Porous organic frameworks for energy related applications

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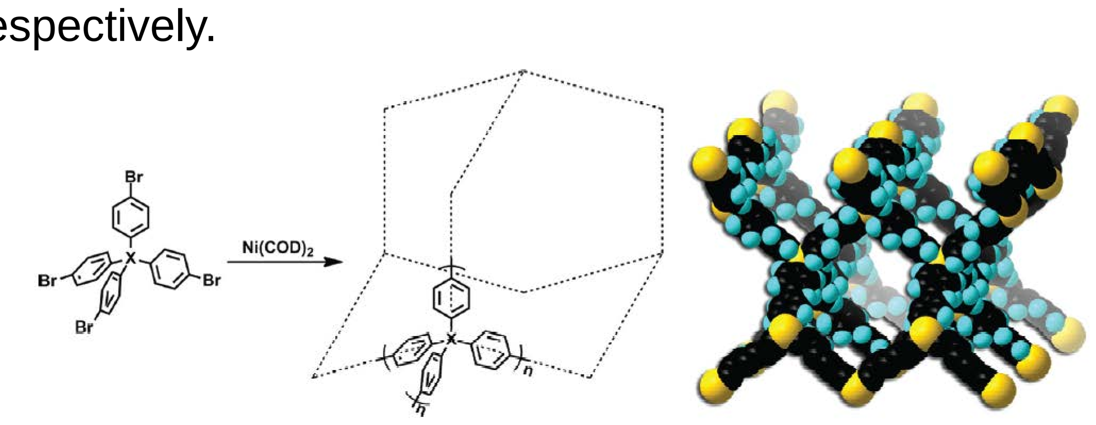
Introduction

Porous materials with high surface area have extensive applications in gas separation, gas storage, catalysis and energy storage. Recently, porous organic frameworks (POFs) emerged as a new microporous material with high stability, high porosity and chemical tailorability. POFs can be easily synthesized from simple starting material by utilizing basic organic coupling reactions. The linkages in POFs are irreversible strong covalent bonds (such as carbon-carbon, carbon-nitrogen or nitrogen-nitrogen bonds), which affords POFs high stability in acid and base environment. In addition, POFs are pure organic materials with no metal elements, thus, they are non-toxic and lighter and less expensive than other chemically synthesized microporous materials such as metal organic frameworks (MOFs). Although POFs are disordered, amorphous material, they possess permanent porosity and high surface area, which can reach more than 6000 m^2/g measured by Brunauer-Emmett-Teller (BET) method. Tunable pore size and functionality of POFs can be achieved by using monomers with specific geometry and functional groups, respectively.



(a) (b)

Figure 1. (a) Synthetic route for POFs with highest BET surface area (PPN-4, 6461 m^2/g). **(b)** The ideal noninterpenetrated diamondoid network of PPN-4 (**Ref. 1**).

Objectives

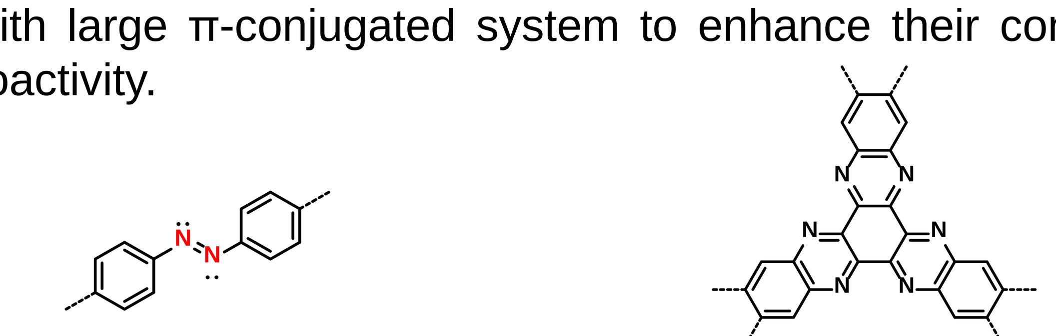
Our goal is to design and synthesize highly porous organic frameworks via (a) incorporating different functional groups and (2) utilizing unique monomer geometry for energy related applications. Two specific objectives are:

- Azo-linked POFs for gas separation

The electron electron pairs in the azo group are believed to have repulsion with totally symmetric molecule such as N_2, while have strong interaction with the partial positively charged carbon in CO_2 (Ref. 2). This thermal-dynamically selective property of azo bond is beneficial for gas separation. Our objective is to synthesize azo-linked POFs with high CO_2/N_2 selectivity.

