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Selective CO₂ Capture in Metal-Organic Frameworks with Azine-Functionalized Pores Generated by Mechanosynthesis

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Supporting Information Placeholder

ABSTRACT: Two new 3D, porous Zn(II)-based metal-organic frameworks, containing azine-functionalized pores, have been readily and quickly isolated via mechanosynthesis, by using a non-linear dicarboxylate and linear N-donor ligands. The use of non-functionalized and methyl-functionalized N-donor ligands has led to the formation of frameworks with different topology, metal-ligand connectivities, and therefore with different pore sizes and accessible volumes. Despite this, both MOFs possess comparable BET surface areas and CO₂ uptakes at 273 and 298 K at 1 bar. The network with narrow and interconnected pores in three dimensions show greater affinity for CO₂ compared to the network with 1D and relatively large pores – attributable to the more effective interactions with the azine groups.

Combustion of fossil fuels results in emission of CO₂ into the atmosphere, which is now known to cause severe global climatic and environmental changes.1,2 One strategy to mitigate these effects is to optimize selective CO₂ capture and storage by developing new adsorbents with high storage capacity and adsorption selectivity for CO₂.3–5 Porous metal-organic frameworks (MOFs) assembled from metal ions and organic linkers have recently begun to be explored as a potential new class of CO₂ adsorbents, owing to their very high surface areas, tunable pore sizes and shapes, adjustable pore surface functionality, and flexible structures.6–8 Tuning of the chemical functionalities of the pore walls in MOFs should help to increase CO₂ uptake and adsorption selectivity.9–10 This can be accomplished by functionalizing the pores with either of two groups: coordinatively unsaturated metal ions11,12; or Lewis basic groups (e.g. amine13,17 and hydroxyl18 groups).

Herein we report that the control of the pore size of MOFs functionalized with azine groups enables greater interactions between the host framework and guest CO₂ molecules.19 Our strategy relies on pillaring 2D layers comprising Zn(II) ions and the V-shaped dicarboxylate ligand 4,4'-oxybisbenzoic acid (H₂oba), with linear pyridyl-based ligands.20,22 The selected pillaring ligands are 1,4-bis(4-pyridyl)-2,3-diazao-1,3-butadiene (4-bpdb) and 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene (4-bpdbh), which lead to [Zn(oba)₂(4-bpdb)] (DMF)_2 (TMU-4: TMU stands for Tarbiat Modares University) and [Zn(oba)₂(4-bpdbh)] (DMF)_2 (TMU-8), respectively.23 Considering that the pores of MOFs constructed from layers pillared by linear ligands are usually delimited by these ligands24, and that the selected ligands contain a bridging azine group in the middle (Scheme 1), we hypothesized -and subsequently confirmed- that the pores of the MOFs should contain two internal Lewis basic sites per ligand. TMU-4 shows 1D (Fig. 1), relatively large pores (size: 6.8 x 7.8 Å, including van der Waals radii), whereas TMU-8 shows 3D, interconnected, narrow pores (Fig. 2) (size: 5.6 x 3.8 Å, including van der Waals radii). We observed that the combination of pore size (narrow and interconnected) and pore functionalization (azine groups) favor the host-guest (CO₂) interactions.25 Interestingly, both MOFs were synthesized easily and rapidly via mechanosynthesis.26–35 Macroscale crystals of each MOF, suitable for single-crystal X-ray diffraction, were prepared by heating a mixture of Zn(NO₃)₂·6H₂O, H₂oba and either 4-bpdb or 4-bpdbh, in DMF at 80 °C for 72 hours.

Scheme 1. Chemical structure of H₂oba, 4-bpdb and 4-bpdbh. Note the bridging azine group at the center of 4-bpdb and 4-bpdbh.

