

Abstract

Carbon dioxide (CO₂) can serve as an ideal C1 source for organic reactions due to its abundance, nontoxicity, and potential as a renewable resource. The chemical transformation of CO₂ into value-added products thus represents an attractive and sustainable means, to mitigate global warming caused by anthropogenic CO₂ emission. In this study, we investigate a porous metal-metalloporphyrin framework, MMPF-10, featuring a high density of Cu(II) sites confined in nanoscopic channels, as a heterogeneous Lewis-acid catalyst for CO₂ chemical transformation with aziridine into oxazolidinones. MMPF-10 was built on a custom-designed octatopic porphyrin ligand of tetrakis-3,5-bis[(4-carboxy)phenyl]phenyl porphine (tbcppp) with the in situ generated Cu₂(CO₂)₄ paddlewheel moieties.

Background

CO₂ as a waste gas is among the most prevalent pollutants in our atmosphere. It is produced at an ever increasing rate and has been implicated in major environmental changes. Ongoing research strives to repurpose CO₂ in usable ways as opposed to simply disposing of it using non-environmentally conscious methods. One such repurposing method is to chemically convert CO₂ into common compounds used in industry such as oxazolidinone. This reaction is performed in the presence of a Lewis Acid catalyst to facilitate it. While multiple options of Lewis Acid catalysts exist, a special type called a metal-metalloporphyrin Frameworks (MMPF) are used in this investigation. MMPFs are a class of Metal Organic Frameworks (MOFs) that are composed of metal containing secondary building units (SBUs) and custom designed metalloporphyrin ligands. They are thermally and chemically stable and have a range of uses in the biological and chemical fields.¹