- Aza-fused π-conjugated POFs for energy storage materials

One major limitation of porous polymer to be used as electrode materials is their poor conductivity in electrochemical process (Ref. 3). Therefore, our objective is to design and synthesize aza-fused porous material with large π-conjugated system to enhance their conductivity and electroactivity.

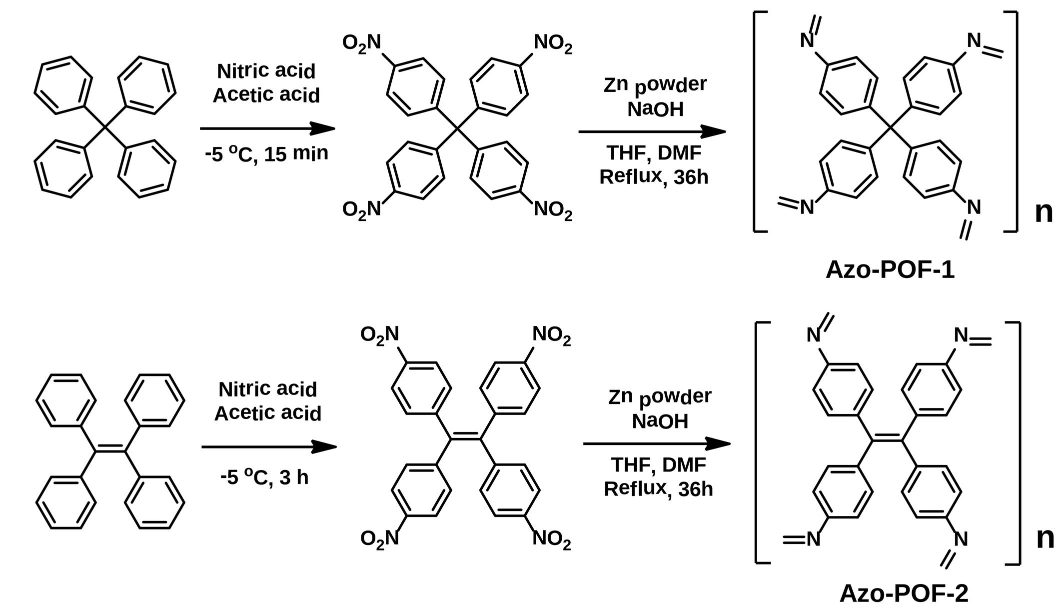


(a) (b)

