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Facile synthesis of azo-linked porous organic frameworks via reductive homocoupling for selective CO$_2$ capture
Facile synthesis of azo-linked porous organic frameworks via reductive homocoupling for selective CO\textsubscript{2} capture

Jingzhi Lu\textsuperscript{a} and Jian Zhang\textsuperscript{*a}

A facile Zn-induced reductive homocoupling reaction was used to synthesize azo-linked porous organic frameworks (azo-POFs) from easily accessed nitro monomers. Azo-POF-2 exhibits the highest CO\textsubscript{2}/N\textsubscript{2} selectivity of 76 at 273 K among all self-coupled azo-linked porous polymers.

Nanoporous organic polymers recently received increasing attention because of their high surface area, low density, wide structural tunability, and most of all, remarkable physicochemical stability resulting from the entirely covalently bonded networks.\textsuperscript{1} They have emerged as a new class of highly desirable materials for practical applications in the storage and separation of a variety of gases including CO\textsubscript{2}, which causes serious environmental concern due to its increasing atmospheric concentration.\textsuperscript{2} For efficient postcombustion capture of CO\textsubscript{2}, both adsorption capacity and CO\textsubscript{2}/N\textsubscript{2} selectivity are important. Therefore, it is necessary to tailor the porosity parameters (surface area, pore volume, pore width, etc.) of porous polymers to achieve high adsorption capacity and/or selectivity. For example, increasing surface area and pore volume\textsuperscript{3} is often an effective method to improve adsorption capacity.\textsuperscript{4} Additionally, incorporating polar functional groups such as amine,\textsuperscript{5} aminal,\textsuperscript{6} imine,\textsuperscript{7} triazine,\textsuperscript{8} triazole,\textsuperscript{9} triethylene glycol monomethyl ether,\textsuperscript{10} and benzimidazole\textsuperscript{11} can often enhance the CO\textsubscript{2}/N\textsubscript{2} selectivity.\textsuperscript{12} Azo-linked porous polymers based on -N=N- bonds are promising CO\textsubscript{2} adsorbents since their electron rich pore surfaces can lead to a high CO\textsubscript{2}/N\textsubscript{2} selectivity.\textsuperscript{13} So far, azo-linked porous polymers have been synthesized either by heterocoupling between aromatic nitro and amine monomers\textsuperscript{13a,13b} or by copper(I)-catalyzed oxidative homocoupling of aromatic amine monomers,\textsuperscript{13c} both of which require a reduction reaction of nitro compounds to prepare the amine monomers. Thus, a simple polymerization method which eliminates the use of amine monomers for synthesizing azo-linked porous polymers is highly desirable. In addition, the porous polymer accessed through the new method should ideally exhibit comparable CO\textsubscript{2}/N\textsubscript{2} selectivity, if not higher, since it has been demonstrated that synthetic conditions can significantly affect the porosity parameters of porous polymers and correspondingly, their gas adsorption performance.\textsuperscript{14}

Herein, we report the first example of synthesis of azo-linked porous organic frameworks (azo-POFs) using a facile Zn-induced reductive homocoupling of aromatic nitro monomers. The obtained azo-POFs exhibit high CO\textsubscript{2}/N\textsubscript{2} selectivity. In particular, azo-POF-2 shows the highest CO\textsubscript{2}/N\textsubscript{2} selectivity of 76 (at 273 K) among all homocoupled, azo-linked porous polymers\textsuperscript{13c} despite its large pore width (1.5 nm). This suggests that an appropriate balance of surface area, pore width, and textural feature is required for a high CO\textsubscript{2}/N\textsubscript{2} selectivity, which is of significant importance for the future rational design and synthesis of porous materials.
We adopted the classic zinc-induced reductive coupling of nitro compounds to synthesize azo-linked POFs since this method is mild, requires only one precursor, and can be performed under air. Two nitro compounds were chosen as the monomers based on their molecular geometry. Tetakis(4-nitrophenoxy)methane (TNPM) serves as a highly symmetric tetrahedral 4-connected building block. Ideally, a dia topology (Fig. 1a) is expected when it is polymerized via self-coupling reaction. 1,1,2,2-Tetrakis(4-nitrophenoxy)ethane (TNPE), on the other hand, is also 4-connected but mostly planar, and we can expect an ideal, 4,4-connected, 2D layer is the targeted structure (Fig. 2a). The geometrical feature of the monomers induces a significant effect on the porosity parameters of the resulting porous polymers (vide infra). In a typical synthesis, the aromatic nitro monomer was dissolved in a solution containing THF, DMF, and NaOH, followed by adding freshly activated zinc powder (Scheme 1). The mixture was heated at 65 °C for 36 hours. The final product was washed by acid, water, acetone, and THF, followed by purification using Soxhlet extraction with water and THF. Common solvents used in the synthesis of azobenzene derivatives such as methanol and ethanol led to the formation of products with poor surface area (90 m²/g), probably due to the low solubility of monomers in such solvents. The ratio of THF and DMF was optimized to achieve the highest yield of azo-POFs. To confirm the importance of azo groups in CO₂ adsorption and CO₂/N₂ selectivity, we also prepared two other POFs (termed as ene-POFs) having the same scaffold structures as azo-POFs but contain -CH=CH- bonds, which lack the CO₂-phobic moieties (see ESI for details of structure, synthesis, and characterization of ene-POFs).

