

REVIEW PAPER

Carbon Dioxide Capture on Metal-organic Frameworks with Amide-decorated Pores

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ABSTRACT

CO₂ is the main greenhouse gas emitted from the combustion of fossil fuels and is considered a threat in the context of global warming. Carbon capture and storage (CCS) schemes embody a group of technologies for the capture of CO₂ from power plants, followed by compression, transport, and permanent storage. Key advances in recent years include the further development of new types of porous materials with high affinity and selectivity toward CO₂ for optimizing the energy penalty of capture. In this regard, microporous metal-organic frameworks (MOFs) represent an opportunity to create next-generation materials that are optimized for real-world applications in CO₂ capture. MOFs have great potential in CCS because they can store greater amounts of CO₂ than other classes of porous materials, and their chemically-adjustable organic and inorganic moieties can be carefully pre-designed to be suitable for molecular recognition of CO₂. Taking into account the nature of physisorption and inherent polarity of CO₂ molecules, addressing materials with both a large surface area and polar pores for strong CO₂ binding affinity is an effective method. Decorating the pores of MOFs with some specific functional groups by directly using functionalized organic linkers or postsynthetic modification, that have high binding affinity to CO₂ molecules, is among the most promising strategies has been pursued to achieve high-performance CO₂ uptake. This review highlights the literature reported on MOFs with amide-decorated pores for CO₂ capture, showing the effects of amide groups on uptake capacity, selectivity and adsorption enthalpies of CO₂.

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INTRODUCTION

Economical and efficient carbon capture and sequestration (CCS) technologies has been attracting tremendous attention due to the escalated global warming [1-3]. A class of crystalline porous materials, metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) that assembled by organic linkers and inorganic nodes (metal ions or metal-containing clusters), is of great promise for their potential use in the strategic storage and separation of hydrogen, methane, and carbon dioxide in clean-energy applications [4-10]. High surface area, large total pore volume

and high adsorption enthalpy involving host-guest interactions are all crucial for high-performance CO₂ storage MOF materials [11]. Therefore, MOF research is currently addressing two issues: (i) increasing CO₂ uptake by generation of MOFs with even higher surface areas and larger pore volumes by the use of larger bridging ligands or highly connected secondary building units (SBUs) [12-15] and (ii) increasing the selectivity of MOFs through enhancement of the adsorption enthalpies for CO₂ through decoration of the materials [16-22]. Until now, several strategies have been pursued to achieve the latter goal, such as narrowing the pore

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size by interpenetration [23-25], tuning of the pore surface charge through variation of the metal cation [26], introducing an alkylamine functionality [27] or water molecules [28] onto the coordinatively unsaturated metal center and decorating MOFs with some specific functional groups (-NH₂, -NO₂, -OH, etc.) that have high binding affinity to CO₂ molecules by postsynthetic modification or directly using functionalized organic linkers [29-34].

The incorporation of pendant amide (-CONH-) groups into MOFs is regarded as a promising approach to enhance CO₂ uptake due to the formation of hydrogen bonds with amides serving as both hydrogen bond acceptors (*via* C=O) and donors (*via* N-H) [35-41]. Amide groups have the same positive effect on adsorption of CO₂ like the widely reported amine (-NH₂) groups by facilitating dipole-quadrupole interactions [20]. However, these two analogous functional groups have some different structural and chemical characteristics. The amide group usually does not coordinate with metal ions and keeps open status in process of constructing MOFs, although it may increase the structural flexibility of MOFs because of its customary position in the main carbon skeleton of the organic ligands. While, the amine group may coordinate with metal ions and loses its function to interact with CO₂ when the amine-functionalized organic ligands are employed in synthesizing MOFs. On the other hand, the amine

group is not located on the main carbon skeleton of the organic ligands and has no apparent influence on the rigidity or flexibility of the MOFs' structures [42]. A series of amide-functionalized MOFs have been synthesized and shown to exhibit high CO₂ uptakes and selectivity (Table 1). However, the incorporation of this functional group generally improves capacity only modestly at low pressures. Likewise, computational studies attribute this to the specific binding and formation of hydrogen bonds between adsorbed CO₂ molecules and free amide groups thus enhancing adsorption affinity and selectivity for CO₂. Several review papers have been published about the MOFs with large CO₂ storage capacity and high selectivity [43-46], but the effects of amide groups in CCS performance of MOFs with amide-decorated pores was not mentioned. This issue is presented in this review.

First evidence

In 2011, Bai and Zaworotko [37] reported how amide groups inside the pores of a Cu-based MOF, [Cu₂₄(TPBTM⁶⁻)₈(H₂O)₂₄] (Cu-TPBTM), can result in a larger CO₂ uptake, enhanced heat of adsorption, and a higher selectivity toward CO₂/N₂ in comparison with an analogous MOF with alkyne groups. Solvothermal reaction of Cu(NO₃)₂·3H₂O with flexible C₃-symmetric hexacarboxylate ligand of TPBTM (TPBTM = N₃N'₃N''-tris(isophthalyl)-1,3,5-benzenetricarboxamide) with

Table 1: A series of amide-functionalized MOFs have been synthesized and shown to exhibit CO₂ uptakes

Chemical formula	Common name	BET (m ² g ⁻¹)	Capacity (wt %)	pressure (bar)	temp (K)	- Q _{st} (kJmol ⁻¹)	Ref.
[Cu ₂ (H ₂ O) ₂ BDPO]	NOTT-125	2447	40.1 [93.3]	1 [20]	273	25.4	[36]
[Cu ₂₄ (TPBTM ⁶⁻) ₈ (H ₂ O) ₂₄]	Cu-TPBTM	3160	103.5	20	298	26.3	[37]
[Cu(pia) ₂ (SiF ₆)](EtOH) ₂ (H ₂ O) ₁₂	UTSA-48	285	5.5	1	296	30	[42]
[Cu ₃ (BTB ⁶⁻) _n]	Cu-BTB	3288	157	20	273	-	[50]
Cu ₃ L ₂ (H ₂ O) ₅	NJU-Bai3	2690	27.3 [97.7]	1 [20]	273	-	[55]
[Cu ₂ PDAI(H ₂ O)]	PCN-124	1372	28.6	1	273	26.3	[59]
[Zn ₄ (bdc) ₄ (bpda) ₄]·5DMF·3H ₂ O	Zn-bpda	331	15.2	35	298	30.2	[61]
[Cu ₂ (TCMBT)(bpp)(μ ₃ -OH)]·6H ₂ O	Cu-TCMBT	808.5	25.5	20	298	26.7	[62]
[Cu ₂ (BDPT ⁴⁻)(H ₂ O) ₂]	HNUST-1	1400	30.7	1	273	22.3	[65]
[Cu ₂ BDPO(H ₂ O) ₄]	HNUST-3	2412	98.9	20	273	24.8	[67]
[CuL ₂ (NO ₃) ₂ ·o-xylene·DMF] _n	1↔NO ₃ ⁻		16.5	1	195	-	[73]
[Mn ₂ (2,6-ndc) ₂ (bpda) ₂]·5DMF	Mn-bpda	372	26.9	35	298	29.6	[74]
[Zn ₂ (oba) ₂ (bpta)]·(DMF) ₃	TMU-22	680	31.7	1	203	26	[76]
[Zn ₂ (oba) ₂ (bpfb)]·(DMF) ₅	TMU-23	0	31.7	1	203	-	[76]
[Zn ₂ (oba) ₂ (bpfn)]·(DMF) ₂	TMU-24	0	27.7	1	203	24	[76]
[Zr ₆ (μ ₃ -O) ₄ (μ ₃ -OH) ₄ (-OH) ₄ (-OH ₂) ₄ (TBAPy) ₂]	SALI-F3G	890	7.3	1	273	27	[77]
-	SALI-DAP	1225	10.1	1	273	28	[77]
[Cu ₂ (PDAD)(H ₂ O)] _n	PCN-124-stu	2153	31.4	1	273	26	[79]
-	MFM-136	1634	63	20	273	25.6	[80]

