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## Enhancing carbon capture capacities of a rigid ultra-microporous MOF through gate-opening at low CO<sub>2</sub> pressures assisted by swiveling oxalate pillars

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**ABSTRACT:** Porosity enhancement from unusual gate opening has been realized in an exceptionally rigid ultra-microporous framework. The gate-opening has been attributed to the presence of symmetrically positioned Zn-O bonds of the Zn-Oxalate units that facilitate subtle swiveling motion resulting in drastic improvement (42%) in CO<sub>2</sub> capacity without compromising the CO<sub>2</sub>/N<sub>2</sub> selectivity.

The area of porous coordination polymers, also known as metal organic frameworks (MOFs), have gained tremendous interest since last few decades due to their profuse applications.<sup>1-3</sup> Their modular structure combined with appropriate choice of ligands and metal ions enables construction of rigid or dynamic architectures.<sup>4</sup> The length and symmetry of the organic linker, generally decides the amount of void space that can be introduced into these materials, additionally, it could promote flexibility of the framework. It can be very advantageous if this flexibility can be manipulated.<sup>4</sup> MOFs with stable and robust frameworks, that maintains its porous structure before and after guest-sorption, are regarded as '2nd generation MOFs' and are good adsorbents analogous to zeolites.<sup>4a</sup> While the '3rd generation' includes the MOFs with dynamic structure, where the flexibility of framework induces reversible response to the external stimuli such as pressure or temperature and that can be gas specific.<sup>4</sup> Some of them exhibit hysteretic isotherms, which originate from a molecular gate opening mechanism.<sup>4-6</sup> In some cases, hysteresis can be manipulated by carefully controlling the external parameters such as heat and pressure.<sup>4-6</sup> In general, this property is associated with MOFs that are built from relatively longer struts and sometimes in large pore frameworks built from short linkers.<sup>4-8</sup> Maximum benefit of a gate-opening can be realized when a subtle

molecular motion produces big change in porosity of the material and thereby in the gas capacity.<sup>7</sup>

MOFs are most commonly synthesized solvothermally, thus solvents play a crucial role in deciding their structure, texture, phase purity. The dynamic role of solvents in deciding the structure of MOFs has been evoked both theoretically and experimentally.<sup>9</sup> The activation energetics and the reaction thermodynamics are, in many cases, determined by the solvents and hence can account for the changes of potential energy barrier and overall free energy via solute-solvent interactions.<sup>9c</sup> Solvents in general can play two important roles, they can be 'structure directing agents' interacting strongly with the framework's component right from their construction of smaller building units and to the final higher dimensional structure. Or, it could form weak interactions with the framework's component, yet be able to co-operatively provide sufficient strength to act as a 'template' by filling up the voids and allowing the framework to grow around them.<sup>9b,10</sup> Earlier we reported, a ultra-microporous MOF synthesized from a methanol-water mixture, with composition  $[\{Zn_2(C_2O_4)(C_2N_4H_3)_2\} \cdot (H_2O)_{0.5}]_n$ , ZnAtzOx\_MeOH (**1**).<sup>11a,b</sup> This material had a 293 K, 1 bar, uptake of 3.8mmol/g and we realized further improving CO<sub>2</sub> capacity of this material could make it a good Vacuum Swing Adsorption (VSA) candidate.<sup>11</sup>

Here in, we report the synthesis, structural characterization, thermal analysis and adsorption studies for a family of topologically related ZnAtzOx frameworks obtained under solvothermal conditions. Importantly, we demonstrate how through choice of solvent we obtain 3rd generation porous material with topology similar to its rigid 2nd generation counterparts, but with much high CO<sub>2</sub> capacities arising from exceptionally subtle 'molecular swiveling' assisted gate opening.

A series of layered-pillared MOFs have been prepared by pillaring ZnAtz layers with oxalate units. The phases were prepared via a solvothermal reaction between ZnCO<sub>3</sub>, aminotriazole (Atz) and oxalic acid (Ox) at 180 °C for 2days, with the only variation being the solvent employed. The