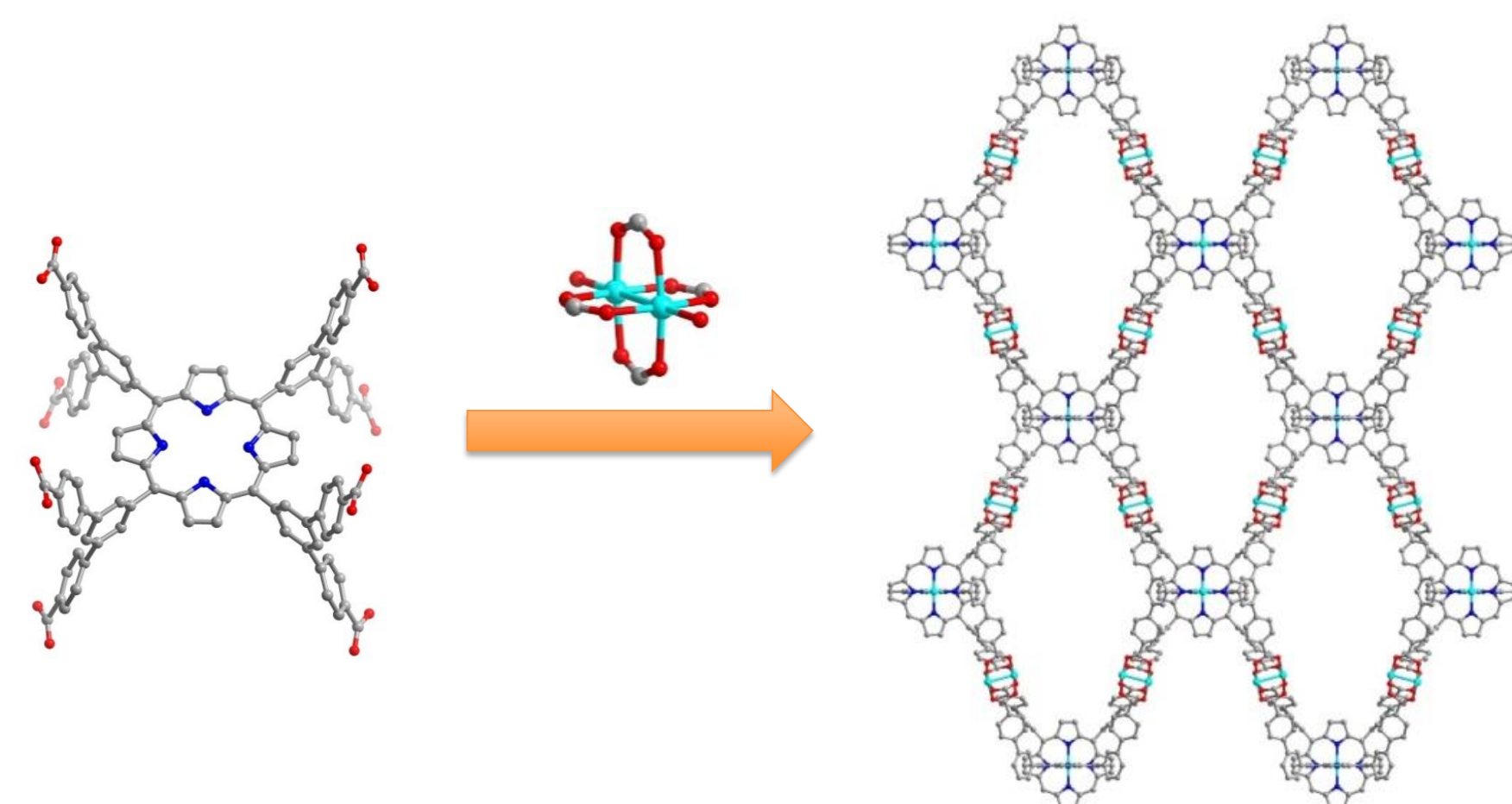


Figure 1: Molecular view of the metalloporphyrin ligand of MMPF-10 (left). Structural view of MMPF-10. Atom Colors: C=Gray, O=Red, N=Blue, Cu=Turquoise.

Objective

To determine to whether the presence of a Lewis Acid catalyst(MMPF-10) plays an appreciable role in the coupling reaction between CO₂ and 2-phenyl-1-propylaziridine.

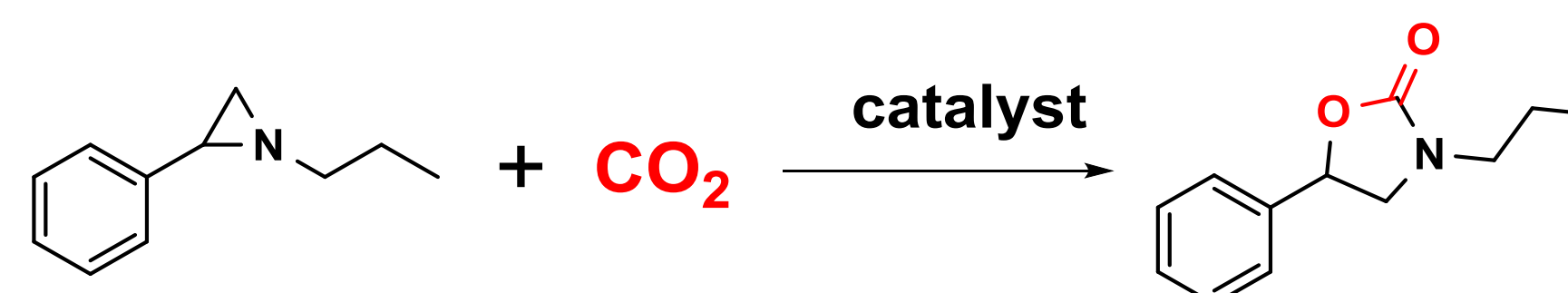


Figure 2: Cycloaddition of CO₂ with 2-phenyl-1-propylaziridine to form 2-oxazolidinone.

Approach

Cycloaddition of CO₂ into oxazolidinone has been previously achieved using multiple methods. The result of these reactions is a homogenous solution in which the catalyst is difficult to separate from the product. In this investigation, we strive to produce a heterogeneous oxazolidinone mixture for ease of separation.

