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Efficient CO_2 Capture by a 3D Porous Polymer Derived from Tröger's Base

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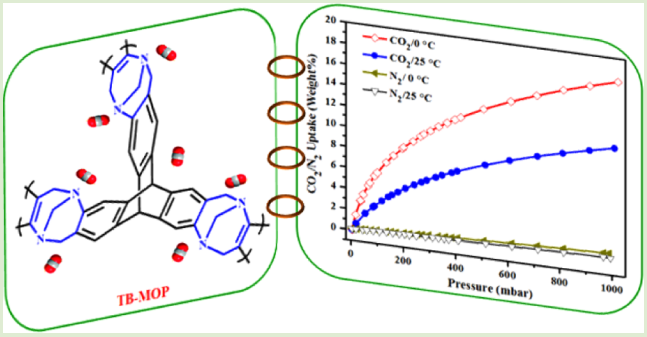
Supporting Information

ABSTRACT: A 3D Tröger's-base-derived microporous organic polymer with a high surface area and good thermal stability was facilely synthesized from a one-pot metal-free polymerization reaction between dimethoxymethane and triaminotriptycene. The obtained material displays excellent CO_2 uptake abilities as well as good adsorption selectivity for CO_2 over N_2. The CO_2 storage can reach up to 4.05 mmol g^{-1} (17.8 wt %) and 2.57 mmol g^{-1} (11.3 wt %) at 273 K and 298 K, respectively. Moreover, the high selectivity of the polymer toward CO_2 over N_2 (50.6, 298 K) makes it a promising material for potential application in CO_2 separation from flue gas.



Carbon capture and sequestration (CCS), a newly emerged strategy to mediate the atmospheric CO_2 concentration for environmental remediation, has attracted significant interest.[1,2] Conventional processes widely employed in industry for CO_2 capture involve chemical absorption of CO_2 with ethanolamine solutions. Though this method is well-established and offers a high CO_2 absorption capacity, it suffers from several serious drawbacks, including solvent loss, a high parasitic energy cost for the regeneration, and equipment corrosion.[3] Therefore, alternative processes such as adsorption separation by porous solid-adsorbents have been proposed.[4−13]

Recently, tremendous attention has been paid to the design and synthesis of microporous organic polymers (MOPs) for CO_2 capture due to their high physicochemical stability and excellent adsorption capacity.[1,2,14−31] Numerous MOPs with good porosities (both surface areas and pore volumes) have been prepared via a variety of organic reactions. Several potential strategies like increasing isosteric heats between sorbent and sorbate have been developed to increase CO_2 loading capacity and the adsorption selectivity for CO_2 over N_2 which is another crucial parameter for CO_2 capture materials.[32] In this regard, various CO_2-philic moieties have been incorporated into the porous polymer networks to enhance the interaction between the material surfaces and CO_2 molecules. Typically, grafting of one ultrahigh-surface-area network (PPN-6) with sulfonic acid, lithium sulfonate, or polyamines attains excellent CO_2 adsorption capacities as well as high CO_2/N_2 selectivity.[1,2] In spite of these beneficial properties, multistep synthesis processes of such attractive adsorbents may limit the scale-up preparation for CO_2 capture. Facile and cost-effective preparation processes combined with excellent gas adsorption properties are the keys to make MOPs as promising candidates for practical applications in post-combustion capture of CO_2.

With these considerations in mind, herein we report the one-pot metal-free synthesis of a three-dimensional (3D) Tröger's-base-derived microporous organic polymer (TB-MOP, Scheme 1) for efficient CO_2 capture. The resulting network showed excellent CO_2 uptake as well as high adsorption selectivity for CO_2 over N_2 at ambient conditions.

TB-MOP was prepared through a trifluoroacetic acid-catalyzed one-pot polymerization reaction between dimethoxymethane and a 3D rigid building block (triaminotriptycene) at room temperature (Scheme 1). CO_2-philic TB units can be facilely in situ generated. This synthesis was inspired by the recent discovery of porous TB based membranes.[33] 2,6,14-Triaminotriptycene, which may allow for a high degree of internal molecular free volume,[24] was selected as the precursor for our polymer network synthesis and can easily be prepared from triptycene in good yield.[34] (Experimental details can be

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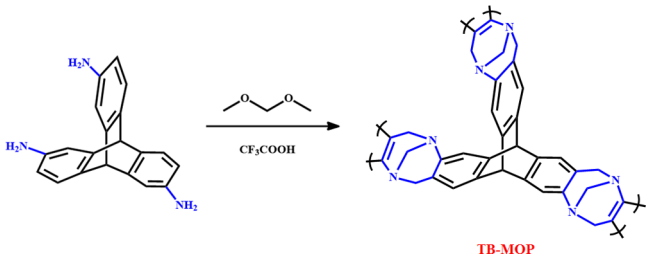
Scheme 1. Synthesis of TB-MOP at Room Temperature



found in the Supporting Information.) The resulting 3D TB-MOP was found to be insoluble in common organic solvents.