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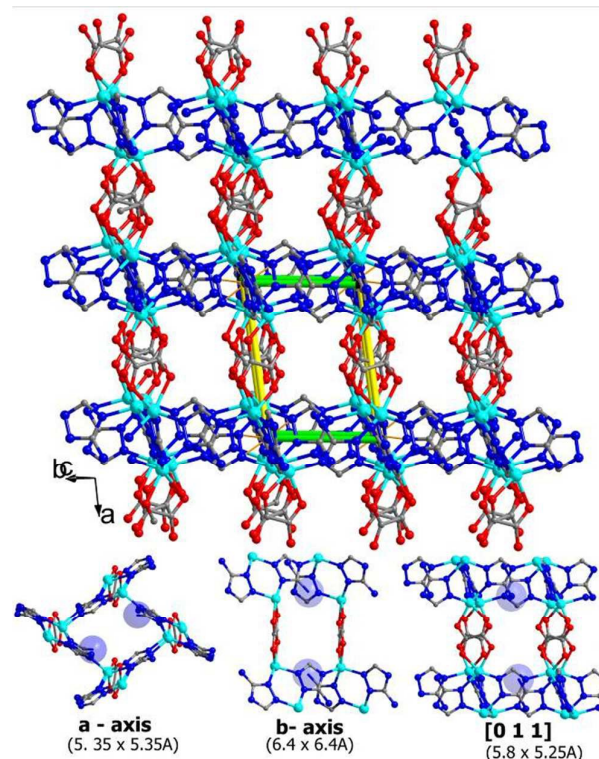
Electronic Supplementary Information (ESI) available: Electronic supplementary information (ESI) available: Experimental procedures, IR spectra, UV spectra, TGA plots, and PXRD data. CCDC CCDC 1428296; CCDC 1428298-1428299; CCDC 1438585-1438586. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x.

solvothermal reaction resulted in four polymorphic phases with a framework composition  $Zn_2(Atz)_2Ox$  (Synthesis solvent:  $H_2O$  (**2**), EtOH (**3**), n-PrOH (**4**) and n-BuOH (**2\***)). An important observation was made during these crystallizations: *though these phases could be formed pure using the single solvent reactions, use of them as a mixture with water resulted in dramatic improvement in crystal quality without any change in phase*. For example, reactions using either water or n-butanol could not grow crystals with sufficient quality for single crystal diffraction, however, when water:n-BuOH (50vol%:50vol%) mixture was used, the quality of the crystals improved significantly. The product MOFs had distinct rigid frameworks and did not show any tendency to interconvert in a single crystal-to-single crystal fashion. All samples could be made as pure phases in bulk (Figure S1) and the most porous phase, **2**, was prepared pure in 5 gm scale by a facile scale up of the mg synthesis (Figure S2). Also, attempts to transform any of the phases to another related polymorph by soaking/boiling them in other solvents were all unsuccessful, which demonstrates the stability of these solvothermally stabilized phases of  $ZnAtzOx$ . The TGA analysis indicated exceptional thermal stability of the compounds ( $>300\text{ }^\circ\text{C}$ ) (Figure S3) which can be attributed to their rigid tridentately linking Atz and the bidentately pillaring oxalate units. Further, high crystallinity observed in the temperature range of RT- $300\text{ }^\circ\text{C}$  from variable temperature PXRD for all the phases were consistent with the TGA results (Figure S4). IR spectra contains the characteristic peaks due to the carboxylate and aminotriazole units (Figure S5). Peaks corresponding to  $CO_2$  could be observed in the IR spectra of a **2** that was exposed to air showing its high affinity for  $CO_2$ .

Structures of all the phases were determined from single crystal x-ray diffraction. Typically, the framework has  $Zn^{2+}$  with distorted trigonal bipyramidal geometry. Their coordinations are from tridentately bridging aminotriazole units and bidentately chelating oxalate units, resulting in highly rigid frameworks. Notably, in all phases the  $-NH_2$  of the aminotriazole remains free. Topologically, the  $ZnAtz$  layers formed by linking of dimeric  $Zn_2Atz_2$  units are pillared in an out-of-plane fashion by the oxalate units. If the  $Zn_2Atz_2$  dimers are reduced to nodes and the Atz and oxalate units to linkers, the resultant topology in all cases is a simple six-connected cubic net (Figure 1). The differences between the structures originate from the extent and mode of puckering of the layers (defined by the angle between the adjacent  $Zn_2Atz_2$  dimers, Figure S6). The Atz and oxalate units together determine the shape and size of the pores (Figure S7). PLATON analyses showed **3**, **4** and **2\*** phase to have an effective solvent accessible volume of 32%, 33%, and 28% respectively. Which was comparable to the parent phase, **1** (31%).<sup>11</sup> As explained earlier, one of the major aim of this study was to improve the capacity of the  $ZnAtzOx\_MeOH$  (**1**) phase without losing its inherent selectivity arising from the ultra-microporous character. To evaluate the porosity experimentally,  $CO_2$  adsorption was carried out on the different phases.

