ChemComm

Cite this: *Chem. Commun.*, 2011, **47**, 2011–2013

www.rsc.org/chemcomm

**COMMUNICATION**

# Amino functionalized zeolitic tetrazolate framework (ZTF) with high capacity for storage of carbon dioxide†

**Tamas Panda,[a] Pradip Pachfule,[a] Yifei Chen,[b] Jianwen Jiang[b] and Rahul Banerjee*[a]**

***Received 1st October 2010, Accepted 2nd December 2010***
**DOI: 10.1039/c0cc04169f**



**A three dimensional –$NH_2$ functionalized Zeolitic Tetrazolate Framework (ZTF-1) has been reported. The framework adopts a dia topology (M–L–M angle is close to 156°). ZTF-1 shows high $CO_2$ (273 K) and $H_2$ (77 K) uptake due to the presence of the free –$NH_2$ group and uncoordinated tetrazolate nitrogen.**

Selective carbon dioxide capture from coal-fired power plants is a critical issue as these plants produce post-combustion flue gases with ~15% $CO_2$ concentration.[1] At present, the separation of $CO_2$ from such a low pressure stream of gases is performed by amine sorbents through chemisorptions.[2] However, researchers are exploring alternative approaches as amine regeneration requires significant heating and has high operational cost. These limitations have prompted investigations on porous materials relying on reversible physisorption of $CO_2$, because it requires less energy for regeneration than materials relying on chemisorption.[3] Adsorbents like Zeolite 13X has been reported to provide an uptake of ~4.7 mmol $CO_2$ per gram sorbent *via* physisorption.[4] Recently, Zeolitic Imidazolate Frameworks (ZIFs), that mimic the zeolite type structure but possess larger and more modifiable pores, has received considerable attention as materials for strategic gases such as $CO_2$ and $H_2$ sorbents.[5] However still there is a necessity of new metal organic frameworks (MOFs) which will exhibit high adsorption capacity,[6] fast $CO_2$ adsorption–desorption and low energy requirement for regeneration. In order to achieve that, a number of feasible avenues for increasing the adsorption capacity of such materials, for instance, the introduction of open metal sites and the use of ligand molecules with specific functionalities (like –OH or –$NH_2$) have been attempted.[7] Recent theoretical work on the interaction of $CO_2$ with functionalized aromatic molecules has shown the effectiveness of introducing specific polar substituent groups, *e.g.* –OH or –$NH_2$, in increasing the $CO_2$–ligand affinity.[8] While the ability of $NH_2$-functionalization of MOFs and ZIFs to enhance $CO_2$ adsorption has been described in the literature.[9] Still there are no reports of a –$NH_2$ functionalized three dimensional zeolitic metal tetrazolate with the uncoordinated tetrazolate nitrogen as well as free –$NH_2$ functionality as the synthesis of such materials has proven to be very challenging.[10]

We describe herein, for the first time, the isolation of a three dimensional amino functionalized Zeolitic Tetrazolate Framework (ZTF-1),‡ where only N1 and N4 are coordinated to metal centers (Zn–5AT–Zn angle is close to 145°, coincident with the Si–O–Si angle) and adopt a tetrahedral framework reminiscent of those found in zeolites.

Our initial attempt to synthesize ZTF-1 by means of solvothermal reactions of $Zn(NO_3)_2{\cdot}6H_2O$ and 5-aminotetrazole (5-AT, $CN_5H_3$) in different molar ratio in aqueous or nonaqueous media (*DMF*/*DEF*/*NMP*) resulted in the precipitation of un-reacted starting material. Usage of diverse structure directing agents (like tetra-butyl ammonium salts) also resulted in similar outcome (Table S1 in ESI†). However after several attempts we discovered that reaction of $Zn(NO_3)_2{\cdot}6H_2O$ (1 ml, 0.2 M) with 5-AT (1 ml, 0.2 M) in a *N*,*N*′-dimethylformamide (DMF) solution in the presence of *N*,*N*′-dimethylformamide–azine–dihydrochloride (DMAz) [1 ml 0.2 M] at 100 °C for 72 h afforded a colorless microcrystalline material with a dodecahedron morphology. So far we are unable to understand the role of DMAz during the synthesis and crystallization of ZTF-1, as it is non-existent in the resulting crystal structure. We anticipate that, it might be acting as a structure directing agent (SDA) as it contains two tetrahedral nitrogens. The as-synthesized compound, was characterized and formulated by X-ray diffraction (XRD) studies as $[Zn(CN_5H_2)_2]{\cdot}DMF$.

