A Supramolecular Porous Organic Cage Platform Promotes Electrochemical Hydrogen Evolution from Water Catalyzed by Cobalt Porphyrins

Peter T. Smith,[a] Bahiru Punja Benke,[b] Lun An,[a] Younghoon Kim,[b, c] Kimoon Kim,*[b, c] and Christopher J. Chang*[a, d]

[a] Department of Chemistry, University of California, Berkeley, Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720-1460 (USA), chrischang@berkeley.edu
[b] Center for Self-assembly and Complexity (CSC), Institute for Basic Science (IBS), Pohang 37673 (Republic of Korea), kkim@postech.ac.kr
[c] Department of Chemistry, Pohang University of Science and Technology, Pohang 37673 (Republic of Korea)
[d] Department of Molecular and Cell Biology, University of California, Berkeley, Berkeley, CA 94720-1460 (USA)

We dedicate this paper to Prof. Jean-Michel Savéant.
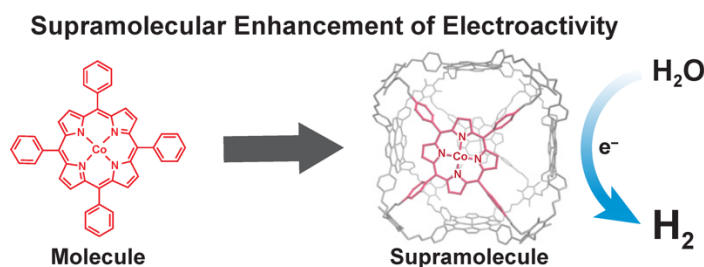
Abstract: We report a supramolecular porous organic cage platform composed of cobalt porphyrins for catalyzing the electrochemical hydrogen evolution reaction (HER) from water at neutral pH. Owing to its permanent porosity, the supramolecular structure yields a catalyst film with a 5-fold increase in the number of electrochemically active cobalt atoms and an improvement in Tafel slope from 170 mV/decade to 119 mV/decade compared to a planar cobalt porphyrin analog, reaching activities over 19,000 turnovers for HER over a 24-hour period with 100% Faradaic efficiency.

The generation of high-purity hydrogen gas from renewable sources for use as a fuel or synthetic feedstock is an attractive alternative over conventional energy-intensive and environmentally harmful processes including natural gas reforming.[1] In this context, water is an abundant and sustainable source of protons that can be reduced to form hydrogen, and the development of catalysts for the electrochemical hydrogen evolution reaction (HER) using earth-abundant metals has been the subject of intense research.[2] In particular, electrochemical HER using a variety of cobalt complexes has been thoroughly investigated,[3] and cobalt porphyrins specifically have been shown to be efficient hydrogen evolving catalysts in homogeneous organic or aqueous conditions,[4] as catalyst films,[5] and even within artificial metalloenzymes.[6] More broadly, porphyrin-based catalysts have proven to be privileged scaffolds for many small-molecule activation reactions owing to facile synthetic tuning of the porphyrin electronics and the associated outer-coordination sphere.[7] In materials platforms for energy catalysis, a common strategy for tuning catalytic activity is altering the nanostructure of the electrode material in an effort to elucidate how different shapes, sizes, or assemblies can influence the active sites.[8] At even smaller length scales, the supramolecular architecture of electrochemical molecular catalysts at the electrode can enable tuning of catalytic activity in confined spaces,[9] with extended framework materials being tailored matrices using a similar approach.[10] As part of a major thrust in our research program in unifying design strategies from molecular, materials, and biological catalysts for sustainable electrosynthesis and photosynthesis,[11] we report here an investigation into the effects of embedding cobalt porphyrin electrocatalysts for HER within a supramolecular porous organic cage.

