3**, was negligible. The CV of the solution was recorded at the beginning for the acid free sample (blue line in Fig. 3c) to get the i_0 value, and after the benzoic acid addition (green line in Fig. 3c) to get the i_{cat} value.

For the CVs that correspond to 1 mM **3** (magenta and brown lines in Fig. 3c), stock solutions of 2 mM **3** in 0.2 M $TBAPF_6$ and 100 mM benzoic acid in 0.2 M $TBAPF_6$ were initially prepared. 2 mL of the 2 mM **3** solution were diluted with electrolyte until final volume 4 mL to give a 1 mM **3** sample. The CV of this acid free solution was recorded (magenta line in Fig. 3c) to obtain the i_0 value. Then, 2 mL of the 2 mM **3** solution, 20 μL of the 100 mM benzoic acid solution and 1980 μL electrolyte (0.2 M $TBAPF_6$) were mixed together to give a 4 mL solution comprising 1 mM **3** and 0.5 mM benzoic acid. The CV of the latter was recorded (brown line in Fig. 3c) to get the i_{cat} value. The two stock solutions were also used for the titration experiment shown in Fig. S6 and described below.

For the titration experiment of a 1 mM **3** solution with benzoic acid shown in Fig. S6, stock solutions of 2 mM **3** in 0.2 M $TBAPF_6$ and 100 mM benzoic acid in 0.2 M $TBAPF_6$ were initially prepared. 2 mL of the 2 mM **3** solution were diluted with electrolyte until final volume 4 mL to give a 1 mM **3** sample. The CV of this acid free solution was recorded to obtain the i_0 value. Appropriate volumes from the two stock solutions were mixed with electrolyte until final volume 4 mL to give the corresponding 1 mM **3** solutions with 0.5, 1, and 3 mM benzoic acid. To the latter (*i.e.* 3 mM) solution, 1.5 and 6.8 mg of benzoic acid was successively added to afford solutions comprising 6 and 20 mM acid concentrations. The CVs of all the above acidic solutions were recorded to get the corresponding i_{cat} values.

CV simulation and generation of working curves

All simulated CVs were calculated using the DigiElchsoftware package.[4] Diffusion coefficients of compounds were determined straightforwardly from the peak currents of reversible waves, and these values were used in the applicable simulations. Symmetry factors (α values) were set as 0.5 for all ET steps.

The working curves shown in Fig. 3b were generated as follows: using the experimentally determined heterogeneous rate constants a CV was simulated for the case of a catalyst at a specified concentration in the absence of substrate (PhCOOH). The peak current associated with the $Co^{+/0}$ couple was recorded as i_0. Next, a CV was simulated for the same catalyst concentration, but with substrate added at an excess factor, γ, of 0.5 for a reaction scheme in which k_{PT2} is 100 times a specified value of k_{PT1} ($\rho = 100$). The peak current associated with this voltammogram was recorded as i_{cat}. The normalized current value $i_{cat}/i_0\gamma$ was calculated. Varying k_{PT1} (and thus, according to Eq. 7, log λ_{PT1}), and determining the corresponding i_{cat} (and therefore $i_{cat}/i_0\gamma$) values, furnished the black curve in Fig. 3b. Although this may also be achieved by modulating other variables (*i.e.* T, v, or $[\mathbf{3}]_{bulk}$) as described by Eq. 7 in the text, alteration of any other variable would also require simulation of a new CV in the absence of substrate to acquire a new i_0. As k_{PT1} was altered, k_{PT2} was set to the appropriate value fixed

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[4] M. Rudolf, *J. Electroanal. Chem.,* 2003, **543**, 23–39; DigiElch from Elchsoft under http://www.elchsoft.com.

by the desired ratio of k_{PT2} to k_{PT1}, ρ (Eq. 8). This was repeated for $\rho = 10$, 1, 0.1, 0.01, and 0.001 to generate the remaining plots in Fig. 3b.

