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 CO_2 uptakes at 273 and 298 K at 1 bar. The network with narrow and interconnected pores in three dimensions show greater affinity for CO_2 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 CO_2 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 CO_2 capture and storage by developing new adsorbents with high storage capacity and adsorption selectivity for CO_2.[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 CO_2 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 CO_2 uptake and adsorption selectivity.[9,10] This can be accomplished by functionalizing the pores with either of two groups: coordinatively unsaturated metal ions[11,12]; or Lewis basic groups (*e.g.* amine[13-17] and hydroxyl[18] 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 CO_2 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-diaza-1,3-butadiene (4-bpdb) and 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene (4-bpdh), which lead to [Zn₂(oba)₂(4-bpdb)]·(DMF)ₓ (**TMU-4: TMU** stands for **T**arbiat **M**odares **U**niversity) and [Zn₂(oba)₂(4-bpdh)]·(DMF)ᵧ (**TMU-5**),

respectively.[23] Considering that the pores of MOFs constructed from layers pillared by linear ligands are usually delimited by these ligands[24], 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-5** 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 (CO_2) 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)₂·6(H₂O), H₂oba and either 4-bpdb or 4-bpdh, in DMF at 80 °C for 72 hours.
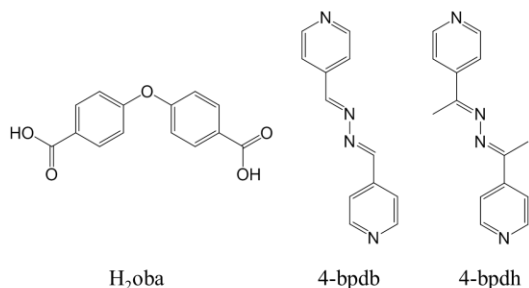
Scheme 1. Chemical structure of H₂oba, 4-bpdb and 4-bpdh. Note the bridging azine group at the center of 4-bpdb and 4-bpdh.

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
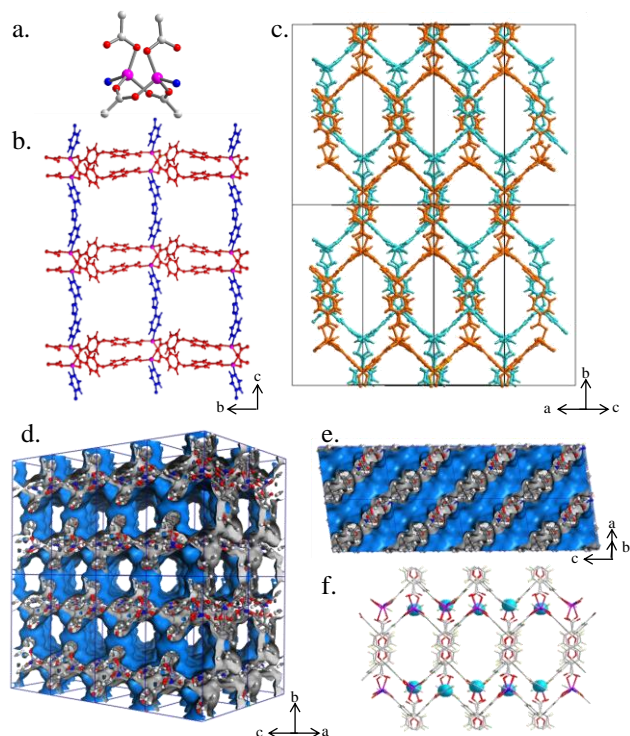
Figure 1. (a) Ball and stick representation of the binuclear Zn_2 unit (O: red; N: blue; C: grey; and Zn: pink). **(b)** Layers of Zn(II)-oba (in red) pillared by 4-bpdb (in blue). **(c)** The packing of the structure leads to a doubly interpenetrated (in orange and cyan) framework possessing 1D pores, **(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 Zn_2 paddlewheel unit within **TMU-5**. **(b)** Layers of Zn(II)-oba (in red) pillared by 4-bpdh (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.

