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Rational design and synthesis of amino-functionalized hydrogen-bonded network with ACO zeolite-*like* topology for gas storage

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Based upon the typically hydrogen-bonded network, metal-organic cubes, the amino functional group was first introduced on the surface of the cube to raise the polarizability of the framework by *in situ* hydrolysis of the precursor 2-amino-4,5-dicyanoimidazole (ADCIm) with octahedral In^{3+} ions in solvothermal condition, resulting in a supramolecular network with very high CO_2 (135.8 cm^3/g at 273K/1atm) and H_2 (2.03 wt% at 77K/1atm) adsorption capacities and exceptional thermostability range up to 416 ℃.

Zeolite-*like* metal-organic frameworks (ZMOFs), as a subset of metal-organic frameworks (MOFs), with structures and properties akin to traditionally zeolitic materials hold promise to meet the needs of society, such as gas storage and separation, ion-exchange for water softening, catalysts, luminescence and chemical sensing.[1] These solid-state materials usually possess fascinating topologies, extra-large cavities, exceptional thermal and chemical stability, making them available platforms for systematic decoration to obtain higher performance (e.g. gas adsorption).[2]

Rational selection of platforms for modification and flexible design of organic ligands in assembly, in some extent, plays an important role in the construction of MOFs with unique properties. For example, the group of Bai has reported a porous framework (NJU-Bai7)[3] with (3,6)-connected structure based on the prototype SYSU,[4] which exhibits very high uptake of CO_2 (72cm^3/g, at 273K/1atm) and CO_2/CH_4 selectivity via delicately shifting the coordination sites of ligands, without changing the topology, surface area and pore volume. Inspired by the intriguing achievement, our group is interested in

exploring a class of potential frameworks which can keep stable porosity after being modified by polar functional groups.

Recent years, hydrogen-bonded metal-organic cubes, as a unique metal-organic polyhedra with adequate coordination sites for cooperative interactions such as hydrogen bonding, usually reveal diverse topologies, extra-large cavities, permanent porosities and functionalized frameworks for selective gas adsorption and separation.[5] Though multiple ZMOFs with fascinating topologies have been synthesized by the directed self-assembly of cubes, the fine decoration of inner surface of channels in iso-reticular frameworks based on the intra-polyhedra functionalization of cubes has not been reported up to now.

Herein, an underlying structure, $[In_8(HImDC)_{12}]\cdot(DMF)_6$ (MOC-2,[6] HImDC = 4,5-imidazoledicarboxylate), H-bonded metal-organic cubes has been applied as a new platform with exceptional stability, ultra-high porosity and highly symmetrical ACO zeolite-*like* topology. In order to enhance the CO_2 uptake capacity of MOFs, several strategies have been employed: (i) tuning pore size by interpenetration;[7] (ii) increasing the quantity of metal sites;[8] (iii) the decoration of pore surface by polar functional groups.[9] Recently, we have reported the synthesis of a novel nitro-functionalized pillared-layer network with high CO_2 adsorption capacity, suggesting that the nitro group has a positive impact on the uptake of CO_2.[9f] In most cases, these strategies may result in a decline in the porosities and surface areas of parent structures, which are harmful to the improvement of gas adsorption capacity. Interestingly, the adjacent cubes in MOC-2 are linked by vertex H-bonded interactions that direct the self-assembly of the **ACO** topological structure. Thus, the new strategy of fine-decorating the intra-surface in cubes through the decoration of polar functional groups (eg. –NH_2 group) on cubes may keep the topology and porosity of MOC-2 unaltered. Furthermore, the imidazole part of HImDC ligand acting as the edges of the cube is approximately coplanar with the face of the In_8 cube, which provides potential possibility to introduce smaller polar groups on the 2-substituent position of imidazole ring, so as to enhance the polarity of framework for gas adsorption.

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d. † Electronic Supplementary Information (ESI) available: Materials and general methods, adsorption measurements, crystal structure, bond valence sum, IR spectrum, PXRD, TGA, gas adsorption data. CCDC 1450997. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x.