Based on recent work from our laboratories using porous supramolecular architectures to enhance the electrochemical activity and selectivity of embedded
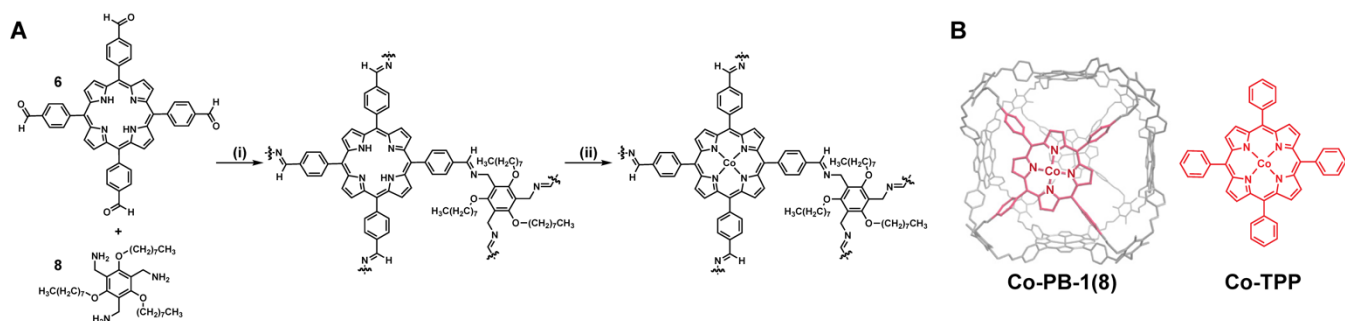
Scheme 1. (A) Synthetic scheme for the preparation of the porous organic cage **Co-PB-1(8)**. (i) Trifluoroacetic acid (cat.), $CHCl_3$, 55 °C, 12 h; (ii) $CoCl_2$, 2,6-lutidine, THF, 70 °C, 12 h. (B) Comparison of a model of the porous organic cage catalyst **Co-PB-1(8)** (left) and its monomeric analog **Co-TPP** (right). Alkyl chains and hydrogen atoms are omitted in the molecular model for clarity.

molecular catalysts for CO_2 reduction reaction (CO_2RR) and O_2 reduction reaction (ORR) processes,[9i, 9j] we reasoned that electrochemical HER would likewise benefit from permanent porosity to more efficiently expose molecular active sites. Indeed, we have focused on exploring porous organic cages as catalyst platforms owing to the ability to rationally design and synthesize supramolecules built from robust covalent linkages that feature permanent porosity.[12] These architectures can provide both chemical and electrochemical stability,[13] effective gas adsorption and separation properties,[14] and promote gas solubility in the liquid phase.[15] We have previously demonstrated the utility of various derivatives of the porphyrin box platform as synthetic ion channels,[16] building blocks for metal-organic frameworks,[17] materials for photoinduced charge separation,[18] and catalysts for electrochemical CO_2 or O_2 reduction.[9i, 9j] These collective efforts establish porphyrin-based porous organic cages as a versatile and modular system where metal and strut substitutions can enable a broad range of applications.[19]

To start, the free-base porphyrin box was first obtained by imine condensation between six tetra(formylphenyl)porphyrins and eight triamine linkers bearing solubilizing C_8H_{17} alkyl groups (Scheme 1). Successful and complete metalation of all six porphyrin moieties in the porphyrin box using $CoCl_2$ to obtain **Co-PB-1(8)** was confirmed using MALDI mass spectrometry and UV/Vis spectroscopy (Figure S1-S2). Gas sorption studies of **Co-PB-1(8)** show permanent porosity and indicate a Brunauer–Emmett–Teller surface area of 519 m^2/g (Figure S3).

