

Supporting Information

Proton-Coupled Electron Transfer of Macrocyclic Ring Hydrogenation: The Chlorinphlorin

Rui Sun,^{a,‡} Mengran Liu,^{a,‡} Shao-Liang Zheng,^a Dilek K. Dogutan,^{a,*} Cyrille Costentin,^{b,c,*} and Daniel G. Nocera^{a,*}

^a *Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, MA 02138, United States.* ^b *Université Grenoble Alpes, CNRS, 38000 Grenoble, France.* ^c *Université de Paris, 75013 Paris, France.*

Emails: [dkiper@fas.harvard.edu](mailto:dkipper@fas.harvard.edu), cyrille.costentin@univ-grenoble-alpes.fr, dnocera@fas.harvard.edu

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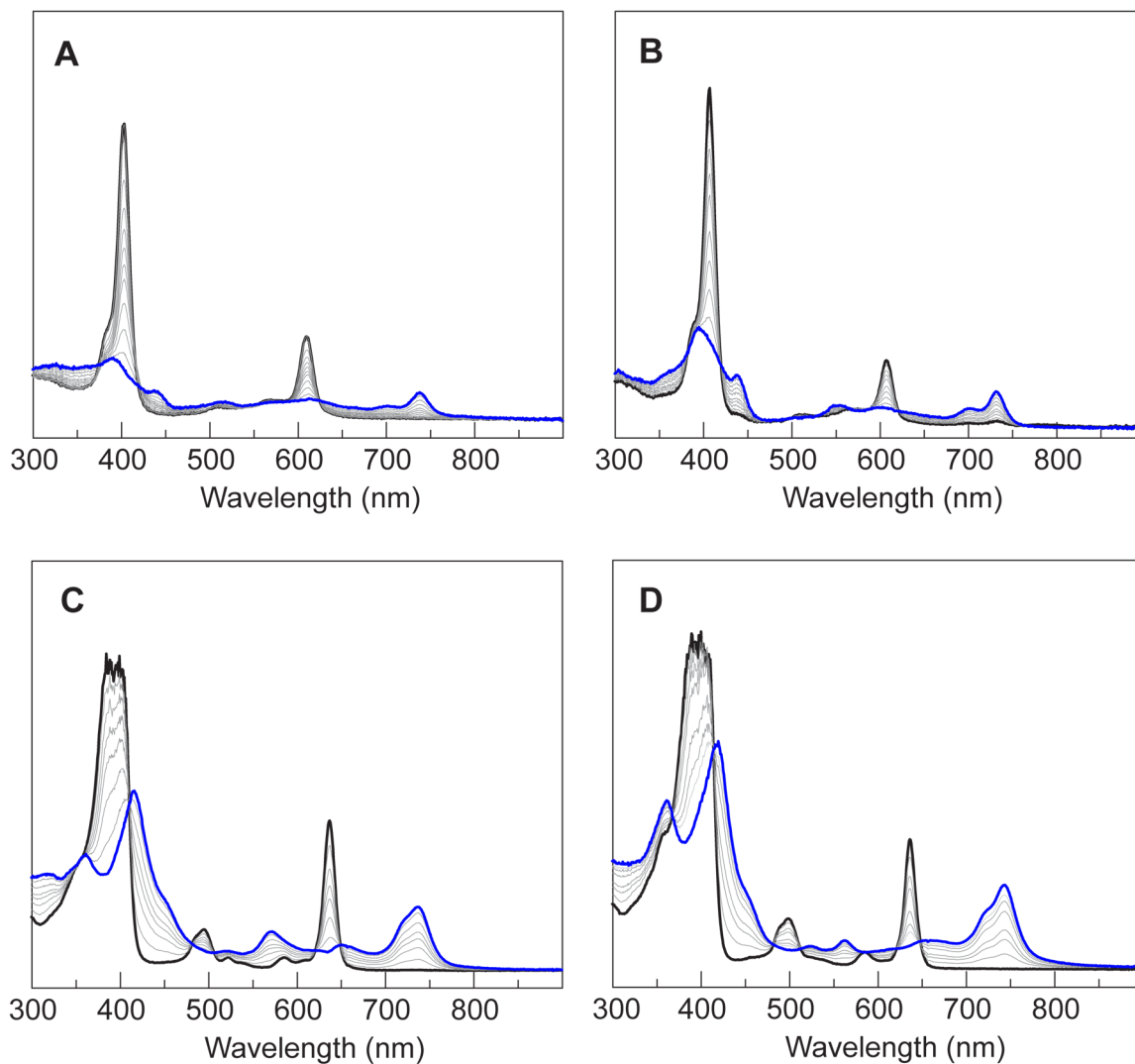


Figure S1. Thin-layer UV-vis spectroelectrochemistry in acetonitrile containing $n\text{-Bu}_4\text{NPF}_6$ (0.1 M) in a nitrogen-atmosphere glovebox at room temperature. The black and blue traces show the initial and final spectra, respectively. (A) Potential held at -2.00 V vs Fc^+/Fc for **ZnCX³-Me** solution without benzoic acid. (B) Potential held at -2.00 V vs Fc^+/Fc for **ZnCX¹⁰-Me** solution without benzoic acid. (C) Potential held at -1.85 V vs Fc^+/Fc for a **H₂CX³-Me** solution without benzoic acid. (D) Potential held at -1.85 V vs Fc^+/Fc for a **H₂CX¹⁰-Me** solution without benzoic acid.