The working curves shown in Fig. 3d were generated as follows: using the experimentally determined heterogeneous rate constants a CV was simulated for the case of a catalyst at a specified concentration in the absence of substrate (PhCOOH). The peak current associated with the $Co^{+/0}$ couple was recorded as i_0. Next, a CV was simulated for the same catalyst concentration, but with substrate added at an excess factor, γ, of 0.5 for a reaction scheme in which k_{PT2} is 10 times a specified value of k_{PT1} ($\rho = 10$). The peak current associated with this voltammogram was recorded as i_{cat}. Thus, the normalized current value $i_{cat}/i_0\gamma$ was calculated. Varying k_{PT1} (and thus, according to Eq. 7, log λ_{PT1}), and determining the corresponding i_{cat} (and therefore $i_{cat}/i_0\gamma$) values, furnished the black curve in Fig. 3d. As k_{PT1} was altered, k_{PT2} was set to the appropriate value fixed by the desired ratio of k_{PT2} to k_{PT1}, $\rho = 10$ (Eq. 8). This was repeated for $\gamma = 1$, 2, 3, 6, 20 and 100 to generate the remaining plots in Fig. 3d.

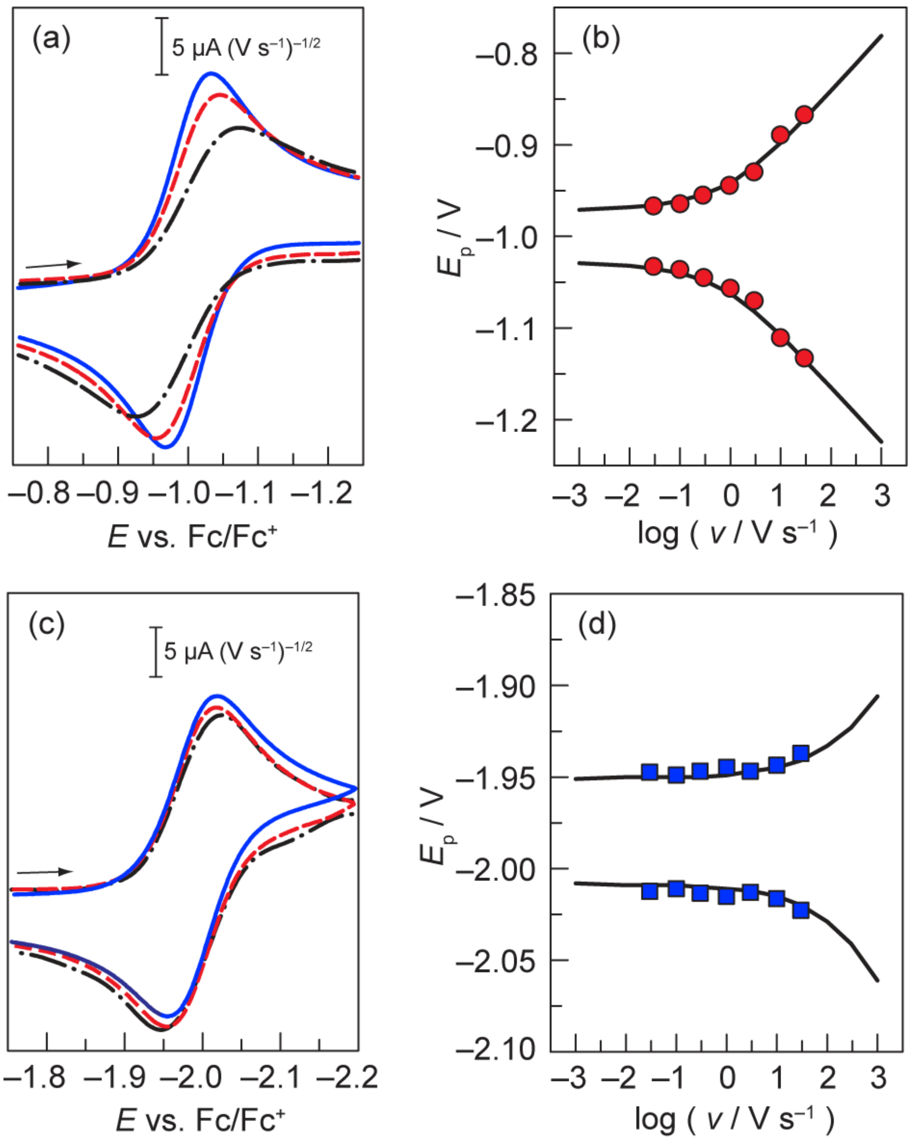

Figure S1. (a) Overlay of representative normalized ($i_{\mathrm{norm}} = i/v^{1/2}$) CVs (waves of the Co$^{2+/+}$ couple) taken of a 0.3 mM solution of **3** in acetonitrile with 0.03 (——), 0.3 (– –), and 3 (— •) V s^{-1} scan rates (v). (b) Plot of the anodic or cathodic peak potential (E_{p}) for the Co$^{2+/+}$ couple *vs.