

Artificial Photosynthesis with Next Generation Molecular Catalysts

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The objective of this project was to develop a new class of molecular photocatalysts for CO₂ reduction that will enable breakthrough advances in artificial photosynthesis. A major limitation of existing photocatalytic assemblies is that only a small fraction of absorbed photons are converted into fuel due to inefficiencies in electron transport between the different system components. In the case of molecular catalysts for reduction of CO₂, highly reducing electron equivalents are required for catalysis. As a result, the electron flux between the photosensitizer and CO₂ reduction catalyst is heavily biased towards the photosensitizer. One method to direct the electron flux towards productive photocatalysis is to design molecular catalysts for CO₂ reduction that operate at more favorable potentials than existing catalysts. The conventional approach is to tune the potential of the catalyst through selection of the supporting ligands, however, this only leads to incremental improvements due to the existence of an unfavorable scaling relationship between the rate and potential of catalysis. Our hypothesis is that the catalytic rate and potential can be simultaneously enhanced using bimetallic catalysts in which one metal improves the potential of catalysis and the second metal increases the rate of catalysis. During the course of this project, a few studies reported some success in improving photocatalytic CO₂ reduction with heterobimetallic complexes,¹⁻² demonstrating the potential of this approach to catalyst design.

Development of heterobimetallic complexes poses a synthetic challenge for several reasons: i) the ligand must possess two binding pockets that are properly positioned for synergistic interaction of the two metals, and ii) each binding pocket must have a high selectivity for one metal over the other. Several different ligand motifs were targeted that possess an azamacrocyclic for binding a transition metal (Co) and an oxomacrocyclic for binding an alkali or alkaline earth metal (Figure 1). The first ligand, **1**, could be formed on a small-scale (< 10 mg) as confirmed by ¹H NMR spectroscopy and high-resolution mass spectrometry; however, attempts to scale up the synthesis of **1** were unsuccessful due to the instability of several reaction intermediates. Several cobalt complexes were prepared: a dicationic complex (**2**), a neutral complex (**3**), and a known complex with a larger oxomacrocyclic (**4**).³ Attempts to bind a second ion (eg Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺) into the oxomacrocyclic unit of **2-4** were met with limited success. Direct synthesis and isolation of heterobimetallic complexes was hindered by the oily and tacky nature of the compounds, preventing the use of X-ray crystallography to determine the complex structure. Cyclic voltammetry (CV) provided some evidence that **3-4** could bind a second metal, resulting in an approximate 500 mV cathodic shift in the Co(II/I) couple. However, the apparent binding constants were very low, and the excess metal ions in solution appeared to electroplate at potentials near the Co(II/I) couple.

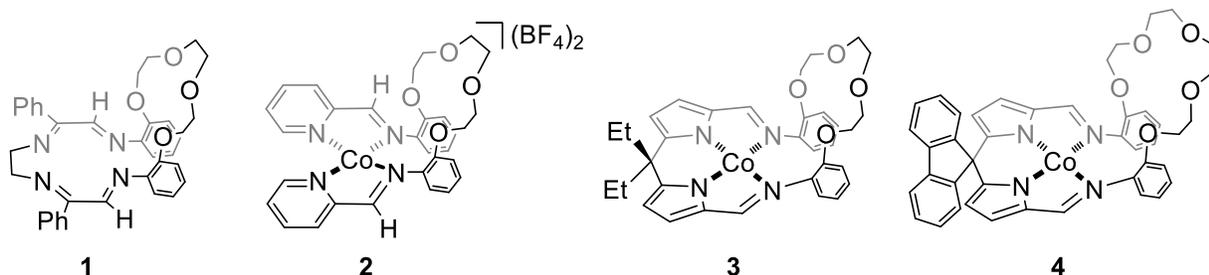


Figure 1. Complexes studied for formation of heterobimetallic complexes.

The dipyrromethane-diimine motif was further explored as a platform for introduction of pendant H-bond donors for improvement of CO₂ binding and reduction. Three complexes were prepared: a parent complex without an H-bond donor (**5**), a complex with pendant OH groups (**6**), and a complex with pendant AcNH groups (**7**), shown in Figure 2. Complex **5** shows a reversible reduction wave at -1.91 V vs Cp₂Fe⁺⁰ that is assigned to the Co(II/I) couple. Support for this assignment comes from control experiments with the analogous Zn complex, which afforded irreversible waves for reduction of the ligand at more negative potentials. Under 1 atm of CO₂, the Co(II/I) couple of **5** remains reversible but shifts positive by 127 mV, indicating the Co(I) state reversibly binds CO₂ with $K_{\text{CO}_2} = 140 \text{ atm}^{-1}$. Complex **6** displays an irreversible Co(II/I) couple, suggesting that intramolecular proton transfer from the pendant OH to Co(I) is rapid and irreversible on the CV timescale. Owing to the decreased acidity of AcNH versus OH, complex **7** displays a reversible Co(II/I) couple at -1.71 V, indicating intramolecular proton transfer is slow on the CV timescale. Under 1 atm of CO₂, the Co(II/I) couple of **7** becomes irreversible and shifts cathodically by 30 mV at a scan rate of 100 mV s⁻¹. Kinetic analysis over a range of scan rates provides a conservative lower limit of $K_{\text{CO}_2} > 280 \text{ atm}^{-1}$ for **7**, indicating that the pendant AcNH groups enhance CO₂ binding relative to the parent complex **5**. Complexes **5** and **7** were also tested for electrocatalytic and photocatalytic CO₂ reduction under a variety of conditions, but in all cases the sole product was observed to be H₂ resulting from competitive proton reduction. *A manuscript describing the preparation and CO₂ binding affinities of these complexes is in preparation.*