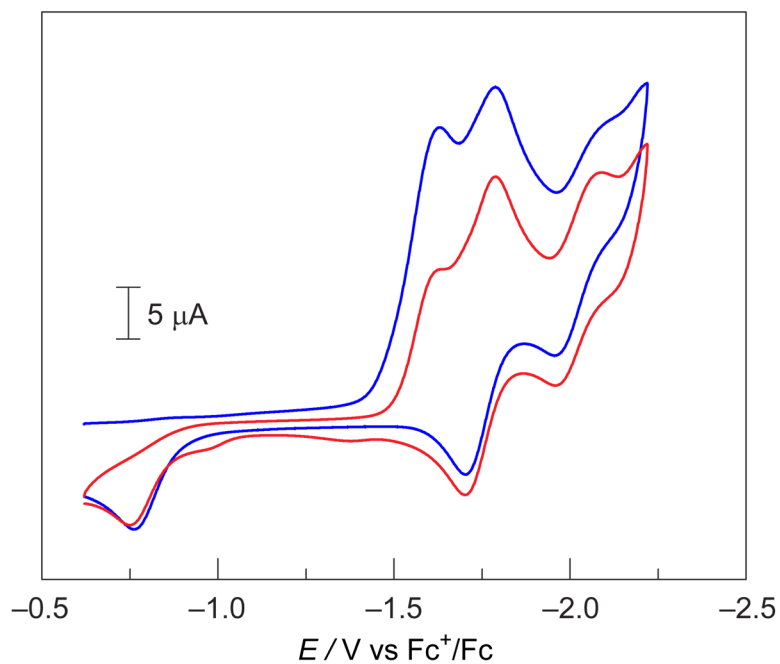
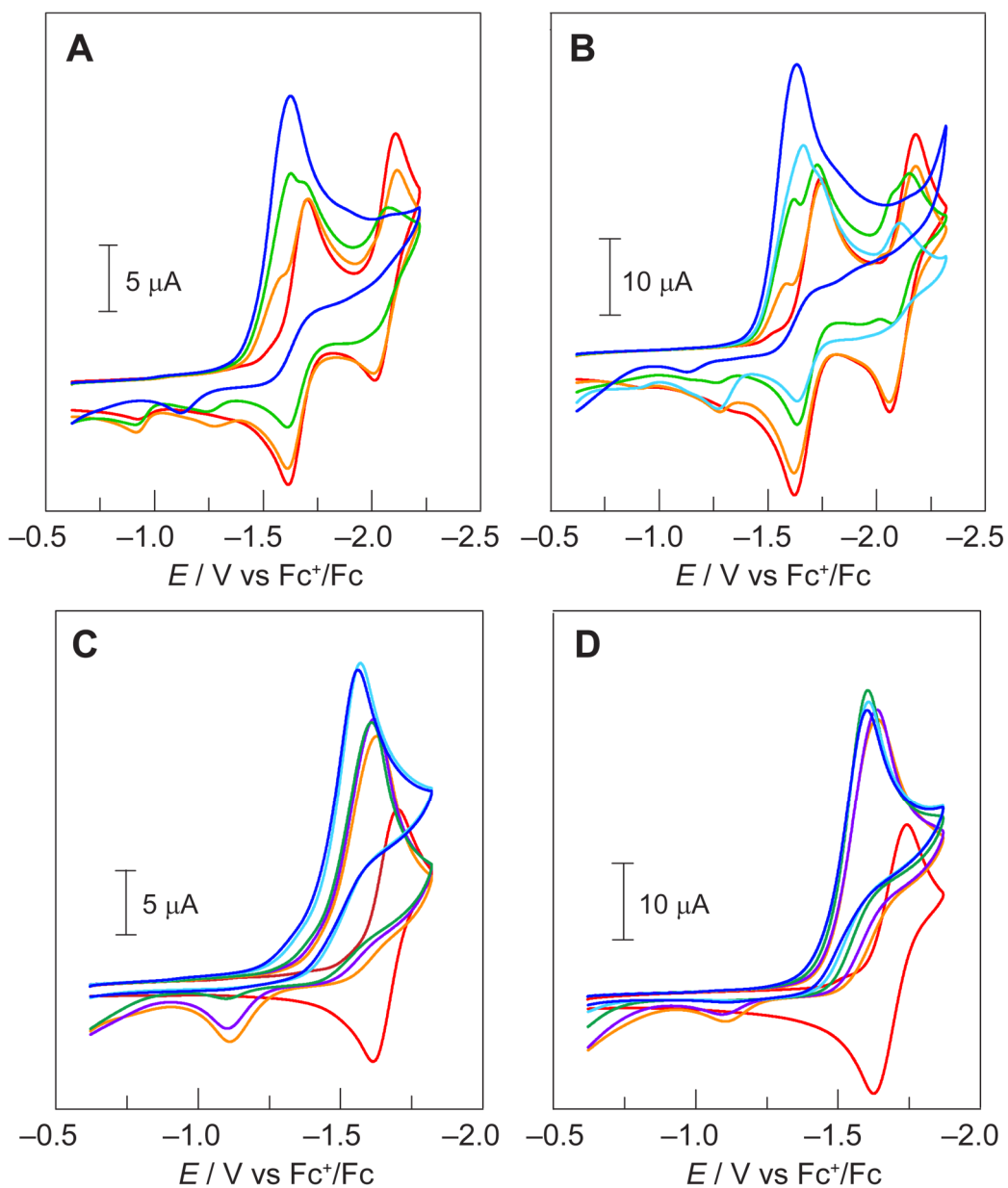


Figure S2. Two successive cyclic voltammograms of H₂CX¹⁰-H (2 mM) in acetonitrile containing *n*-Bu₄NPF₆ (0.1 M) collected using a 3 mm glassy carbon working electrode. $\nu = 0.1$ V/s. The blue trace shows the first scan while the red trace shows the second.



