

An amine-functionalized metal organic framework for preferential CO₂ adsorption at low pressures†

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A metal organic framework with amine-lined pores gives high values for surface area and heat of adsorption with CO₂ gas.

Metal organic frameworks (MOFs) show great promise for gas sorption and storage.^{1,2} For carbon dioxide, notable advances have occurred with respect to both capacity (MOF-177 is capable of storing up to 33.5 mmol g⁻¹ of CO₂³) and demonstrating the ability of MOFs to separate CO₂ from mixtures of gases.⁴ While large pore MOFs could be effective for storing high capacities of the gas, usually at higher pressures, they may not be as efficient at lower pressures. They also would be expected to be less selective in their sorption properties based on pore size alone. These issues become very significant for removal of trace amounts of CO₂ from industrially recyclable gases such as H₂ as the partial pressure of CO₂ is very low. Conventional methods of CO₂ capture, using amine solutions as scrubbing agents, involve a high energy penalty and are inefficient when it comes to the regeneration of the adsorbed CO₂ gas molecules.⁵ The kinetics of gas sorption in MOFs can be controlled both by complex pore structures^{4,6} and by chemical functionalization of pores with groups capable of interacting strongly with the adsorbates.⁷

The potential of amine groups to interact with CO₂ molecules is by now reasonably well understood.⁸ Some investigations on the ability of amine-derivatized MOFs to adsorb CO₂ gas molecules have appeared in the recent literature.⁹ Our efforts are focused in the design and synthesis of MOFs, from readily accessible components, with amine-functionalized micropores. For this purpose we have chosen 3-amino-1,2,4-triazole (Atz) as a ligand as it has excellent tendencies towards forming robust networks.^{10–14} However, most of these are either dense frameworks or have cages occupied by counter anions. zur Loye and co-workers¹³ reported an interesting microporous ZnFAtz compound, with amine-lined 1D pores.

Since our initial attempts to synthesize MOFs by combining Atz with different metals did not yield highly crystalline structures, we decided to employ oxalic acid as a co-ligand

based on our prior success with the use of such a strategy in other systems.¹⁵ The result is a porous Zn-aminotriazolato-oxalate compound, with a formula Zn₂(C₂O₄)(C₂N₄H₃)₂·(H₂O)_{0.5} (**1**), that shows rapid uptake at low pressures and high enthalpy of adsorption for CO₂.‡

Compound **1** was synthesized *via* a solvothermal reaction with zinc carbonate, 3-amino-1,2,4-triazole and oxalic acid carried out at 180 °C for 2 days. The three-dimensional framework is built from the pillaring of Zn-aminotriazolite layers by the oxalate groups. The aminotriazolite ligands bind to trigonal bipyramidal zinc centres in a tridentate fashion ($\mu_{1,2}$) through the three N-atoms of the ring, while the amino groups remain free (Fig. 1a). The adjacent zinc atoms, in the 1,2-positions, from two Atz ligands create dimeric Zn₂ units within the layer. Alternating dimeric units on the *ac*-plane are rotated by 90° with respect to each other (Fig. 1a). The free amino groups of the Atz ligands running along the *a*-axis are disordered about a 2-fold ligand axis. This layer is the same as that observed for Zn-Atz-carboxylates.^{10–13} The oxalate ligands bind to the zinc in a bidentate mode through two oxygen atoms from different carboxylate groups to form five-membered rings (Fig. 1b).

Considering the Zn₂ dimers to be nodes, the three-dimensional framework has a 6-connected α -Po topology (Fig. 1b). This creates channels with a cross section of 3.5 × 4.0 Å (all pore dimensions reported factor in van der Waals radii) along the *a*-axis (Fig. 1b). These channels are cross-linked by smaller channels (3.9 × 2.1 Å) along the *b*-axis, thus creating a 2D pore system in the *ab*-plane (Fig. 3). There are also small slit-shaped windows (3.0 × 1.6 Å)

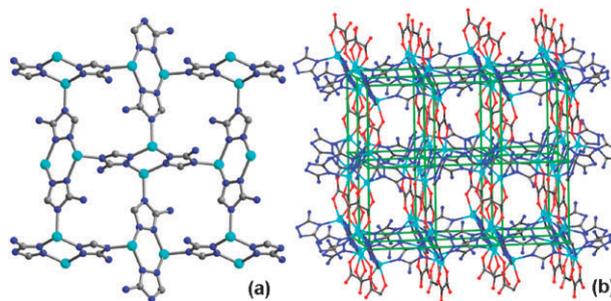


Fig. 1 (a) Zn-aminotriazolite layer in **1**. The layer is made up of Zn₂ dimers rotated by 90° with respect to each other. (b) The three-dimensional structure formed by pillaring the above Zn-aminotriazolite layers by oxalate units. Colour scheme: Zn—cyan; N—blue; O—red; C—grey. The cubic 6-connected network of **1** is indicated as green grids.

