ChemComm

COMMUNICATION



View Article Online View Journal | View Issue



Cite this: Chem. Commun., 2014, 50, 15055

Received 16th September 2014, Accepted 3rd October 2014

DOI: 10.1039/c4cc07255c

www.rsc.org/chemcomm

Thiazolothiazole-linked porous organic polymers†

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Thiazolothiazole-linked porous organic polymers have been synthesized from a facile catalyst-free condensation reaction between aldehydes and dithiooxamide under solvothermal conditions. The resultant porous frameworks exhibit a highly selective uptake of CO_2 over N_2 under ambient conditions.

Porous organic polymers (POPs) have emerged as a new class of advanced porous materials because of their potential applications in heterogeneous catalysis, gas separation and storage, energy, and electronic devices.¹ The intriguing issue of such materials is the salient advantages of their functionalities. One effective approach is to integrate task-specific groups like basic N-heterocycle units and acidic motifs into the purely organic framework using covalent bonds.² As such, a rapidly increasing number of designed structures, synthetic methods and applications for this kind of porous solids have been intensively studied, yielding a wide variety of POPs including crystalline polymers such as covalent organic frameworks³ (COFs), covalent triazine frameworks (CTFs),⁴ amorphous polymers such as polymers of intrinsic microporosity (PIMs)⁵ and porous aromatic frameworks (PAFs).⁶ Remarkable examples of this sort are seen in the porous polymer networks (PPNs). Grafting an ultrahigh-surfacearea porous polymer network (PPN-6) with task-specific groups like sulfonic acid, lithium sulfonate, polyamines or sulfonate ammonium leads to excellent CO₂ adsorption capacities as well as high CO₂/N₂ selectivity.⁷ However, the synthesis of such attractive materials as well as many other conventional POPs

that involve expensive transition-metal-based catalysts and extra purification efforts may limit the scale-up preparation.⁸ Facile and cost-effective preparation processes are the key to fully realize the potential of POPs for practical applications.

Recently, a new biheterocyclic system based on thiazolothiazole (TzTz) has been increasingly studied owing to the steadily growing interest in its potential applications in electronic and optoelectronic devices.⁹ Despite the importance of the TzTz group that contains N-heterocycle units that may facilitate gas binding and thereby enable potential application in gas separation within porous platforms, so far it has never been introduced into porous polymer networks. It is believed that the incorporation of TzTz into porous polymeric architectures can not only expand the range of applications of this biheterocyclic system, but also extend the library of POPs.

Herein, we contribute to the rising array of POPs by presenting a new synthesis method to generate TzTz-linked porous organic polymers (TzTz-POPs). The key to this novel preparation strategy lies in a catalyst-free solvothermal process. The resultant conjugated porous polymers exhibit good porosities with a surface area of up to 488 m² g⁻¹. We further demonstrate that the TzTz moieties integrated in the networks give rise to highly selective uptake of CO_2 over N_2 under ambient conditions.

As shown in Scheme 1, 1,3,5-triformylbenzene (M1) with three aldehyde groups, was polymerized with dithiooxamide through a one-pot catalyst-free procedure to demonstrate the feasibility of the strategy. CO₂-philic TzTz units can be facilely formed in situ. This synthesis was inspired by the recent discovery of the TzTz-based Cu2+ colorimetric and fluorescent sensor.¹⁰ Multiple attempts to generate porous polymers under conventional reflux conditions failed, and the materials were obtained with negligible porosities. Therefore, we utilized a solvothermal method, which has been widely considered as the most promising methodology to construct COFs,^{1a} to prepare TzTz-POPs with good porosities. In addition, tetrakis(4formylphenyl)methane (M2), which is expected to produce a three-dimensional (locally diamond-like) network, was further selected as the tetrahedral building block to show the features of this new class of TzTz-POPs.¹¹ Both TzTz-POPs were isolated

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[†] Electronic supplementary information (ESI) available: Experimental section, Fig. S1–S5, and Table S1. See DOI: 10.1039/c4cc07255c





in good yields and were insoluble in common organic solvents. (Experimental details can be found in the ESI.[†])