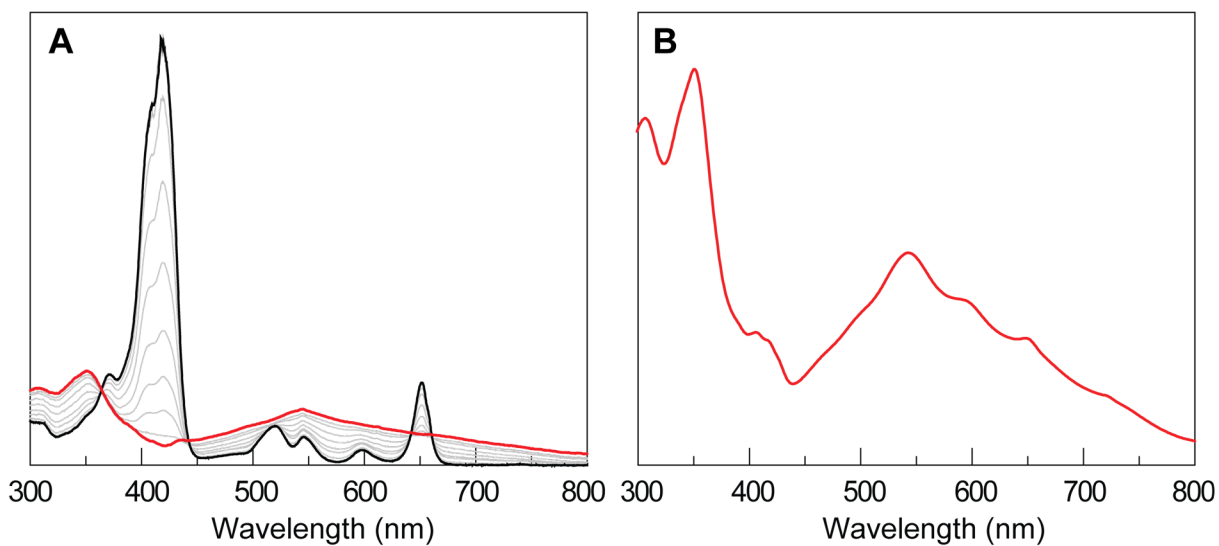


Figure S4. UV-vis characterization of chemically prepared chlorinphlorin. **(A)** Thin-layer UV-vis spectroelectrochemistry in a N_2 -filled glovebox on a solution of 15 mM *meso*-tetraphenylchlorin and 100 mM benzoic acid in CD_2Cl_2 with $n-Bu_4NPF_6$ (0.1 M) as an electrolyte under an applied potential of -1.78 V vs Fc^+/Fc . The black and red traces show the initial and final spectra, respectively. **(B)** UV-vis spectrum of the isolated *meso*-tetraphenylchlorinphlorin product from chemical reduction in DCM.

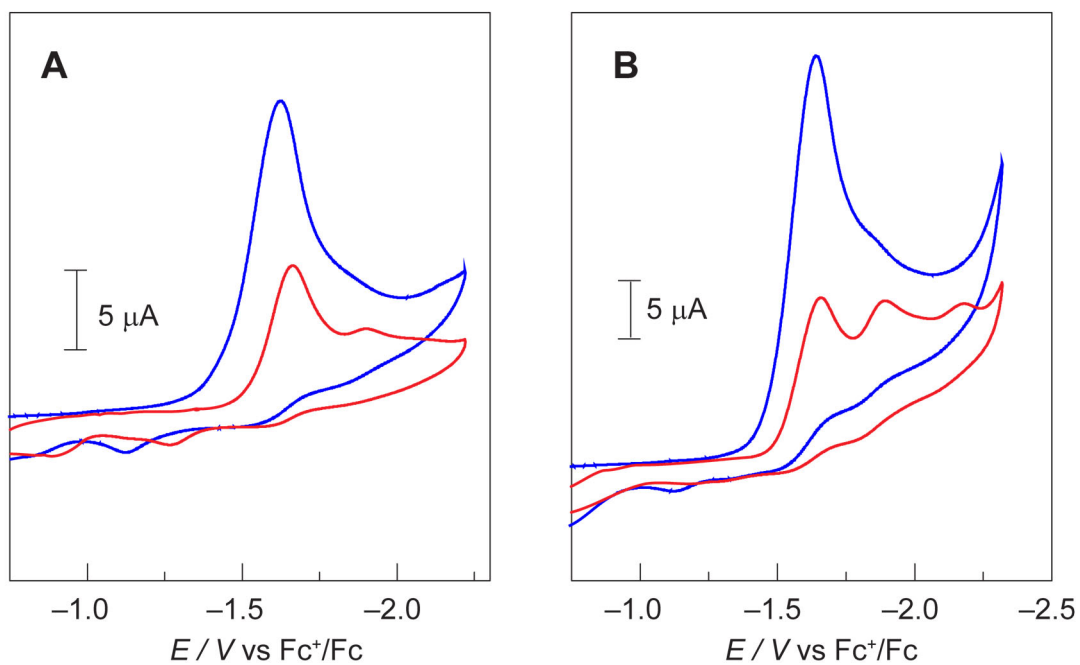


Figure S5. (A) Two successive cyclic voltammograms of $\text{H}_2\text{CX}^3\text{-Me}$ (1 mM) in the presence of 2 mM benzoic acid. (B) Two successive cyclic voltammograms of $\text{H}_2\text{CX}^{10}\text{-Me}$ (1.6 mM) in the presence of 3 mM benzoic acid. The blue trace shows the first scan while the red trace shows the second. In all cases, the solvent was acetonitrile containing $n\text{-Bu}_4\text{NPF}_6$ (0.1 M) and the measurements were performed using a 3 mm glassy carbon working electrode. $\nu = 0.1$ V/s.