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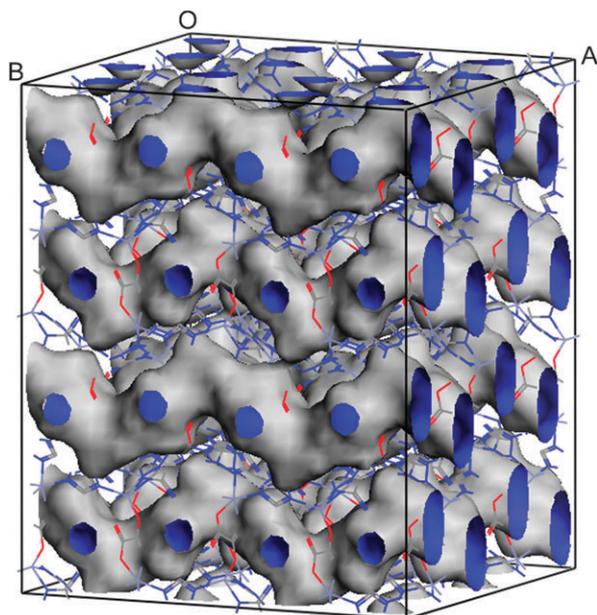


Fig. 2 (a) The Connolly surface diagram of **1** made using a probe radius of 1.3 Å. The larger one dimensional column (3.5 × 4.0 Å) running along the *a*-axis and the smaller (3.9 × 2.1 Å) cross-linking tunnels running along the *b*-axis have been shown. The inner surfaces of the channels have been shown in blue, while the outer surfaces are represented in grey. Framework atoms: Zn—cyan; N—blue; O—red; C—grey.

along the *c*-axis, which cross-link the 2D channel system in the *ab*-plane into three dimensions. The connectivities between these orthogonal apertures generate cube-shaped spaces within the framework with approximate dimensions of 4.0 × 4.0 × 4.0 Å. Notably, the free amine groups protrude into the pores giving a zig-zag arrangement to the largest pore

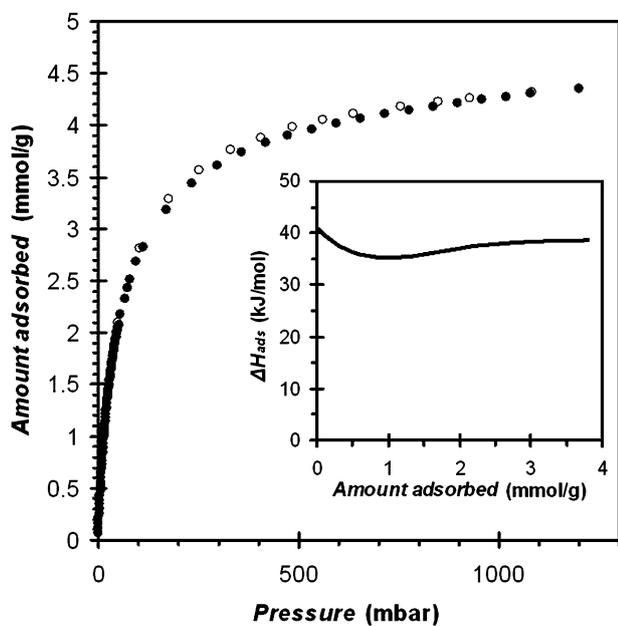


Fig. 3 CO₂ sorption isotherm of **1** carried out at 273 K, closed circles adsorption, open circles desorption. Inset shows the enthalpy of adsorption (ΔH_{ads}) as a function of loading.

down the *a*-axis (Fig. 2). The spaces within the pores are filled by solvent water molecules.

A zinc-triazolato-oxalate with 6-connected α -Po topology has been reported.¹⁶ This has a framework different from that of **1**. Rather than the 4,4-connected Zn-Atz layer of **1**, it forms a 3D Zn-triazolate framework with spaces occupied by the oxalate ligand. Unlike **1**, this framework does not appear to be porous. On the other hand, Chen and co-workers studied a series of zinc aminotriazolates, the same layer motif observed here, pillared with carbonate and carboxylates, excluding oxalate.¹⁰ In this case, N₂ sorption studies showed a surface area of 104 m² g⁻¹ for the carbonate derivative and no gas uptake for the carboxylate pillared compounds. In these zinc-Atz layered structures, the porosity appeared to be limited by the efficient packing of the pillaring dicarboxylates within the inter-lamellar spaces. Oxalate appears well-suited to bridge the Zn-Atz layers as the use of other carboxylates like formate¹¹ or glutarate,¹⁴ which cannot form 5-membered chelate rings, form entirely different dense frameworks. The use of Atz with NO₃⁻ ions forms a cage structure trapping ions in the cages.¹¹ A noteworthy structural feature in most of these frameworks is the presence of Atz in a μ_2 or $\mu_{1,2}$ coordination mode; however, the latter is the most common.

