

## PERSPECTIVE

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[rsc.li/chemical-science](https://rsc.li/chemical-science)Direct air capture of CO<sub>2</sub> via crystal engineering

Radu Custelcean \*

This article presents a perspective view of the topic of direct air capture (DAC) of carbon dioxide and its role in mitigating climate change, focusing on a promising approach to DAC involving crystal engineering of metal–organic and hydrogen-bonded frameworks. The structures of these crystalline materials can be easily elucidated using X-ray and neutron diffraction methods, thereby allowing for systematic structure–property relationships studies, and precise tuning of their DAC performance.

## Introduction

Our continuing reliance on fossil fuels as a major source of energy created the impetus for effective emissions reductions through large-scale deployment of carbon capture and storage (CCS) technologies for mitigating climate change. While CCS technologies have traditionally been implemented at point sources of CO<sub>2</sub> emissions, such as coal- or gas-fired power plants, recent integrated assessment models have increasingly emphasized the need for negative emissions technologies (NETs), that is, technologies that remove CO<sub>2</sub> out of the atmosphere, to limit global warming below 2 °C by 2100.<sup>1,2</sup>

Direct air capture (DAC) refers to NETs that capture CO<sub>2</sub> from ambient air using engineered chemical processes.<sup>3–7</sup> DAC technologies have the potential to remove past emissions and restore the atmospheric CO<sub>2</sub> concentration to an optimal level below 350 ppm, and lower the global temperature back within

the optimum range of the pre-industrial Holocene period.<sup>8</sup> DAC can also compensate for the CO<sub>2</sub> emissions from the economy sectors that are difficult to decarbonize, such as steel and cement industries, long-distance transportation and shipping, and on-demand reliable electricity, which together account for about 27% of the global CO<sub>2</sub> emissions.<sup>9</sup> Furthermore, DAC offers the potential for high capacity (Gt-CO<sub>2</sub> scale), the flexibility of placement near the storage sites, and the possibility to generate high-purity CO<sub>2</sub> streams that can be converted into value-added products.<sup>1,2</sup>

To achieve these ambitious goals, DAC technologies must overcome a number of technical and economic challenges. First, the very low atmospheric CO<sub>2</sub> concentration (currently about 415 ppm) dictates that DAC sorbents bind CO<sub>2</sub> strongly and selectively against other components in the air. Indeed, simple thermodynamic considerations define the lower end of the CO<sub>2</sub> binding constant (log *K*) to 3.7, corresponding to a free energy of binding of at least −21 kJ mol<sup>−1</sup>.<sup>10</sup> Furthermore, considering the entropy of binding is typically negative, the enthalpy of CO<sub>2</sub> binding needs to be significantly exothermic (at least −50 kJ mol<sup>−1</sup>). With regard to selectivity, DAC sorbents need to be selective for CO<sub>2</sub> against water, which is 10–100 times more abundant than CO<sub>2</sub> in the atmosphere and tends to bind relatively strongly to most sorbents. Second, considering the enormous magnitude of DAC technologies deployment required to make an impact on the climate – up to 10 Gt CO<sub>2</sub> need to be captured annually by 2050<sup>1,2</sup> DAC sorbents will have to be manufactured on a massive scale (Mt per year), need to be chemically robust to survive tens of thousands of loading/unloading cycles, and cost less than \$10 per kg.<sup>11</sup> As a result of these stringent requirements, there are currently few viable CO<sub>2</sub> sorbents for DAC, mostly based on aqueous alkaline bases (e.g., NaOH, KOH),<sup>12</sup> solid-supported amines,<sup>13,14</sup> or moisture-swelling anion-exchange resins.<sup>15</sup>

With their ordered, well-defined structures, crystalline organic materials (e.g., metal–organic frameworks, hydrogen-bonded frameworks) offer a unique and promising approach to DAC. Their crystalline structures can be easily elucidated



*Radu Custelcean is a senior research scientist at Oak Ridge National Laboratory, where for the past 18 years has been involved in basic and applied research in molecular recognition, crystal engineering, separation science and technology, and carbon capture. Following a serendipitous discovery of atmospheric CO<sub>2</sub> capture by crystallization of a simple guanidine compound in 2016, direct*

*air capture (DAC) became his favorite research topic. His ultimate goal is to develop energy-efficient, cost-effective DAC technologies that will help address climate change.*

Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA. E-mail: [custelceanr@ornl.gov](mailto:custelceanr@ornl.gov)



using X-ray and neutron diffraction techniques, leading to a precise understanding of the relationship between their structures and functions. Moreover, their DAC performance could in principle be tuned and systematically improved by employing crystal engineering principles. Indeed, crystal engineering, whose primary objective has been the design and synthesis of functional organic and metal–organic crystals, has seen significant progress over the last decades, evolving from analysis of crystal structures and intermolecular interactions, to design of crystals with predetermined topologies, to property design and optimization. Thus, crystal engineering, which for many years has been limited to crystal structure engineering, is now transforming into crystal property engineering.<sup>16</sup> The crystal property of interest here, which will be discussed in detail in this perspective article, is atmospheric CO<sub>2</sub> capture, towards development of effective and energy-efficient DAC technologies.