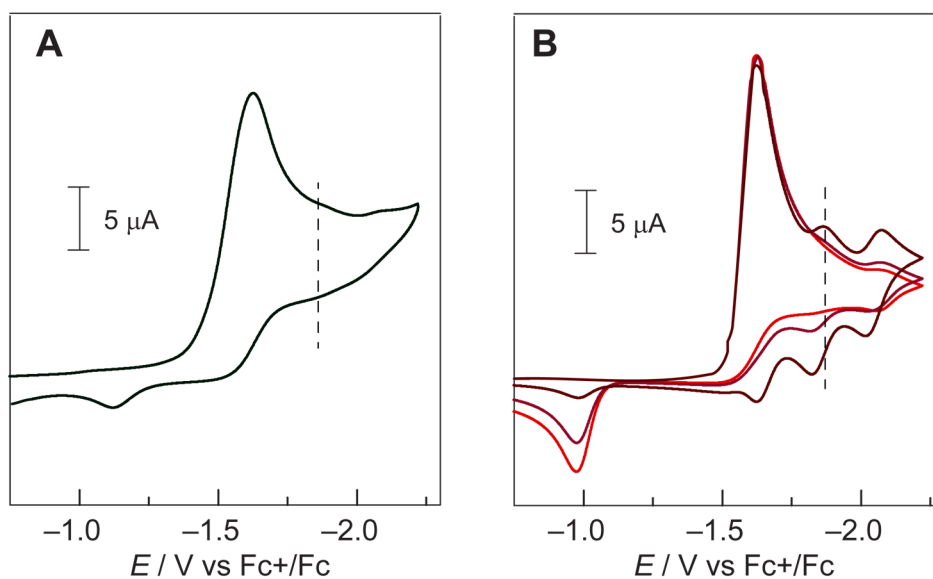


Figure S6. (A) $\text{H}_2\text{CX}^3\text{-Me}$ (1.0 mM) in the presence of 1 mM benzoic acid in anhydrous acetonitrile with $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte (0.1 M) using a 3 mm glassy carbon working electrode. $\nu = 0.1$ V/s. (B) Simulated CVs of $\text{H}_2\text{CX}^3\text{-Me}$ (1.0 mM) in the presence of 1 mM benzoic acid with $k_{\text{H}_2} = 10$ (red), 100 (burgundy) and 1000 (brick red) $\text{M}^{-1} \text{s}^{-1}$. The dotted vertical line indicates the location of the $\text{CHI}(\text{H}_2)$ reduction wave. Simulation reproduces experimental CV for $k_{\text{H}_2} = 10 \text{ M}^{-1} \text{s}^{-1}$.