amide groups afforded a high yield of octahedron shaped crystals of Cu-TPBTM. This MOF exhibits the same topology as the prototypical *rht*-type MOF [47] and other isorecticular MOFs such as the PCN-61 series [48] and NOTT-112 [49] (Fig. 1a). The N₂ adsorption for Cu-TPBTM at 77 K exhibited a reversible type-I isotherm with BET surface area of ~3160 m² g⁻¹, which is close to PCN-61 (~3000 m² g⁻¹) and smaller than those reported for PCN-68 (~5109 m² g⁻¹) [48]. The effect of the amide groups upon CO₂ uptake on Cu-TPBTM is compared to its analogue PCN-61, which possesses the same pore sizes, surface area, and number of open Cu^{II} sites, where the only difference between Cu-TPBTM and PCN-61 is the substitution of the acetylene moiety in PCN-61 with an amide moiety (Fig. 1b). Interestingly, Cu-TPBTM exhibits a stronger binding affinity for CO₂ than PCN-61. CO₂ adsorption capacity of Cu-TPBTM is ca. 23.53 mmol g⁻¹ at 298 K and 20 bar, with a corresponding isosteric heat of adsorption of - 26.3 kJ/mol. These results are higher than PCN-66 (21.5 mmol g⁻¹; -22

kJ/mol) and PCN-68 (22.1 mmol g⁻¹; -21.2 kJ/mol), although the latter has larger surface areas (Fig. 1c, d). Moreover, better selectivity for CO₂/N₂ separation has been achieved at 298 K for Cu-TPBTM (~22 at 1 bar and 33 at 20 bar) compared to PCN-61 (15 at 1 bar and 22 at 20 bar). These suggest that polar -CONH- functionalities have a positive effect on adsorption of CO₂ by enhancing the initial slopes of CO₂ isotherms for Cu-TPBTM, resulting in greater Q_{st} uptake, and selectivity.

In a similar study by the same group, nanosized triangular amide-bridging hexacarboxylate linkers of H₆BTB and H₆TATB have been used to expand isorecticular *rht*-type MOFs of [Cu₃(BTB⁶⁻)_n] (Cu-BTB) and [Cu₃(TATB⁶⁻)_n] (Cu-TATB) [50] (Fig. 2a). Cu-BTB and Cu-TATB exhibit a high apparent BET surface area of 3288 and 3360 m² g⁻¹, respectively, which is slightly higher than that of Cu-TPBTM. Both materials display uncommon pseudo type IV isotherms with stepwise adsorption behavior and a noticeable hysteresis, which is characteristic

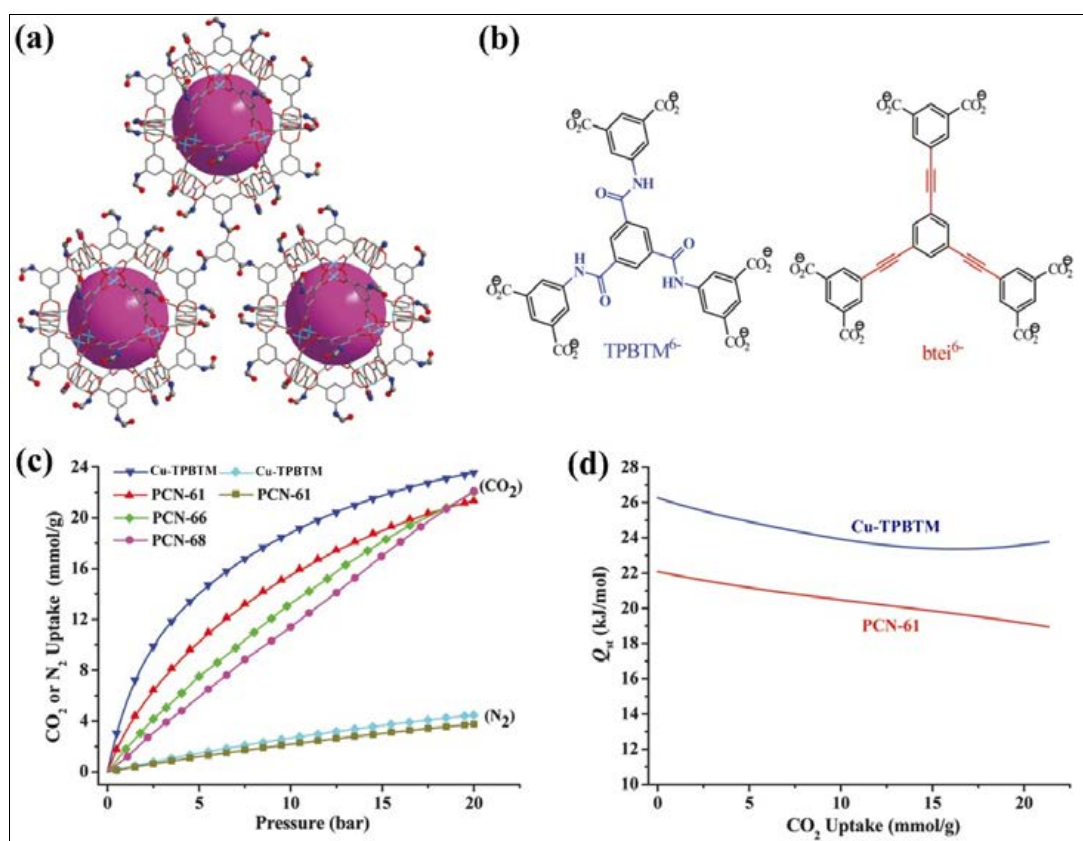


Fig. 1: (a) Portion of the structure of the (3, 24)-connected *rht*-type framework of Cu-TPBTM showing surface decoration by amide groups. Cu, blue-green; C, gray; O, red; N, blue. (b) Bridging ligands of TPBTM⁶⁻ and bte1⁶⁻ for Cu-TPBTM and PCN-61, respectively. (c) High-pressure gravimetric excess CO₂ and N₂ sorption isotherms of Cu-TPBTM and the PCN-6X series at 298 K. (d) Isothermic heats of CO₂ adsorption for Cu-TPBTM and PCN-61. Adapted from Ref. [37].

of flexible MOFs with hierarchically-assembled mesopores. High-pressure gravimetric CO₂ adsorption isotherms show that compared to the parent Cu-TPBTM MOF, the CO₂ sorption isotherm of expanded framework Cu-BTB demonstrates a type-IV-like profile with a marked gate-opening process with an exceptionally high unsaturation excess CO₂ uptake of 111 wt% at 298 K. This CO₂ storage capacity is just lower than that of MOF-177 (123.2 wt%) [12] and MOF-205 (114.4 wt%) [15], but far greater than that of any other high surface area MOFs reported such as MOF-210 (70.4 wt%) [15] and NU-100 (95 wt%) [51] under the same conditions. Interestingly, in sharp contrast to CO₂, Cu-BTB can only absorb limited amounts of CH₄ (13 wt%) and N₂ (11 wt%) at 273 K and 20 bar, representing the CO₂/CH₄ and CO₂/N₂ selectivity of 8.6 and 34.3, respectively, which are much higher than the corresponding value of MOF-177 (4.4 and 17.5) [52] and most other MOF materials [53].

The introduction of N-heteroaryl moieties into MOFs may generally lead to the improvement of their CO₂ storage abilities which was confirmed by theoretical studies [54]. However, in the case of Cu-TATB, it was almost useless, and Cu-TATB had almost the same gas sorption behavior as Cu-BTB, despite that the surface is decorated by nitrogen containing triazine rings. Moreover, grand canonical Monte Carlo (GCMC) and first-principles calculations have been performed to further probe

the advantages of amide groups upon CO₂ adsorption at the molecular level, which demonstrated that CO₂ molecules prefer to locate at both the open Cu(II) metal sites and amide groups within the Cu-BTB framework. More interestingly, the CO₂ binding energy of the carbonyl site (C=O) is up to -9.24 kJ mol⁻¹ and is very comparable with that of open Cu^{II} metal sites (-9.03 kJ mol⁻¹), and far from the amide site (-NH-) (-0.168 kJ mol⁻¹) (Fig. 2b). The reason for this difference could be attributed to the possibility that the carbonyl moiety can yield an enhanced lone pair polarization on the CO₂ molecule. These results verified that the amide groups within both structures act as strong interaction sites and play an important role in the high and selective CO₂ uptake.