The crystal structure of ZTF-1 was found to be related to the diamond (*dia*) topology.[11] The T atoms are Zn and the linkers are 5-AT bonding to Zn *via* the N atoms of the five-membered tetrazolate ring (Fig. 1a). The Zn···Zn distance (~5.9 Å) in ZTF-1 like ZIFs is extended by replacing oxide ions with tetrazolate linkers (the corresponding Si···Si distance in aluminosilicates is about 3.0 Å).[12] This leads to an expanded metal tetrazolate with voids (Fig. 1b) and an extended 3-D ZTF structure with a pore size of 4.5 Å in diameter (Fig. 1b). The *dia* framework of the ZTF-1 is illustrated in Fig. 1c, which shows only the vertices (T atoms), edges (links between the

[a] *Physical/Materials Chemistry Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, India. E-mail: r.banerjee@ncl.res.in; Tel: +91 2025902535*
[b] *Department of Chemical & Biomolecular Engineering, National University of Singapore, 117576, Singapore*

† Electronic supplementary information (ESI) available: Experimental procedures, crystallographic data (CIF) and additional supporting data. CCDC 779031. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc04169f

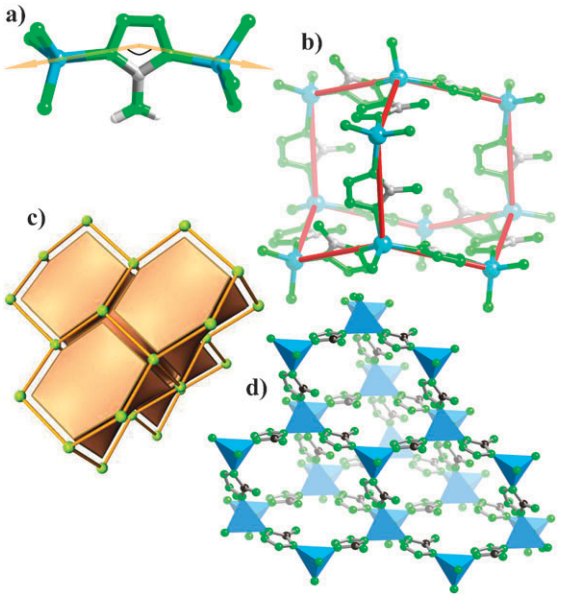


**Fig. 1** Crystal structure of ZTF-1. (a) The Zn–TET–Zn bridging angle in ZTF-1. (b) Zn(II) and 5-amino tetrazolate clusters are bridged together to generate an extended 3D porous structure with channels along the crystallographic *c* direction. (c) The framework adopts a *dia* topology. The structure is shown as an exploded tiling of adamantane (brown) with all the tetrahedral Zn(II) atoms (green) linked. (d) 3D packing diagram of ZTF-1. [Zn(II) blue; C, black; N, green.]