The structure of TB-MOP can be characterized at the molecular level by solid state ^{13}C cross-polarization magic-angle spinning (CP/MAS) NMR (Figure 1A). The existences of in situ generated TB units within the network are confirmed by the signals at ca. 55, 68, 111, 124, and 146 ppm.[35,36] The peak at 136 ppm corresponds to carbon atoms of the substituted benzene rings.[35,36] High thermal stability of TB-MOP was revealed by thermogravimetric analysis (TGA, Figure S1). TB-MOP retains more than 60% of its mass at 800 °C under N_2 atmosphere. It is worth mentioning that high thermal stabilities of MOPs are beneficial for considering their potential application in postcombustion processes at higher temperatures and CO_2 scrubbing operations.[30,37] Moreover, TB-MOP is shown to be amorphous as indicated by X-ray powder diffraction measurement (Figure S2), which is similar to previous triptycene derived MOPs.[24,35]

The porosity of TB-MOP was evaluated by a nitrogen adsorption isotherm measured at 77 K (Figure 1B), which exhibited a Type I adsorption profile. A rapid uptake at low pressure (0−0.1 bar) indicated a permanent microporous nature of the polymeric network. The calculated Brunauer−Emmett−Teller (BET) surface area is shown to be ∼694 m^2 g^{-1} and can be comparable to that reported for conjugated microporous polymer-derived adsorbents.[18] The level of microporosity in the material was assessed by the ratio of micropore volume to the total pore volume (V_{micro}/V_{total}).[38] The total pore volume (calculated at P/P_0 ∼ 0.98) and micropore volume derived from the t-plot method were 0.398 cm^3 g^{-1} and 0.179 cm^3 g^{-1}, respectively. For TB-MOP, a V_{micro}/V_{total} value of 0.45 was obtained, indicating the existence of mesopores.[28] Moreover, the pore size distribution (PSD) analysis based on nonlocal density functional theory (NLDFT) further confirmed the presence of primarily micropores with a small mesopore contribution (Figure 1B). The presence of mesopores may be a result of the intrinsic porosity and expanded networks of the 3D rigid building blocks.[35]

In view of the fact that TB-MOP possesses two key properties of high CO_2 uptake capacity, for example, good microporosity and abundant nitrogen-containing CO_2-philic sites, the CO_2 adsorption of TB-MOP was measured up to 1 bar (Figure 1C) using a gravimetric microbalance (IGA, Hiden Isochema). Uptakes of 4.05 mmol g^{-1} (17.8 wt %) and 2.57 mmol g^{-1} (11.3 wt %) were obtained at 273 and 298 K, respectively. To directly compare CO_2 capture performance for different MOPs, we have plotted the CO_2 uptake at both 273 and 298 K and 1 bar for a range of MOP-based adsorbents as a function of BET surface area measured by N_2 adsorption at 77 K (Figure S3A and B). TB-MOP, as can be seen, shows a higher CO_2 adsorption capacity than many previously reported MOPs under the same conditions despite possessing a lower BET surface area (Table S1).[32] Moreover, although benzimidazole-linked polymers with higher surface areas show better CO_2 uptake (filled circles in Figure S3A and B), the preparation of their building blocks are more challenging than our facile