Framework TMU-4 was prepared by mechanosynthesis (grinding by hand) of a mixture of Zn(OAc)₂·2H₂O, H₂oba and 4-bpdb for 15 minutes. The resulting powder was washed once with a small amount of DMF to remove any traces of unreacted organic ligands or/and metal salts, and then dried in air to afford a yellow crystalline powder (yield: 85%).36 The simulated (derived from the single crystal structure of TMU-4) and experimental (resulting from the mechanosynthesized powder) powder X-ray diffraction (PXRD) patterns are consistent (Figure S3 in the SI), confirming...
that the mechanosynthesized TMU-4 is structurally identical to TMU-4 prepared through conventional heating, and that it can be obtained as a pure phase (as also evidenced by elemental analysis; see SI). TMU-4 is based on a binuclear ZnII unit (Zn#1 and Zn#2), in which both tetrahedral Zn(II) centers are coordinated to three carboxylate O atoms (for Zn#1: O1, O4, O10, and for Zn#2: O5, O6, O9) from three fully deprotonated oba ligands, and one N atom (Zn#1: N1 and Zn#2: N4) from the 4-bpdb ligand (Figure 1a). The distance between Zn#1 and Zn#2 is 3.44 Å. Each nonlinear (angle: 125.12°) dicarboxylate oba ligand binds three consecutive Zn(II) centers from two different ZnII units, thereby forming 2D sheets (Fig. 1b and S1 in the SI). The coordination modes of a single oba ligand within TMU-4 differ according to the carboxylate functional group: one of the carboxylate groups is bidentate and bridges both Zn#1 and Zn#2 centers of the unit in a syn-syn mode (mean distance: 1.994 Å), whereas the other one is monodentate and binds to either Zn#1 or Zn#2 (distance: 1.939 Å). The 2D sheets are connected through the linear 4-bpdb, extending the structure in three dimensions. Although TMU-4 is doubly interpenetrated, it still possesses large 1D pore channels (size: 6.8 x 7.8 Å; 40% void space per unit cell) running along the [1 0 1] direction (Fig. 1c-e). As shown in Fig. 1f, the internal surface of these pores is functionalized with the azine groups (shown in sky blue) of the 4-bpdb ligands.

TMU-5 was prepared using the same mechanochemical conditions as for TMU-4, but instead of 4-bpdb, we used 4-hpdb (yield: 80%). Interestingly, the simple introduction of two methyl groups in the N-donor pillar ligand induced the formation of a different structure to that of TMU-4. TMU-5 is based on a binuclear paddlewheel Zn(II) unit (Fig. 2a), in which four carboxylate O atoms from four adjacent oba ligands form an approximate equatorial square plane (Zn–O carboxylate distances: 2.025 to 2.054 Å). The coordination environment of each Zn(II) center is completed by one N atom from 4-hpdb in the axial position (mean distance: 2.033 Å). The separation of the Zn(II) centers within the paddle-wheel unit is 2.937 Å, meaning that the Zn(II) ions are closer together than in TMU-4. As in TMU-4, the orientation of the oba ligands (angle: 120.7°) around the paddle-wheel Zn(II) units leads to the formation of 2D layers pillared by 4-hpdb ligands to yield a 3D framework (Fig. 2b and S2 in the SI). TMU-5 possesses narrower channels than those in TMU-4 (size: 5.6 x 3.8 Å; 34% void space per unit cell) running along the b-axis; however, these are interconnected along the three dimensions (Figures 1c-d), due to the large separation (distance: 8.192 Å) of the neighboring (oba or 4-bpdb) ligands. As seen in Fig. 2e, these channels are also functionalized with azine groups (shown in sky blue).