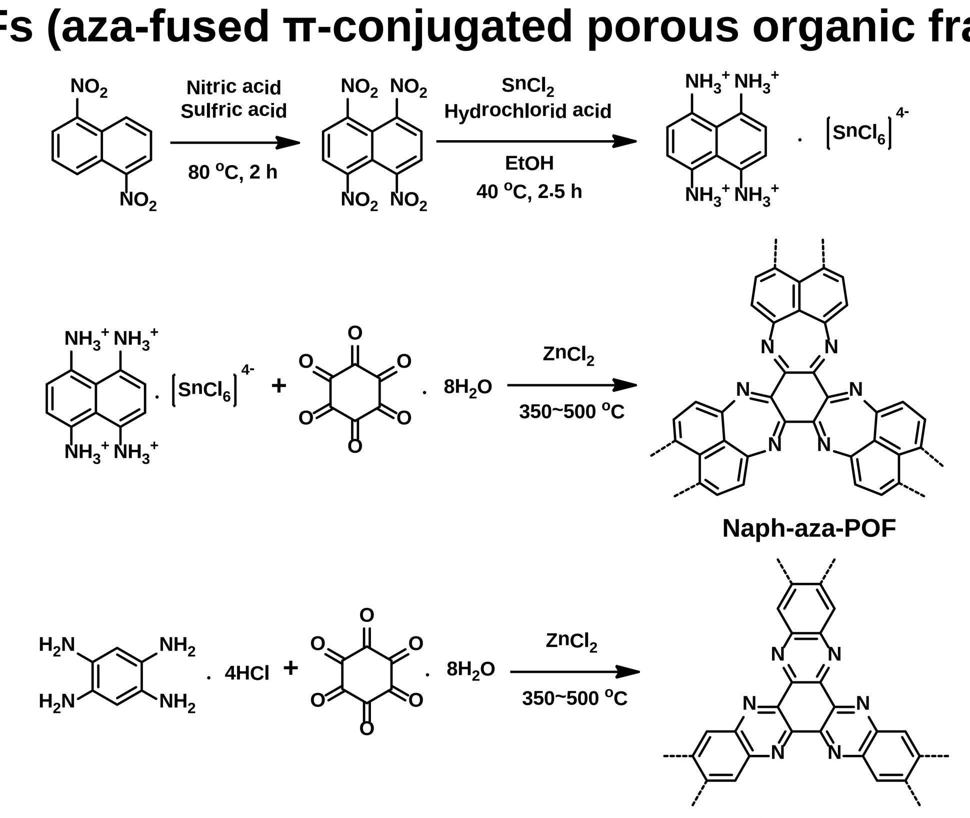
Figure 2. Structures of (a) Azo-linked porous organic frameworks, (b) Aza-fused, π-conjugated porous organic frameworks.

