Supramolecular Enhancement of Electrochemical Nitrate Reduction Catalyzed by Cobalt Porphyrin Organic Cages for Ammonia Electrosynthesis in Water

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We present a supramolecular strategy for electrochemical nitrate reduction by embedding two-dimensional (2D) molecular cobalt porphyrin units into a three-dimensional (3D) porous box architecture. By augmenting porosity and electrochemically active sites as well as facilitating catalyst-substrate interactions, the resulting supramolecular electrocatalyst platform enables selective nitrate reduction to ammonia in water with greater than 90% Faradaic efficiency and turnover numbers exceeding 200,000, representing a 15-fold increase in activity for ammonia electrosynthesis and higher catalytic stability for the 3D structure over its 2D counterpart.
Abstract: The electrochemical nitrate (NO$_3^-$) reduction reaction (NO$_3^-$RR) to ammonia (NH$_3$) represents a sustainable approach for denitrification to balance global nitrogen cycles and an alternative to traditional thermal Haber-Bosch processes. Here, we present a supramolecular strategy for promoting NH$_3$ production in water from NO$_3$RR by integrating two-dimensional (2D) molecular cobalt porphyrin (CoTPP) units into a three-dimensional (3D) porous organic cage architecture. The porphyrin box CoPB-C8 enhances electrochemical active site exposure, facilitates substrate-catalyst interactions, and improves catalyst stability, leading to turnover numbers and frequencies for NH$_3$ production exceeding 200,000 and 56 s$^{-1}$, respectively. These values represent a 15-fold increase in NO$_3$RR activity and 200-mV improvement in overpotential for the 3D CoPB-C8 box structure compared to its 2D CoTPP counterpart. Synthetic tuning of peripheral alkyl substituents highlights the importance of supramolecular porosity and cavity size on electrochemical NO$_3$RR activity. These findings establish the incorporation of 2D molecular units into 3D confined space microenvironments as an effective supramolecular design strategy for enhancing electrocatalysis.

Introduction
Denitrification, a microbially-facilitated process that reduces nitrate (NO$_3^-$) and nitrite (NO$_2^-$) to dinitrogen (N$_2$), plays a pivotal role in balancing the global nitrogen cycle.$^{[1]}$ Rising NO$_3^-$ levels in soil and water, largely triggered by anthropogenic activities, continue to induce serious environmental and health issues by disrupting endogenous nitrogen stores.$^{[2]}$ Indeed, reactive nitrogen (N$_r$) generation has increased from ca. 30 Tg N yr$^{-1}$ in 1968 to 226 Tg N yr$^{-1}$ in 2020, and continues to climb.$^{[3]}$ Excess N$_r$ in the environment, particularly NO$_3^-$, has contributed to hydrosphere deterioration,$^{[4]}$ ozone depletion,$^{[5]}$ and damage to the human endocrine system.$^{[6]}$ As such, developing eco-friendly processes for artificial denitrification and remediation of N$_r$ pollution are highly needed. While physical NO$_3^-$ removal technologies, including ion exchange,$^{[7]}$ reverse osmosis,$^{[8]}$ and electrodialysis,$^{[9]}$ are effective for wastewater purification, the resulting highly concentrated NO$_3^-$ solutions require further treatment.$^{[10]}$
In this context, the electrochemical nitrate reduction reaction (NO₃RR) is a potentially attractive approach to nitrogen cycle remediation as it can be powered by sustainable energy sources to form more environmentally benign and/or value-added nitrogen-based chemical products. Moreover, when ammonia is the product of NO₃RR, it offers an alternative route to this important industrial material and carbon-free fuel compared to the traditional thermal Haber-Bosch process. However, because the reduction of NO₃⁻ to NH₃ involves the coupled transfer of multiple electron and proton equivalents, NO₃RR selectivity is a significant challenge as various products are accessible (e.g., NO₂⁻, NO, N₂O, N₂, NH₂OH). Against this background, we sought to contribute to the development of molecular electrocatalysts for NO₃RR, which are far less studied relative to heterogeneous materials systems, but offer untapped potential to incorporate molecular design elements to facilitate substrate-catalyst interaction and stabilize downstream reduction intermediates.