Generally, the replacements of functional groups on the imidazole ring has found to be vital to the synthesis of thermostable and porous ZMOFs.[10]

In this work, we present a new three-dimensionally hydrogen-bonded framework, namely, $[In_8(AHImDC)_{12}] \cdot 6H_2O$ (**1**, AHImDC = 2-amino-4,5-imidazoledicarboxylate), with two types of amino-functionalized channels and **ACO** topological structure. Notably, rational modification of inner surface of channels in prototype MOC-2 with amino groups not only enhances the polarity of the framework, but also doesn't reduce surface area obviously, which is very rare in functionality of iso-reticular MOFs.
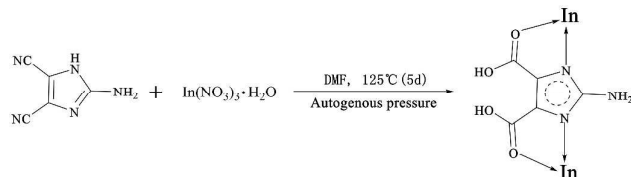
Scheme 1 Schematic representation of *in situ* generated AHImDC from the precursor ADClm ligand.

Solvothermal reaction of AHImDC which is formed from *in situ* synthesis of the precursor ADClm (2-amino-4,5-dicyanoimidazole) with $In(NO_3)_3 \cdot H_2O$ resulted in the formation of pale-yellow polyhedral microcrystalline material, which is stable in common organic solvents (Scheme 1). The hydrolysis degree of -CN group on ADClm was confirmed by IR spectrum (Fig. S1, ESI†). The replacement of characteristic adsorption peak of 2230 cm^{-1} related to cyano group by typical adsorption peak (3428 cm^{-1} and 1661 cm^{-1}) of carboxyl group indicates that ADClm completely hydrolysed to corresponding carboxylate.[11] The purity of **1** was confirmed by the positive matching of the diffraction peaks between experimental and simulated X-ray diffraction (XRD) patterns (Fig. S2, ESI†).

Single-crystal analysis demonstrates that compound **1** consists of In_8 cubes extended by hydrogen-bond interactions, and crystallizes in the high symmetry cubic Fm-3n space group. Twelve doubly deprotonated AHImDC ligands self-assemble with eight In^{3+} ions forming the rigid cubic SBUs (secondary building units). Each vertex of the cube is occupied by an In^{3+} ion which is six-coordinated by three nitrogen atoms and three carboxyl oxygen atoms from three separate AHImDC ligands in a distorted octahedral geometry, where the bond lengths of In-O and In-N are 2.181 Å and 2.240 Å, respectively (Fig. 1a). Meanwhile, each ADClm ligand bridging two neighbouring In^{3+} ions in a bi-cheating fashion, constructs the twelve edges of the cube. Fig. 1b illustrates the cubic structure of **1**, where the In···In distances of 6.653 Å and In···In···In angles of 90° indicate no deviations from the ideal cube geometry. Moreover, the orientation and construction of the ligands composing the molecular cube are different from the previously reported metal-organic squares[12] based on four-membered ring SBUs (two up and two horizontals with respect to the corresponding faces, Fig. S4, ESI†). Each cubic SBU is linked in a vertex-to-vertex fashion with eight adjacent SBUs via 24 intermolecular O-H···O hydrogen bonds (O···O distances of 2.825 Å) between
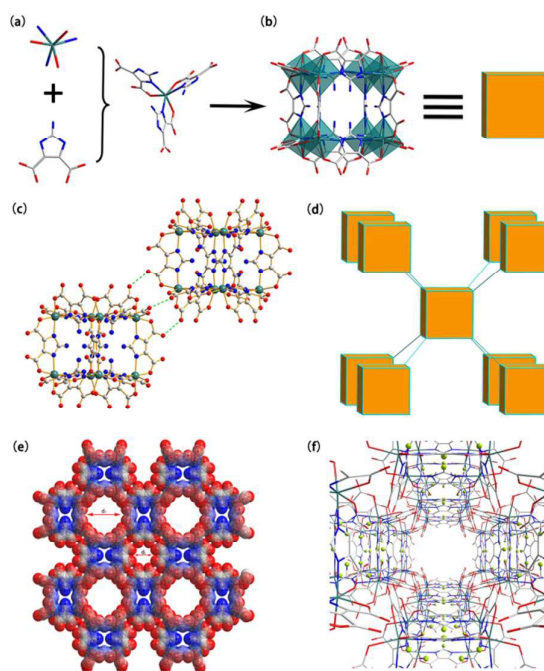