Characterization of MMPF-10

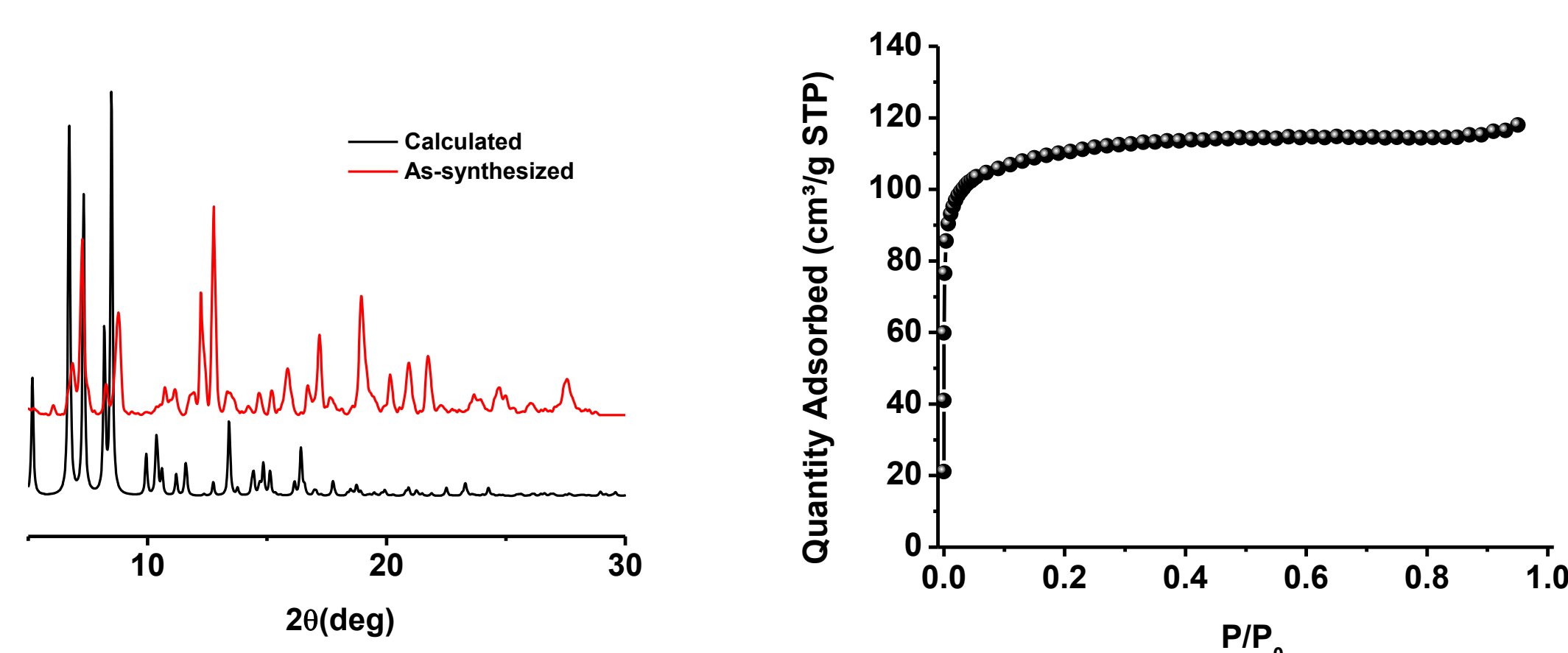


Figure 3: Powder X-ray diffraction patterns of MMPF-10 (left); N₂ adsorption isotherm of MMPF-10 at 77 K (right).