Along these lines, integrating molecular catalysts into discrete porous supramolecular architectures, such as organic cages, represents an effective strategy to combine molecularly structural tailorability with material porosity and stability and offers potential to bridge the gap between homogeneous and heterogenous catalysis; this approach has gained increasing attention in electrocatalysis design. The resulting supramolecular electrocatalyst retains the intrinsic reactivities of the molecular subunits, but augments their properties by embedding them within a confined space microenvironment with size-tunable cavities. As part of a larger program in our laboratory in hybrid bioinorganic catalysis, we have leveraged individual facets of site isolation or increased surface area for achieving electrochemical
oxygen reduction reaction (ORR),[17] carbon dioxide reduction reaction (CO₂RR),[18] and hydrogen evolution reaction (HER).[19] Inspired by supramolecular systems for NO₃⁻ recognition[20] and transport[21] and noting that porphyrin box organic cages[22] are capable of serving as synthetic ion channels to transport nitrate ions across lipid bilayers,[23] we sought to exploit these dual features of supramolecular porosity and intrinsic NO₃⁻ affinity for electrochemical NO₃RR. We now report that integrating two-dimensional (2D) molecular cobalt porphyrin (CoTPP) catalyst units into a three-dimensional (3D) porous organic cage structure (CoPB-C8) markedly improves its activity and stability for electrochemical NO₃RR (Scheme 1A).[16a] This supramolecular catalyst promotes efficient NO₃RR in water with high selectivity for ammonia production (>90% Faradaic efficiency), achieving total turnover number (TON) and turnover frequency (TOF) values that exceed 200,000 (33,858 per [Co]) and 56 s⁻¹ (9.4 s⁻¹ per [Co]), respectively. These values represent a 15-fold improvement in NH₃ production relative to parent CoTPP, which can be attributed to an increase in electrochemically active cobalt centers and facilitated interactions between the supramolecular CoPB-C8 catalyst and NO₃⁻ substrate. Further synthetic tuning by modifying peripheral alkyl substituents reveals the importance of cage porosity and cavity size on electrochemical NO₃RR.

Figure 1. The supramolecular cobalt porphyrin box organic cage CoPB-C8 shows an increase in electroactive metal sites and superior electrochemical nitrite reduction reaction (NO₂RR) activity relative to the parent cobalt tetraphenylporphyrin (CoTPP) control analog. Scan rate dependence from 0.1 to 0.5 V/s of the Co(III)/Co(II) redox couples for (A) supramolecular CoPB-C8 and (B) molecular CoTPP catalyst electrodes in 0.5 M pH 7.3 aqueous Na₂SO₄ solution under an Ar atmosphere. Each catalyst electrode was prepared by depositing 30 nmol/cm² Co (5.0 nmol/cm² of CoPB-C8 and 30.0 nmol/cm² of CoTPP).
CoTPP). Plotting the corresponding cathodic and anodic peak currents against the scan rate indicated 1.4% of Co centers are electroactive in the CoTPP film and 7.2% of the Co centers are electroactive in the CoPB-C8 film. (C) CV traces for CoPB-C8 (red), CoTPP (blue), and electrode background (black) obtained in 0.5 M Na$_2$SO$_4$/0.1 M NaNO$_3$ saturated with Ar. (D) Chemical structure of the zinc porphyrin cage (ZnPB) modified for solubility used for $^1$H-NMR titration experiments. (E) $^1$H NMR titration of a diamagnetic analog of the supramolecular porphyrin catalyst, ZnPB (1 eq.), with varying concentrations of tetrabutylammonium nitrate (TBANO$_3$) (0-40 eq.), revealing a host-guest interaction between the porphyrin box host and nitrate anion guest.