Fig. 1 a) The coordination environments of In^{3+} in compound **1**; b) Wireframe and schematic representation of a cubic **SBU**; c) Intermolecular hydrogen-bond interaction linking two adjacent cubes; d) Schematic representation of the **ACO** topology; e) Space filling mode of **1** exhibiting two types of channels (approximate diameter, d_1 = 9.5 Å and d_2 = 5.5 Å); (f) Central projection showing the inner surface of the first type of channel (the lime balls represent the $-NH_2$ groups).

the peripherally uncoordinated carboxyl oxygen atoms, leading to an eight-connected body-centered cubic net (Fig. 1c). From the view of topology, the $[In_8(AHImDC)_{12}]$ units and hydrogen bonds can be respectively viewed as eight-connected nodes and linear linkers, then compound **1** adopts a **ACO** zeolite-*like* topology (Fig. 1d) that is iso-reticular with those hydrogen-bonded supramolecular assemblies (MOC-2[6] and Zn_{14}-MBB,[13a] Co_{14}-MBB[13b]). The compound exhibits two types of channels: (i) approximately square channels with the opening diameter of 9.5 Å; (ii) rounded channels with the opening diameter of 5.5 Å, considering the van der Waals radii of the nearest atoms (Fig. 1e). Furthermore, the first type of channels possesses unique cages which can accommodate a dummy sphere with a maximum diameter of 13.1 Å (Fig. S5, ESI†). It is worth mentioning that both the amino groups and the non-coordinated carboxyl oxygen atoms are exposed on the surfaces of the channels, effectively improving the polarity of inner surfaces of channels (Fig. 1f).

The total potential solvent-accessible volume is 4,595.9 $Å^3$ for **1**, equal to 56.1% of the unit cell volume, using PLATON program[14] by removing the guest molecules.

The TGA measurement was performed in N_2 atmosphere from room temperature up to 700 ℃ with a heating rate of 10 ℃/min. TGA curve of as-synthesized **1** indicated that the guest molecules (water and DMF) escaped in the range of 30-250 ℃
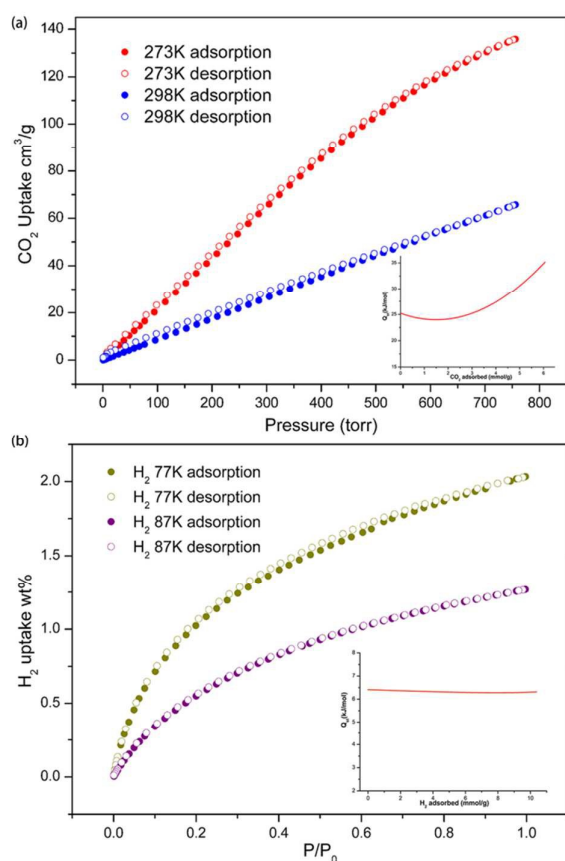
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Fig. 2 a) CO_2 adsorption-desorption isotherms of **1** at 273K and 298K (inset: CO_2 adsorption enthalpy); b) H_2 adsorption-desorption isotherms measured at 77K and 87K (inset: H_2 adsorption enthalpy).

and the structure decomposed at about 416 ℃ (Fig. S6, ESI†).