In a follow-up study by the same group, an *agw*-type porous MOF with the inserted amide functional groups, [Cu₃L₂(H₂O)₅] (NJU-Bai3), has been reported based upon a relatively small multidentate ligand, 5-(4-carboxybenzoylamino)-isophthalic acid (H₃L) (Fig. 3a) [55]. The overall structure of NJU-Bai3 is well packed by three types of cages with densely decorated amide units that are directly exposed to each individual cavity, in which, the bowl-like cage includes 12 amide groups (Fig. 3b), exhibited the BET surface area of 2690 m²g⁻¹. The CO₂ uptake for NJU-Bai3 at 273 K and 1 bar reaches 6.21 mmol g⁻¹, which is substantially larger than that of UCMC-150 (4.68 mmol g⁻¹), which the latter has the same topology as the prototypical

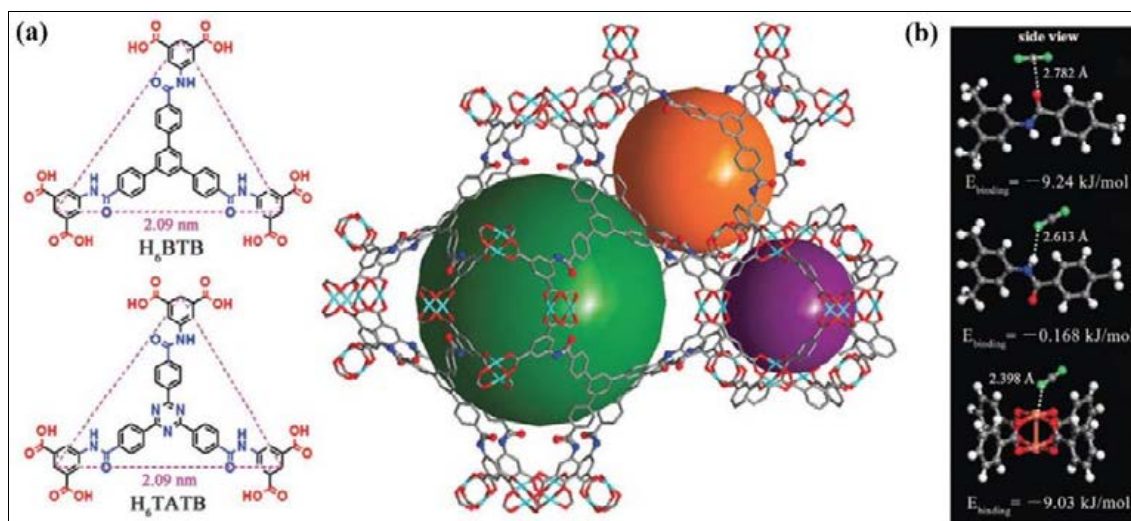


Fig. 2: (a) Nanosized amide-bridging ligands (H₆BTB and H₆TATB) and the 3D polyhedra packing in Cu-BTB. Cu, blue-green; C, gray; O, red; N, blue. (b) Preferential CO₂ adsorption sites and corresponding binding energies in Cu-BTB obtained from first-principles calculations. Adapted from Ref. [50].

agw-type framework but without amid-decorated pores [56]. Moreover, its high-pressure adsorption shows the unsaturation excess CO₂ uptake of 22.12 mmol g⁻¹ at 273 K and 20 bar, which is among the highest values for porous MOFs (IRMOF-1: 19.0 mmol g⁻¹; IRMOF-3: 17.2 mmol g⁻¹; and MOF-177: 28.7 mmol g⁻¹). However, it is worthy of note that the corresponding N₂ and CH₄ uptake of NJU-Bai3 was only 3.96 mmol g⁻¹ and 6.9 mmol g⁻¹, respectively.

Furthermore, the amide-functionalized NJU-Bai3 exhibits a strong binding affinity for CO₂ (36.5 kJ mol⁻¹) at zero coverage, which is significantly higher than that of its prototype, UCMCM-150 (20.3 kJ mol⁻¹) [57]. Moreover, similar to the previous example, the authors used GCMC simulations to further investigate the positive effect of decorated amide groups on CO₂ uptake in NJU-Bai3, which clearly reveal that both Cu^{II} metal sites and the amide groups are the main adsorption sites of CO₂ molecules in the framework. Interestingly, in terms of adsorption selectivity of CO₂/N₂ (60.8) and CO₂/CH₄ (46.6), NJU-Bai3 represents one of the highest selectivities reported up to now for adsorbent

materials, except that of the Co(II)-carborane coordination polymers (CO₂/N₂: 95 and CO₂/CH₄: 47), which has very low CO₂ uptake (1.7 mmol g⁻¹, 17 bar and 298 K) [58] (Fig. 3c). Therefore, NJU-Bai3 is one of the best examples of MOFs combining two interesting characters of high storage and high selectivity toward CO₂.

Zhou and coworkers reported a microporous multi-functional MOF PCN-124, which is constructed from Cu paddlewheel motifs and 5,5'-((pyridine-3,5-dicarbonyl)bis-(azanediyl)) diisophthalate (PDAI) ligand with two isophthalate and one pyridine groups connected through amide bonds [59]. PCN-124 possesses a self-interpenetrated (3, 36)-connected 3D structure with the BET surface areas are of 1372 m²g⁻¹ and moderate hydrostability, which is particularly relevant for potential applications in CO₂ capture technologies. Interestingly, the linearly arranged open metal sites and amide groups in its framework provide a favorable environment for CO₂ adsorption. CO₂ adsorption capacity of PCN-124 is 28.6 wt% at 273 K and 1 bar, with a corresponding heat of adsorption at

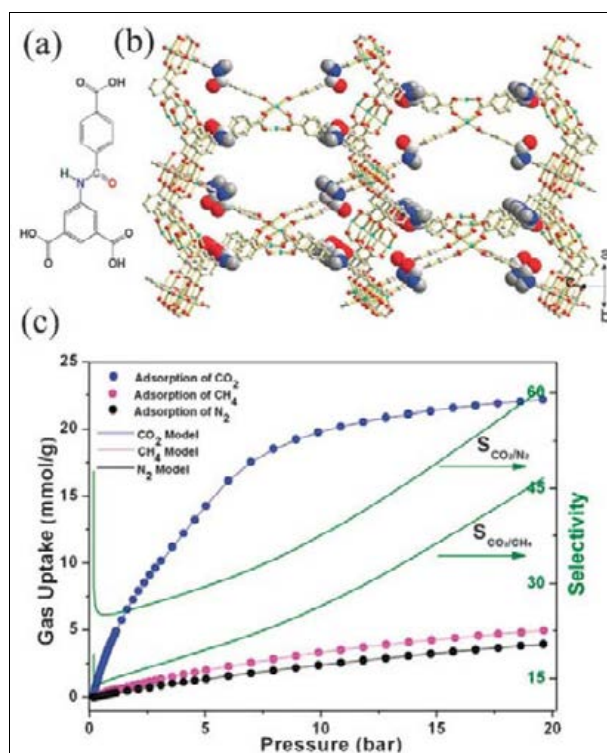


Fig. 3: (a) The organic building block of amide-functionalized H₃L. (b) The densely decorated amide groups in the pores from the crystal structure of NJU-Bai3. (c) High pressure gases adsorption isotherms and the dual-site Langmuir-Freundlich fit lines of CO₂, CH₄ and N₂ in NJU-Bai3 at 273 K. The green lines show the IAST predicted selectivity of CO₂ over N₂ and CH₄, respectively. Adapted from Ref. [55].

zero CO₂ loading of 26.3 kJ mol⁻¹. Interestingly, these results are higher than those for the isostructural MOF, PMOF-3, consisting of bridging ethynyl bonds instead of amide ones, despite higher N₂ adsorption of the latter.