Results and Discussion

Supramolecular Integration of Molecular Cobalt Porphyrin Units Increases Electroactive Metal Centers and Responses to Nitrate

To build a three-dimensional (3D) porous organic cage from two-dimensional (2D) porphyrin building blocks, the free-base porphyrin box (PB-C8) was first self-assembled from six tetraformylphenylporphyrin units and eight tri-amine linkers (Scheme 1B). Metalation of the six porphyrin subunits in PB-C8 with CoCl$_2$ yields the desired cobalt porphyrin box (CoPB-C8) as confirmed by MALDI mass spectrometry and UV/Vis spectroscopy (Figure S2 and S26). A monomeric cobalt tetraphenylporphyrin (CoTPP) was used as a control compound to evaluate the effects of the supramolecular architecture. To assess electrochemical NO$_3$RR under aqueous conditions, both catalysts were mixed with multi-walled carbon nanotubes (MWNTs) and further deposited onto a glassy carbon electrode. These working electrodes contain a catalyst loading of 5 nmol/cm$^2$ of CoPB-C8 or 30 nmol/cm$^2$ of CoTPP, which normalizes the concentration of cobalt atoms in both electrodes to 30 nmol/cm$^2$. The CV measurements of both electrodes in 0.5 M pH 7.3 sodium sulfate (Na$_2$SO$_4$) electrolyte showed a clear Co$^{II}$/Co$^{III}$ redox wave under argon (Ar), which confirms the successful immobilization of catalysts and indicates that the intrinsic electronic properties of molecular porphyrin subunits in the supramolecular structure are not perturbed (Figure 1A and 1B). The slight positive shift of the Co$^{III}$/Co$^{II}$ redox couple observed for CoPB-C8 ($E_{1/2} = -0.34$ V vs. saturated calomel electrode, SCE) relative to that of CoTPP ($E_{1/2} = -0.39$ V vs. SCE) is likely to arise from the electron-withdrawing effect of the imine linkages in the porphyrin box. Plotting the cathodic and anodic peak currents of the Co$^{III}$/Co$^{II}$ redox couple versus the scan rate gave linear correlations for both catalysts (Figure S1), enabling us to calculate the electrochemically active Co centers (EA$_{Co}$) for each compound. The calculated EA$_{Co}$ concentration normalized per metal center was 2.16 ± 0.17 nmol/cm$^2$ for the CoPB-C8 electrode and 0.44 ± 0.05 nmol/cm$^2$ for CoTPP electrode, corresponding to a 5-fold increase in electrochemically active sites upon embedding the 2D Co porphyrin unit within a 3D porous supramolecular structure. Upon titration with sodium nitrate (NaNO$_3$) (Figure S2A and S2B), a much larger catalytic current was observed for CoPB-C8 over CoTPP electrode (Figure
indicating superior NO₃RR activity for CoPB-C8. As a control experiment, the catalyst-free glassy carbon electrode shows negligible NO₃RR activity, confirming that the catalytic currents indeed arise from the cobalt compounds (Figure S2C).

We hypothesized that compared to gaseous CO₂ and O₂ substrates, studies of potential substrate-catalyst interactions within supramolecular electrocatalyst systems would be more feasible with solution NO₃⁻ via spectroscopic techniques such as nuclear magnetic resonance (NMR) spectroscopy. Indeed, we were able to observe direct interactions between the supramolecular catalyst platform and NO₃⁻ substrate by ¹H-NMR spectroscopy titration experiments (Figure S3). The addition of tetrabutylammonium nitrate (TBANO₃) to a diamagnetic and soluble zinc porphyrin box congener (Figure 1D) in CD₃CN solvent led to apparent upfield shifts of protons on the porphyrinic phenyl rings, whereas no shift was observed for the imine protons (a) or the pyrrolic protons (b) (Figure 1E). Interestingly, only the protons at the ortho-position (c) of the imine substituent shifted while the chemical shift of protons at the meta-position (d) remained unchanged, which indicates a possible anion-π interaction of the negative charged NO₃⁻ and partially positive charged porphyrinic phenyl rings induced by the adjacent electron-withdrawing imine group. We reasoned that the interaction between the supramolecular cage and NO₃⁻ substrate could potentially facilitate mass transport and thus enhance catalytic performance.