To confirm the permanent porosity of compound **1**, N_2 sorption isotherms at 77K were measured volumetrically on fully degassed samples after exchange in acetone for three days. As shown in Fig. S7 (ESI†), the fully reversible Type-I isotherm for N_2 sorption demonstrates that **1** is a microporous material. The Langmuir surface area is 1476 m^2/g (BET surface area is 1164 m^2/g), while the iso-reticular MOC-2 is 1420 m^2/g ($SA_{Langmuir}$), indicating that the porosity is almost unchanged.

The CO_2 sorption isotherms were measured at 273 K and 298 K (0-1atm), respectively. Compound **1** exhibits very high CO_2 uptake capacity of 135.8 cm^3/g (STP, 26.9 wt% and 6 mmol/g) at 273K/1atm and 65.7 cm^3/g (STP, 13.0 wt% and 2.7 mmol/g) at 298K/1atm (Fig. 2a). The values are higher than those of Hydrogen-bonded networks and functionalized MOFs (Zn_{14}-MBB,[13a] 56 cm^3/g; $Zn_2(atz)_2(ox)$,[15a] 97.5 cm^3/g; PCN-61,[15b] 128 cm^3/g; NJU-Bai7,[3] 72 cm^3/g; SYSU,[4] 118 cm^3/g, Table S3, ESI†). Based on the sorption isotherms measured at 273K and 298K, the adsorption enthalpy (Q_{st}) for compound **1** was calculated to be 25.2 KJ/mol at zero-coverage adsorption, reflecting a strong interaction between CO_2 molecules and the framework.[3] With increasing the loading, the Q_{st} value sharply increases to 35.2 KJ/mol (the curves of Q_{st} for most MOFs usually exhibit declining or horizontal tendencies). Actually,

uncoordinated $-NH_2$ groups provide not only the binding sites to interact with CO_2 molecules through N-H⋯O (CO_2) hydrogen bond but also an interaction between the N lone pair and the C atom of CO_2.[16] Two stages in adsorption may account for the special heat of adsorption cure. In the first stage, the Q_{st} of 25.2 KJ/mol for **1** may ascribe to the single N-H⋯O (CO_2) H-bond and the interaction between the framework and CO_2 molecules. In intermediate stage, the cure reveals a rapid increasement to 35.2 KJ/mol from intermediate loading, which is likely due to the formation of further N-H⋯O (CO_2) H-bond, interaction between the electronegative N atom of amino group and electropositive C atom of CO_2 and CO_2⋯CO_2 interaction (Fig. 3).[15a] The value (35.2 KJ/mol) is quite comparable to those of well-known MOFs (HKUST-1,[17] 29.8 KJ/mol; $Zn_2(atz)_2(ox)$,[15] 40.8 KJ/mol; Zn_{14}-MBB,[13] 38 KJ/mol). The high CO_2 capacities and adsorption energies demonstrate the obviously enhanced interaction between the CO_2 molecules and the framework due to the introduction of amino groups on the internal surface of channels of **1**.
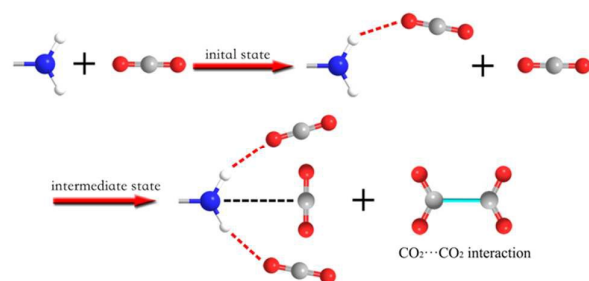

Fig. 3 The speculation of potential CO_2 adsorption progress in amine-functionalized **1** [Dash lines represent N-H⋯O (red) hydrogen bonds and C⋯N (black) electrostatic interaction, while CO_2⋯CO_2 interaction is indicated as a blue bond].