In another report, a 3D microporous MOF with the formula of [Cu(pia)₂(SiF₆)](EtOH)₂(H₂O)₁₂ (UTSA-48; pia = N-(pyridin-4-yl)isonicotinamide) with functional -CONH- groups on the pore surfaces has been synthesized, and its CO₂ capture properties were compared to its isostructural amide-free MOFs, [Cu(bipy)₂(SiF₆)] and [Cu(bpe)₂(SiF₆)] [42]. The small pores and the functional amide groups within the activated UTSA-48 have enabled their strong interactions with CO₂, representing adsorption enthalpy of 30.0 kJ mol⁻¹, which is higher than the values of [Cu(bipy)₂(SiF₆)] (27 kJ mol⁻¹) and [Cu(bpe)₂(SiF₆)] (22 kJ mol⁻¹). Moreover, UTSA-48 exhibits CO₂/CH₄ separation with a Henry's Law selectivity of 20.7 at 273 K, which is

higher than its isostructural non-functionalized MOFs [60], indicating that amide groups have the positive effect on adsorption of CO₂ by facilitating dipole-quadrupole interactions between -CONH- groups and CO₂ or NH...OCO hydrogen bonds.

Current developments

After the previous finding presented in the last section, researchers focused their efforts on studying the effect of amide on the CO₂ capture in MOFs. A unique spatial arrangement of amide groups for CO₂ adsorption was found in the open-ended channels of a zinc(II)-organic framework [Zn₄(BDC)₄(bpda)]·5DMF·3H₂O (Zn-bpda; BDC = 1,4-benzylidicarboxylate, bpda = N,N'-bis(4-pyridinyl)-1,4-benzenedicarboxamide) [61]. Zn-bpda consists of 4⁺-sql [Zn₄(BDC)₄] sheets that are further pillared by a long amide-functionalized linker of bpda and forms a 3D porous framework with an α-Po 4¹²·6³ topology (Fig. 4a). The N₂

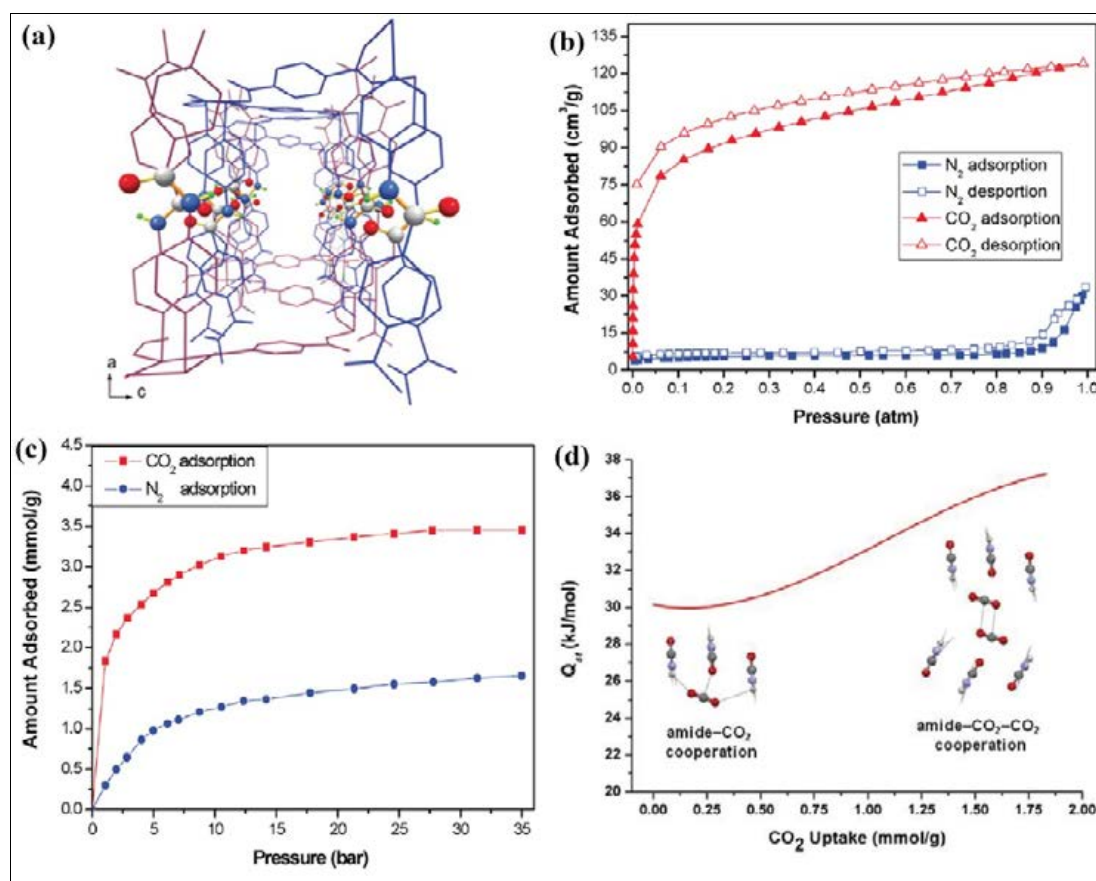


Fig. 4: (a) Spotlight of the larger channel opening showing a nearly unique arrangement of the unsheltered amide groups in Zn-bpda. Adsorption isotherms of N₂ and CO₂ measured at (b) 77 and 195 K and (c) 298 K and high pressure. (d) Isosteric heat (Q_{st}) of CO₂ adsorption. Adapted from Ref. [61].

adsorption isotherms of the MOF showed only a minor uptake at 77 K and 1 bar, which can be attributed to the framework contraction and a lack of appropriate intermolecular interactions at low temperature, where the CO₂ adsorption at 195 K exhibited a reversible type I isotherm, representing a BET surface area of 331 m² g⁻¹ (Fig. 4b). Remarkably, the MOF takes up 3.45 mmol g⁻¹ of CO₂ and 1.65 mmol g⁻¹ of N₂ at 35 bar and 298 K, where displays a distinct selective adsorption capacity for CO₂ over N₂ at low pressure, (Fig. 4c). Interestingly, the amount of captured CO₂ molecules at 1 bar is nearly equivalent to the number of exposed amide groups of the framework. This fact, which was further approved by density functional theory (DFT) calculations, implies that the amide groups inside the framework are involved in efficient intermolecular interactions with the adsorbed CO₂ molecules at ambient pressure and temperature. Furthermore, due to the positive cooperative effect of the unsheltered amide groups on the adsorption of CO₂ molecules, the isosteric heat of CO₂ adsorption (Q_{st}) of Zn-bpda presented a strong binding affinity for CO₂ (30.2 kJ mol⁻¹), which exhibits a significant increase with increasing CO₂ uptake to 37.2 kJ mol⁻¹, depending on the adsorbed amount of CO₂ molecules (Fig. 4d).

Considering future practical applications, a good gas storage or separation material must be stable toward moisture. Bai and coworkers have presented an evolution approach for constructing a water stable pillar-layered porous MOF, [Cu₂(TCMBT)(bpp)(μ₃-OH)]·6H₂O (Cu-TCMBT), using amide-containing flexible N,N',N''-tris(carboxymethyl)-1,3,5-benzenetricarboxamide (TCMBT) ligand [62]. Interestingly, Cu-TCMBT is quite stable in room temperature and boiling water for 2 months, as confirmed by PXRD patterns. The N₂ adsorption for activated Cu-TCMBT at 77 K exhibits a typical type I curve, with the BET surface area of 808.5 m² g⁻¹. In spite of possessing a relatively low BET surface area, the CO₂ uptake of Cu-TCMBT at 1 bar (44.8 cm³ g⁻¹) outperforms those of most of the ZIF materials [30, 63]. Moreover, the adsorption enthalpies for CO₂, CH₄, and N₂ were calculated to be 26.7, 19.1 and 16.0 kJ mol⁻¹, respectively. The higher CO₂ adsorption enthalpy is mainly attributed to incorporated bridging amide groups along the small channels. Because of a much larger quadrupole moment of CO₂ (13.4 × 10⁻⁴⁰ C m²) than that of N₂ (4.7 × 10⁻⁴⁰ C m²) and CH₄ (nonpolar) [64], the large dipole moment of the

bridging amide groups along the small channels facilitated the dipole-quadrupole interactions with CO₂, leading to the selectivity of CO₂ over CH₄ and N₂.