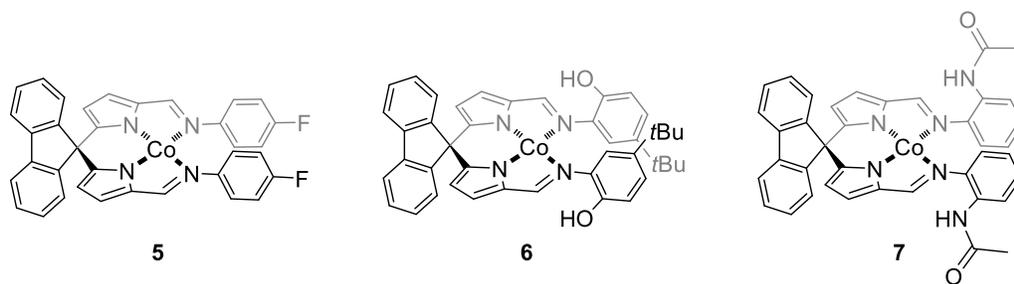


Figure 2. Complexes studied for CO₂ binding and reduction.

During the course of this project, PNNL acquired benchtop XAS/XES instruments (easyXAFS300 and easyXES150), a capability would be very beneficial for studying the electronic structure of the complexes targeted in this project. A study was undertaken to develop the methodology for XANES measurement of solution-phase complexes (cell design, analyte concentration, collection times, etc.). Ni(cyclam)²⁺ was selected as a model complex for methodology development since it is a known CO₂ reduction catalyst,⁴⁻⁵ is easily prepared in large quantities, and the experimental spectra can be compared the spectra of similar complexes.⁶⁻⁷ The solution cell, shown in the bottom left of Figure 3, consisted of a Teflon spacer with two analyte windows, a layer of Kapton film on either side of the spacer, and screw-mounted aluminum plates to hold the cell together. Analyte solution was loaded into the assembled cell through screw-capped ports at the top of the Teflon spacer. XANES spectra were collected in water, nitromethane, and acetonitrile solvents using a concentration of 0.10 M (water, nitromethane) or 0.04 M (acetonitrile). A technical limitation was encountered where organic solvents were observed to slowly leak through the cell seam, however, this did not preclude the acquisition of spectra in these solvents. A pre-edge peak is observed at ~8338 eV in water and nitromethane but not in acetonitrile, indicating Ni(cyclam)²⁺ is four-coordinate in the former solvents and six-coordinate in acetonitrile solvent. Calculations show very good agreement between the experimental spectra and the theoretical spectra obtained from TDDFT-

based⁸ Ni K-edge XANES calculations, indicating that theory will be a valuable tool for the prediction and interpretation of the absorption and emission spectral transitions observed in experimental spectra of new molecular complexes. *A manuscript is in preparation that will describe the experimental and theoretical x-ray absorption and emission spectra of this complex and analyze the influence of the ligand conformation on the electronic structure.*

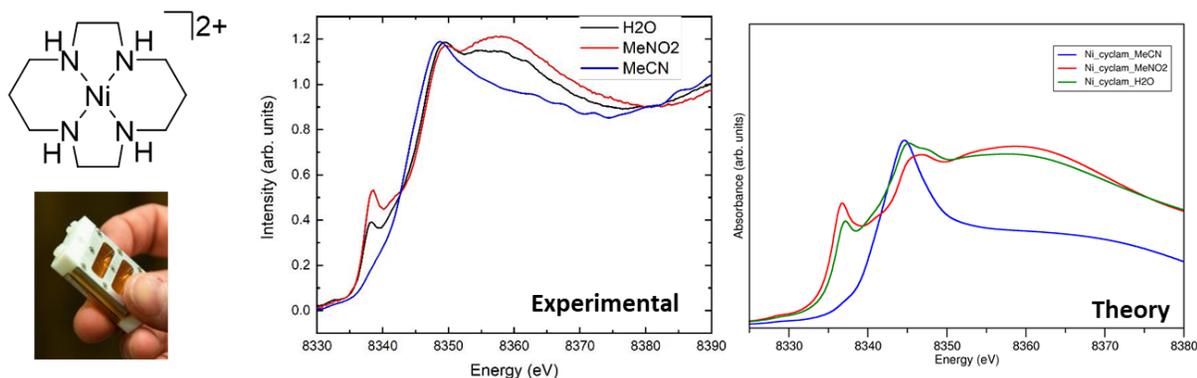


Figure 3. Experimental and theoretical XANES spectra of Ni(cyclam)²⁺ in different solvents using a benchtop XAS instrument.

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