Thermogravimetric analysis performed on bulk samples showed that **1** loses solvent molecules from 30 to 130 °C and then shows no further mass losses up to 300 °C (see Fig. S1, ESI†). Also, **1** could be activated by evacuating the sample at 100 °C under reduced pressure ($\sim 10^{-3}$ mbar) after soaking in dry acetone for 72 hours. Both samples showed PXRD patterns that matched the (single crystal) parent phase (Fig. S1 and S2, ESI†). Based on these promising results and a PLATON calculation that showed **1** had an effective solvent accessible volume of 31%, gas sorption studies were performed.

Adsorption of various gases by activated **1** was studied using a Micromeritics ASAP 2020 gas adsorption analyzer. CO₂ sorption at 273 K gave a reversible Type I isotherm (Fig. 3). A surface area of 782 m² g⁻¹ and pore volume of 0.19 cm³ g⁻¹ were calculated from the fit to the density functional theory model (Fig. S9–S12, ESI†). A notable aspect of the CO₂ adsorption was the abrupt uptake at lower pressures; the uptake was 4.35 mmol g⁻¹ (97.5 cm³ (STP) g⁻¹) at partial pressures as low as 1.2 bar ($P/P_0 = 0.034$) at 273 K. Adsorption and desorption cycles were repeated eight times with complete reversibility. This integrity was also corroborated by the PXRD and TGA (Fig. S4, ESI†). This stability can to a large extent be attributed to the fact that **1** is made up of small but rigid linkers each multiply chelated. Surprisingly, **1** did not show any appreciable uptake of N₂, Ar or H₂ under comparable conditions (Table 1, Fig. S6, ESI†). This apparent selectivity for CO₂ is attributed to the small pores in **1** restricting the adsorption of gases giving rise to a diffusion barrier. In the case of CO₂ this diffusion barrier can be overcome by extremely favourable host-guest interactions.

To further understand the adsorption properties, the enthalpy of adsorption (ΔH_{ads}) of CO₂ was determined by carrying out a second isotherm at 293 K and fitting the data to the virial model. At zero loading, indicative of the interaction of CO₂ with the most energetically favoured sites in the

Table 1 Summary of gas adsorption data for **1**

Gas	T/K	Surface area ^a /m ² g ⁻¹	Pore volume ^a /cm ³ g ⁻¹	Amount adsorbed ^b /	
				cm ³ (STP)g ⁻¹	mmol g ⁻¹
CO ₂	273	782	0.19	97.50	4.35
CO ₂	293	—	—	84.80	3.78
N ₂	77	7	<0.01	2.06	0.09
N ₂	273	—	—	5.98	0.27
H ₂ ^c	273	—	—	1.70	0.08
Ar	87	3	<0.01	7.90	0.35
Ar	273	—	—	5.35	0.24

^a Surface area and pore volume determined from density functional theory model. ^b Amount of gas adsorbed taken at 0.8 P/P₀ for N₂ and Ar at 77 and 87 K, respectively, for all other isotherms values taken at maximum pressure. ^c Attempts were made to measure the 77 K H₂ isotherm but the adsorption kinetics were too slow to allow a reliable analysis.

framework, ΔH_{ads} was determined to be 40.8 kJ mol⁻¹. At maximum loading the ΔH_{ads} was still remarkably high at 38.6 kJ mol⁻¹ (Fig. 3). Also, the curve indicated a slight upward trend from intermediate loadings (Fig. 3 inset), which is likely due to favourable adsorbate–adsorbate interactions between CO₂ molecules trapped in the pores. This ΔH_{ads} exhibited by **1** is slightly lower than the highest values observed in materials used in pressure swing adsorption devices (zeolite NaX = 48.2 kJ mol⁻¹).¹⁷ The high ΔH_{ads} is believed to arise from a combination of CO₂–amine interactions and the small pores of **1** allowing overlap of the attractive potential of proximal surfaces.

The high adsorption energy and the uptakes associated with CO₂ gas, coupled with the lack of uptake for other gases, imply that these solids could be very useful for selectively capturing CO₂ at low partial pressure from a mixture of gases. Breakthrough experiments with **1** and with related materials are ongoing as well as physical characterization of the adsorbed CO₂ molecules.

Notes and references

‡ Zn₂(C₂O₄)(C₂N₄H₃)₂·(H₂O)_{0.5}, *M*_r = 393.951, orthorhombic, *Pbca*, *a* = 13.838(3), *b* = 12.784(3), *c* = 16.885(3) Å, *V* = 2987.0(10) Å³, *Z* = 8, λ = 0.71073 Å, *T* = 173(2) K, *R*₁(obs) = 0.0504, *R*_w(obs) = 0.1204; GOF = 1.113.

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