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A pillared metal–organic framework incorporated with 1,2,3-triazole moieties exhibiting remarkable enhancement of CO₂ uptake†

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The replacement of the pillar ligand, 4,4'-bipyridine, in the prototypal pillared MOF, MOF-508, with the custom-designed ligand, 4,4'-(2H-1,2,3-triazole-2,4-diyl)dipyridine, affords a porous metal–triazolate framework, MTAF-3, which demonstrates remarkable enhancement of CO₂ uptake capacity by a factor of ~3 compared to the parent MOF-508.

Over the last decade, MOFs¹ have been developed into a promising class of functional porous materials by judiciously custom-designing organic linkers and carefully selecting metal ions or clusters as nodes.² *Via* self-assembly of the custom-designed organic ligands and the metal-containing secondary building blocks (SBUs), the modular construction of MOFs has been well established, and the structural topology of MOFs could also be predicted. Owing to high porosity, tuneable pore sizes, and pore walls that can be functionalized,³ MOFs have exhibited potential for a wide range of applications such as gas storage,⁴ separation,⁵ heterocatalysis,⁶ sensors⁷ and other areas.⁸ Of particular interest among these applications for MOFs is CO₂ capture, which has attracted escalating attention due to global warming mainly triggered by the emission of CO₂ from the combustion of fossil fuels.⁹ An important context of CO₂ capture by MOFs lies in developing various strategies to enhance the CO₂ adsorption capacity at ambient temperatures.¹⁰ One of the well-studied strategies to enhance CO₂ capacity is to expose coordinatively unsaturated open metal sites typically *via* thermal liberation of coordinated labile ligands,¹¹ and this has afforded exceptionally high CO₂ uptake capacities in some MOFs, *e.g.* MOF-74 series.¹² However, the open metal sites can rapidly re-adsorb water molecules thus inevitably leading to a remarkable drop in CO₂ uptake capacity upon exposure to moisture.¹³ Another widely explored strategy is to introduce chemical bonding with CO₂ molecules by grafting functional amine groups into MOFs *via*

the route of post-synthetic modification.^{8e,14} Although amine-grafted MOFs have demonstrated significant enhancement of CO₂ uptake¹⁵ or even exhibited record isosteric heats of adsorption of 90–100 kJ mol⁻¹,¹⁶ a substantial amount of energy is required to break the CO₂–amine chemical bonding during the regeneration process. In this contribution, we report a different strategy by incorporating 1,2,3-triazolate moieties that feature exposed N atoms as relative moderate Lewis base centers compared to amine groups to enhance the CO₂ uptake in MOFs. The incorporation of 1,2,3-triazolate moieties into a pillared MOF has led to remarkable enhancement of CO₂ uptake capacity as well as significant boost of heats of adsorption for CO₂.

Pillared MOFs have recently been widely explored as a type of platform for gas storage/separation, and they consist of two-dimensional (2D) layers that have ligating sites for linkage with ditopic pillars usually of dipyridine derivatives into three-dimensional (3D) architectures.¹⁷ The structures and properties of pillared MOFs are readily tuned by functionalizing either the linkers within the 2D layers or the ditopic pillared ligands. One of the prototypal pillared MOF structures is MOF-508 (Fig. 1a),¹⁸ in which the 2D layers based upon 1,4-benzenedicarboxylate (bdc) and the dizinc paddle-wheel cluster are pillared by 4,4'-bipyridine (bpy) to afford a 3D two-fold interpenetrating α -Po network (Scheme 1). To decorate MOF-508 with 1,2,3-triazolate moieties, we designed a new dipyridine derivative ligand, 4,4'-(2H-1,2,3-triazole-2,4-diyl)dipyridine (tadp). As expected, the self-assembly of tadp with bdc and dizinc paddle-wheel cluster generated *in situ* gave rise to MTAF-3 (Metal–TriAzolate Framework, MTAF) (Scheme 1),¹⁹ which is isostructural with MOF-508 but exhibits much higher CO₂ uptake capacity than the parent MOF-508.