Thermogravimetric analysis (TGA) of TMU-4 and TMU-5 revealed a first weight loss in the temperature range of 100-315 °C (15.9 %) and 100-290 °C (16.1 %), respectively, attributed to the loss of guest DMF molecules adsorbed during the washing step. Then, a second weight loss was observed in the range of 315-500 °C for TMU-4 and 290-500 °C for TMU-5, corresponding to the decomposition of the frameworks (Figure S6 in the SI). These observations confirmed that the pores of the mechanosynthesized TMU-4 and TMU-5 were available for the adsorption of DMF molecules. This result is similar with what is found for the corresponding TMU-4 and TMU-5 synthesized by conventional heating, for which TGA showed additional weight losses of 16.5% (100-315 °C) in TMU-4 and 18% (100-290°C) in TMU-5 (Fig. S6 in the SI), both of which we ascribed to the removal of guest DMF molecules. We also investigated the stability of both frameworks in H2O for 24 h at room temperature. In both cases, a new crystalline phase was formed as confirmed by PXRD (Fig. S5 in the SI). Single crystal X-ray diffraction experiments were not successful due to the poor quality of the crystals after being exposed in H2O.17

Figure 1. (a) Ball and stick representation of the binuclear ZnII unit (O: red; N: blue; C: grey; and Zn: pink). (b) Layers of Zn(II)-oba (in red) pillared by 4-bpdb (in blue). (c) The packing of the structure leads to a doubly interpenetrated (in orange and cyan) framework possessing 1D pores. (d) and (e) 3D Connolly surface representation of porous TMU-4 along [1 0 1] direction and that the channels formed are one dimensional respectively, and (f) Representation of the pores highlighting the azine groups (sky blue balls) pointing towards the pores of TMU-4. In the Connolly surface representations, gray represents outside the surface and blue, inside the surface.

Figure 2. (a) Representation of the ZnII paddlewheel unit within TMU-5. (b) Layers of Zn(II)-oba (in red) pillared by 4-bpdb (in blue). (c) and (d) Connolly surface representation along b- and a-axis respectively, showing that TMU-5 is porous and comprises interconnected pores. (e) Representation of the pores, highlighting the azine groups (in sky blue). Color code: O: red; N: blue; C: grey; and Zn: pink. Connolly surface: gray represents outside the surface and blue, inside the surface.
A type II N₂ isotherm collected at 77 K and 1 bar on the mechanochemically synthesized TMU-4 (after activation at 40 °C) revealed that N₂ molecules couldn’t diffuse within its pores under these conditions. Interestingly, TMU-4 is porous to CO₂ at 195 K and 1 bar (148.90 cm³/g at 1 bar; BET surface area calculated over p/p° = 0.02-0.3: 517.9 m²/g) (Fig. 3a). The pore volume calculated from the CO₂ adsorption is 0.298 cm³/g (compared to 0.367 cm³/g in the rigid host structure). TMU-4 shows a pore size of 6.8 x 7.8 Å, large enough to be, in principle, accessible for both N₂ and CO₂ (kinetic diameters for CO₂: 3.30 Å and N₂: 3.75 Å) adsorption. We reasoned that this selectivity could be partially explained by the existence of structural changes during gas adsorption, the existence of structural defects and/or the surface functionalization and consequently to the interactions between the CO₂ molecule and the electron-donating, uncoordinated nitrogen atoms of the azine groups decorating the pores.

Surprisingly, even though TMU-5 has narrower pores than TMU-4, we found that it is porous to both CO₂ (142.88 cm³/g at 1 bar; BET surface area: 502.7 m²/g at 195 K and N₂ (144.49 cm³/g at 1 bar; BET surface area: 408.8 m²/g) at 77 K, for which it showed reversible type-I isotherms (Fig. 3a). The pore volumes for TMU-5, derived from the CO₂ and N₂ adsorption branches, were found to be 0.286 cm³/g and 0.227 cm³/g, respectively (compared to 0.235 cm³/g in the static structure). These results suggest that N₂ can almost fill all the pores of TMU-5, whereas (polar) CO₂ can fill the pores and at the same time induce structural re-arrangements that expand the pores and consequently, the structural architecture. Similar behavior has been recently described in other MOFs: the adsorption of bulky xylene molecules within a flexible framework induced structural changes. PXRD study after the sorption studies revealed that both TMU-4 and TMU-5 are robust (Fig. S8 in the SI).