The adsorption measurements were carried out on the activated samples of **2**, **3**, **4** and **2\***. The  $CO_2$  uptake of **2** and **2\*** were similar and were considerably higher than the rest of the phases, including, **1** (Figure 2). **3** showed lower porosity

compared to **1** and **2**, while **4** was found to be practically non-porous (Figure 2A).



**Figure 1.** Three dimensional structure of  $ZnAtzOx$ , **2**, grown from water/butanol solvent. The  $ZnAtz$  layers are pillared by the oxalate units resulting in ultra-micropores along three different axes. The dimensions do not factor in the van derWaal radii. Colour code: Zn - cyan; O - red; N - blue; C - grey.

From here onwards phases **2** and **2\*** has not been differentiated, unless required. The relatively higher  $CO_2$  uptake of **2** is achieved by a process of  $CO_2$  assisted gate-opening. Thus, the gate opening is characterized by a sharp increase in  $CO_2$  uptake at a  $P/P_0$  of 0.2 at 273K, but lacks any noticeable hysteresis.<sup>12</sup> Also the profile, particularly in terms of the abruptness of the isotherms at low pressures (0-0.03bar), agree well between the isotherms of phases **1** and **2**. Due to the stepped nature of the 273K isotherm surface areas or pore volume determinations from routine DFT models were not feasible. However, taking a logical approach, the 195K isotherm seem to represent the saturation capacity of the material, while the 303K isotherm without the gate-opening seemed to represent the capacity due to only one of the adsorption sites or say one type of pore. Thus from 195K isotherm a BET surface area of  $573\text{ m}^2/\text{g}$  was calculated. And, separately by fitting the low pressure and high pressure regions of the 273K data using the standard BET model,  $307.631\text{ m}^2/\text{g}$  ( $R^2 = 0.999802$ ) and  $206.144\text{ m}^2/\text{g}$  ( $R^2 = 0.995646$ ) were obtained (Figure S11). Thus the sum of the surface areas from the low pressure and high pressure regions would yield a surface area comparable to the one from 195K  $CO_2$  isotherm. This can be explained by considering a dual site model for the  $CO_2$ 's filling up the pores in **2**. In fact, the abrupt increase in  $CO_2$  capacity at the gate opening is accompanied likely by an increase in pore volume and this opens up

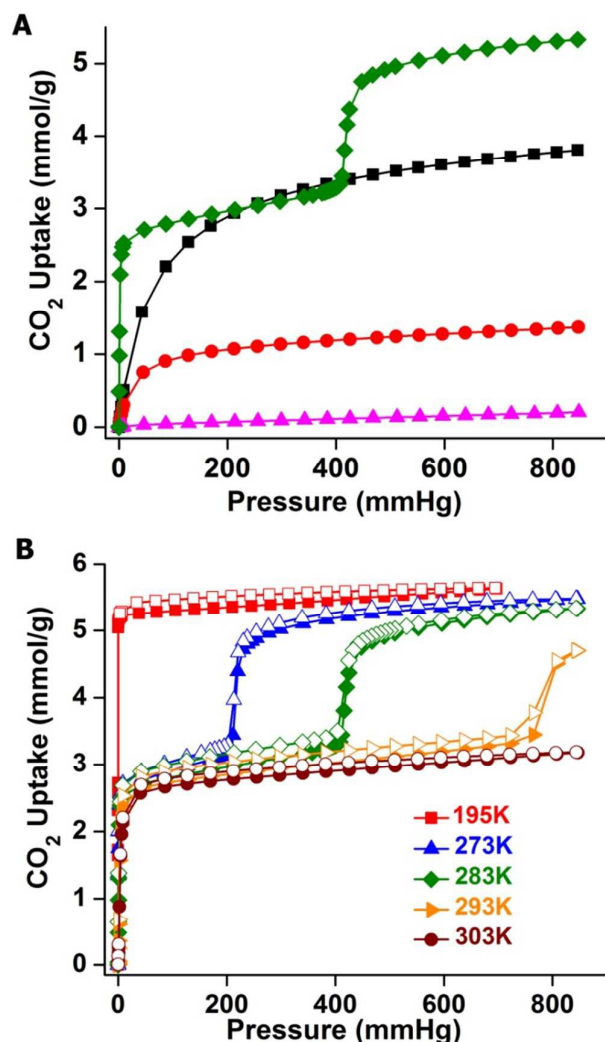


Figure 2. (A) CO<sub>2</sub> adsorption comparison for various phase of ZnAtzOx, all measured at 283K, Colour Code: green: 2, black: 1, red: 3, pink: 4. (B) CO<sub>2</sub> adsorption curve at different temperatures for the 2.