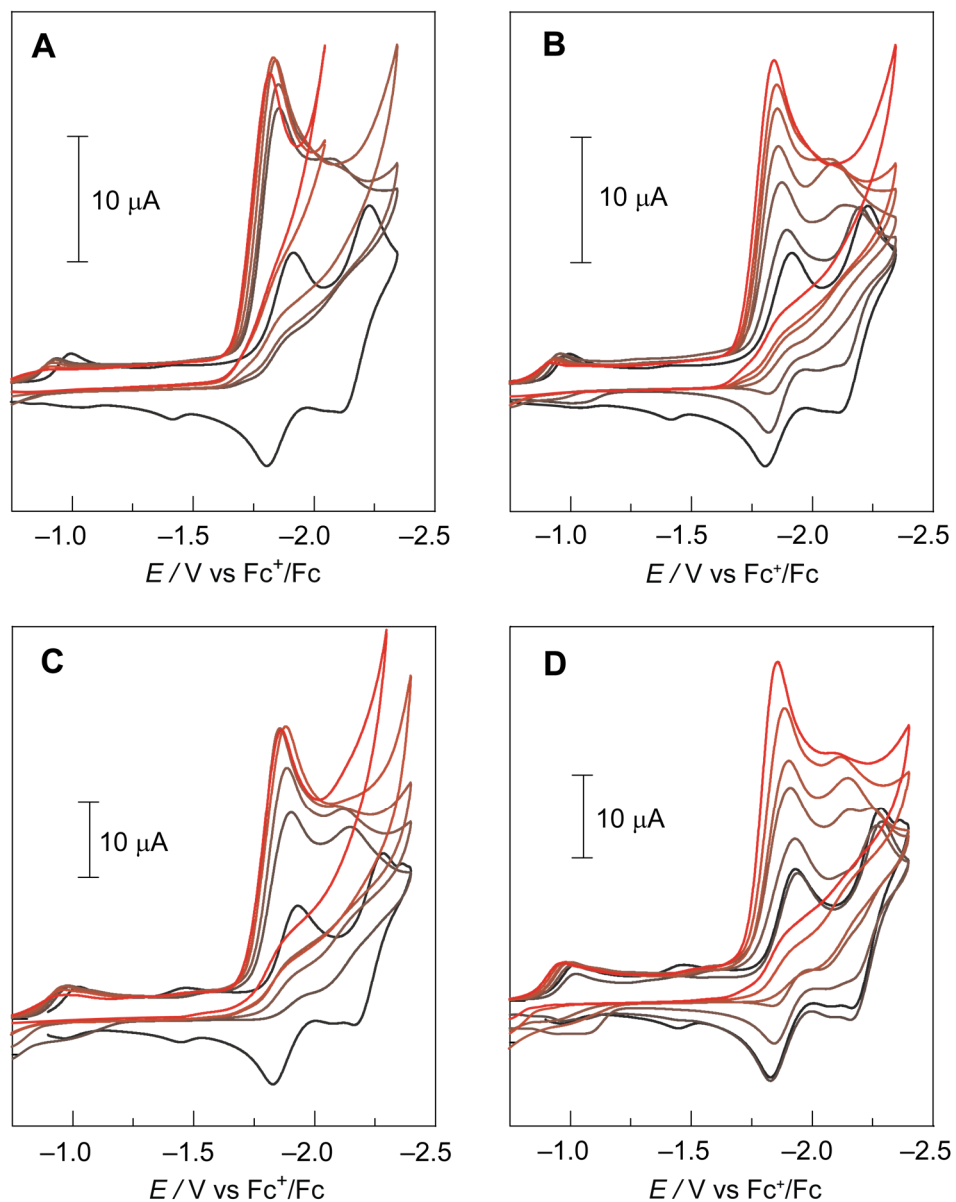


Figure S7. Cyclic voltammograms of $\text{ZnCX}^3\text{-Me}$ (0.8 mM) in the presence of benzoic acid (from black to red): (A) 0, 2, 3, 5, 10, 20 mM, (B) 0, 0.2, 0.5, 1, 2, 3, 5 mM. Cyclic voltammograms of $\text{ZnCX}^{10}\text{-Me}$ (1 mM) in the presence of benzoic acid (from black to red): (C) 0, 2, 3, 5, 10, 20 mM, (D) 0, 0.2, 0.5, 1, 2, 3, 5 mM. In all cases, the solvent was acetonitrile containing $n\text{-Bu}_4\text{NPF}_6$ (0.1 M) and the measurements were performed using 3 mm glassy carbon electrodes. $\nu = 0.1$ V/s. Electroactive impurities are observed for both samples at ca. -0.9 V vs. Fc^+/Fc .

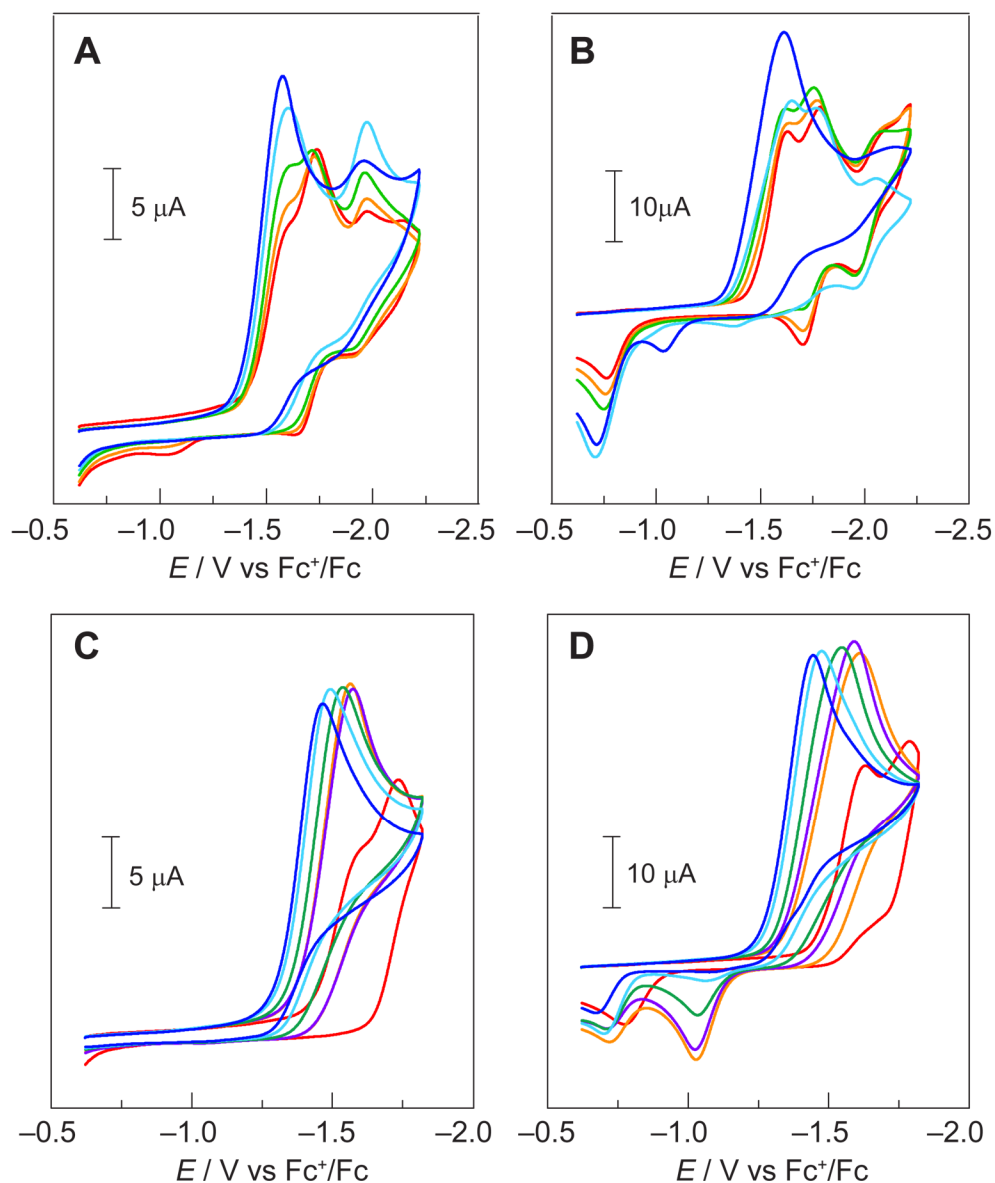


Figure S8. CVs of (A) $\text{H}_2\text{CX}^3\text{-H}$ (1.0 mM) and $\text{H}_2\text{CX}^{10}\text{-H}$ (2.0 mM) in the presence of low benzoic acid concentrations: for (A): 0 (red), 0.2 (orange), 0.5 (green), 1 (cyan), 2 (blue) mM and for (B) 0 (red), 0.2 (orange), 0.5 (green), 1 (cyan), 2 (blue) mM. CVs of (C) $\text{H}_2\text{CX}^3\text{-H}$ (1.0 mM) and (D) $\text{H}_2\text{CX}^{10}\text{-H}$ (2.0 mM) in the presence of high benzoic acid concentrations: for (C) 0 (red), 2 (orange), 3 (purple), 5 (green), 10 (cyan), 20 (blue) mM and for (D) 0 (red), 2 (orange), 3 (purple), 5 (green), 10 (cyan), 20 (blue) mM. All CVs were taken in anhydrous acetonitrile with $n\text{-Bu}_4\text{NPF}_6$ as the supporting electrolyte (0.1 M) using a 3 mm glassy carbon working electrode. $v = 0.1$ V/s.