Yellow block crystals of MTAF-3 were obtained *via* solvothermal reaction of bdc, tadp and Zn(NO₃)₂·6H₂O in *N,N*-diethylformamide (DEF) at 85 °C for 48 hours. Single-crystal X-ray crystallographic studies reveal that MTAF-3‡ crystallizes in the space group *C2/c* with a formula [Zn₄(bdc)₄(tadp)₂](DEF)₂(H₂O) as estimated from crystallographic data, elemental analysis, and TGA studies. As predicted, MTAF-3 is isostructural with MOF-508, and is composed of paddle-wheel dinuclear zinc carboxylate units [Zn₂(COO)₄] that are bridged by the bdc ligands to form distorted 2D square grids, which are further pillared by tadp ligands instead of bpy *via* coordinating the axial sites of the [Zn₂(COO)₄] paddle wheels to result in a 3D framework

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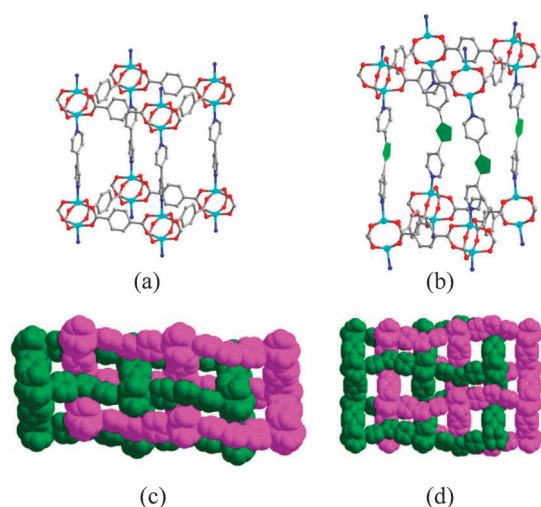
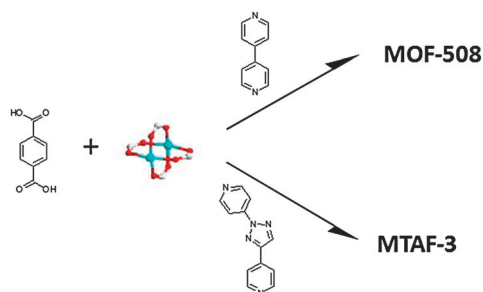


Fig. 1 (a) Building unit of MOF-508; (b) building unit of MTAF-3; (c) space-filling picture of interpenetrating MTAF-3 viewed from the *b* direction; (d) space-filling picture of interpenetrating MTAF-3 viewed from the *c* direction.



Scheme 1 Illustration of approaches to constructing MOF-508 and MTAF-3.

with α -Po topology (Fig. 1b). It's worth noting that the nitrogen atoms at the 1 and 3 positions of the 1,2,3-triazole moieties are oriented to the channels and are accessible for guest molecules to interact with. Similar to MOF-508, MTAF-3 also possesses two-fold interpenetration, which reduces its pore size to ~ 4.6 Å (Fig. 1b and c). However, MTAF-3 is still porous and has a solvent accessible volume of 39.4% calculated using PLATON, which is higher than that of MOF-508 (12.1%).²⁰

The phase purity of the bulk sample MTAF-3 was confirmed by powder X-ray diffraction (PXRD) studies (Fig. S1, ESI†). Thermogravimetric analysis (TGA) of the fresh MTAF-3 sample revealed a weight loss of about $\sim 32\%$ from 30 to ~ 200 °C corresponding to the loss of guest solvent molecules of DEF and H₂O trapped in the channels; it is followed by a steady plateau from ~ 200 to 400 °C before complete decomposition of the framework (Fig. S2, ESI†). TGA studies on the solvent-free MTAF-3 sample (Fig. S2, ESI†) further confirmed its thermal stability up to ~ 400 °C, and also highlighted the robustness of the two-fold interpenetrating pillared framework of MTAF-3 (Fig. 1d).

To assess the permanent porosity of MTAF-3, gas adsorption studies were conducted on the activated sample. As shown in Fig. 2(a), the N₂ isotherm at 77 K reveals that MTAF-3 exhibits an uptake capacity of ~ 300 cm³ g⁻¹ at the saturation pressure with typical type-I adsorption behaviour, as expected for microporous