a second adsorption site (discussed later in the text).<sup>11</sup>

The CO<sub>2</sub> gating in **2** shows temperature dependence, the gating occurs at a CO<sub>2</sub> pressure of 200mbar at 273K and shifts to as high as 765mbar at 293K. This 565mbar difference in gate opening pressures for a mere 20°C increase in temperature is quite unusual and is reflective of the ultra-microporous character of **2**. By which we mean that a subtle difference in orientation of the organic linkers causes massive difference in the pore accessibilities. One possible explanation for the increase of the gate-opening pressures with increasing temperature could be as follows. The CO<sub>2</sub>-framework interactions are expected to weaken with increasing temperature, this would mean that more CO<sub>2</sub> molecules would have to act co-operatively to provide sufficient force to create the molecular motion required for the gate-opening, which translates to higher CO<sub>2</sub> pressures. To provide a plausible explanation for the origin of gate opening in **2**, possible molecular motion associated with both Atz and oxalate units needed to be considered. Given the rigid tridentate linking

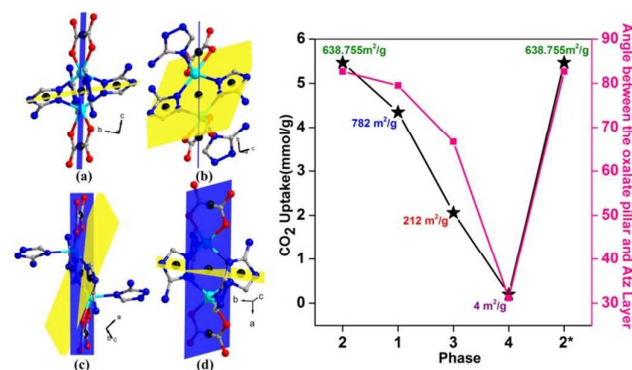
mode of the Atz units and the typically strong Zn-N covalent bonds, it is unlikely that they would go through any significant rotation about the Zn-N bond, particularly under this low CO<sub>2</sub> pressures. On the other hand, an examination of the bond distances reveal that the Zn-O distances are not all symmetrical, in fact, there are shorter (2.0Å) and longer (2.2Å) distances in **2**. Such relatively longer Zn-O bonds are found also in **3** and **4**, but they are non-porous to CO<sub>2</sub> and no gating phenomenon are observed for these phases. This is explained by the symmetrical positioning of the longer Zn-O bonds in **2**. The longer Zn-O bonds (2.2Å) from Zn and oxalate are positioned diagonally about the oxalate C-C bond, this could facilitate a spindle like rotation or 'swiveling' of the oxalates (Figure S14). Whereas in **1**, where even weaker Zn-O bond (2.4 Å) are present yet no gate opening is observed, which indirectly suggests that the symmetric arrangement of relatively weaker bonds (Figure S14) is crucial. However, if they spin by larger angles (for example, >90) it would be resulting in considerable structural rearrangement, which would be expected to show changes in the PXRD pattern. Lack of any major structural change during gate opening, except for the mere volume expansion, was confirmed using a PXRD of **2** that was sealed under 900mbar of CO<sub>2</sub> pressure in a capillary (Figure S15a). Furthermore, when this sealed sample was subjected to heating (30°-150°C), no appreciable change in structure was noticed (Figure S15b). Thus a subtle molecular motion could be opening up an additional site for CO<sub>2</sub> to fill up.

To provide further support to our hypothesis, a dual site Langmuir-Freundlich model was employed to calculate the energetics associated with the CO<sub>2</sub>-framework interactions for both these sites. It turns out that a site I has a HOA of 46kJ/mol, while the site II has a value of 32kJ/mol (See supporting information). Comparison of these values against the HOA's observed for **1** brings some excellent observations. **1** also had a dual site CO<sub>2</sub> filling and had one site with relatively higher HOA (40kJ/mol) dominated by amine-CO<sub>2</sub> interactions, and the other site with HOA of 32kJ/mol dominated by CO<sub>2</sub>-CO<sub>2</sub> interactions, which were well partitioned in energy contributions via simulations. Now, comparing the 195K or 273K CO<sub>2</sub> isotherms of **2** with **1**'s, it can be seen that **2** has even more abruptness or steepness at low CO<sub>2</sub> pressures, which indicates stronger interactions between the framework and CO<sub>2</sub>. This is consistent with the higher HOA obtained for the site I of **2** (46kJ/mol vs 40kJ/mol for **1**). Meanwhile, the HOA corresponding to the site II of **2** has a value comparable to the one obtained for the second site in **1**, which is mostly due to CO<sub>2</sub>-CO<sub>2</sub> interactions. In addition, in **2**, the gate opening significantly enhances the pore volume (from 0.13 to 0.18cc/g). Considering that the increase in CO<sub>2</sub> capacity is associated with increase in pore volume resulting from gate opening, it is possible that the second CO<sub>2</sub> site is generated only via this gate opening. Based on the uptakes it can be calculated that the site I holds 1.3 moles of CO<sub>2</sub>/FU, while the site II would accommodate 0.95 moles/FU. Thus the saturated CO<sub>2</sub> uptake results in **2**.(CO<sub>2</sub>)<sub>2.25</sub>, which is almost 1 CO<sub>2</sub>/FU higher than what was observed for **1**.