Figure 2. Supramolecular cobalt porphyrin box organic cage shows superior electrochemical nitrate reduction (NO₃RR) activity relative to a parent cobalt tetraphenylporphyrin control analog. (A) Faradaic efficiency (FE) for electrochemical nitrate reduction to ammonia, plotted by NH₃ production, catalyzed by CoPB-C8 (red) and CoTPP (blue) over a range of applied

1C)
potentials after 1 h electrolysis. (B) NH₃ yield rate for **CoPB-C8** (red), and **CoTPP** (blue). (C) NH₃ production during 4 h electrolysis at -1.34 V vs. SCE for **CoPB-C8** (red), and **CoTPP** (blue). (D) Comparison of turnover number (TON) values per Co over a range of applied potentials after 1 h electrolysis. (E) NH₃ production and TON for various amounts of **CoPB-C8** loading at -1.54 V vs. SCE. (F) ¹H NMR spectra showing direct detection of NH₃ product with ¹⁵N labeling of substrate for electrolysis runs, after three independent nitrate reduction tests at -1.44 V vs SCE, 0.5 M Na₂SO₄/0.1 M NaNO₃, 0.5 M Na₂SO₄/0.1 M NaNO₃, and 0.5 M Na₂SO₄. Maleic acid (C₄H₂O₄) was added as an internal standard.

**Supramolecular Cobalt Porphyrin Box Catalyst Shows Enhanced Reactivity and Stability Over Parent Porphyrin for Electrochemical NO₃RR With Ammonia as the Major Product**

We next performed controlled potential electrolysis (CPE) experiments with product detection in 0.5 M Na₂SO₄ with added 0.1 M NaNO₃ under an Ar atmosphere. Under these conditions, both **CoPB-C8** and **CoTPP** selectively produced NH₃ with Faradaic efficiencies (FE) reaching greater than 90% over a range of applied potentials (-1.04 to -1.54 V vs. SCE) (Figure 2A). Importantly, **CoPB-C8** showed superior reactivity for NH₃ production, which starts to generate NH₃ at an onset potential of -0.94 V vs. SCE with an NH₃ yield rate of 16.7 μg h⁻¹ (Figure 2B), while **CoTPP** required a 200 mV more negative applied potential (-1.14 V vs. SCE) to achieve a similar NH₃ production rate (14.2 μg h⁻¹). These results are in line with the CV data (Figure 1C) and establish a supramolecular enhancement for electrochemical NO₃RR. Along the applied potentials, **CoPB-C8** showed superior NH₃ partial current density than **CoTPP** (Figure S6), of which the largest difference in catalytic activity for the two compounds was observed at -1.14 V vs. SCE with a 15-fold increase in NH₃ yield rate for the **CoPB-C8** electrode (221.5 μg h⁻¹) over the **CoTPP** electrode (14.2 μg h⁻¹), thus demonstrating the advantages of integrating a molecular electrocatalyst into a supramolecular matrix. After electrolysis at -1.54 V vs. SCE for 1 h, **CoPB-C8** produced 2,729 μg of NH₃ with a turnover number (TON) per cobalt center of 5,343 (Figure 2D). Further optimization of catalyst loading showed that the concentration of **CoPB-C8** can be lowered to 0.5 nmol/cm² while still maintaining good electrochemical NO₃RR activity, resulting in TON values reaching 208,998 (TON = 34,833 per Co) after 1 h, corresponding to a turnover frequency (TOF) of 56 s⁻¹ (TOF = 9.4 s⁻¹ per Co) (Figure 2E), rendering **CoPB-C8** a highly efficient electrochemical NO₃RR catalyst under aqueous conditions (Table S2).