* log of scan rate (trumpet plot). Simulated curves are plotted for k_{s} = 0.011 cm s^{-1} (——). (c) Overlay of representative normalized ($i_{\mathrm{norm}} = i/v^{1/2}$) CVs (waves of the Co$^{+/0}$ couple) taken of a 0.3 mM solution of **3** in acetonitrile with 0.03 (——), 0.3 (– –), and 3 (— •) V s^{-1} scan rates. (d) Plot of the anodic or cathodic peak potential (E_{p}) for the Co$^{+/0}$ couple *vs.* log of scan rate (trumpet plot). Simulated curves are plotted for k_s = 0.2 cm s^{-1} (——). The diffusion coefficient (D) for **3** was determined to be 8 × 10^{-6} cm^2 s^{-1} from the peak current, i, in the reversible limit: $i = 0.446FAC^{o}D^{1/2}(\mathrm{F}v/\mathrm{R}T)^{1/2}$ (where F is the faraday constant, A is the area of the electrode and C^{o} is the bulk porphyrin concentration).

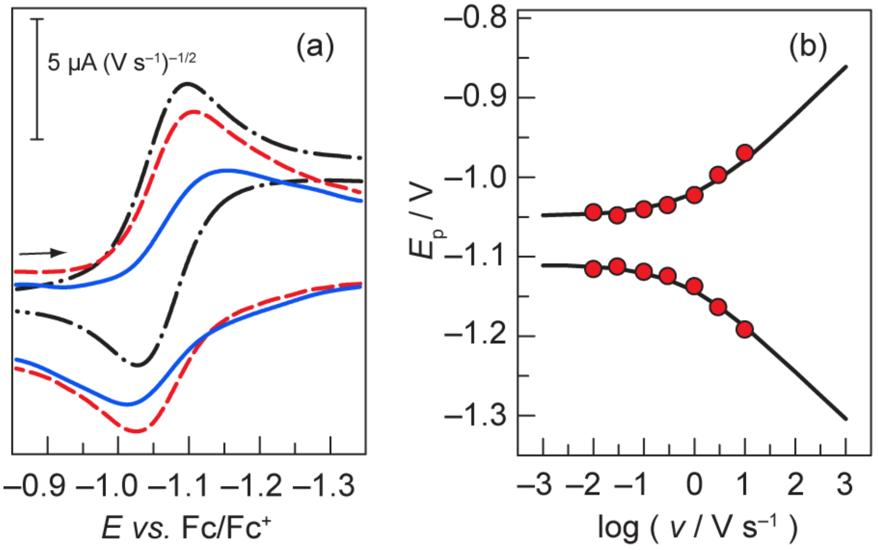

Figure S2. (a) Overlay of representative normalized ($i_{\text{norm}} = i/v^{1/2}$) CVs (waves of the Co$^{2+/+}$ couple) taken of a 0.2 mM solution of **1** in acetonitrile with 0.03 (━ •), 0.3 (— —), and 3 (━━) V s^{-1} scan rates (v), using a glassy carbon electrode. (b) Plot of the anodic or cathodic peak potential (E_p) for the Co$^{2+/+}$ couple *vs.* log of scan rate (trumpet plot). Simulated curves are plotted for k_s = 0.012 cm s^{-1} (━━). The diffusion coefficient (D) of **1** was determined to be 5 × 10^{-6} cm^2 s^{-1} from the peak current, i, in the reversible limit: $i = 0.446FAC^{o}D^{1/2}(\mathrm{F}v/\mathrm{R}T)^{1/2}$ (where F is the faraday constant, A is the area of the electrode and C^{o} is the bulk porphyrin concentration).