### DAC with metal–organic frameworks

**DAC by physisorption.** Physisorption by crystalline porous solids is typically more suitable for CO<sub>2</sub> capture at relatively high pressures and concentrations, attributes that are not compatible with DAC. Nevertheless, the recently developed hybrid ultramicroporous materials (HUMs) that can tightly encapsulate CO<sub>2</sub> with high selectivity against other components in air (*e.g.*, N<sub>2</sub>, O<sub>2</sub>) have been proposed for DAC applications.<sup>17–21</sup> These crystalline frameworks consist of [M(pyrazine)<sub>2</sub>]<sup>2+</sup><sub>n</sub> square grids linked by counter anions acting as pillars (Fig. 1a).<sup>18</sup> The combination of small pore sizes and strong electrostatics from the inorganic anionic pillars provide a tailored fit and enhanced selectivity for small polarizable gases such as CO<sub>2</sub>.

In an initial study, Zaworotko *et al.* performed screening of five porous sorbents for their ability to capture CO<sub>2</sub> under DAC conditions: SIFSIX-3-Ni, HKUST-1, Mg-MOF-74/Mg-dobdc, zeolite-13X, and TEPA-SBA-15.<sup>17</sup> These sorbents represent four classes of porous materials: HUMs (SIFSIX-3-Ni), MOFs (HKUST-1, Mg-MOF-74/Mg-dobdc), zeolites, and amine-modified mesoporous silicate (TEPA-SBA-15) as a representative chemisorbent for comparison with the physisorbents. Temperature-programmed desorption (TPD) measurements under DAC conditions found that, while the SIFSIX-3-Ni performed best among the MOFs, the CO<sub>2</sub>/H<sub>2</sub>O selectivity was poor for all physisorbents. In contrast, the chemisorbent TEPA-SBA-

15 showed far superior DAC performance and CO<sub>2</sub>/H<sub>2</sub>O selectivity. Nevertheless, the promising performance of the SIFSIX-3-Ni HUM compared to the other MOF sorbents indicated that tuning pore size and functionality could lead to improved DAC by this class of materials.

Fine tuning the pores of the HUMs can be easily done by substituting the SiF<sub>6</sub><sup>2−</sup> anionic pillars with TiF<sub>6</sub><sup>2−</sup>, which leads to the isostructural TIFSIX-3-Ni sorbent with tighter binding sites for CO<sub>2</sub>, and as a result about three times higher uptake of CO<sub>2</sub> under DAC conditions.<sup>19</sup> The measured enthalpy of CO<sub>2</sub> adsorption for TIFSIX-3-Ni, of −50 kJ mol<sup>−1</sup>, is slightly higher than for the SIFSIX-3-Ni analogue (*Q*<sub>st</sub> = 45 kJ mol<sup>−1</sup>), and significantly higher than the corresponding values for other MOF materials (*e.g.*, Mg-MOF-74, −42 kJ mol<sup>−1</sup>; UiO-66-NH<sub>2</sub>, −38 kJ mol<sup>−1</sup>; HKUST-1 −23 kJ mol<sup>−1</sup>). Accordingly, the CO<sub>2</sub> capacity (0.41 mmol g<sup>−1</sup>) and CO<sub>2</sub>/H<sub>2</sub>O selectivity (12.8) measured under DAC conditions for TIFSIX-3-Ni, was significantly higher compared to other physisorbents. A related crystalline material, with anionic pillars consisting of NbOF<sub>5</sub><sup>−</sup> (NbOFFIVE-1-Ni) was described by Eddaoudi *et al.* (Fig. 1b).<sup>20</sup> This sorbent has slightly higher gravimetric uptake (1.3 mmol g<sup>−1</sup>) and enthalpy of CO<sub>2</sub> adsorption (−54 kJ mol<sup>−1</sup>) than TIFSIX-3-Ni. Its crystal structure obtained in the presence of carbon dioxide revealed the CO<sub>2</sub> is tightly bound within the square-shaped channels, surrounded by four electronegative F atoms from the NbOF<sub>5</sub><sup>−</sup> anions interacting with the electropositive C atom of CO<sub>2</sub> (Fig. 1b). These strong and complementary interactions provide an optimal CO<sub>2</sub> binding site, consistent with the relatively high enthalpy of adsorption compared with other physisorbents. Unfortunately, for both TIFSIX-3-Ni and NbOFFIVE-1-Ni, the binding sites also strongly bind water, which competes with the CO<sub>2</sub> adsorption.<sup>21</sup> Nevertheless, the regeneration of these materials can be done at relatively low temperatures (90–100 °C), under purging with an inert gas or vacuum.