Moreover, embedding the molecular cobalt porphyrin unit into a supramolecular porous cage increases catalyst stability. Stable NH₃ production was observed for **CoPB-C8** over longer-term CPEs at -1.34 V vs. SCE (Figure 2C), where this catalyst kept producing NH₃ at a relatively constant rate of 1,358 μg/h to produce a total of 5,432 μg of NH₃ during the 4-h electrolysis, while maintaining a high FE of 95%. In contrast, **CoTPP** loses significant activity after 1.5 h with the NH₃ yield nearing a plateau, resulting in
only 825 μg of NH₃ being produced after 4 h with a lower FE of 78% (Figures S7 and S8). We speculate that this improved stability likely arises from the isolated cobalt site in the PB architecture, which can prevent intermolecular decomposition pathways.\[^{17a, 30}\] Next, we used \(^1\)H-NMR to validate the generation of NH₃ by electrochemical NO₃RR catalysis, including with \(^{15}\)N-labeled substrate. Indeed, a set of three symmetric peaks with a spacing of 51 Hz corresponding to \(^{14}\)NH₄⁺ were observed after electrolysis at -1.44 V vs. SCE in NaNO₃ electrolyte (Figure 2F). Moreover, a doublet peak \((J_{N-H} = 72 \text{ Hz})\) attributed to \(^{15}\)NH₄⁺ was detected when using isotopic \(^{15}\)N labeled Na\(^{15}\)NO₃ electrolyte (Figure 2F), thus confirming that NO₃⁻ is indeed the nitrogen source for the observed NH₃ product.

**Nitrite and Hydroxylamine Are Competent Intermediates in Ammonia Electrosynthesis Catalyzed by the Supramolecular Cobalt Porphyrin Box**

Nitrite (NO₂⁻), the two-electron reduction product of NO₃⁻, is another major water pollutant that is even more potentially harmful than NO₃⁻.\[^{11d}\] Thus, efficient catalysts for the electrochemical NO₂⁻ reduction reaction (NO₂RR) are desired for developing effective denitrification and chemical production. While several types of molecular catalysts have shown activity towards electrochemical NO₂RR, achieving NH₃ selectivity with a sufficiently high rate of product generation remains challenging.\[^{31}\] Recently, a graphite conjugated diimine macrocyclic cobalt catalyst has been reported to reduce NO₂⁻ selectively to NH₃ with TOF up to 14.4 s\(^{-1}\) when using a glassy carbon electrode.\[^{32}\] We performed electrochemical NO₂RR with the CoPB-C8 catalyst to compare its reactivity with reported systems and determine whether NO₂⁻ could be a competent intermediate during our electrochemical NO₃RR system. Electrochemical NO₂RR was assayed in a similar manner to electrochemical NO₃RR except for the use of NaNO₂ as a substrate (0.1 M). As shown in Figure 3A, a greater catalytic current was observed for the CoPB-C8 electrode compared to the CoTPP electrode by CV (Figure S9), indicating higher electrochemical NO₂RR for the former catalyst. Indeed, CPE experiments revealed that CoPB-C8 showed superior activity to CoTPP for NO₂RR (Figures 3B and S10), with NH₃ detected as the major product (Figure S11). Under optimized conditions, the highest NO₂RR TON of 238932 (39822 per Co center) was obtained with 0.5 nmol/cm² CoPB-C8 loading at -1.44 vs. SCE after 1 h, corresponding to a TOF of 66.6 s\(^{-1}\) (11.1 s\(^{-1}\) per [Co]) (Figure S12). These data establish that CoPB-C8 is an efficient catalyst for electrochemical NO₂⁻ reduction, comparable to the high-performing NO₂RR systems reported in the literature.\[^{33}\] The magnitude of the observed activity enhancement for CoPB-C8 over CoTPP is smaller for NO₂RR than for NO₃RR. For example, at the applied potential of -1.14 V vs. SCE, CoPB-C8 exhibited a ca. 2.6-fold increase in NH₃ yield rate over CoTPP for NO₂RR, relative to the 15-fold enhancement for NO₃RR, thus demonstrating
that the porous supramolecular structure of CoPB-C8 more strongly facilitates the rate-determining step of nitrate to nitrite reduction in the electrochemical NO₃RR.