Azo-POFs are insoluble in common organic solvents such as dichloromethane, acetone, THF, methanol, DMF, and DMSO, indicating they are crosslinked organic frameworks. Scanning electron microscopy (SEM) images (Fig. 2) show that both azo-POFs contain the same scaffold structures as azo-POFs but contain -CH=CH- bonds, which lack the CO₂-phobic moieties (see ESI for details of structure, synthesis, and characterization of ene-POFs). The porosity of both azo-POFs and ene-POFs was investigated by nitrogen gas adsorption/desorption measurements at 77 K (Fig. 3). A rapid uptake at low pressure (0−0.1 bar) indicates a permanent microporous nature. The apparent hysteresis between adsorption and desorption suggests that all POFs are networks containing both meso- and micropores, which is attributed to the pore network effects, that is, mesopores are accessible only through micropores. Using Brunauer-Emmett-Teller (BET) model in the pressure range of P/P₀ = 0.01−0.15, the apparent surface areas (SA_BET) were calculated as 712 m²/g (azo-POF-1), 439 m²/g (azo-POF-2), 755 m²/g (ene-POF-1), and 622 m²/g (ene-POF-2). It is also noted that POFs containing 3D linkage (tetrakisphenylmethane) exhibit higher surface areas than those containing 2D linkage (tetrakisphenylethene), a trend similar to a previous report of BILP polymers. Pore-size distribution (Fig. 3b) based on nonlocal density functional theory (NLDFT) was estimated by fitting the N₂ adsorption isotherm, leading to pore sizes centered at 0.54, 1.50, 0.65, and 0.70 nm for azo-POF-1, azo-POF-2, ene-POF-1, and ene-POF-2, respectively. Indeed, the synthetic method significantly affects the porosity parameters of the resulting porous polymers. For example, azo-POF-1 has the same chemical structure as azo-COP-1 and ALP-2 that were previously synthesized using a metal-catalyst-free method and a copper (I)-catalyzed method, respectively, but its SA_BET is larger than that of azo-COP-1 (634 m²/g), but smaller than that of ALP-2 (1065 m²/g). In addition, the major pore width of azo-POF-1 (0.54 nm) is smaller than that of both azo-COP-1 (0.7 nm) and ALP-2 (1.1 nm).

Fig. 2 SEM images of azo-POF-1 (a), azo-POF-2 (b), ene-POF-1 (c), and ene-POF-2 (d).
azo groups, which was confirmed by the calculated isosteric heats of adsorption (Qst).

As shown in Table 1, the Qst values at zero coverage are 27.5 and 26.2 kJ/mol for azo-POF-1 and azo-POF-2, respectively, higher than those of ene-POFs (24 kJ/mol), indicating the strong dipole-quadrupole interaction between the polarizable CO2 molecules and the nitrogen sites on azo groups. Moreover, the moderate Qst values of azo-POFs are weak enough to allow for material reactivation without applying heat, an attractive property since other materials with strong acidic or basic sites (e.g. alkanolamine) exhibiting high CO2 affinities require large energy inputs to regenerate the active sites.

<table>
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<tr>
<th>polymer</th>
<th>CO2</th>
<th>N2</th>
<th>selectivity</th>
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<tr>
<td>azo-POF-1</td>
<td>131</td>
<td>298</td>
<td>69(52)</td>
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<tr>
<td>azo-POF-2</td>
<td>84.5</td>
<td>55.1</td>
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<td>40.2</td>
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*Gas uptake in mg g−1 and the isosteric heats of adsorption (Qst) in kJ mol−1. Selectivities (mg mg−1) were calculated by initial slope method. 

The CO2/N2 selectivities were calculated using both initial slope ratios estimated from Henry’s law constants15 based on the pressure below 0.10 bar and the ideal adsorbed solution theory (IAST) based on single-component adsorptions of CO2 and N2 colleted at 273 and 298 K (Table 1 and ESI).22 At 273 K, eene-POFs exhibit lower selectivities (50-54) than azo-POFs, exemplifying again the importance of azo groups as polar functionalities to the high CO2/N2 selectivities of azo-linked polymers. The CO2/N2 selectivity of azo-POF-1 (69) is comparable to azo-COP-1 (73, 273 K)3a and higher than ALP-2 (46, 273 K),13b confirming that the facile Zn-induced reductive coupling method does not compromise the CO2 adsorption of azo-POFs. Of particular interest is the high CO2/N2 selectivity of azo-POF-2 (76, 273 K). Generally, a small pore width is considered to be responsible for the high CO2/N2 selectivity, described as the “sieving effect”.13c Thus, it is quite unusual for azo-POF-2 (major pore width: 1.5 nm) exhibiting a high CO2/N2 selectivity of 76 when compared to azo-COP-1 (pore width: 0.7 nm, CO2/N2: 73)13a,13b and ALP-3 (pore width: 1.24 nm, CO2/N2: 68).13b Hence, besides pore width, other pore metrics also contribute to the observed high CO2/N2 selectivity in azo-POF-2, which require further investigation.

Note: For further discussion, please refer to the original manuscript for detailed experimental procedures, characterization methods, and gas adsorption studies. See DOI: 10.1039/c000000x/

**Fig. 4** CO2 and N2 uptake isotherms of azo-POFs and ene-POFs at 273 K and 298 K.

**Table 1** CO2 and N2 uptakes, isosteric heats of adsorption, and CO2/N2 selectivity of POFs

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**Notes and references**