Synthetic procedure of 2-phenyl-1-propylaziridine

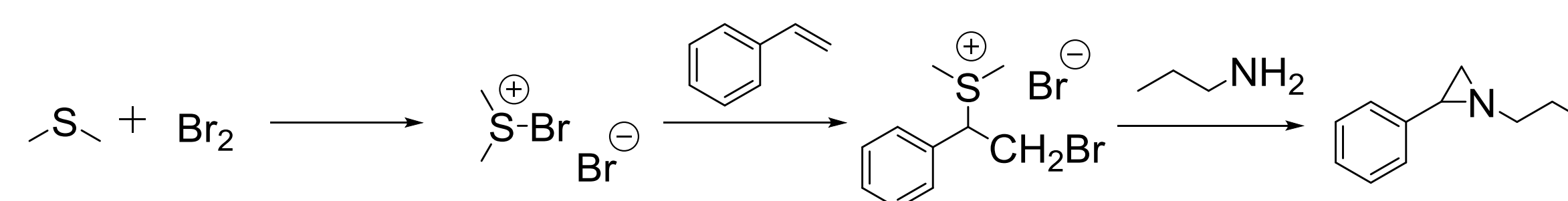


Figure 4: Schematic representation of synthetic details of 2-phenyl-1-propylaziridine for CO₂ cycloaddition reaction.

Table 1: CO₂ cycloaddition reactions with aziridine under different catalytic reaction conditions.

Entry ^a	Substrate	Lewis Acid	Co-catalyst	Yield (%)
1	2-phenyl-1-propylaziridine	NA	NA	~0
2 ^b	2-phenyl-1-propylaziridine	Cu(NO ₃) ₂	NA	4
3 ^c	2-phenyl-1-propylaziridine	Cu(NO ₃) ₂	TBAB	37.5
4 ^d	2-phenyl-1-propylaziridine	MMPF-10	NA	3
5 ^e	2-phenyl-1-propylaziridine	MMPF-10	TBAB	33.0

^aAll of the reactions were carried out using 1mmol substrate of 2-phenyl-1-propylaziridine in presence of 0.5 mL isopropanol solvent under 2.5 MPa CO₂ at 50 °C for 2 hrs. The reaction yield was quantified by NMR spectroscopy; ^bCopper nitrate (0.0125 mmol) was used as homogeneous Lewis acid; ^cMMPF-10 (0.0125 mmol) was used as heterogeneous Lewis acid; ^dCopper nitrate (0.0125 mmol) and tetra-*n*-butylammonium bromide (TBAB, 0.0125 mmol) were used as catalysts; ^eMMPF-10 (0.0125 mmol) and TBAB (0.0125 mmol) were used as catalysts.

Conclusions

- As illustrated in Figure 3, the powder X-ray diffraction patterns of MMPF-10 are in agreement with the calculated ones, which verifies the phase purity of MMPF-10. The nitrogen (N₂) adsorption isotherm at 77 K demonstrates an uptake capacity of ~110 cm³/g at 1 atm of pressure, which belongs to a typical type I adsorption isotherm of microporous materials. It also reveals that MMPF-10 owns a BET surface area of 420 m²/g, along with a Langmuir surface area of 480 m²/g.
- The substrate of 2-phenyl-1-propylaziridine can be easily prepared by a three-step synthetic experiment, as shown in Figure 4.
- Different catalytic conditions of CO₂ cycloaddition reaction have been examined carefully by use of a 50 mL high-pressure reaction vessel. TBAB as a co-catalyst plays an very important role in the reaction. MMPF-10 featuring a high-density accessible Cu(II) sites within nanoscopic channels, remains a useful heterogeneous catalyst, which exhibits comparable efficiency to the homogeneous catalyst of copper nitrate.
- Future research attention focuses on how to further improve catalytic efficiency of CO₂ cycloaddition reactions with aziridines.

Referenced Resources

- Gao, W.-Y.; Chrzanowski, M.; Ma, S. *Chem. Soc. Rev.*, 2014, 43, 5841-5866.
- Gao, W.-Y.; Chen, Y.; Niu, Y.; Williams, K.; Cash, L.; Perez, P. J.; Wojtas, L.; Cai, J.; Chen, Y.-S.; Ma, S. *Angew. Chem. Int. Ed.*, 2014, 53, 2615-2619.
- Gao, W.-Y.; Wojtas, L.; Ma, S. *Chem. Commun.*, 2014, 50, 5316-5318.