The structure of TzTz-POPs was unambiguously unraveled at the molecular level by ¹H-¹³C cross-polarization magic-angle spinning (CP-MAS) ¹³C NMR spectra (Fig. 1). TzTz-POPs showed two peaks at ca. 132 ppm and 128 ppm, corresponding to the aromatic carbons from the building blocks. Most importantly, the existence of an in situ generated thiazolothiazole ring within the networks can be confirmed by the presence of sp² carbons (~150 and 168 ppm). Additionally, for TzTz-POP-1, a carbonyl peak attributed to unreacted aldehyde groups, was also observed at 192.7 ppm. The aliphatic carbon from the tetrahedral center inside TzTz-POP-2 was located at 64.9 ppm. The Fourier transform infrared (FT-IR) spectra of TzTz-POPs (Fig. S1, ESI[†]) further confirmed the high-efficiency of condensation. Absorption peaks at *ca*. 1600 cm^{-1} can be ascribed to the stretching vibration of the carbon-nitrogen double bond (-C==N-) of the thiazolothiazole ring.¹² The absence of a C=O stretching band (at $ca.1700 \text{ cm}^{-1}$) in the spectra of TzTz-POP-2 indicates consumption of the tetrahedral monomer (M2).¹³ The nitrogen content of the TzTz-POP-1 is found to be 11.3% by elemental



Fig. 1 Solid state ¹³CNMR of thiazolothiazole-linked POPs.

analysis and higher than that of **TzTz-POP-2** (7.7%). Thermal gravimetric analysis (TGA) shows that both polymers possess good thermal stability (Fig. S2, ESI[†]). Moreover, as shown by the powder X-ray diffraction (XRD) analysis, TzTz-POPs were obtained as amorphous solids though solvothermal conditions were utilized for the polymerizations (Fig. S3, ESI[†]). It is worth noting that preparation of crystalline POPs requires enormous efforts in the screening of diverse reaction conditions.¹⁴

The porous nature of TzTz-POPs was evaluated by nitrogen adsorption-desorption isotherms measured at 77 K (Fig. 2). The fully reversible isotherms show rapid uptake at low relative pressures indicating that both polymers are mainly microporous. The increase in the nitrogen adsorption at a high relative pressure above 0.9 may arise in part from interparticulate porosity associated with the meso- and macrostructures of the samples and interparticulate voids. The desired high microporosity is successfully created using the tetrahedral building block (M2). The BET (Brunauer-Emmett-Teller) surface area of **TzTz-POP-2** calculated over a relative pressure (P/P_0) range from 0.01 to 0.1 is 488 m² g⁻¹ and higher than that of TzTz-POP-1 (299 $m^2 g^{-1}$, Table 1). Though the achieved surface areas are lower than those of the reported benzimidazole-linked POPs,¹⁵ they are comparable to some classical zeolites and POPs.¹² The transmission electron microscopy (TEM) images of TzTz-POPs also revealed their porous nature (Fig. S4, ESI⁺). In addition, the pore size distribution (PSD) analysis of TzTz-POPs, performed using nonlocal density functional theory (NLDFT), suggests primary narrow micropores of the polymeric networks (Fig. S5A and B, ESI†). To gain a better understanding of micropores inside TzTz-POPs, we further used CO2 gas as the adsorbate to calculate their PSDs.¹⁶ According to NLDFT pore size distribution curves (Fig. S5C and D, ESI⁺), both TzTz-POPs show narrow micropore peaks at around 0.3-0.7 nm. Clearly, these narrow ultra-micropores (<7 Å) are essential and advantageous for potential gas separation.¹⁷ The total pore volumes of TzTz-POP-1 and TzTz-POP-2 estimated from the amount of nitrogen gas adsorbed at $P/P_0 = 0.99$, are 0.38 and 0.59 cm³ g⁻¹, respectively. These results from PSD studies further confirm that the solvothermal method may provide good porosities for TzTz-linked porous networks.

Table 1 Characteristics of thiazolothiazole-linked POPs

Polymers	Surface area $(S_{\text{BET}})/\text{m}^2 \text{ g}^{-1}$	$V_{\text{total}}^{a}/\text{cm}^{3}\text{ g}^{-1}$	CO ₂ uptake ^b / mmol g ⁻¹ (273/298 K)	CO ₂ /N ₂ selectivity (initial slope, 273 K)	$Q_{\rm st}/{ m kJ}~{ m mol}^{-1}$
TzTz-POP-1	299	0.38	1.9/1.3	54	32
TzTz-POP-2	488	0.59	2.5/1.5	35	30