Synthesis of POFs

- **Azo-POFs (azo-linked porous organic frameworks)**



- **Aza-POFs (aza-fused π-conjugated porous organic frameworks)**



Structural Characterization

- **Infrared spectra**

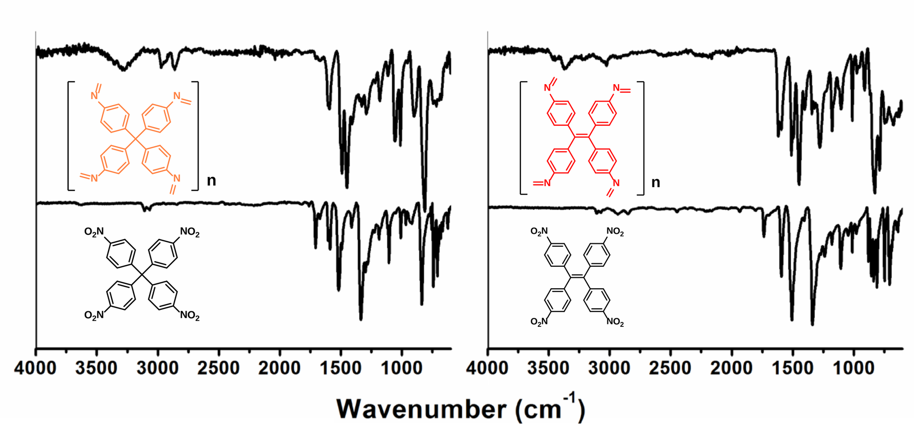


Figure 5. Infrared spectra of azo-POFs and corresponding monomers

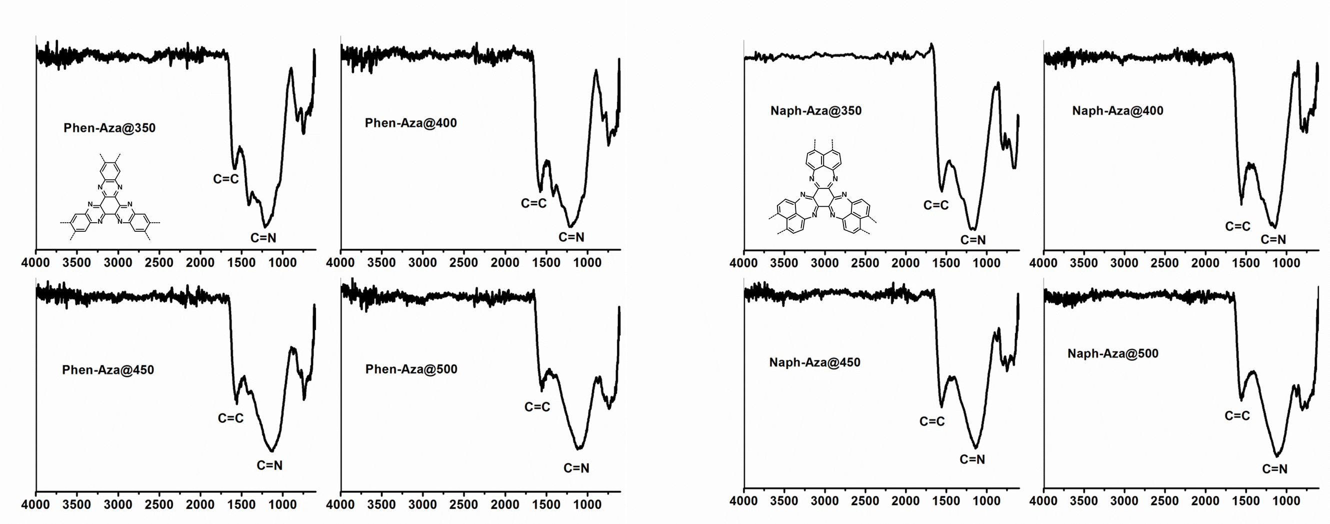
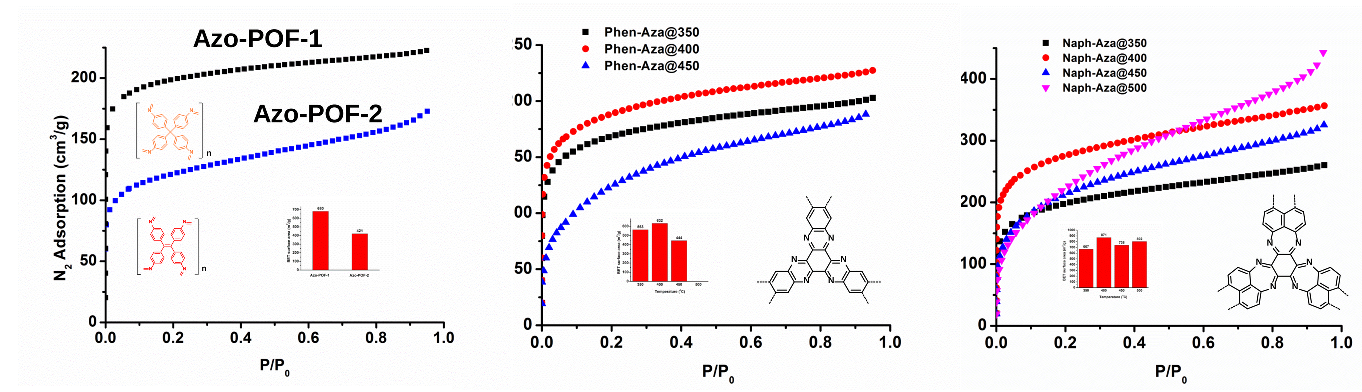


Figure 6. Infrared spectra of aza-POFs synthesized at different temperature.