In order to utilize the porous organic cage system with an aqueous electrolyte, the supramolecular **Co-PB-1(8)** catalyst was heterogenized by drop-casting onto a glassy carbon working electrode that had first been coated with carbon nanotubes to enhance conductivity. Linear sweep voltammetry (LSV) of this heterogeneous **Co-PB-1(8)** electrode in 1 M pH 7 phosphate buffer shows a large cathodic current enhancement when scanning beyond –0.45 V vs. the reversible hydrogen electrode (RHE), suggesting catalytic proton reduction to

hydrogen (Figure 1). For comparison, we investigated **Co-TPP** as an electrochemical HER catalyst under the same conditions since it is the base molecular unit of the supramolecular **Co-PB-1(8)** architecture. Six molar equivalents of **Co-TPP** were deposited onto the electrode in order to normalize to the number of Co centers in the **Co-PB-1(8)** and **Co-TPP** heterogeneous catalyst films. Accordingly, LSV of this **Co-TPP** electrode shows a much weaker current enhancement with an onset potential for HER shifted slightly more negative compared to **Co-PB-1(8)**. This enhanced catalytic response is observed despite the supramolecular catalyst possessing electron-withdrawing imine groups that may reduce the nucleophilicity of the metal center and thus hinder catalysis, as observed in reported scaling relationships.[20]
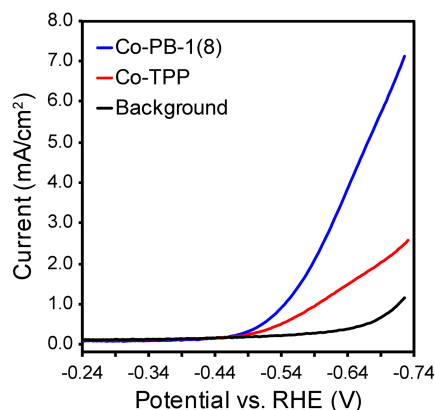

Figure 1. LSV traces for supramolecular porous cage catalyst **Co-PB-1(8)** (blue), its planar molecular analog **Co-TPP** (red), and electrode background (black) obtained in 1 M pH 7 phosphate buffer saturated with N_2.

Notably, Tafel analyses plotted in Figure 2 indicate that the supramolecular **Co-PB-1(8)** catalyst displays improved kinetics compared to the molecular **Co-TPP** congener. **Co-PB-1(8)** exhibits a Tafel slope of 119 mV/dec, which is in agreement with the theory that a single electron transfer to a proton from water is rate-determining.[21] In contrast, **Co-TPP** has a larger Tafel

slope of 170 mV/dec. We attribute this observed difference to inferior electron transfer throughout the **Co-TPP** catalyst film and/or to a lower local concentration of water within the film relative to the **Co-PB-1(8)** system. We speculate that the structural porosity of **Co-PB-1(8)** facilitates the delivery of both electrons and protons to the active Co centers. Indeed, heterogeneous molecular electrochemical catalysts commonly suffer from large Tafel slopes, indicating that the initial electron transfer is greatly hindered and/or that substrate adsorption or product desorption steps are slow.[22] As such, embedding the catalyst into a supramolecular architecture may accelerate this rate-limiting step by facilitating charge, electrolyte, and substrate transport.
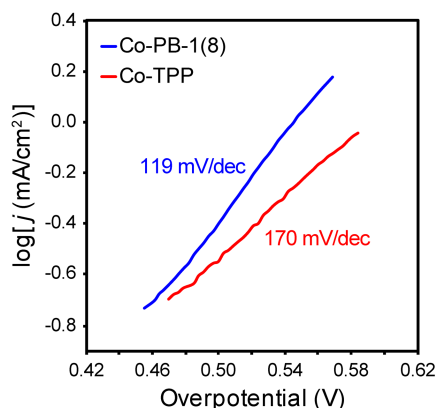

Figure 2. Tafel plot for **Co-PB-1(8)** and **Co-TPP** catalysts. Each catalyst electrode was prepared by depositing 13.8 nmol/cm^2 of Co centers (2.3 nmol/cm^2 of hexa-cobalt **Co-PB-1(8)** and 13.8 nmol/cm^2 of mono-cobalt **Co-TPP**).