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 Zn_2 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 3.441 Å. Each non-linear (angle: 125.12°) dicarboxylate oba ligand binds three consecutive Zn(II) centers from two different Zn_2 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)[37] 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-bpdh (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 pad-
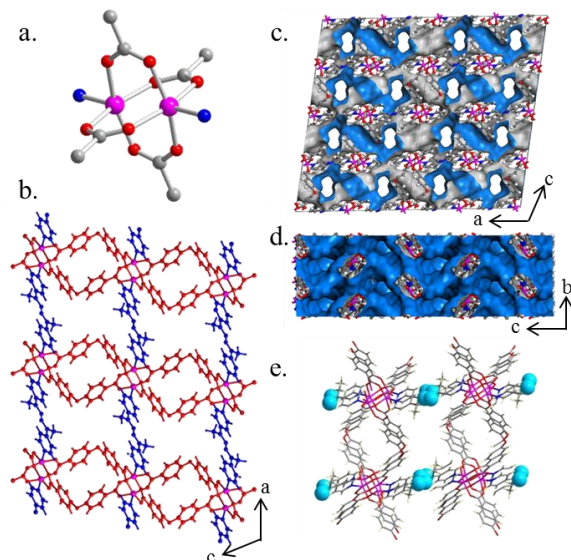
dlewheel Zn(II) unit (Fig. 2a), in which four carboxylate O atoms from four adjacent oba ligands form an approximate equatorial square plane (Zn–O carboxylate distances: 2.025 to 2.054 Å). The coordination environment of each Zn(II) center is completed by one N atom from 4-bpdh in the axial position (mean distance: 2.033Å). The separation of the Zn(II) centers within the paddlewheel 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: 120.70°) around the paddle-wheel Zn(II) units leads to the formation of 2D layers pillared by 4-bpdh ligands to yield a 3D framework (Fig. 2b and S2 in the SI). **TMU-5** possess narrower channels than those in **TMU-4** (size: 5.6 x 3.8 Å; 34% void space per unit cell)[37] 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-bpdh) 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 H_2O 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 H_2O.[17]
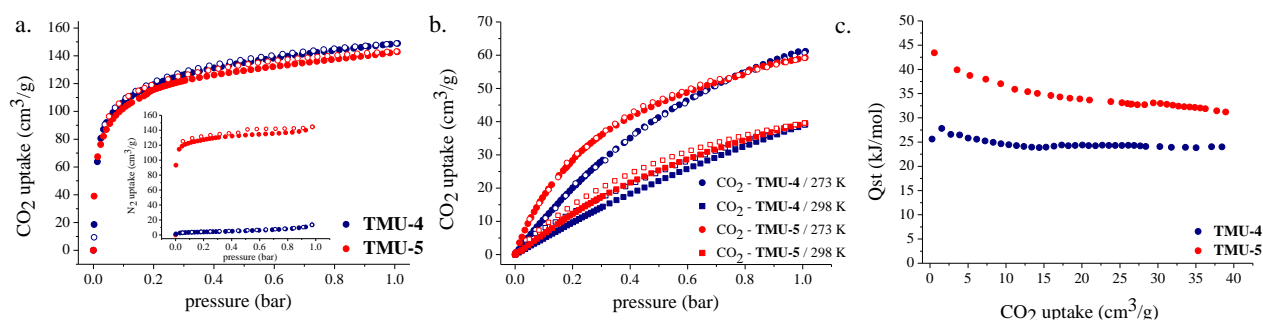
Figure 3. (a) Type I CO_2 isotherms at 195 K and 1 bar collected on mechanosynthesized **TMU-4** and **TMU-5** after activating each one at 40 °C overnight under vacuum. Inset shows N_2 isotherms. **(b)** CO_2 isotherms collected at 273 K and 298 K. **(c)** Isosteric heat of adsorption (Q_{st}) for CO_2 at different CO_2 loadings.