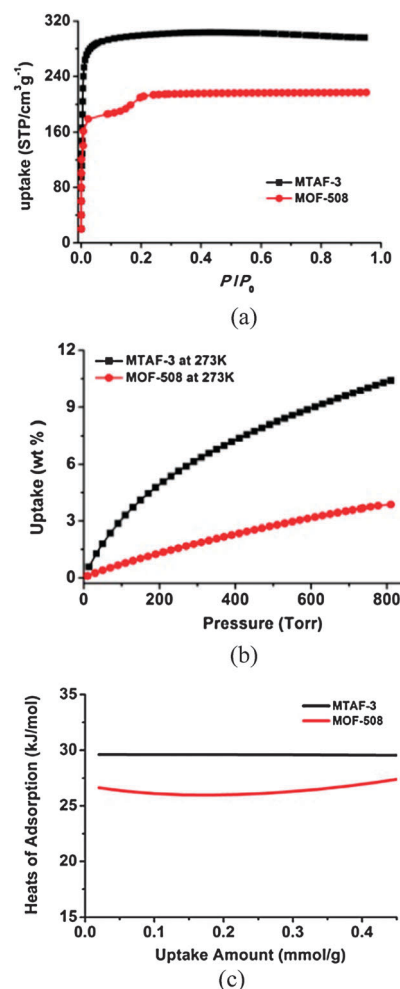


Fig. 2 (a) N₂ adsorption isotherms of MTAF-3 and MOF-508 at 77 K; (b) CO₂ adsorption isotherms of MTAF-3 and MOF-508 at 273 K; (c) heats of adsorption of CO₂ for MTAF-3 and MOF-508.

materials. Derived from the N₂ isotherm at 77 K, MTAF-3 possesses a Brunauer–Emmett–Teller (BET) surface area of 1175 m² g⁻¹ ($P/P_0 = 0.01$ – 0.1) corresponding to a Langmuir surface area of 1307 m² g⁻¹ ($P/P_0 = 0.9$). The BET surface area of MOF-508 is 743 m² g⁻¹ (Langmuir surface area: ~ 900 m² g⁻¹), which is comparable to that reported in the literature.¹⁸ Therefore, the decoration of MOF-508 with 1,2,3-triazole moieties has resulted in an increase of $\sim 60\%$ in BET surface area.

The orientation of two open nitrogen atoms in each 1,2,3-triazole moiety toward the channels may facilitate the interactions with CO₂ molecules, and this prompted us to evaluate the CO₂ uptake performances of MTAF-3. As shown in Fig. 2(b), MTAF-3 can adsorb a substantial amount of CO₂ with an uptake capacity of 10.0 wt% at 273 K under 1 atm of pressure, meaning an enhancement by a factor of 2.7 compared to MOF-508 under the same conditions. It has been well documented that the enlargement of pore sizes will lead to decrease of low pressure CO₂ uptake of MOFs at ambient temperatures despite the increase in surface area.^{10a} Therefore, we speculate that the remarkable enhancement of CO₂ uptake observed for MTAF-3 could be mainly attributed to the stronger CO₂–framework interactions exerted by the Lewis base nitrogen

atoms of 1,2,3-triazole moieties. This could be inferred from the shapes of the CO₂ adsorption isotherms for MTAF-3 and MOF-508, and the steeper slope is the stronger interactions between the framework and CO₂ gas molecules.²¹ We calculated the heats of adsorption (Q_{st}) of CO₂ for MTAF-3 and MOF-508 based upon the CO₂ adsorption isotherms at 273 K and 298 K using the virial method.²² As shown in Fig. 2(c), MTAF-3 exhibits a constant Q_{st} of ~ 29 kJ mol⁻¹, which is ~ 3 kJ mol⁻¹ higher than that of MOF-508 (Q_{st} of ~ 26 kJ mol⁻¹). These results further validate the contribution of 1,2,3-triazole moieties to the enhancement of CO₂ uptake in MTAF-3.

In summary, the incorporation of 1,2,3-triazole moieties into the prototypal pillared MOF, MOF-508, using the custom-designed pillar ligand, 4,4'-(2H-1,2,3-triazole-2,4-diyl)dipyridine, afforded a porous metal-triazolate framework, MTAF-3, which demonstrates remarkable enhancement of CO₂ uptake capacity by a factor of ~ 3 and a significant increase in Q_{st} of CO₂ by an average of ~ 3 kJ mol⁻¹ compared to the parent MOF-508. The strategy of incorporating 1,2,3-triazole functional groups that provide moderate Lewis base centers into MOFs represents a promising way to construct new types of porous MOFs with enhanced CO₂ uptake performances. Ongoing work in our laboratories includes the custom-design of new variants of 1,2,3-triazole-based ligands for the construction of functional MTAFs and exploring them for application in CO₂ capture, sensors and catalysis.

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Notes and references

† X-ray crystal data for MTAF-3: C₆₆H₅₆N₁₂O₁₉Zn₄, $f_w = 1582.71$, monoclinic, C2/c, $a = 34.6925(7)$ Å, $b = 16.6027(4)$ Å, $c = 13.7633(3)$ Å, $V = 7646.4(3)$ Å³, $Z = 4$, $T = 228(2)$ K, $\rho_{\text{calcd}} = 1.375$ g cm⁻³, R_1 ($I > 2\sigma(I)$) = 0.0416, wR_2 (all data) = 0.1176.

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