We next analyzed the electrochemically active surface areas of the **Co-PB-1(8)** and **Co-TPP** heterogeneous electrodes by measuring the scan rate dependence of the reversible Co^{III}/Co^{II} redox couple observed at 0.76 V vs. RHE for both **Co-PB-1(8)** and **Co-TPP** in 1 M pH 7 phosphate buffer (Figure 3A, B). Both catalyst films were prepared by depositing 13.8 nmol/cm^2

of Co centers (2.3 nmol/cm^2 of **Co-PB-1(8)** and 13.8 nmol/cm^2 of **Co-TPP**). Variation of the cathodic and anodic peak currents with the scan rate was linear for both catalysts, (Figure 3C, D) indicating catalyst immobilization and reversible electron transfer.[23] From these data, we calculated that the **Co-PB-1(8)** electrode had 1.0 ± 0.1 nmol/cm^2 of electrochemically active Co centers compared to 0.2 ± 0.05 nmol/cm^2 in the **Co-TPP** electrode. These values correspond to 1.4% of Co centers being electroactive in the **Co-TPP** film and 7.2% of the Co centers are electroactive in the **Co-PB-1(8)** film, resulting in a 5-fold enhancement in electrochemically active surface area observed for the supramolecular **Co-PB-1(8)** catalyst over the molecular **Co-TPP** control, reinforcing that the permanent porosity derived from supramolecular incorporation of the Co-porphyrin unit can contribute to making the active sites more accessible in the film. Indeed, aggregation of planar macrocyclic catalysts has been shown to greatly hinder electrocatalytic activity.[24]

With these data in hand, we performed controlled potential electrolysis experiments with both **Co-PB-1(8)** and **Co-TPP** heterogeneous electrodes as HER electrocatalysts (13.8 nmol/cm^2 Co deposited for each) in 1 M pH 7 phosphate buffer. A potential of –0.6 V vs. RHE was applied for 24 h, and **Co-PB-1(8)** and **Co-TPP** consumed 114 C and 52 C of charge, respectively (Figure 4). Analyzing the headspace after each experiment by gas chromatography revealed that both catalysts gave *ca.* 100% Faradaic efficiency for HER, with **Co-PB-1(8)** producing more than twice the amount of H$_2$ compared to **Co-TPP** (14.0 mL vs. 6.6 mL of hydrogen). For **Co-PB-1(8)**, these results correspond to a turnover number (TON) of 19,030 [TON per electroactive Co (TON$_{EA}$) = 262,660] and an average turnover frequency (TOF) of 0.22 s^{-1} [TOF per electroactive Co (TOF$_{EA}$) = 3.04 s^{-1}]. For **Co-TPP**, these data give a TON of 8,710 (TON$_{EA}$ = 601,090) and an average TOF of 0.10 s^{-1} (TOF$_{EA}$ = 6.96 s^{-1}). The data support the notion that the supramolecular structure allows for more of the deposited catalytic cobalt
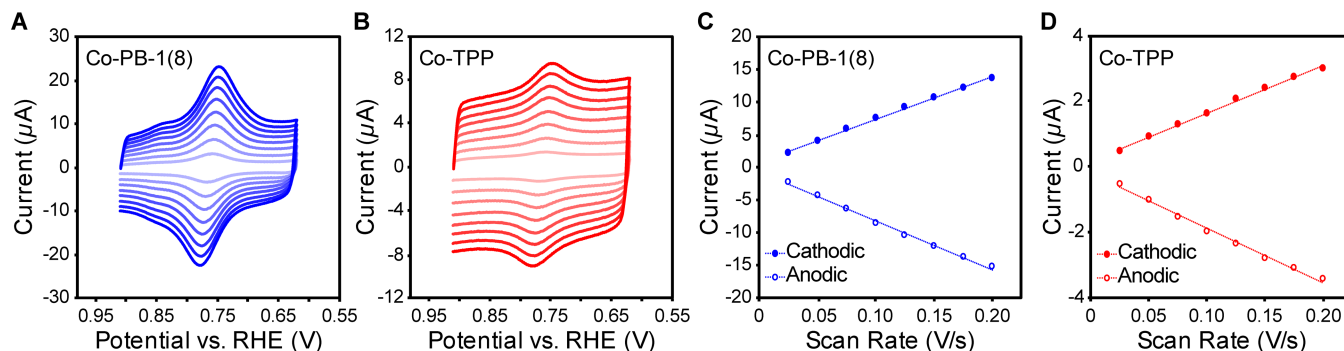