In 2013, Zheng *et al.* reported an expanded microporous NbO-type MOF formulated as [Cu₂(BDPT⁴⁻)(H₂O)₂] (HNUST-1; H₄BDPT = bis(3,5-dicarboxyphenyl)terephthalamide), designed from a nanosized rectangular amide-bridging tetra-carboxylate linker by solvothermal reaction of H₄BDPT and Cu(NO₃)₂·3H₂O in a mixture of DMF, ethanol, and H₂O [65]. The single crystal X-ray structure reveals that the framework of HNUST-1 is constructed from paddlewheel [Cu₂(COO)₄] SBUs bridged by BDPT to form a 3D non-interpenetrated (4,4)-connected net and contains two different types of the shuttle shaped and spherical pores (Fig. 5a-e) [66]. HNUST-1 exhibits a reversible type-I adsorption isotherm and takes up large amounts of N₂ at 77 K (370 cm³ g⁻¹ at 1 bar), featuring a moderate BET surface area of 1400 m² g⁻¹. HNUST-1 shows large CO₂-storage capacity of 53.3 wt. % at 20 bar and 273 K, as well as good selectivity of CO₂/CH₄ (7.2) and CO₂/N₂ (39.8), that is much higher than the corresponding value of MOF-177 (4.4 and 17.5) [52] and most other MOF materials [53]. Furthermore, the adsorption enthalpy of CO₂ was 31.2 kJ mol⁻¹, where a weaker CH₄ binding affinity was observed with Q_{st} of 23.4 kJ mol⁻¹ (Fig. 5f). The authors attributed this behavior to be a result of the large quadrupolar moment of the CO₂ molecule which facilitates strong dipole-quadrupole interactions between the amide groups in HNUST-1 and CO₂.

In a similar study by the same group, a microporous NbO-type MOF, [Cu₂BDPO(H₂O)₄] (HNUST-3), has been designed and synthesized by using a tetracarboxylate ligand of N,N'-bis(3,5-dicarboxyphenyl)oxalamide (H₄BDPO) with the "double amide" [-NHC(O)C(O)NH-] oxalamide motif whereby two back-to-back amides comprise the bridge between two isophthalate groups [67]. The 3D framework of HNUST-3 is the first example of a porous oxalamide-functionalized MOF, made up of four connected square [Cu₂(COO)₄] paddlewheels bridged through four branched BDPO linkers, while each Cu(II) center is coordinated to one water molecule along the axis of the paddlewheel. HNUST-3 exhibits a high BET surface area of 2412 m² g⁻¹, which is among the highest surface area of NbO-type MOF series reported to date. Moreover, HNUST-3 gives a

maximum excess H₂ uptake of 6.1 wt % (41.8 g L⁻¹) at 20 bar and 77 K which is moderate compared to the highest capacity MOF materials. Interestingly, this MOF adsorbs substantial amounts of CO₂ with uptake capacities of 33.15 wt % at 273 K and 16.6 wt % at 298 K under 1 atm of pressure, which are quite larger than that of the best performing ZIF material (ZIF-20, 13.7 wt % at 273 K and 1 atm) [68] and PCN-46 (ca. 13.2 wt % at 298 K and 1 atm) [70]. Notably, the CO₂ uptake amounts of HNUST-3 at 273 K were not saturated at 20 bar, with the values of 98.9 wt % (about 22.47 mmol g⁻¹). Interestingly, a container filled with HNUST-3 can store about 16 times the amount of CO₂ in an empty container at 20 bar and room temperature, which is higher than that for Cu-TPBTM (13 times), MOF-177

and PCN-61 (~14 times). Significantly, the strong interaction of CO₂ with the framework resulted in higher enthalpy of adsorption compared to CH₄ and N₂, leading to the high selectivity of CO₂/CH₄ (7.9) and CO₂/N₂ (26.1) at 298 K, which can be attributed to the large quadrupole moment of CO₂ as well as the presence of coordinatively unsaturated metal sites and polar oxalamide groups in HNUST-3.

In a follow-up study, Schröder and coworkers reported the uptake of CO₂ in a Cu-based porous MOF, [Cu₂(H₂O)₂BDPO] (NOTT-125), using the same oxalamide H₄BDPO ligand [36]. The amide-containing linker connects Cu₂(OOCR) paddlewheels to form NOTT-125 with fof topology in which the oxalamide is incorporated and placed

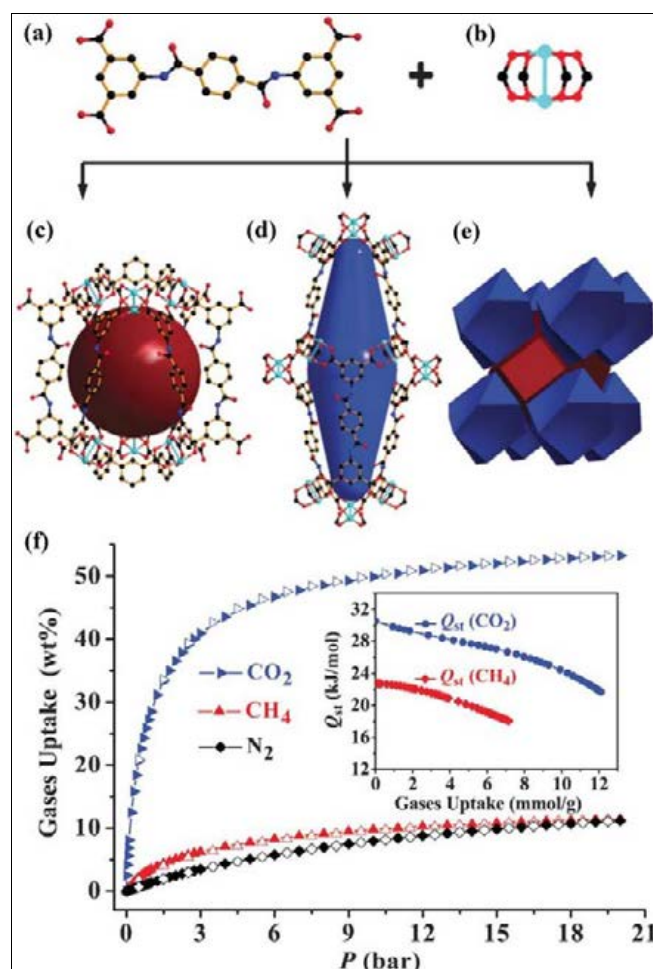


Fig. 5: (a and b) BDPT⁺ and [Cu₂(COO)₄] paddlewheel cluster. (c and d) The spherical and shuttle shaped cage. (e) A natural tiling of HNUST-1. Cu, blue-green; C, black; O, red; N, blue. (f) Gas sorption properties of HNUST-1. High-pressure gravimetric excess CO₂, CH₄ and N₂ isotherms collected at 273 K (inset: isosteric heats of CO₂ and CH₄ adsorption). Filled and open symbols represent adsorption and desorption, respectively. Adapted from Ref. [65].

within the pore walls (Fig. 6a-d). The N₂ sorption isotherm for activated NOTT-125 at 77 K exhibits reversible type I adsorption behavior with the BET surface area of 2447 m² g⁻¹. The oxalamide groups in the pore walls, combined with the large pore volume of this MOF has afforded the enhanced CO₂ uptake of 40.1 wt % at 273 K and 1 bar, which approaches the highest reported values for MOFs, such as Cu-TDPAT (44.5 wt%) [70] and Cu-TPBTM (42.6 wt%) [37], and is higher than the related amide-functionalized MOFs of Cu-NJU-Bai3 and PCN-124 (Fig. 6e,f). Moreover, its high pressure CO₂ uptake (21.2 mmol g⁻¹ at 298 K and 20 bar) and adsorption enthalpy (25.35 kJ mol⁻¹) could be attributed to the specific CO₂-oxamide interactions, including dipole-quadrupole

interactions and hydrogen-bond formation between the amide NH and the oxygen atoms of CO₂, which further verified by GCMC simulations.