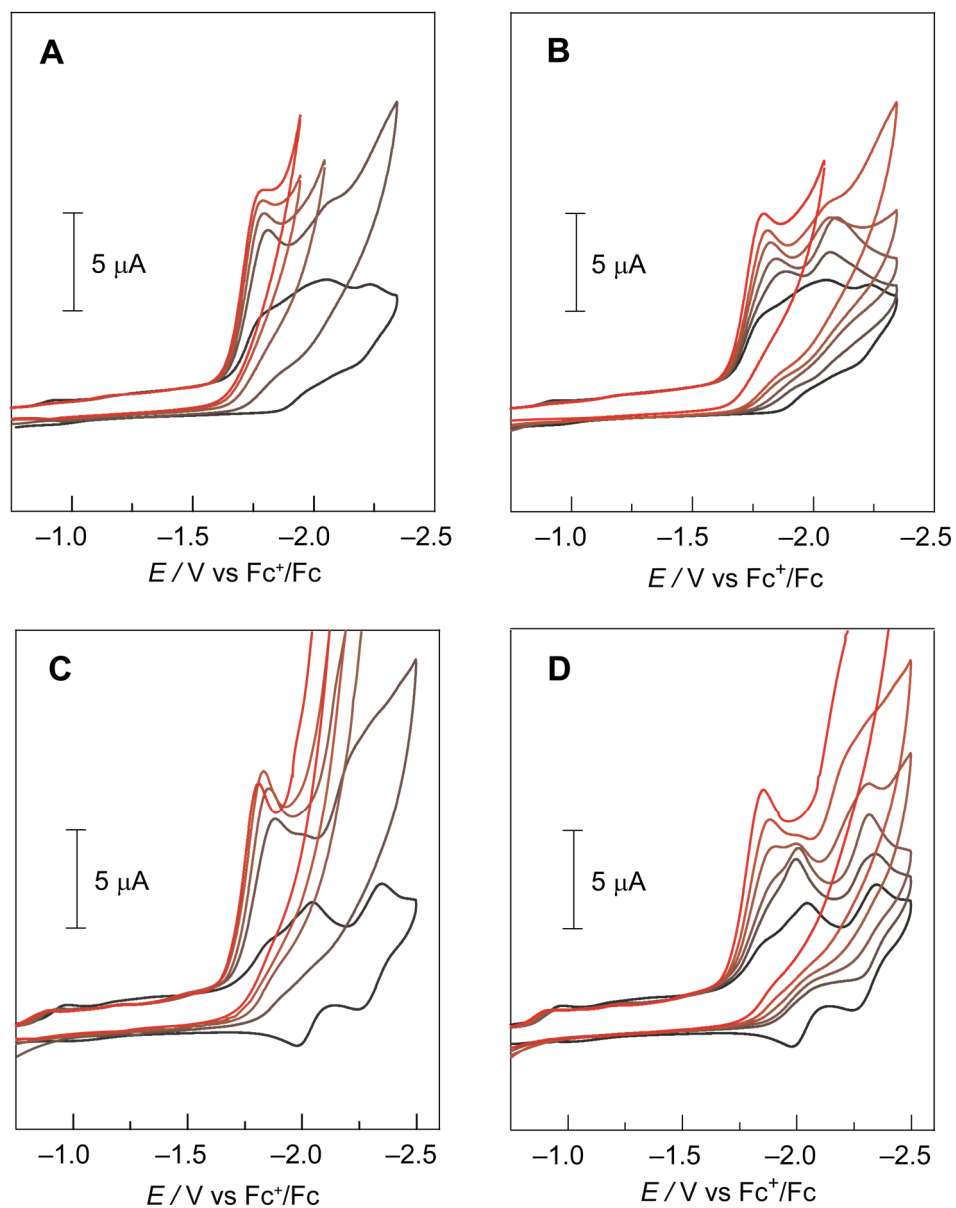
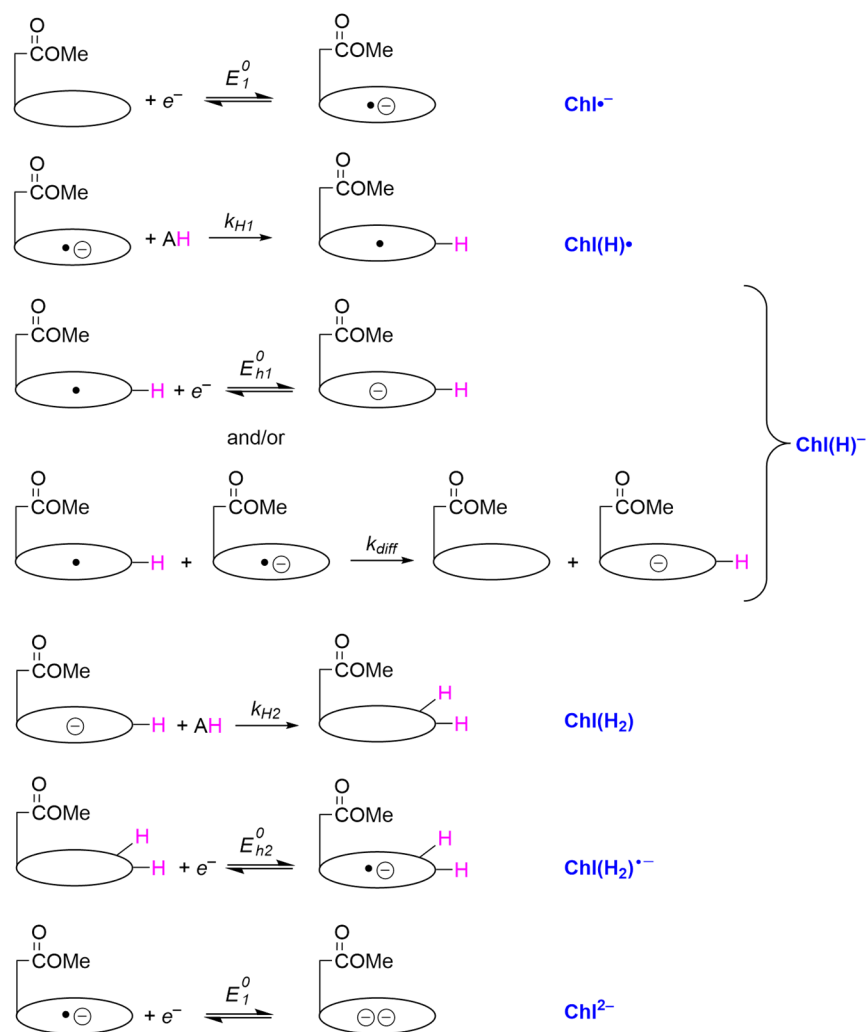