A good CO<sub>2</sub>/N<sub>2</sub> apparent selectivity can be realized by comparing the initial slope of the room temperature isotherms of **2** (Figure S18a). This room temperature selectivity realized at low pressure of CO<sub>2</sub>, to our knowledge, is among some of the best performing ultra-microporous MOFs (Table S3). In a

performance point of view, the increase in CO<sub>2</sub> uptake due to gate opening from 3.2 mmol/g (700 mbar) to 4.7 mmol/g (1.1 bar) at 293 K, in fact translates to a 65% increase (0.7 to 2 mmol/g) in working capacity for a 1–0.15 vacuum swing at 293 K, considering the pure component isotherms. This truly represents the exceptional tunability of the capacity and selectivity that ultra-microporous materials bring. However, the selectivity does drop appreciably as we approach ambient pressures (Figure S18b). The selectivity observed is considerably higher than many MOFs, but lower than some of the best-performing ones.<sup>1b,11c</sup> The exceptional stability of **2** is reflected in the complete maintaining of crystallinity even after 16 adsorption-desorption cycles (RT–150 °C heating-cooling). **2** poses high hydrolytic stability towards both steam and boiling water (Figures S2, S19 and S20).

Pre-gate opening CO<sub>2</sub> uptake (0–200 mbar) in **2** is also higher than all the other phases, particularly the **1**.<sup>11</sup> Now this is not due to any structural rearrangements under CO<sub>2</sub>, but is inherent to the as-synthesized framework's structure. This can be explained considering the pillar orientations. The pillaring oxalates are aligned all along the *ab*-plane, thus controls the accessibility from two orthogonal directions. Given this, their orientation with respect to the Atz layer can also have significant impact in determining the free space volumes. A comparison of the angles between the mean planes defined by aminotriazolate layer and the oxalate pillars shows that the



**Figure 3.** (A) Comparison of the angle between the oxalate pillar and the aminotriazolate layer: (a) **1**, (b) **3**, (c) **4** and (d) **2**. Colour Code: Yellow: ZnAtz layer and Blue: Oxalate pillar. (B) A plot showing the role of solvents in controlling the porosity of the ultra-microporous ZnAtzOx MOF phases.

porous phases, **1** and **2**, have these values close to 80°, while for the non-porous **3** and **4** they are much lower than this (Table in Figure S6).

We also observed some strong solvent dependence on the framework structure of the ZnAtzOx polymorph. There are two key roles of the solvents. Solvents as 'structure directing agent (SDA)' or as 'template'. It can be expected that solvents with high hydrogen bonding abilities would interact strongly with the polar walls of the framework and such solvents can direct the structure. On the other hand solvents which are bulkier are generally good at templating. Now between the solvents employed in this work, water and methanol are the most polar and hydrogen bonding, while butanol is the bulkiest. As can be rationalized from figure 3, only the polar solvents acting as

SDA or the bulky solvent acting as a template, both assist the ZnAtz layer and the oxalate pillars to take a more symmetrical arrangement (angle close to 90°) giving rise to a near-cubic pores with maximum accessibility. At the same time, the inherent molecular-sieving assisted selectivity is not compromised. Thus, an appropriate choice of solvent can aid in rational synthesis of ultra-microporous solids for gas storage and separation.

In conclusion, the present study demonstrates a 42% enhancement of CO<sub>2</sub> capacity of a rigid ultra-microporous MOF via a counterintuitive gate opening phenomenon. The gating has been attributed to the swiveling motion of the oxalate pillars favored by the presence symmetrically positioned weak Zn–O bonds from the Zn–Oxalate units. A dual site model has been proposed to explain the opening up of a CO<sub>2</sub> site via this gate opening. The openness of the ZnAtzOx 3D framework has been tuned by choosing solvents with right polarity or bulkiness.

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