Figure 3. Supramolecular cobalt porphyrin box organic cage shows superior electrochemical nitrite reduction activity relative to a cobalt tetraphenylporphyrin control analog. (A) CV traces for CoPB-C8 (red), CoTPP (blue), and electrode background (black) obtained in 0.5 M Na₂SO₄/0.1 M NaNO₂ saturated with Ar. (B) NH₃ yield rate for CoPB-C8 (red), and CoTPP (blue).

Finally, hydroxylamine (NH₂OH) has been proposed as another key intermediate in both electrochemical NO₃RR and NO₂RR but often requires the use of a special metal electrode, such as Hg or Cu, to ultimately form NH₃.[11c] For our CoPB-C8 electrode, a CPE experiment in 0.5 M Na₂SO₄/0.1 M NH₂OH electrolyte with potential holding at -1.34 V vs. SCE exhibited >99% FE for NH₃ production, confirming that NH₂OH can also behave as a substrate for electrocatalytic NH₃ generation in our platform (Figure S13). The collective results show that the supramolecular porphyrin box catalyst platform is capable of sequential electrochemical reductions to convert NO₃⁻ to NH₃, but under catalytic conditions does not release partially reduced NO₂⁻ or NH₂OH intermediates. These findings highlight the ability of this supramolecular architecture to funnel intermediates to desirable product pathways.

**Synthetic Tuning of Peripheral Alkyl Substituents on the Supramolecular Box Structure Highlight the Importance of Box Porosity and Cavity Size on Ammonia Electrosynthesis by NO₃RR**
Figure 4. The effect of peripheral alkyl substituents on the eNO$_3$RR activity of CoPBs. NH$_3$ yield rate comparison for CoPB-C4 (green), CoPB-C6 (purple), CoPB-C8 (red), CoPB-C13' (orange), and CoTPP (blue).

With these results in hand, we sought to further optimize the catalytic performance of this supramolecular electrocatalyst platform for NO$_3$RR by tuning peripheral structure. We have achieved gains in CO$_2$RR by appending remote positive charges into supramolecular scaffolds.[28] In this instance, we hypothesized that tuning the lengths of peripheral alkyl chains on these CoPB catalysts with a conserved supramolecular core would show measurable effects on electrochemical NO$_3$RR activity and provide direct structure-activity relationships to assess contributions of supramolecular porosity. To this end, we synthesized CoPB-C4 bearing shorter butyl (-C$_4$H$_9$) substituents and CoPB-C13' bearing longer 6-(hexyloxy)hexyl (-(CH$_2$)$_6$OC$_6$H$_{13}$) substituents relative to the octyl (-C$_8$H$_{17}$) groups in CoPB-C8. The electrochemical NO$_3$RR activities of these CoPBs are summarized in Figure 4. While CoPB-C4 showed a similar supramolecular enhancement for NH$_3$ production, the porous cage effect on electrochemical NO$_3$RR of CoPB-13' was totally suppressed, resulting in a similar reactivity to the nonporous CoTPP. We suggest that the loss of the supramolecular enhancement for NO$_3$RR in CoPB-13' is likely due to substantial blocking of the cage windows and access to the porous cavity by the longer alkyl chains, with subsequent suppression of nitrate binding and transport. To further assess the effects of alkyl substituent lengths on box porosity and cavity size, we performed molecular dynamics (MD) simulations to obtain the lowest energy conformers of these CoPBs (Figure S14).[17a, 34] We then used a python package, named pywindow,[35] to calculate the average window diameter ($D_{\text{window}}$) and intrinsic void diameter ($D_{\text{void}}$) of this family of CoPBs (Table S1). As expected, the inclusion of longer alkyl chains in the CoPB structures results in decreased $D_{\text{window}}$ values as listed in Table S1. While CoPB-C8 (4.2 Å) still retain comparable $D_{\text{window}}$ to CoPB-C4 (6.0 Å), the $D_{\text{window}}$ of CoPB-C13' decreased to 2.1 Å, which is much smaller than the hydrodynamic radius of nitrate (3.16 Å),[36] thus suppressing NO$_3$RR for this catalyst. It is noteworthy that the calculated $D_{\text{window}}$ for CoPB-C4 (6.0 Å) is close to the window size obtained from the crystal structure of the metal free PB-C4 (6.6 × 8.5 Å),[24] thus demonstrating the reliability of current calculation.
and indicating negligible structure change of PBs after metalation. Interestingly, the calculated $D_{\text{void}}$ values for CoPB-C4 (18.92 Å) and CoPB-C8 (18.71 Å) remained constant, indicating that even the octyl substituent is not long enough to occupy the space inside the cage. However, the calculated $D_{\text{void}}$ value decreased significantly for CoPB-C13' (11.85 Å), presumably due to its much longer alkyl substituents. Taken together, these findings reveal the importance of box porosity and cavity size on electrochemical NO$_3$RR, which will be helpful in establishing design rules for broader exploration of supramolecular electrocatalysis.