T atoms) and the network topological connectivity (ball–stick).[13] It is simply made up of four coordinated [$6^4$] tiling with a transitivity of 1111 (vertex, edge, face, tile). A monoclinic unit cell of ZTF-1 contains 4 zinc ions within a unit cell volume of 1349.7(5) Å$^3$. The density ($T/V$) of metal atoms per unit volume is 2.09 nm$^{-3}$, which is comparable to ZIFs (2.08–3.7 nm$^{-3}$) and much less than that of zeolites (12–20 nm$^{-3}$). Fig. 1b shows the separate adamantane type cage in the structure of ZTF-1. The adamantane cage consists of 10 Zn ions and 12 5-AT and each cage is surrounded by 6 similar cages (Fig. 1d). Note that, because of the way the 5-AT linkers are oriented, there are six 5-AT links pointing inwards each cage while six are pointing outwards. Apart from the –$NH_2$ functionality, uncoordinated N2 and N3 nitrogen are exposed to the pore. As shown in Fig. 1b, the largest 6-membered ring has a pore aperture of 4.3 Å. The reason for ZTF-1 adopting the *dia* topology is not very clear to us. We calculated the M–L–M angle of all ZIFs reported so far (Table S3 and Fig. S5, ESI†) to elucidate the reason for the formation of the *dia* topology with 5-AT rather than the *sod* topology (obtained with 2-methylimidazolate and 2-nitroimidazolate). The *dia* topology is found to withstand a wide variation of the M–L–M angle (from 135° to 149°) compared to any other topology reported (*sod* withstands a variation of 141° to 147°).[14]

The as-synthesized ZTF-1 consists of 23.5 wt% of DMF, as quantified from XRD, corroborated by thermogravimetric analysis (TGA) (Fig. S6, ESI†). The activated sample was prepared by exchanging the solvent in the as-synthesized ZTF-1 with dry methanol, followed by evacuation at room temperature. The methanol-exchanged and activated compounds were characterized by TGA measurements to assure full activation was achieved. The architectural stability

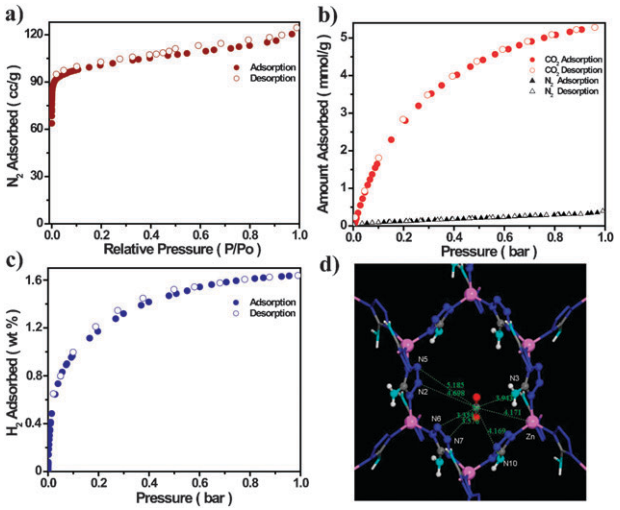


**Fig. 2** Gas adsorption isotherms of ZTF-1. (a) Nitrogen adsorption isotherm (77) K. (b) Adsorption isotherms for $CO_2$ (red circles) and $N_2$ (black triangles) at 273 K. (c) Hydrogen adsorption isotherms at 77 K. The filled and open circles represent adsorption and desorption, respectively. (d) Distances between $CO_2$ molecule and different N atoms in ZTF-1.