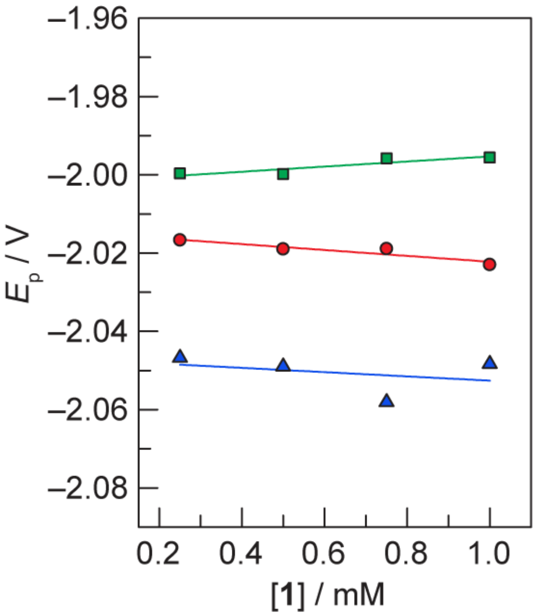

Figure S3. Concentration dependence studies of the Co$^{+/0}$ reduction wave peak potential of **1**. Experimental data obtained at scan rates of 0.03 (■), 0.3 (●), and 3 (▲) V s^{-1}.

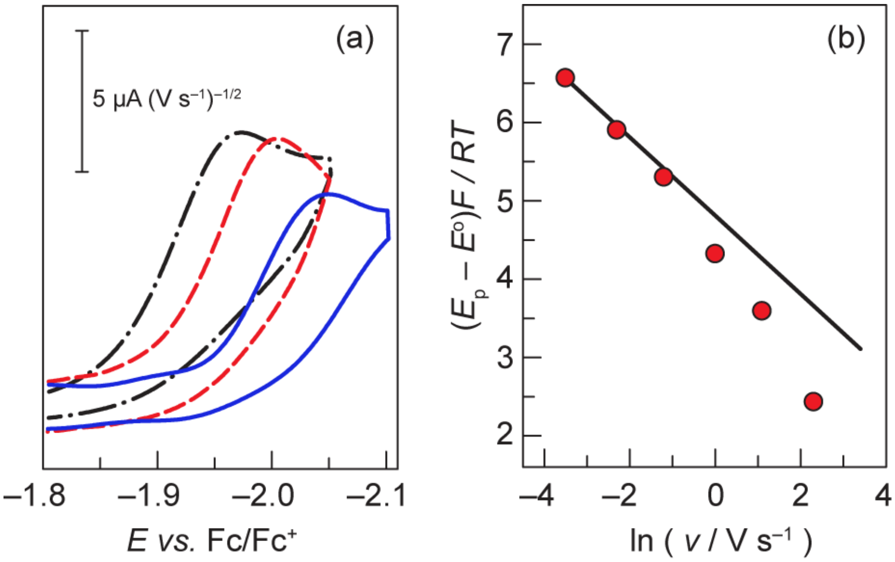

Figure S4. (a) Overlay of representative background-subtracted normalized ($i_{\text{norm}} = i/v^{½}$) CVs taken of a 0.2 mM solution of **1** in acetonitrile at scan rates (v) of 0.03 (— •), 0.3 (– –), and 3 (——) V s^{-1}. (b) Plot of (E_p – E^o)F/RT *vs.* ln of scan rate (E^o = –2.14 V, taken from **2**). Experimental data (●), theoretically predicted line (——) derived from Eq. 3 of the main text (*i.e.* assuming fast, unconditionally reversible ET followed by irreversible PT) using as k_{PT} the value calculated from the CV recorded with 0.03 V s^{-1} scan rate (k_{PT} = 3 × 10^6 s^{-1}).