In light of the narrow ultra-microporosities of TzTz-POPs and abundant N-heterocycle units within the networks, we next investigated their CO₂ uptake capacities. The CO₂ adsorption was measured up to 1 bar at both 273 K and 298 K (Fig. 3A and B). Interestingly, TzTz-POP-1 and TzTz-POP-2 show uptake capacities of 1.9 mmol g^{-1} (8.4 wt%) and 2.5 mmol g^{-1} (11.0 wt%), respectively, at 273 K. Though the uptake capacities are lower than those of some reported porous adsorbents (e.g., carbonaceous solids and porphyrin based POPs),¹⁸ they are comparable to those of many other porous materials. And for TzTz-POP-2, it is worth mentioning that the CO₂ adsorption capacity is not only higher than those of previously reported conjugated microporous polymers (CMPs) which were prepared by cross-coupling reactions involving expensive transition-metals,¹⁹ but it is also comparable to that of the "knitting" approach-derived hypercrosslinked pyrrolic POP (Py-1, 2.7 mmol g^{-1}).²⁰ It is important to note that large amounts of solvents are usually required for the removal of metalbased Lewis acid catalysts which are extensively used in the synthesis of such "knitted" POPs. Clearly, our catalyst-free approach is a more facile route for the preparation of task-specific POP-based CO₂ adsorbents. Previous work showed that chemical functional groups may have a large effect on CO₂ uptake besides the contribution of the surface area and the pore volume.²¹ In addition, a good cycling of CO₂ uptake for TzTz-POP-2 was also observed (Fig. S6, ESI[†]), indicating good desorption during each regeneration cycle.^{7b} To provide a better understanding of the CO₂ storage properties,



Fig. 3 (A) and (B) CO_2 and N_2 adsorption isotherms of TzTz-POPs measured at 273 K and 298 K, respectively. (C) The isosteric heat of adsorption for TzTz-POPs. (D) The selectivity of **TzTz-POP-1** for CO_2 over N_2 obtained from the initial slope method.

the isosteric heats of adsorption for TzTz-POPs were calculated by fitting the CO₂ adsorption isotherms measured at 273 and 298 K and applying a variant of the Clausius–Clapeyron equation (see ESI†).²² At low adsorption values, both TzTz-POPs show high adsorption heats (Table 1 and Fig. 3C), exceeding those reported for many other POPs (Table S1, ESI†) such as the amine integrated CMP (CMP-1-NH₂, 29.5 kJ mol⁻¹) and the benzimidazole-linked POP (BILP-4, 28.7 kJ mol⁻¹).¹⁹ Accordingly, the existence of TzTz groups within the networks plays an important role in their exceptionally high CO₂ affinity. However, the heats still remain below the energy of chemisorptive processes (>40 kJ mol⁻¹),²³ indicating strong interactions of the polarizable CO₂ molecules through dipole–quadrupole interactions with the networks, and also the inherent ultra-microporosities of TzTz-POPs, which are more favourable for CO₂ desorption.

Selectivity is another important parameter for POP-based CO2 adsorbents since the industrial emission stream also comprises $\sim 70\% N_2$.²⁰ To examine the separation abilities of TzTz-POPs, N₂ sorption experiments were carried out at 273 K and 298 K, respectively. Attributed to the incorporation of TzTz moieties, the selectivity for CO2 over N2 was calculated to be 54 and 35 for TzTz-POP-1 and TzTz-POP-2 at 273 K by the ratios of the initial slopes of CO₂ and N₂ adsorption isotherms (see Fig. 3D and Fig. S7, ESI⁺), respectively. Though this value is lower than that reported for azo-linked N2-phobic POPs,²³ TzTz-POPs show better CO₂/N₂ selectivity than those reported for many other POPs like polycarbazole (CPOP-1, 25).²⁴ For POPs based CO₂ capture materials, upon increasing the temperature the selectivity usually decreases rapidly due to smaller uptake of gases. Interestingly, at 298 K, the CO₂/N₂ selectivities of TzTz-POP-1 and TzTz-POP-2 remain at a good level and reach 34 and 23, respectively. Accordingly, the TzTz-rich units within purely organic networks may account for such high CO₂/N₂ selectivities. The reason can be ascribed to the enhanced dipole-quadrupole interaction between the large guadrupole moment of CO₂ molecules $(-1.4 \times 10^{-39} \text{ Cm}^2)$ and the polar sites associated with N-doped sites. Therefore, the high selectivities of TzTz-POPs toward CO2 over N2 may make them promising materials for potential CO₂ separation.

In conclusion, we have demonstrated a one-pot catalyst-free synthesis of new thiazolothiazole-linked porous organic polymers from a simple condensation reaction between aldehydes and dithio-oxamide under solvothermal conditions. The resultant materials display good porosities with a surface area of up to 488 m² g⁻¹. Attributed to the narrow ultra-microporosities and abundant N-heterocycle units within the networks, TzTz-POPs exhibit a highly selective uptake of CO₂ over N₂ under ambient conditions.

XZ, JH and HLL thank the National Basic Research Program of China (2013CB733501), the National Natural Science Foundation

of China (No. 91334203 and 21176066), the 111 Project of China (No. B08021) and the Fundamental Research Funds for the Central Universities of China. This work (SM and SD) was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and the Biosciences Division.

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