Advances in the field of porous solids have been recently realized through the development of MOFs that are flexible. These so-called “third generation materials” are unique in their ability to undergo structural changes during the adsorption and desorption of guests, inducing highly-selective guest accommodation and magnetic modulation [71, 72]. The first gate-opening behavior of amide-functionalized MOF has been reported by Ghosh and co-workers, where the amide integrated framework of [CuL₂(NO₃)₂·o-xylene·DMF]_n (1-NO₃⁻), based on a flexible neutral amide-based N-donor ligand, was discriminated between CO₂

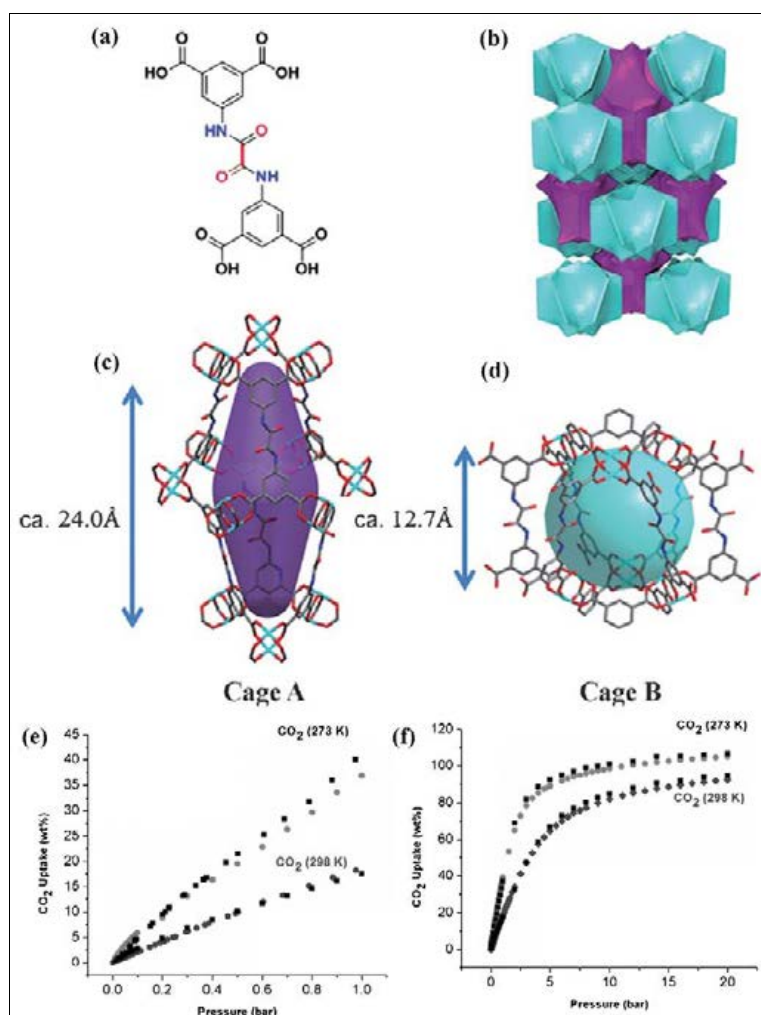


Fig. 6: View of: (a) Chemical structure of H₄BDPO; (b) Tiling of NOTT-125; (c) Cage A, and (d) Cage B. Experimental (circles) and simulated (squares) CO₂ isotherms of NOTT-125 at 273 and 298 K in the pressure range (e) 0-1 and (f) up to 20 bar. Adapted from Ref. [36].

as a polar gas molecule and other nonpolar gases [73] (Fig. 7a,b). Upon desolvation, this compound undergoes a dynamic structural transformation from a 1D porous phase to a 2D non-porous phase. Interestingly, 1-NO₃⁻ showed a CO₂ uptake of around 84 cm³ g⁻¹, whereas the compound shows a negligible uptake for other gases (N₂, H₂, Ar, and CH₄) (Fig. 7c). Such selectivity of CO₂ and corresponding transformation from the nonporous phase to microporous phase can be ascribed to the strong dipole-quadrupolar interaction of the -CONH- groups with the incoming CO₂ molecules.

In a similar study, the amide-CO₂ interaction was induced gate-opening behavior for CO₂ adsorption in flexible 2-fold interpenetrating network of [Mn₂(2,6-ndc)₂(bpda)]·5DMF (Mn-bpda) with amide groups exposed in the channels [74]. The N₂ adsorption isotherms of MOF showed only a minor uptake at 77 K, which can be attributed to framework contraction and a lack

of appropriate intermolecular interactions at low temperature, where the adsorption isotherms for CO₂ at 195 K displayed a gate-opening adsorption, with a total amount of CO₂ adsorption of 143 cm³ g⁻¹, and a corresponding isosteric heat of adsorption of 26.9 kJ mol⁻¹ which increases to 36.2 kJ mol⁻¹ with increasing CO₂ uptake. Moreover, the high pressure CO₂ adsorption isotherm of the flexible species Mn-bpda indicated a marked gate-opening process at P=5-8 bar, which was not found for N₂ adsorption (Fig. 8). These results show that amide-CO₂ interactions and possible amide-CO₂-CO₂ interactions play important roles in causing structural variations and in inducing the gate-opening behavior for CO₂ adsorption [75].

Recently, a pillaring strategy has been used for the design and synthesis of three interpenetrated amide-functionalized MOFs, TMUs-22/-23/-24, with the V-shaped dicarboxylate ligand of 4,4'-oxybisbenzoic acid (H₂oba) and linear

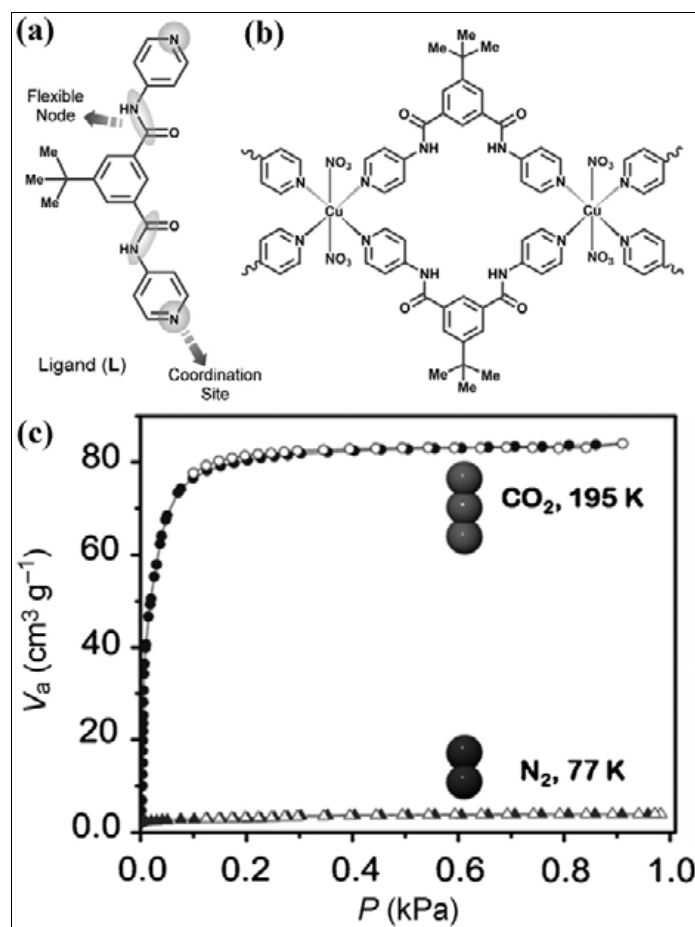


Fig. 7: (a) The ligand L and (b) the coordination environment around the copper center in 1-NO₃⁻. (c) CO₂ and N₂ adsorption isotherm at 195 K and 77 K respectively showing separation. Adapted from Ref. [73].