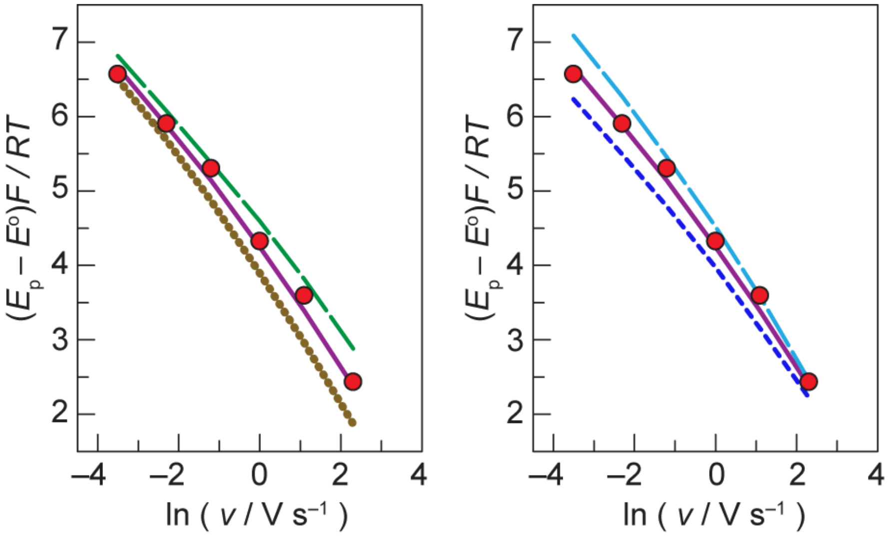

Figure S5. Plots of (E_p – E^o)F / RT *vs.* ln of scan rate (E^o = –2.14 V, taken from **2**) for **1**. Experimental data taken from Fig. S4a (●), simulated curves plotted for: k_s = 0.24 cm s^{-1} and k_{PT} = 8.5 × 10^6 s^{-1} (——); k_s = 0.35 cm s^{-1} and k_{PT} = 8.5 × 10^6 s^{-1} (– –); k_s = 0.18 cm s^{-1} and k_{PT} = 8.5 × 10^6 s^{-1} (•••); k_s = 0.24 cm s^{-1} and k_{PT} = 3 × 10^7 s^{-1} (– –); and k_s = 0.24 cm s^{-1} and k_{PT} = 3 × 10^6 s^{-1} (– –).

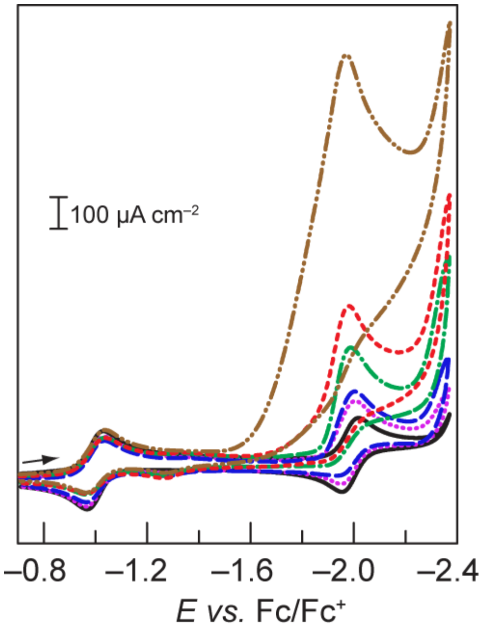

Figure S6. CVs of a 1.0 mM solution of **3** in the absence of benzoic acid (—) and in the presence of 0.5 (•••), 1.0 (– –), 3.0 (— •), 6.0 (– –), and 20 mM (— ••) benzoic acid. Scan rate, 30 mV s^{-1}; 0.2 M TBAPF$_6$ in acetonitrile. Glassy carbon working electrode, Ag/AgNO$_3$ reference electrode, and Pt wire counter electrode.