

Summary of Findings

Reported herein is the work accomplished during the tenure of the Academic Year Undergraduate Research Grant for the project titled "Synthesis and Characterization of Porous Organic Polymers with Tunable Nucleophilicity and Pore Size for CO₂ Sequestration." The project consisted of two main phases: (1) synthesis of building blocks **A** and **B** (Figure 1) for nucleophilic porous organic polymers (POPs), and (2) synthesis and characterization of the nucleophilic POPs **A1**, **B1** and **C1** (Figure 1).

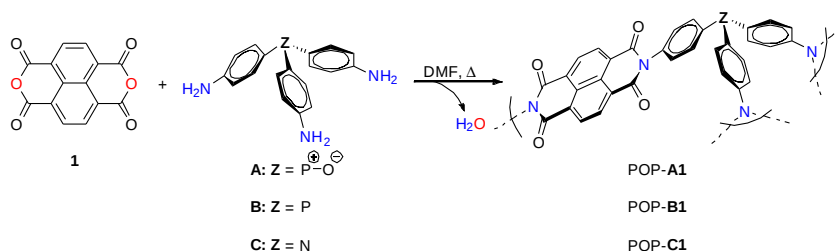
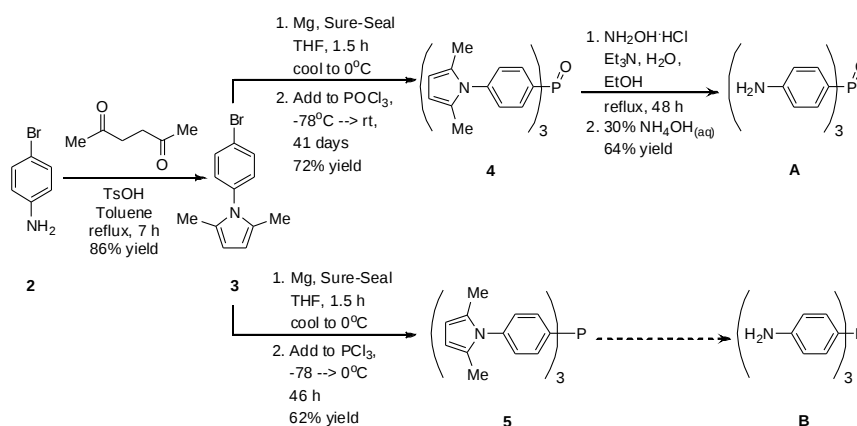


Figure 1. Synthesis of POPs from **1** and building blocks **1** and **A**, **B**, or **C**

Synthesis of building block **A** was carried out as depicted in Scheme 1. Bis-protection of the amine functionality in 4-bromoaniline (**2**) afforded aryl bromide **3**. The latter was subsequently converted to a Grignard reagent, which was added to phosphorus (V) oxychloride to form tertiary phosphine oxide **4**. Removal of the pyrrole protective groups unveiled building block **A** in overall 40 % yield.

A similar route to building block **B** was envisioned. Encouragingly, using phosphorus trichloride instead of phosphorus (V) oxychloride in the second step afforded phosphine **5**, as desired. To our surprise, however, no conversion of **5** was observed during the final de-protection step. Lack of conversion was ascribed to the insolubility of phosphine **5** in the ethanol/water solvent system used in the original protocol. Alternate conditions and reagents are currently being explored, with first trace conversion observed for the reaction system consisting of **5**, *O*-^tbutylhydroxylammonium chloride and triethylamine in tetrahydrofuran.

Scheme 1. Synthesis of building blocks **A** and **B**



With building blocks **A** and **C** in hand (**C** is commercially available), the synthesis of the corresponding nucleophilic POPs was commenced. POPs **A1** and **C1** were prepared

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by heating the corresponding building blocks in *N,N*-dimethylformamide (DMF) at 80°C for 5-6.5 h and then raising the temperature to 133°C for the following 48 h for **A1** and 24 h for **C1**. Filtration and activation afforded the desired POPs in good yield (65 % for POP **A1**, 96 % for POP **C1**).

Structural characterization of the POPs was achieved through solid state nuclear magnetic resonance (ssNMR) and Fourier transform infrared (FT-IR) spectroscopy. The ¹³C ssNMR spectra of both POPs (and ³¹P ssNMR spectrum for POP **A1**) displayed peaks corresponding to their respective building blocks, indicating that these building blocks were incorporated into the POP. Moreover, the observed peak shifts and broadening suggested that the synthesized materials were polymers. In FT-IR spectra of the POPs, the peaks corresponding to the primary amine and anhydride functionalities were replaced by characteristic imide stretches. Hence, the prepared materials were polyimides, as expected.

Our expectation that the adsorption properties of these materials would vary with building block functionality was also validated. POPs **C1**, based on the building block **C** containing an sp²-hybridized nitrogen atom, exhibited adsorption of both N₂ at 77 K and CO₂ at 273 K. Based on adsorption of the former, the specific surface area (SSA) of POP **C1** was calculated to be 304 m²/g, while adsorption of the latter yielded an SSA of 717 m²/g. Moreover, the steep rise of the N₂ adsorption curve of POPs **C1** at low relative pressure followed by a saturation region classified these curves as Type 1B, characteristic of microporous materials. On the other hand, the porosity type (*e.g.* micro-, meso-, etc.) of POP **A1** could not be determined because it adsorbed virtually no N₂ at 77 K (SSA = 6.13 m²/g). Yet, it adsorbed a significant amount of CO₂ (SSA = 458 m²/g). Thus, while both POPs were porous, the data suggests that POP **A1** would be more selective than POP **C1** for adsorption of CO₂ over N₂. Additionally, POP **A1** (as well as **C1**) was demonstrated by thermogravimetric analysis to be stable up to 500°C. Hence, POP **A1** is a promising material for selective capture of CO₂ from power plant emissions, the long term goal of this project.

At present, new batches of POPs **A1** and **C1** are being synthesized to reproduce the results cited above. Also, once building block **B** is synthesized, it will be polymerized with building block **1** to make POP **B1**. It is our hope that ultimately, the materials prepared during this project will result in the development of more energy-efficient CO₂ capture technology.