and permanent porosity of ZTF-1 were also confirmed by measuring the $N_2$ gas adsorption of the guest-free material (Fig. 2a). The BET and Langmuir surface area were calculated to be 355.3 and 443.8 m$^2$ g$^{-1}$. Recently researchers have shown that MOFs and ZIFs can hold large amounts of carbon dioxide and have demonstrated that ZIFs can capture $CO_2$ selectively from CO and $CH_4$ (see Table S4 in ESI† for a detailed list of MOFs with high $CO_2$ uptake).[5] Fig. 2b shows the $CO_2$ adsorption isotherms for ZTF-1, which shows high capacity for $CO_2$ than $N_2$ at 273 K. The $CO_2$ uptake at 760 Torr for ZTF-1 is 10 times higher than $N_2$ at 273 K. Although ZTF-1 has lower $CO_2$ uptake (5.6 mmol g$^{-1}$ at 273 K) than the Mg–MOF-74 (8.08 mmol g$^{-1}$ at 298 K), the $CO_2$ uptake of ZTF-1 compares well with the recently reported bio-MOF-11[15] (6 mmol g$^{-1}$ at 273 K) and outperforms other ZIFs. Recently, Yaghi and Simuzu reported free –$NH_2$ functionalised zeolitic MOF, ZIF-96[9] and Zn–aminotriazolato-oxalate.[9] However, ZTF-1 contains *both* free tetrazole nitrogen and free –$NH_2$ functionality to interact strongly with $CO_2$. As a result in terms of $CO_2$ uptake ZTF-1 outperforms ZIF-96 (2.16 mmol g$^{-1}$ at 298 K) and Zn–aminotriazolato-oxalate (4.3 mmol g$^{-1}$ at 273 K). Since ZTF-1 has small pores and exposed –$NH_2$ functionality like the bio-MOF-11, which has a high (1.5 wt% at 77 K) $H_2$ uptake, we decided to collect $H_2$ adsorption isotherms for ZTF-1 at 77 K (Fig. 2c). It should be noted that the repeatability of the $H_2$ adsorption behavior was confirmed by reproducing the same isotherm three times at 77 K (Fig. S10, ESI†). The uptake at 760 Torr at 77 K is 1.6 wt%, which is comparable to bio-MOF-11[15] and higher than those for ZIF-11 (1.4 wt%),[5] ZIF-8 (1.3 wt%)[5] and ZIF-20 (1.1 wt%).[5] The initial uptake of ZTF-1 is also higher than that of ZIF-8 (1.3 wt%) and ZIF-11 (1.4 wt%). This suggests that a relatively strong interaction between the ZTF-1 framework and $H_2$ exists at low pressure and low temperature. A recent theoretical study suggests that nitrogen atoms on aromatic rings in a framework can enhance the adsorption energy of $H_2$.[16] In ZTF-1, two tetrazole nitrogen atoms and amino nitrogen

 

atoms are available to bind $H_2$ and thereby possibly enhancing the $H_2$ uptake compared to other ZIFs.

Next we wish to investigate the adsorption sites inside the gas-loaded crystal structure of ZTF-1. Grand canonical Monte Carlo (GCMC) simulations were employed to investigate $CO_2$ adsorption in de-solvated ZTF-1 to further confirm the adsorption mechanism (Fig. S11, ESI†). The framework and individual $CO_2$ molecule were considered to be rigid. The interactions between $CO_2$ molecules and framework were represented by electrostatic and Lennard-Jones (LJ) potentials. The atomic charges in ZTF-1 framework were estimated by density functional theory and the LJ potential parameters were adopted from the Universal Force Field (UFF). $CO_2$ adsorption in ZTF-1 was simulated in Materials Studio using the Metropolis algorithm. The simulated isotherm (Fig. S13a, ESI†) agrees quite well with experiment. The high $CO_2$ capacity is attributed to the narrow pores, exposed $-NH_2$ functionality and free tetrazole nitrogen. We have also calculated the isosteric heat $Q_{st}$ for $CO_2$ adsorption in ZTF-1 at 273 K (Fig. S13b, ESI†). At zero coverage, $Q_{st}$ is approximately 25.4 kJ mol$^{-1}$. With increasing loading, $Q_{st}$ increases; which is similar to $CO_2$ adsorption in IRMOF-1. The isosteric heat predicted is consistent with the high capacity observed in the experiment. To identify the favorable binding sites for $CO_2$ in ZTF-1, we have calculated the density distributions of adsorbed $CO_2$ molecules along the *YZ* plane at 273 K and 100 kPa. We see that $CO_2$ molecules are primarily adsorbed in the pores along the *X* axis and the binding sites are mostly located in the pore centers. To better understand the nature of the binding sites, we have calculated the distances between a single $CO_2$ molecule and different N atoms in a six membered adamantane ring consisting of Zn atoms (Fig. 2d). It is observed that $CO_2$ is closer to the both $-NH_2$ nitrogen atoms (3.94 Å) and to the uncoordinated tetrazole nitrogen (3.45 Å).