Figure S9. Cyclic voltammograms of $\text{ZnCX}^3\text{-H}$ (0.4 mM) in the presence of benzoic acid (from black to red): (A) 0, 2, 5, 10, 20 mM, (B) 0, 0.2, 0.5, 1, 2, 5 mM. Cyclic voltammograms of $\text{ZnCX}^{10}\text{-H}$ (0.4 mM) in the presence of benzoic acid (from black to red): (C) 0, 2, 3, 5, 10, 20 mM, (D) 0, 0.2, 0.5, 1, 2, 5 mM. In all cases, the solvent was acetonitrile containing *n*-Bu₄NPF₆ (0.1 M) and the measurements were performed using 3 mm glassy carbon electrodes. $\nu = 0.1$ V/s. Electroactive impurities were observed for both samples at ca. -0.9 V vs. Fc^+/Fc .



Scheme S1. Simulation model using the parameters in Table S1 as well as $D = 5 \times 10^{-6} \text{ cm}^2/\text{s}$, $v = 0.1 \text{ V/s}$, $T = 293 \text{ K}$, $S = 0.071 \text{ cm}^2$.

Table S1. Summary of Parameters used in CV Simulation.

	H ₂ CX ¹⁰ -Me (1.6 mM)	H ₂ CX ³ -Me (1 mM)
E_1^0 (V vs. Fc ⁺ /Fc)	-1.68	-1.65
k_{H1} (M ⁻¹ s ⁻¹)	5×10^5	5×10^5
E_h^0 (V vs. Fc ⁺ /Fc)	> -1	> -1
k_{H2} (M ⁻¹ s ⁻¹)	1 to 10 ³	1 to 10 ³
E_{h2}^0 (V vs. Fc ⁺ /Fc)	-1.85	-1.85
E_2^0 (V vs. Fc ⁺ /Fc)	-2.12	-2.05
k_{diff} (M ⁻¹ s ⁻¹)	10 ¹⁰	10 ¹⁰