Furthermore, H_2 sorption isotherms were also measured at 77 K and 87 K, indicating that **1** can store up to 2.03 wt% (STP, 232.4 cm^3/g, 10.4 mmol/g) at 77K/1atm and 1.27 wt% (STP, 143.8 cm^3/g, 6.4 mmol/g) at 87 K/1atm, and the adsorption enthalpies calculated using the Virial equation are 6.4-6.3 KJ/mol (Fig. 2b). These values are slightly lower than the high hydrogen adsorptive material (MOC-2, 2.17 wt% and 6.5-5.7 KJ/mol) at the same condition. To systematically investigate the gas storage capacity of compound **1**, the CH_4 adsorption measurements compound **1** were also conducted. The maximum CH_4 capacity is 39.2cm^3/g (1.7mmol/g) at 273K/1atm and 16cm^3/g (0.7mmol/g) at 298K/1atm, respectively (Fig. S9, ESI†). The values of adsorption heat of **1** for CH_4 are 22.7-34.3 KJ/mol.

In conclusion, an amino-functionalized assembly of hydrogen-bonded framework has been successfully synthesized by in situ linker generation method, exhibiting fascinating **ACO** zeolite-*like* topology. The porous material possesses very high thermal stability up to 416°C, which is critical to the practical application of MOFs. Compared with the prototype structure (MOC-2), the introduction of amino groups onto the inner surface of the channels remarkably

increases the polarity of the framework without leading to a decline in the surface and porosity. Additionally, this ZMOFs exhibits very high CO_2 adsorption capacity of 135.8 cm^3/g at 273K/1atm and H_2 uptake of 2.03 wt% at 77K/1atm, which are comparable to those of well-known MOFs, making it potential candidate for gas storage. Commonly, the self-assembly of metal-organic cubes based on vertex- and edge-transitive nets has led to several zeolite-*like* metal-organic frameworks with interesting topology (eg. ACO, LTA and AST) to reticular chemistry. Nevertheless, our work provides a new pathway to decorate this type of iso-reticular framework for better properties.

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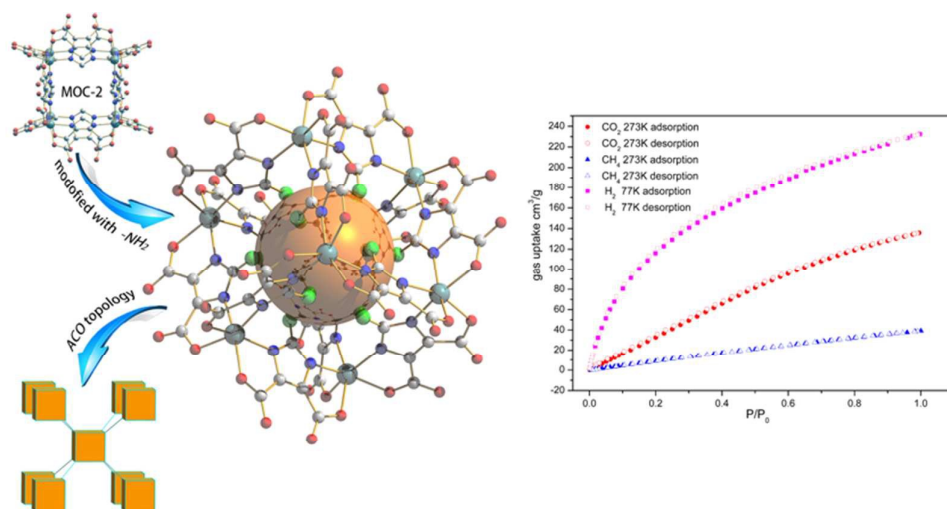
The modification of amino groups on the surface of the In_8 cubic SBUs comprising hydrogen-bonded networks with **ACO** zeolite-*like* topology resulted in a great improvement in gas adsorption.