A type II N_2 isotherm collected at 77 K and 1 bar on the mecha-nochemically synthesized **TMU-4** (after activation at 40 °C) revealed that N_2 molecules couldn't diffuse within its pores under these conditions. Interestingly, **TMU-4** is porous to CO_2 at 195 K and 1 bar (148.90 cm³/g at 1 bar; BET surface area calculated over p/p^0 = 0.02-0.3: 517.9 m²/g) (Fig. 3a). The pore volume calculated from the CO_2 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 N_2 and CO_2 (kinetic diameters for CO_2: 3.30 Å and N_2: 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 CO_2 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 CO_2 (142.88 cm³/g at 1 bar; BET surface area: 502.7 m²/g) at 195 K and N_2 (144.49 cm³/g at 1 bar; BET surface area: 400.8 m²/g) at 77 K, for which it showed reversible type-I isotherms (Fig. 3a).[38] The pore volumes for **TMU-5**, derived from the CO_2 and N_2 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 N_2 can almost fill the pores of **TMU-5**, whereas (polar) CO_2 can fill the pores and at the same time induce struc-tural re-arrangements that expand the pores and consequently, the structural architecture. Similar behavior has been recently de-scribed in other MOFs: the adsorption of bulky xylene molecules within a flexible framework induced structural changes.[39] 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 CO_2 and N_2 led us to investigate their respective CO_2/N_2 selectivities at 298 K based on the ratio of single-component uptakes and using the IAST model for the equimolar gas mixture.[40] The calculated CO_2/N_2 selectivity for **TMU-5** (32:1) is slightly greater than that of **TMU-4** (28:1) (ratio of single-component uptakes). The selec-tivity of the equimolar mixture of CO_2 and N_2 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 $Zn_2(TCBP)(DMF)_2$, which is found to be ~45.[41]

To assess the strength of interactions between CO_2 and each host framework, we also collected CO_2 isotherms at 273 K at 1 bar. The CO_2 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 CO_2, respectively. A compa-rable uptake at 1 bar was also observed at 298 K from both frameworks (Figure 2b). However, an important feature derived from these isotherms is that at low pressure, **TMU-5** adsorbed higher amounts of CO_2 than **TMU-4**. For example, at 273 K and 0.25 bar **TMU-5** adsorbed 32.71 cm³/g, whereas **TMU-4** ad-sorbed 24.39 cm³/g. This observation reveals that the interactions between the azine groups pointing towards the narrow pores of **TMU-5** and CO_2 are more pronounced than those in **TMU-4**. The isosteric heat of adsorption (Q_{st}) was calculated using the Clausi-us-Clapeyron equation[42] 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 CO_2. The Q_{st} of **TMU-5** for CO_2 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 CO_2 compared with the interactions occurred within the large 1D pores in **TMU-4**, which are functionalized with azine groups.[20,43] It is also in corre-lation with the fact that azine groups of **TMU-5** are more elec-tron-rich than those of **TMU-4**.[38] As seen in Fig. 3c, the strength of interactions of **TMU-4** and **TMU-5** with CO_2 at high loadings are gradually decreased.

To conclude, the mechanochemical grinding of N-donor ligands with Zn(II) and H_2oba resulted in the formation of two frame-works − **TMU-4** and **TMU-5** possessing different structural to-pologies, metal-ligand connectivities and therefore different pore sizes. Despite this, the pore surface in both networks is azine decorated available for the CO_2 capture. Detailed sorption studies revealed that both MOFs introduce moderately strong interactions with CO_2, which are more pronounced within **TMU-5** (narrow pores). This study demonstrates that the size of the azine func-tionalized pores are key factors for the capture of CO_2 and since both frameworks can be obtained within only 15 minutes via mechanosynthesis, can be therefore used for industrial studies on CO_2 capture.

ASSOCIATED CONTENT

Supporting Information

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### Notes

The authors declare no competing financial interest.

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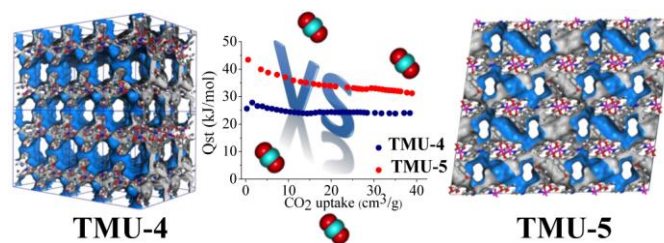
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Title: Selective CO₂ Capture in Metal-Organic Frameworks with Azine-Functionalized Pores Generated by Mechanosynthesis

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