Electrocatalytic Production of Hydrogen Peroxide Enabled by Post-Synthetic Modification of a Self-Assembled Porphyrin Cube

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Supplementary Information

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Figure S1. Paramagnetic $^1$H NMR of Co$_2$-cube. ($500$ MHz, CD$_3$CN, $25^\circ$C).
High-Resolution Mass Spectrometry:

Figure S2. ESI-FT-ICR high resolution mass spectrum of FeCu-cube acquired in CH$_3$CN in positive mode. M = (C$_{408}$H$_{264}$Cu$_6$Fe$_8$N$_{72}$)(OTf)$_{16}$.

Figure S3. The 7+ base peak in Figure S2 corresponding (top) Experimental data, (bottom) simulated spectrum with loss of 7 OTF$^-$ counterions [M−7OTf]$^{7+}$. M = FeCu-cube = (C$_{408}$H$_{264}$Cu$_6$Fe$_8$N$_{72}$)(OTf)$_{16}$.
Figure S4. The 7+ peak in Figure S2. (top) Experimental data, (bottom) simulated spectrum with loss of 8 OTf⁻ and gain of 1 Cl⁻ counterions [M−8OTf+Cl⁻]⁻. M = FeCu-cube = (C₄₈H₂₆₄Cu₆Fe₈N₇₂)(OTf)₁₆.

**UV-Vis Spectroscopy:**

Figure S5. UV-Vis spectrum of FeCu-cube in CH₃CN.
Figure S6. UV-Vis spectrum of **CoCo-cube** in CH\textsubscript{3}CN.

**Infrared Spectroscopy:**

Figure S7. ATR-FTIR spectra of (top) **FeCu-cube** and (bottom) **CoCo-cube**.
Electrochemical Characterization

Figure S8. Cyclic voltammogram of CuTAPP (0.1 mM) in CH$_3$CN with 100 mM TBAPF$_6$.

Figure S9. Cyclic voltammogram of FeCu-cube (0.1 mM) in CH$_3$CN with 100 mM TBAPF$_6$. (top) Red trace shows the first cycle when scanned reducing first. (bottom) Blue trace shows the first cycle when scanned oxidizing first. Notably, the large oxidation event observed in the red trace is absent until reducing potentials are scanned.
Figure S10. Cyclic voltammogram of FeCu-cube (0.1 mM) in CH$_3$CN with 100 mM TBAPF$_6$, cycled scanning only oxidizing potentials.

Figure S11. Cyclic voltammogram of FeCu-cube (0.1 mM) in CH$_3$CN with 100 mM TBAPF$_6$, cycled scanning only reducing potentials.
Figure S12. Cyclic voltammogram of CoCo-cube (0.05 mM) in CH$_3$CN with 100 mM TBAPF$_6$. (top) Red trace shows the first cycle when scanned reducing first. (bottom) Blue trace shows the first cycle when scanned oxidizing first. Note, the oxidation events observed in the red trace are absent until reducing potentials are scanned.

Figure S13. Cyclic voltammogram of CoCo-cube (0.05 mM) in CH$_3$CN with 100 mM TBAPF$_6$, isolating first reduction event (porphyrin Co(II/I) couple).
Figure S14. UV-Vis spectroelectrochemical study of the first reduction event of CoCo-cube. Platinum mesh electrode held at –1.2 V vs. Fc\(^{+/0}\). The growth of the band at ~360 and 520 nm are consistent with the formation of a Co(I) porphyrin species.

Figure S15. Cyclic voltammograms of CoCo-cube (0.05 mM) in CH\(_3\)CN with 100 mM TBAPF\(_6\), cycled 3 times.

Figure S16. Cyclic voltammograms of CoCo-cube (0.01 mM) in CH\(_3\)CN with 100 mM TBAPF\(_6\), cycled 3 times at 300 mV/sec. Concentration was reduced and scan rate increased to reduce film formation; however, evidence of film formation persists.
Figure S17. Cyclic voltammograms of CoCo-cube (0.05 mM) in CH$_3$CN with 100 mM TBAPF$_6$ and 100 mM TFA after sparging with N$_2$ (blue) and O$_2$ (green).

Figure S18. CV of heterogeneous catalyst ink of CoCo-cube deposited on a glassy carbon working electrode, in 0.5 M H$_2$SO$_4$, after sparging with O$_2$ (green trace), and N$_2$ (blue trace).
Figure S19. Acid stability study of CoCo-cube under catalytic conditions. Solid CoCo-cube was soaked in 0.5 M H$_2$SO$_4$, rinsed with water, isopropanol, and dissolved in acetonitrile.

As a control study, we synthesized tris(N-phenyl-pyridinaldimine)cobalt(II) hexafluorophosphate as a model complex for the nodes of the CoCo-cube following literature protocol: 1

Figure S20. Heterogeneous CV of CoCo-cube and tris(N-phenyl-pyridinaldimine)cobalt(II) hexafluorophosphate deposited on a glassy carbon electrode under catalytic conditions (0.5 M H$_2$SO$_4$, saturated O$_2$).
Figure S21. RRDE study of CoTPP as a model for the faces of the **CoCo-cube**. Films were formed identically to the **CoCo-cube** and analysis under identical conditions (0.5 M H₂SO₄, saturated O₂).

**Koutecký–Levich Analysis and Selectivity:**

\[
\frac{1}{i} = \frac{1}{B} \omega^{-\frac{1}{2}} + \frac{1}{i_K} \tag{S1}
\]

Where \(i\) is the reductive current response due to ORR, \(B\) is the Levich constant, \(\omega\) is the rotation rate in rad/sec, and \(i_K\) is the theoretical current that would pass absent mass transport effects (the kinetic current). The kinetic current is related to the heterogeneous electron transfer rate constant as follows:

\[
i_K = nF A k_{het} [O_2] \Gamma_{cat} \tag{S2}
\]

Where \(n\) is the number of electrons transferred, determined by the Faradaic efficiency, \(F\) is Faraday’s constant, \(A\) is the electrode surface area, \([O_2]\) is the dissolved concentration of O₂ in 0.5 M H₂SO₄, and \(\Gamma_{cat}\) is the ideal active site density, or moles of catalyst per unit area. The standard rate constant \((k_s)\) is related to \(k_{het}\) by:

\[
k_{het} = k_s e^{-\frac{\alpha F \eta}{kT}} \tag{S3}
\]

Where the exponential term contains \(\alpha\) the transfer coefficient, \(F\) is Faraday’s constant, \(R\) the gas constant, and \(T\) the temperature in Kelvin, and \(\eta\) is the overpotential.
The following equation can be used to determine selectivity:

$$\% H_2 O_2 = \frac{2i_{ring}}{N \left( i_{disk} + \frac{i_{ring}}{N} \right)} \cdot 100$$

(S4)

Where $i_{ring}$ and $i_{disk}$ refer to the ring and disk currents, respectively, and $N$ is the collection efficiency (0.36), which was experimentally determined using $K_3[Fe(CN)_6]$.2,3


References