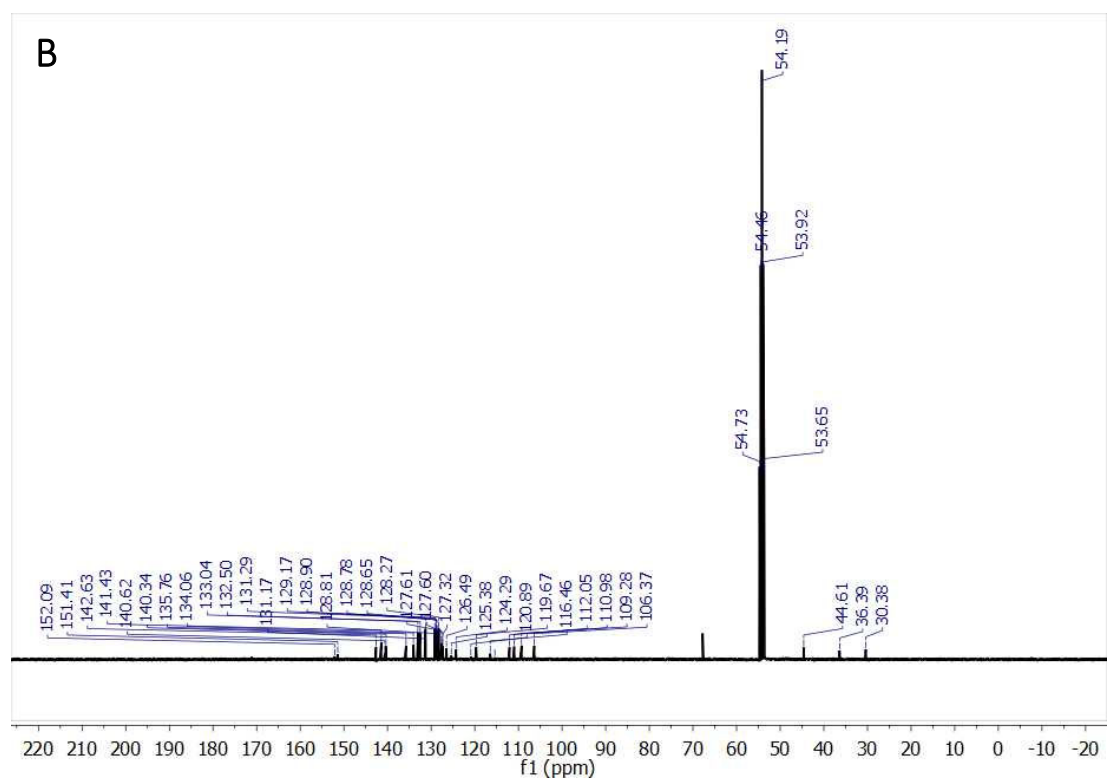
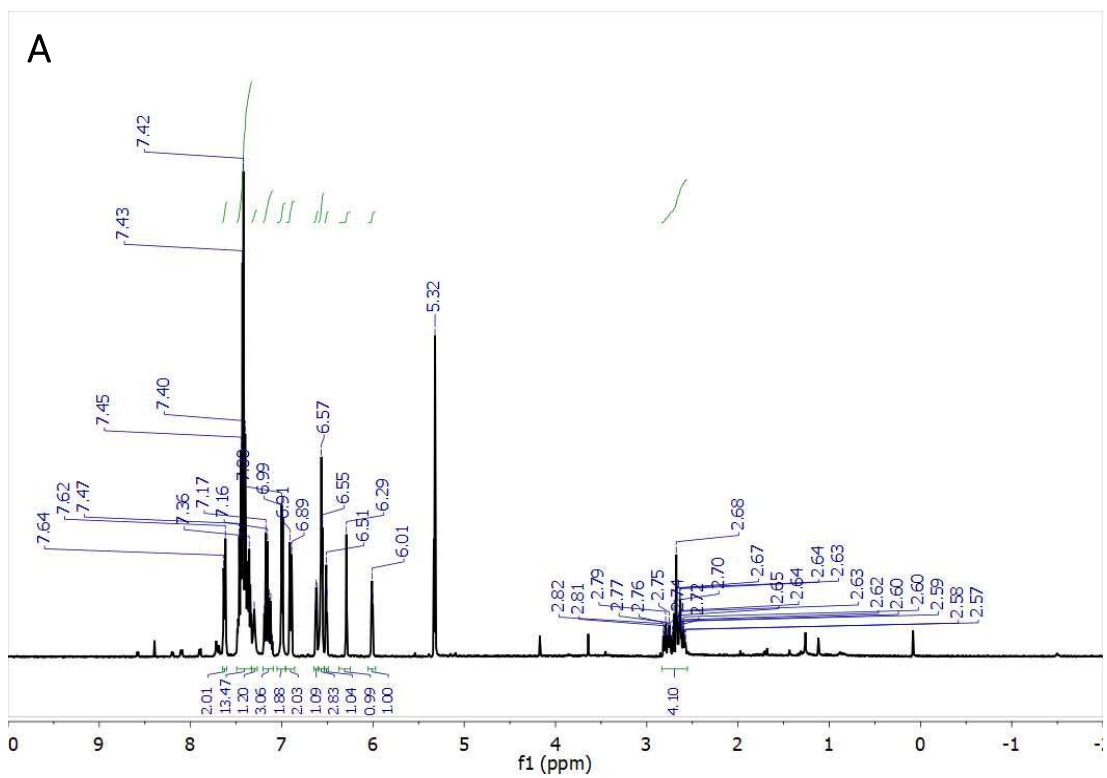


Figure S10. NMR spectra for *meso*-tetraphenylchlorinphlorin. (A) ^1H NMR (400 MHz, CD_2Cl_2) and (B) ^{13}C NMR (101 MHz, CD_2Cl_2).

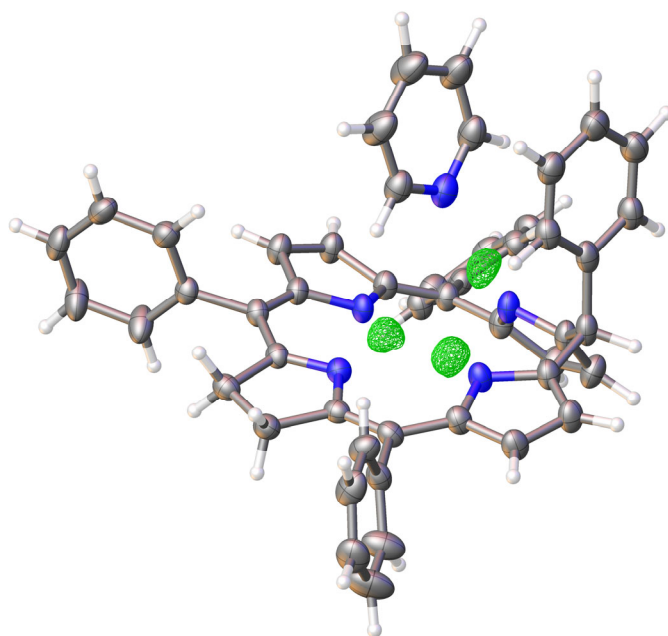


Figure S11. Crystal structure with the difference-Fourier map (green) used to locate hydrogen atoms bound to pyrrolic nitrogen atoms.

Table S2. Crystal data and structure refinement for *meso*-tetraphenylchlorinphlorin.

Empirical formula	C ₄₉ H ₃₉ N ₅
Formula weight	697.85
T (K)	100
λ (Å)	0.41328
Crystal system	Monoclinic
Space group	<i>P2₁/n</i>
<i>a</i> (Å)	16.617(4)
<i>b</i> (Å)	11.878(2)
<i>c</i> (Å)	20.263(7)
α (°)	90
β (°)	110.077(7)
γ (°)	90
<i>V</i> (Å ³)	3731.9(17)
<i>Z</i>	4
ρ_{calcd} (Mg/m ³)	1.242
μ (mm ⁻¹)	0.034
θ range for data collection (°)	2.29 to 14.15
Index ranges	$-19 \leq h \leq 19, -14 \leq k \leq 12, -24 \leq \ell \leq 24$
Reflections collected	6673
<i>R</i> _{int}	0.0694
Completeness to θ_{max}	99.4%
Data/restraints/parameters	6673 / 0 / 644
GOF on <i>F</i> ²	1.055
<i>R</i> ₁	0.0537
w <i>R</i> ₂	0.1394
Largest diff. peak, hole (e Å ⁻³)	0.324, -0.258