**Concluding Remarks**

To close, we have presented a supramolecular strategy to enhance electrochemical NO$_3$RR catalysis through integrating a monomeric two-dimensional (2D) cobalt porphyrin electrocatalyst into a three-dimensional (3D) porphyrin-based porous organic cage architecture. The resulting supramolecular electrocatalyst, CoPB-C8, is capable of increasing active site exposure and electrochemically active sites, as well as facilitating catalyst-substrate interactions. These combined features enable selective NO$_3$RR to NH$_3$ product in water with greater than 90% Faradaic efficiency and turnover numbers exceeding 200,000, representing a 15-fold increase in activity, a 200-mV improvement in overpotential, and higher catalytic stability for ammonia electrosynthesis catalyzed by the 3D structure over its 2D counterpart. Moreover, this 3D box platform is competent for selective nitrate-to-ammonia conversion via sequential multi-electron reduction processes, without releasing nitrite or hydroxylamine intermediates. Finally, synthetic tuning of peripheral alkyl substituents reveal the importance of box porosity and cavity size on electrochemical NO$_3$RR activity. This work provides a starting point for using bioinspired, supramolecular design principles for developing catalysts for electrochemical reduction processes related to the nitrogen cycle and a broader range of small-molecule substrates, particularly oxyanions that are important in water remediation and energy storage.

**Acknowledgements**

This work was supported by the U.S. Department of Energy, Office of Science, Office of Advanced Scientific Computing, Office of Basic Energy Sciences, via the Division of Chemical Sciences, Geosciences, and Bioscience of the U.S. Department of Energy at Lawrence Berkeley National Laboratory (Grant No. DE-AC02-05CH11231 to C.J.C.). L.A. thanks SIOC/Pharmaron for a postdoctoral fellowship. M.R.N. acknowledges NSERC (Canada) for a postdoctoral fellowship. P.T.S. and P.D.T. acknowledge the NSF for Graduate Research Fellowships. We thank Dr. Hasan Celik in the UC Berkeley College of Chemistry NMR facility (CoC-NMR) for technical assistance and Prof. Kimoon Kim
(POSTECH) for helpful discussions. Instruments in the CoC-NMR are supported in part by NIH (S10OD024998). We also thank the College of Chemistry’s Molecular Graphics and Computation Facility, which is supported by the NIH (S10OD023532), for computational resources.

**Keywords:** electrocatalysis • supramolecular chemistry • nitrate reduction • porous organic cage • ammonia electrosynthesis

**References**