dipyridyl-based ligands, which are isorecticular to the imine-functionalized TMUs-6/-21 MOFs [76] (Fig. 9a). The similarities (structure and stability) and differences (functional group and accessibility) of these MOFs allow study of the influence of

the amide and the imine groups on their N₂ and CO₂ sorption properties as well as on their selective sorption of CO₂ over N₂. Interestingly, extensive study of their CO₂ sorption properties and selectivity, evaluated by performing kinetics

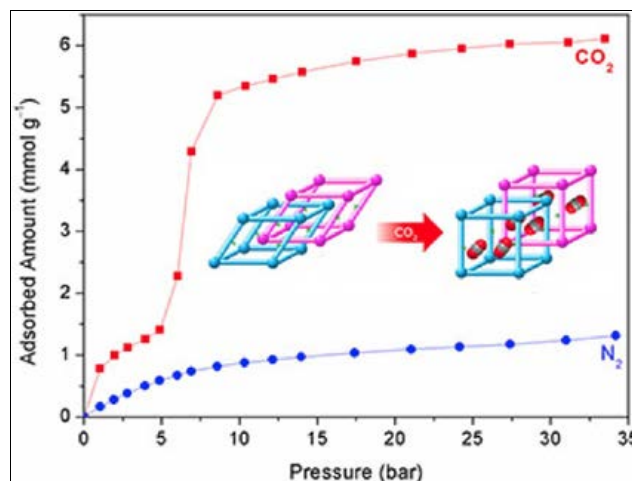


Fig. 8: Amide-CO₂ interactions induced gate-opening behavior for CO₂ adsorption at 298 K. Adapted from Ref. [74].

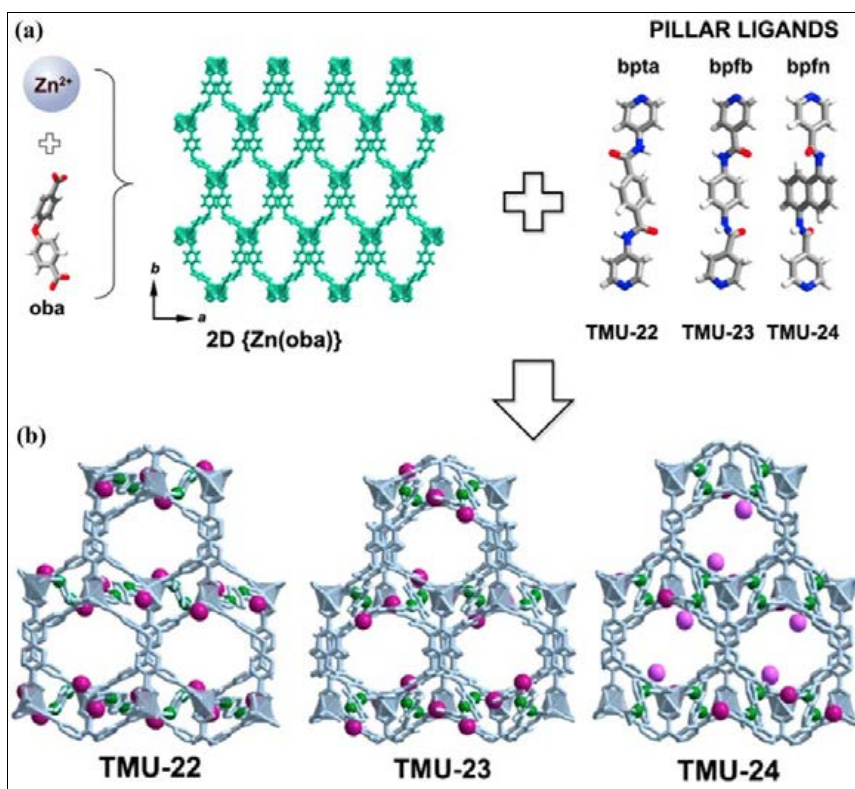


Fig. 9: (a) 2D layers formed by the association between Zn(II) ions and oba linkers are further pillared by amide/imine-functionalized dipyrrolic-based ligands yielding to threefold interpenetrated porous pcu-MOFs. (b) View of the pore channels of TMUs-22/-23/-24, highlighting the amide groups. Color code: N (green), O (purple), the more accessible O atoms in TMU-24 (lavender). Adapted from Ref. [76].

and breakthrough experiments for a CO₂/N₂ gas mixture, revealed that not only the incorporation of amide groups but also their accessibility is crucial to obtain enhanced CO₂ sorption and CO₂/N₂ selectivity (Fig. 9b). Therefore, the MOF with more accessible amide groups (TMU-24) shows a CO₂/N₂ selectivity value of ca. 10 (as revealed by breakthrough experiments), which is ca. 500% and 700% of the selectivity values observed for the other amide-containing (TMUs-22/-23) and imine-containing (TMUs-6/-21) MOFs, respectively.

MOFs are amenable to various post-synthesis manipulations to incorporate desired chemical moieties into nanoscale pores. In a valuable work performed by Hupp and Farha, two complementary amide-containing organic motifs (Fig. 10 a,b), which have a partial charges ($\delta^+ \dots \delta^- \dots \delta^+$) precisely

positioned via polar organic functionalities to complement the quadrupolar charge distribution in O=C=O, were post-synthetically incorporated into the robust NU-1000 MOF using solvent-assisted ligand incorporation (SALI) for CO₂ capture and separation [77] (Fig. 10c-e). Previous studies have established that SALI relies on Zr(IV)-carboxylate bond formation on the NU-1000 node to incorporate chemical moieties, provides a platform to evaluate the performance of new chemical functionalities in a porous solid environment without the need to prepare a new MOF linker containing the chemical functionality of interest, and enhances chemical and water vapor stability [77, 78]. Both of the amide-decorated SALI-derived samples entailed a slightly steeper CO₂ uptake in the CO₂ adsorption profiles at low