Synthesis of zeolitic MOFs with free amino decorated pores was always a challenge for researchers as the free amine group tends to coordinate with the metal, resulting in hindering its 3D structure generation. Successful synthesis and crystallization of ZTF-1, the first zeolitic MOF with *both* exposed $-NH_2$ functionality and free tetrazole nitrogen, could only become possible once we found a possible structure directing agent DMAz. ZTF-1 has high $CO_2$ capacity. This material is comparable to recently reported bioMOF-11 and outperforms other amine-functionalized MOFs[8] and ZIFs.[5] The high $CO_2$ in ZTF-1 compared to $-NH_2$ functionalised ZIF-96 is also validated as we found the location of $CO_2$ is closer to the both $-NH_2$ nitrogen atoms and to the uncoordinated tetrazole nitrogen. It is hard to quantify the exact contributions of exposed $NH_2$ functionality or free tetrazole nitrogen for the high $CO_2$ capacity of ZTF-1 but these results point toward the value of utilizing amino functionalized links and free aromatic nitrogen atoms as a building block for constructing MOFs for high and reversible $CO_2$ capture.

## Notes and references

‡ ZTF-1: $C_5H_{10}N_{11}OZn$, $M_r$ = 305.61, monoclinic, *Cc*, $a$ = 13.330(3) Å; $b$ = 15.327(3) Å; $c$ = 8.7796(17); $\beta$ = 131.20 (2) Å, $V$ = 1349.7(5) Å$^3$, $D_c$ = 1.504 g cm$^{-3}$, $\mu$ = 1.829 mm$^{-1}$, 7544 total reflection, 2879 unique ($R_{int}$ = 0.0693), $T$ = 293(2), final $R$ indices ($I > 2\sigma(I)$): $R_1$ = 0.0510, w$R_2$ = 0.1283, The final w$R(F^2)$ was 0.001 (all data). CCDC 779031.


1 E. Kintisch, *Science*, 2007, **317**, 184; H. Herzog, E. Drake, and E. Adams, *$CO_2$ Capture, Reuse, and Storage Technologies for Mitigating Global Climate Change*, Report No. DE-AF22-96PC01257, U.S. Department of Energy, Washington, D.C., 1997; D. Reichle, *et al.*, *Carbon Sequestration Research and Development*, Department of Energy, Washington, D.C., 1999, Ch. 2; E. J. Granite and H. W. Pennline, *Ind. Eng. Chem. Res.*, 2002, **41**, 5470.

2 J. D. Figueroa, T. Fout, S. Plasynski, H. McIlvried and R. D. Srivastava, *Int. J. Greenhouse Gas Control*, 2008, **2**, 9.

3 J. D. Figueroa, T. Fout, S. Plasynski, H. McIlvried and R. D. Srivastava, *Int. J. Greenhouse Gas Control*, 2008, **2**, 9; D. Aaron and C. Tsouris, *Sep. Sci. Technol.*, 2005, **40**, 321.

4 R. S. Franchi, P. J. E. Harlick and A. Harlick, *Ind. Eng. Chem. Res.*, 2005, **44**, 8007; S. Cavenati, C. A. Grande and A. E. Rodrigues, *J. Chem. Eng. Data*, 2004, **49**, 1095.

5 K. S. Park, N. Zheng, A.-P. Cöté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 10186; X.-C. Huang, Y.-Y. Lin, J.-P. Zhang and X.-M. Chen, *Angew. Chem., Int. Ed.*, 2006, **45**, 1557; R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Science*, 2008, **319**, 939; B. Wang, A. P. Cöté, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Nature*, 2008, **453**, 207; A. J. Cairns, J. A. Perman, L. Wojtas, V. Ch. Kravtsov, M. H. Alkordi, M. Eddaoudi and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2008, **130**, 1560.

6 Material with high $CO_2$ should possess high adsorption enthalpy like Mg–MOF-74 (47 kJ mol$^{-1}$) and high $CO_2$ uptake like MOF-177 (761.6 cc g$^{-1}$) at 42 bar and 298 KC. Lastoskie, *Science*, 2010, **330**, 595.