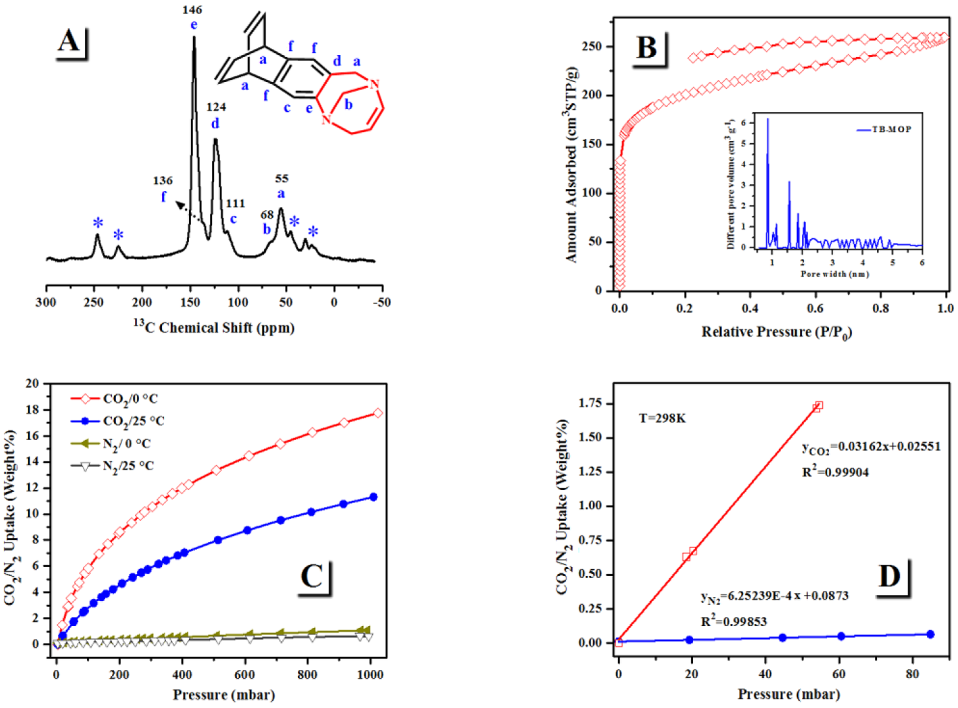


Figure 1. (A) Solid state ^{13}C-CP/MAS NMR spectrum of TB-MOP. The asterisk denotes spinning sidebands. (B) Nitrogen gas adsorption isotherms measured at 77 K and corresponding pore size distribution curve (inset) of TB-MOP. (C) CO_2 and N_2 adsorption isotherms of TB-MOP measured at 273 and 298 K. (D) Initial slope calculation for CO_2 and N_2 isotherms collected at 298 K.

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synthesis.[24−26] Previous work has shown that CO_2-philic sites such as acid groups and N-containing heterocyclic rings may have a large effect on CO_2 uptake besides the contribution of porosity (surface area and pore volume).[18] To provide a better understanding of the CO_2 storage properties, the isosteric heat of adsorption for TB-MOP was calculated by fitting the CO_2 adsorption isotherms measured at 273 and 298 K and applying a variant of the Clausius−Clapeyron equation (see Supporting Information).[11] TB-MOP shows a heat in the range of 24.5−29.5 kJ mol^{-1} (Figure S4). This value is higher than that reported for many other MOPs.[32] However, the value still remains below the energy of chemisorptive processes (>40 kJ mol^{-1}),[30] indicating strong interactions of the polarizable CO_2 molecules through dipole−quadrupole interactions with the network, along with the inherent microporosity of TB-MOP, which is more favorable for facile CO_2 desorption. The readily reversible adsorption/desorption behavior (Figure S5) further indicates that interactions between CO_2 molecules and TB-MOP are weak enough to allow for adsorbent regeneration without applying heat.[26] Additionally, CO_2 uptake at 10 bar for TB-MOP was measured to be 8.39 mmol g^{-1} (36.9 wt %, 273 K) and 6.18 mmol g^{-1} (27.2 wt %, 298 K), respectively, showing good adsorption abilities at high pressure (see Figure S5).

Inspired by the excellent CO_2 uptake abilities and high isosteric heat for TB-MOP, N_2 adsorption experiments were carried out at 1 bar to examine the separation capability since industrial emission stream also contains ∼70% N_2 (see Figure 1C). The selectivity for CO_2 over N_2 was calculated to be 45.2 at 273 K by the ratios of the initial slopes of CO_2 and N_2 adsorption isotherms (Figure S6),[22] indicating increased selectivity as compared to previously reported MOPs. For example, much smaller CO_2/N_2 selectivity (25) at 273 K for carbazole-based porous organic polymer is observed though it possesses a higher CO_2 loading capacity (21.2 wt %, 273 K).[21] Interestingly, at a higher temperature (298 K), the selectivity for TB-MOP was shown to be even larger and increased to 50.6 (Figure 1D). A similar trend has recently been indicated in N_2-phobic azo-based MOPs.[30] It should be noted that the CO_2/N_2 selectivity as well as CO_2 uptakes for many MOPs have been reported only at 273 K though CO_2/N_2 separation at the higher temperature of 298 K is closer to the conditions required for postcombustion capture.[17] Accordingly, the in situ generated TB units within the network may play a role similar as the azo group, leading to a higher CO_2/N_2 selectivity at 298 K. The stronger affinity between CO_2 molecules and TB-MOP can be ascribed to the enhanced dipole−quadrupole interaction between the large quadrupole moment of CO_2 molecules (-1.4×10^{-39} C m^2) and the polar TB sites.[22] Moreover, given the effect of water on CO_2 uptake process,[23] a water droplet was brought in contact with the surface of a mechanically compressed TB-MOP thin pellet for the contact angle (CA) measurement.[39] However, the CA could not be obtained because, upon touching the pellet, the water droplet was absorbed immediately by TB-MOP. This indicates that the selectivity of TB-MOP toward CO_2 over N_2 will likely be affected by the presence of water under more realistic carbon capture conditions.

In conclusion, a 3D Tröger's-base-derived microporous organic polymer with a high surface area and good thermal stability can be facilely synthesized from a one-pot metal-free polymerization reaction between dimethoxymethane and triaminotriptycene. The obtained material displays excellent CO_2 uptake abilities as well as high adsorption selectivity for CO_2 over N_2. The CO_2 storage can reach up to 4.05 mmol g^{-1} (17.8 wt %) and 2.57 mmol g^{-1} (11.3 wt %) at 273 K and 298 K, respectively, which can be competitive with many other CO_2 adsorbents. Moreover, the high selectivity of the polymer toward CO_2 over N_2 (50.6, 298 K) makes it a promising material for potential application in CO_2 separation from flue gas. Work on expansion of triptycene derived materials along with Tröger's base units for membrane based CO_2/N_2 separation is currently underway in our lab.

■ ASSOCIATED CONTENT

Supporting Information

Synthesis details, gas adsorption experiments, Figures S1−S9, and Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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