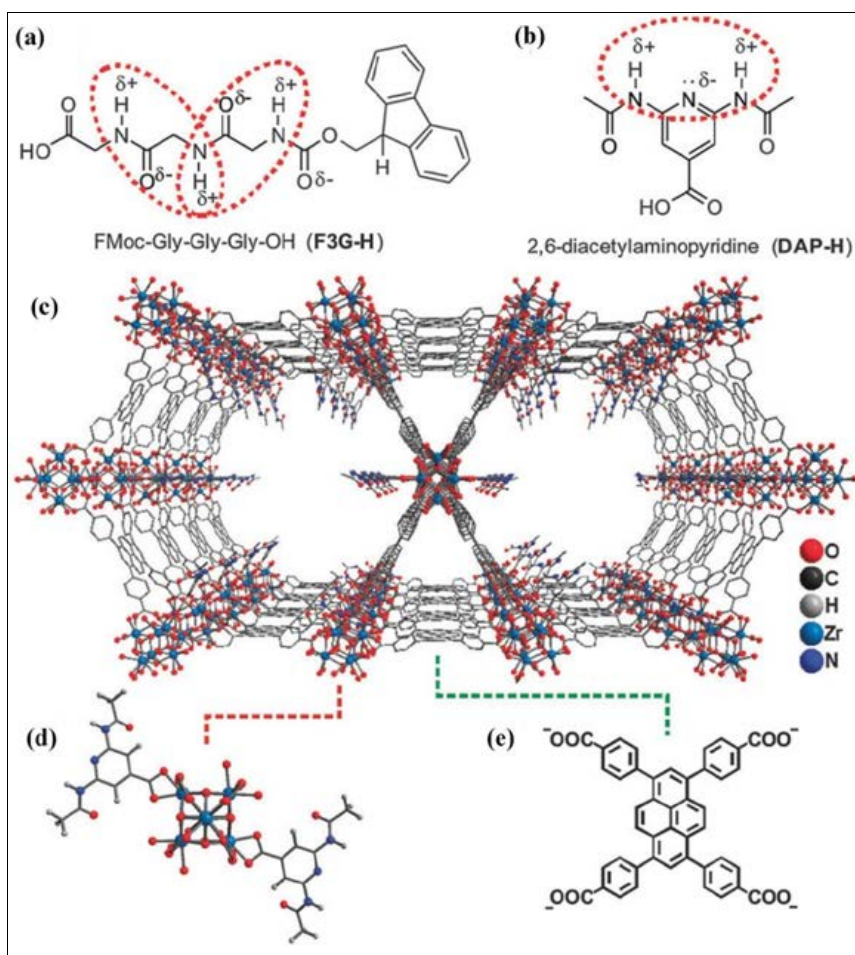


Fig. 10: Schematic representations of (a) N- α -fluorenylmethoxycarbonyl protected triglycine and (b) 2,6-diacetylaminopyridine-4-carboxylic acid. SALI, a heterogenization strategy for carboxylic acid-derived functional groups, applied to the MOF NU-1000: (c) molecular representation of SALI-derived SALI-DAP (along the c-axis), (d) the corresponding functionalized node, and (d) the linker of NU-1000. Adapted from Ref. [77].

pressure, resulting in higher volumetric uptake at lower pressure (~0.2 bar) relative to the unmodified NU-1000. Moreover, the post-modified samples showed higher values for Q_{st} at the zero-loading limit (27-28 kJ mol⁻¹) than the parent NU-1000 (17 kJ mol⁻¹), as qualitatively predicted by the GCMC simulations.

Very recently, an exceptionally water stable highly porous 3D MOF, [Cu₂(PDAD)(H₂O)]_n (PCN-124-stu, H₄PDAD = 5,5'-(pyridine-3,5-dicarbonyl)bis(azanediyldiisophthalic acid), has been synthesized with amide-functionalized cages [79]. PCN-124-stu maintains its framework in water with different pH values (pH 2-12) for at least one week, as monitored by PXRD, while only a limited number of MOFs have excellent stability in such a wide pH range of aqueous solutions, including those constructed MOFs with relatively expensive metals such as Zr which have higher metal-oxygen coordination bond energies. Compared to prototypical MOF PCN-124, PCN-124-stu exhibits larger pore sizes, higher porosity, and larger surface area. However, compared to the CO₂ capacities of PCN-124 under the same conditions, those of MOFs PCN-124-stu are reduced to some extent, which this may be attributable to the larger surface area and porosity of the latter. Through GCMC simulation at 273 K and 1 bar, the zero-loading heats of adsorption were found to be 26 kJ mol⁻¹ for CO₂ and 15 kJ mol⁻¹ for CH₄, which show significant selective adsorption of CO₂ over CH₄. Furthermore, the GCMC simulations revealed that both open Cu^{II} metal sites and the amide groups in the framework are clearly the main adsorption sites of CO₂ molecules, where H-bonding and van der Waals forces are the main interactions between CO₂ molecules and amide groups in the lowest-energy framework.

In 2016, Schröder and coworkers reported an amide-functionalized pyrimidyl Cu(II)-carboxylate MOF, MFM-136, which shows a CO₂ uptake of 14.3 mmol g⁻¹ at 20 bar and 273 K, representing the highest CO₂ uptake in mono-amide-functionalized MOFs reported to date [80]. In contrast, MFM-136 gives a lower uptake of CH₄ (8.3 mmol g⁻¹) and negligible uptake of N₂ under the same conditions, leading to selectivities of 6.3:1 and 27:1 for CO₂/CH₄ and CO₂/N₂, respectively. In this MOF, all Cu(II) sites are fully coordinated to carboxylate and pyrimidyl groups, affording a pore environment without open metal sites, which provides an ideal environment for

studying the binding interaction between amides and adsorbed CO₂ molecules, since it eliminates the competitive binding of CO₂ on the open Cu(II) sites. It is noteworthy that despite the good CO₂ uptake properties of MFM-136, combined neutron diffraction and inelastic neutron spectroscopy indicate no direct binding between adsorbed CO₂/CH₄ and free amides in this case. This suggests that introduction of functional groups solely may not necessarily induce specific guest-host binding in the porous material, but it is a combination of pore size, geometry, and functional group that leads to enhanced gas adsorption properties. However, for further comparison it would be well to perform the CO₂ uptake of the isostructural MOF, which has the same pore size and geometry as MFM-136 but without amide functional groups inside the pores.

CONCLUSIONS AND PERSPECTIVES

Currently, there is no unique solution to solve the problem of CO₂ capture, and this complicated challenge will almost certainly require the integration of several technology options. This review article has sought to highlight the effects of amide groups in the pores of MOFs on the CO₂ storage and separation abilities, which are dramatically enhanced by generation of specific metal-free polar functional groups within the porous MOFs because the functional moieties directly recognize CO₂ molecules through strong interactions. Furthermore, in parallel with experimental studies, in some cases, computational modeling methods such as grand canonical Monte Carlo (GCMC) and first-principles calculations have been applied as a tool to further probe the advantages of amide groups upon CO₂ adsorption at the molecular level, which demonstrated that CO₂ molecules prefer to locate at amide groups within the frameworks. Finally, we anticipate that this review article can provide useful information on the significant progress of the enhancement of CO₂ capture by decorating amide functional groups within the pores of MOF materials, which is very promising for real-world applications where MOF materials could be capable of serving as next-generation CO₂ capture systems.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this paper.

ABBREVIATIONS

BDC = 1,4-benzoyldicarboxylate
 bipy = 4,4'-bipyridine
 bpe = 1,2-bis(4-pyridyl)-ethene
 bpda = N,N'-bis(4-pyridinyl)-1,4-benzene dicarboxamide
 bpfb = N,N'-bis-(4-pyridylformamide)-1,4-benzenediamine
 bpfm = N,N'-bis(4-pyridylformamide)-1,5-naphthalenediamine
 bpta = N,N'-bis(4-pyridinyl)terephthalamide
 bpp = 1,3-bis(4-pyridyl)propane
 bteif⁶ = 5,5',5''-benzene-1,3,5-triyltris(1-ethynyl-2-isophthalate)
 CCS = Carbon capture and sequestration
 H₃L = (5-(4-carboxybenzoylamino)-isophthalic acid)
 H₄BDPT = bis(3,5-dicarboxyphenyl)terephthalamide
 H₄BDPO = N,N'-bis(3,5 dicarboxyphenyl)oxalamide
 H₄PDAD = 5,5'-(pyridine-3,5-dicarbonyl) bis(azanediyl)diisophthalic acid
 H₆BTB = 5,5',5''-((5'-(4-formylphenyl)-[1,1':3,1''-terphenyl]-4,4''-dicarbonyl)tris(azanediyl)) triisophthalic acid
 H₆TATB = 5,5',5''-((4,4',4''-(1,3,5-triazine-2,4,6-triyl) tris(benzoyl))tris(azanediyl))triisophthalic acid
 GCMC = Grand canonical Monte Carlo
 MOFs = Metal-organic frameworks
 2,6-ndc = 2,6-naphthalene dicarboxylate
 PDAI = 5,5'-(pyridine-3,5-dicarbonyl)bis-(azanediyl) diisophthalate
 pia = N-(pyridin-4-yl)isonicotinamide
 TBAPy = 1,3,6,8-tetrakis(p-benzoic acid)pyrene
 TPBTM = N,N',N''-tris(isophthalyl)-1,3,5-benzenetricarboxamide
 TCMBT = N,N',N''-tris(carboxymethyl)-1,3,5-benzenetricarboxamide

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