7 A. R. Millward and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 17998; S. R. Caskey, A. G. Wong-Foy and A. J. Matzger, *J. Am. Chem. Soc.*, 2008, **130**, 10870; O. K. Farha, C. D. Malliakas, M. G. Kanatzidis and J. T. Hupp, *J. Am. Chem. Soc.*, 2010, **132**, 950; J. An and N. L. Rosi, *J. Am. Chem. Soc.*, 2010, **132**, 5578.

8 A. Torrisi, C. M. Draznieks and R. G. Bell, *J. Chem. Phys.*, 2009, **130**, 194703; A. Torrisi, C. M. Draznieks and R. G. Bell, *J. Chem. Phys.*, 2010, **132**, 13; A. Torrisi, R. G. Bell and C. M. Draznieks, *Cryst. Growth Des.*, 2010, **10**, 2839; B. Arstad, R. Blom and O. Swang, *J. Phys. Chem. A*, 2007, **111**, 1222; K. D. Vogiatzis, A. Mavrandonakis, W. Klopper and G. E. Froudakis, *ChemPhysChem*, 2009, **10**, 374.

9 S. Couck, J. F. M. Denayer, G. V. Baron, T. Remy, J. Gascon and F. Kapteijn, *J. Am. Chem. Soc.*, 2009, **131**, 6326; A. Sayari and Y. Belmabkhout, *J. Am. Chem. Soc.*, 2010, **132**, 6312; B. Arstad, H. Fjellvag, K. O. Kongshaug, O. Swang and R. Blom, *Adsorption*, 2008, **14**, 755; A. Demessence, D. M. D'Alessandro, M. L. Foo and J. R. Long, *J. Am. Chem. Soc.*, 2009, **131**, 8784; R. Vaidhyanathan, S. S. Iremonger, K. W. Dawson and G. K. H. Shimizu, *Chem. Commun.*, 2009, 5230; W. Morris, B. Leung, H. Furukawa, O. K. Yaghi, N. He, H. Hayashi, Y. Houndonougbo, M. Asta, B. B. Laird and O. M. Yaghi, *J. Am. Chem. Soc.*, 2010, **132**, 11006; R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi and T. K. Woo, *Science*, 2010, **330**, 650.

10 There are reports of $-NH_2$ functionalized metal triazolates/tetrazolates but none with a 3D nature and all M–L–M angle close to 145°. X. W. Wang, J. Z. Chen and J. H. Liu, *Cryst. Growth Des.*, 2007, **7**, 1207; X. He, C. Z. Lu and D. Q. Yuan, *Inorg. Chem.*, 2006, **45**, 5760; Q.-G. Zhai, X.-Y. Wu, S.-M. Chen, Z.-G. Zhao and C.-Z. Lu, *Inorg. Chem.*, 2007, **46**, 5046.

11 http://www.iza-structure.org/databases/.; Reticular Chemistry Structure Resource (RCSR), http:// rcsr.anu.edu.au/home.; M. O'Keeffe and B. G. Hyde, *Crystal Structures I. Patterns and Symmetry*, Mineralogical Society of America, Washington, DC, 1996.

12 J. C. Jansen, in *Introduction to Zeolite Science and Practice*, A. van Bekkum, P. A. Jacobs, E. M. Flanigen and J. C. Jansen, ed. Elsevier, Amsterdam, 2001; C. Baerlocher, W. M. Meier and D. H. Olson, *Atlas of Zeolite Framework Types*, Elsevier, Amsterdam, 2001.

13 O. D. Friedrichs, M. D. Foster, M. O'Keeffe, D. M. Proserpio, M. Treacy and O. M. Yaghi, *J. Solid State Chem.*, 2005, **178**, 2533.

14 Diamond has also been described as the underlying topology of a MOF structure that actually has low crystallographic symmetry, M. O'Keeffe, M. A. Peskov, S. J. Ramsden and O. M. Yaghi, *Acc. Chem. Res.*, 2008, **41**, 1782.

15 J. An, S. J. Geib and N. L. Rosi, *J. Am. Chem. Soc.*, 2010, **132**, 38.

16 A. Samanta, T. Furuta and J. Li, *J. Chem. Phys.*, 2006, **125**.