Gas Adsorption

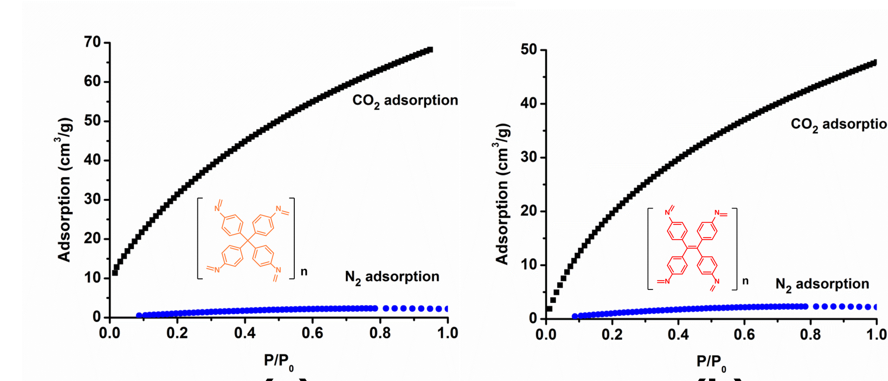
- **N_2 adsorption isotherm and BET surface area**



(a) (b) (c)

Figure 3. N_2 adsorption isotherm (at 77K) and BET surface area of (a) azo-POF-1 and azo-POF-2, (b) Phen-aza-POF synthesized at different temperature and (c) Naph-aza-POF synthesized at different temperature.

- **CO_2/N_2 selectivity at 273K**

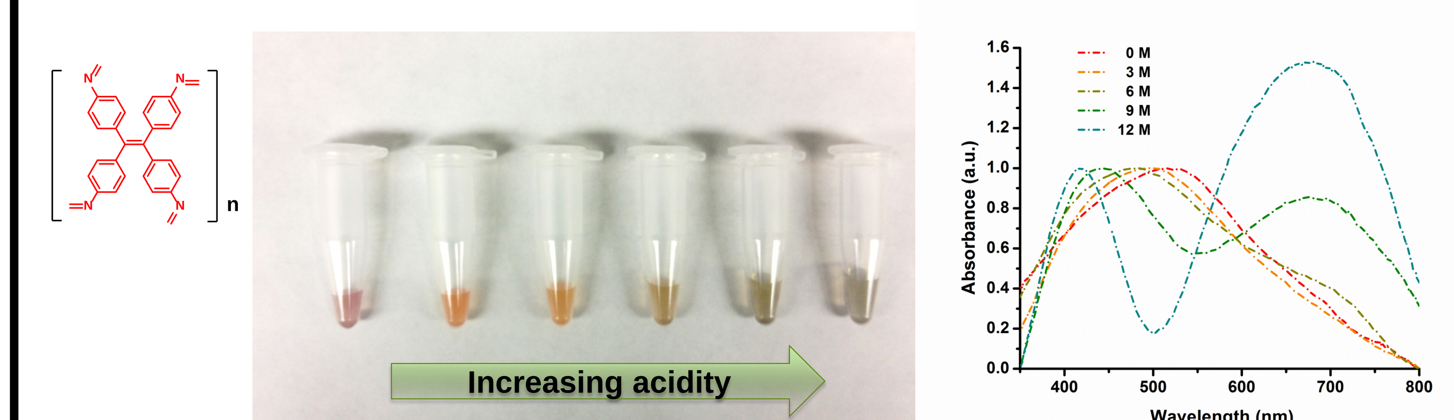


	CO_2 adsorption at 273K (cm^3/g)	N_2 adsorption at 273K (cm^3/g)	CO_2/N_2 selectivity (mol/mol)
Azo-POF-1	67.1	2.3	29.2
Azo-POF-2	47.8	2.1	22.8

(a) (b) (c)

Figure 4. CO_2 and N_2 adsorption isotherm (at 273K) of (a) Azo-POF-1 and (b) Azo-POF-2. (c) CO_2 and N_2 uptakes and selectivity of azo-POFs.

Color change of azo-POF-2 induced by acidity



(a) (b)

Figure 7. (a) Photograph of azo-POF-2 in HCl solutions of different concentration; (b) UV-Visible absorbance spectra of azo-POF-2 in HCl solutions of different concentration.

Conclusion and Future work

We successively synthesized target azo-POFs and aza-POFs with high BET surface area. The CO_2/N_2 selectivity of azo-POF-1 and azo-POF-2 are 29.2 and 22.8, respectively. In the future, we will test the electroactivity of aza-POFs in supercapacitor and lithium-ion battery.

Acknowledgement

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References

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