The sorption behavior of TMU-4 and TMU-5 towards CO₂ and N₂ led us to investigate their respective CO₂/N₂ selectivities at 298 K based on the ratio of single-component uptakes and using the IAST model for the equimolar gas mixture. The calculated CO₂/N₂ selectivity for TMU-5 (32:1) is slightly greater than that of TMU-4 (28:1) (ratio of single-component uptakes). The selectivity of the equimolar mixture of CO₂ and N₂ was also estimated using IAST calculations. It was found a similar tendency for both frameworks, with selectivity values of 20.9 for MTU-4 and 25.2 for TMU-5. These selectivity values gradually decrease from 25.2 to 23.2 and from 20.9 to 18.4 at 1 bar for TMU-5 and TMU-4, respectively (Fig. S9-10 in the SI). These are moderate values for MOFs, lower than that of Zn(TCBP)(DMF)₂, which is found to be ~45.

To assess the strength of interactions between CO₂ and each host framework, we also collected CO₂ isotherms at 273 K at 1 bar. The CO₂ isotherms for both frameworks show reversible type I behavior (Fig. 3b). At 273 K and 1 bar, TMU-4 and TMU-5 adsorbed 61.16 and 59.15 cm³/g of CO₂, respectively. A comparable uptake at 1 bar was also observed at 298 K from both frameworks (Fig. 2b). However, an important feature derived from these isotherms is that at low pressure, TMU-5 adsorbed higher amounts of CO₂ than TMU-4. For example, at 273 K and 0.25 bar TMU-5 adsorbed 32.71 cm³/g, whereas TMU-4 adsorbed 24.39 cm³/g. This observation reveals that the interactions between the azine groups pointing towards the narrow pores of TMU-5 and CO₂ are more pronounced than those in TMU-4. The isosteric heat of adsorption (Qₑ) was calculated using the Clausius-Clapeyron equation using the adsorption branches of the isotherms measured at 273 and 298 K in order to check how the pore functionalization and size can influence the affinity of TMU-4 and TMU-5 for CO₂. The Qₑ of TMU-5 for CO₂ was 43.4 kJ/mol at zero coverage - a much higher value than that for TMU-4 (25.6-27.8 kJ/mol) (Fig. 3c). This observation confirms that the narrow and interconnected pores functionalized with azine groups of TMU-5 generates greater interactions with CO₂ compared with the interactions occurred within the large 1D pores in TMU-4, which are functionalized with azine groups. It is also in correlation with the fact that azine groups of TMU-5 are more electron-rich than those of TMU-4. As seen in Fig. 3c, the strength of interactions of TMU-4 and TMU-5 with CO₂ at high loadings are gradually decreased.

To conclude, the mechanochemical grinding of N-donor ligands with Zn(II) and Hzoa resulted in the formation of two frameworks – TMU-4 and TMU-5 possessing different structural topologies, metal-ligand connectivities and therefore different pore sizes. Despite this, the pore surface in both networks is azine decorated available for the CO₂ capture. Detailed sorption studies revealed that both MOFs introduce moderately strong interactions with CO₂ which are more pronounced within TMU-5 (narrow pores). This study demonstrates that the size of the azine functionalized pores are key factors for the capture of CO₂ and since both frameworks can be obtained within only 15 minutes via mechansynthesis, can be therefore used for industrial studies on CO₂ capture.

**ASSOCIATED CONTENT**

**Supporting Information**

Detailed synthetic procedures for the isolation of TMU-4 and TMU-5, additional graphs determining their structure, PXRD patterns and TGA profiles are provided. The supplementary crystallographic data were deposited with the Cambridge Crystallographic Data Centre (CCDC) as entry CCDC 973905 and 973906. 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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