Figure 3. Scan rate dependence from 0.025 to 0.2 V/s of the Co^{III}/Co^{II} redox couple for supramolecular **Co-PB-1(8)** (A) and molecular **Co-TPP** (B) catalyst films in 1 M pH 7 phosphate buffer saturated with N$_2$. Each catalyst electrode was prepared by depositing 13.8 nmol/cm^2 of Co centers (2.3 nmol/cm^2 of **Co-PB-1(8)** and 13.8 nmol/cm^2 of **Co-TPP**). The corresponding cathodic and anodic peak currents are plotted against the scan rate in (C) for **Co-PB-1(8)** and in (D) for **Co-TPP**.

porphyrin moieties to participate in electrochemical HER. Normalizing to the number of electroactive Co centers reveals that the monomeric **Co-TPP** catalyst can outperform **Co-PB-1(8)** in terms of TON_{EA} and TOF_{EA}; however, in a practical sense we emphasize the performance of the entire catalyst film owing to the importance of the electrode assembly and the challenges of achieving a high percentage of active metal centers when heterogenized. Recently, various catalyst immobilization strategies or additives have shown how influential these can be to the electrocatalyst activity,[25] and supramolecular incorporation to achieve permanent porosity offers a viable strategy to improve catalyst film design. We can also attribute this slight difference in the intrinsic catalytic activity by the presence of electron-withdrawing imine groups present in the **Co-PB-1(8)** catalyst, which may reduce the nucleophilicity of the metal center compared to **Co-TPP** at the same applied potential. Nevertheless, the supramolecular architecture enables the **Co-PB-1(8)** catalyst to electrochemically generate significantly more hydrogen than the monomeric analogue **Co-TPP**, under identical conditions and at an overpotential of 0.6 V, which compares favorably with canonical molecular HER catalysts under neutral aqueous conditions.[2a, 3f, 3r, 4, 6a]
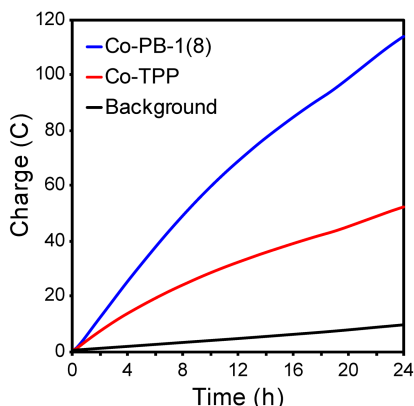

Figure 4. Charge accumulation during long-term controlled potential electrolysis experiments with supramolecular **Co-PB-1(8)** (blue), molecular **Co-TPP** (red), and electrode background (black) at −0.6 V vs. RHE in 1 M pH 7 phosphate buffer saturated with Ar. Each catalyst electrode was prepared by depositing 13.8 nmol/cm^2 of Co centers (2.3 nmol/cm^2 of **Co-PB-1(8)** and 13.8 nmol/cm^2 of **Co-TPP**).

To close, we have established that incorporation of molecular cobalt porphyrin catalysts into supramolecular porous organic cages can enhance their ability to catalyze electrochemical HER from water at neutral pH, with turnover numbers reaching over 19,000 and stability for at least 24 hours. Tafel analysis reveals that electron transfer and/or proton availability are superior for the supramolecular **Co-PB-1(8)** catalyst over its molecular **Co-TPP** counterpart, and the measured electrochemically

active surface areas show that the **Co-PB-1(8)** electrode displays more than 5 times as many electroactive Co centers over **Co-TPP**. These data further establish this supramolecular approach as an effective strategy to enhance catalytic activity of molecular electrocatalysts. We anticipate that the versatility of porous organic cages as a supramolecular platform for developing tunable and efficient catalysts will continue to expand, particularly for reactions that can be effected by sustainable electrical and/or light energy input.

Conflict of Interest
The authors declare no conflict of interest.

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