The superior DAC performance of TIFSIX-3-Ni and NbOFFIVE-1-Ni compared to SIFSIX-3-Ni highlights how subtle changes in pore size and chemistry can have a dramatic effect on the CO<sub>2</sub> sorption performance of a series of isostructural materials. However, competition with water vapor remains a significant challenge, especially for DAC applications. Even though the incorporation of strong electrostatics from the inorganic pillars combined with ultramicropores offers improved CO<sub>2</sub> capture performance from moist air, it is not enough to compete with chemisorbents.<sup>21</sup> Furthermore, like

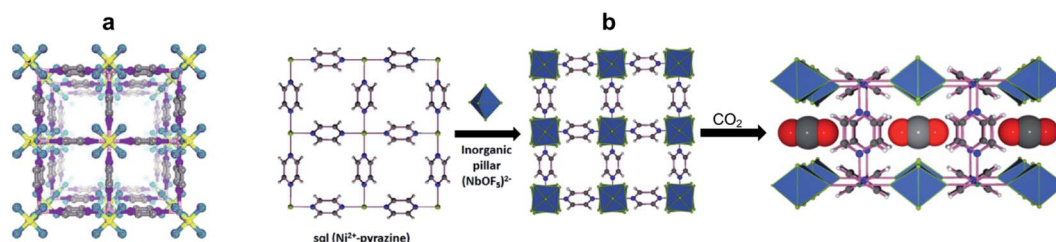


Fig. 1 MOFs/HUMs for DAC by physisorption. (a) Crystal structure of SIFSIX-3-Ni. (b) Crystal structure of NbOFFIVE-1-Ni and binding of CO<sub>2</sub> in its pores. Adapted with permission from ref. 20. Copyright (2016) American Chemical Society.



zeolites that have high affinity to water, water adsorption in the pores of MOFs or HUMs competes with the CO<sub>2</sub> adsorption, leading to longer regeneration times, higher regeneration energies, and reduced working capacity for the DAC process.

**DAC by chemisorption.** Chemisorbents typically offer stronger CO<sub>2</sub> binding and superior CO<sub>2</sub>/H<sub>2</sub>O selectivity than physisorbents, due to specific covalent interactions between amine or hydroxide functional groups and CO<sub>2</sub>. While this comes with higher CO<sub>2</sub> binding enthalpy, the overall regeneration energy can still be considerably lower than for aqueous amine or alkaline bases, due to the significantly lower heat capacity of solids compared to aqueous solvents.

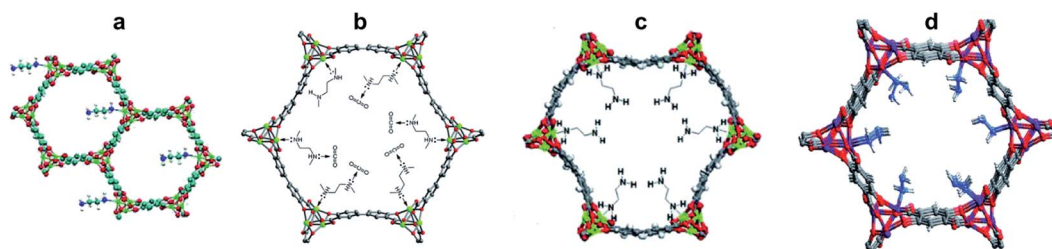
Functionalization of magnesium dioxymethylene dicarboxylate (Mg/dobdc, or Mg-MOF-74) with ethylenediamine (ed) led to an early example of MOF capable of multiple cycles of CO<sub>2</sub> adsorption/release *via* chemisorption under practical DAC conditions using simulated dry air (400 ppm CO<sub>2</sub>).<sup>22</sup> Ethylenediamine was grafted to the pores of this MOF through coordination of the open metal sites with one of the amine groups, which left the second NH<sub>2</sub> group pendent inside the pore and available to react with CO<sub>2</sub> (Fig. 2a). The measured cyclic capacity of ed-Mg/dobdc was about 1.50 mmol g<sup>-1</sup>, sustained over 4 consecutive cycles. For comparison, under the same conditions, the measured cyclic capacity of Mg/dobdc was 1.35 mmol g<sup>-1</sup> in the first cycle, and dropped to 1.06 mmol g<sup>-1</sup> after 4 cycles.

An expanded analogue of Mg/dobdc, magnesium 4,4'-dioxido-3,3'-biphenyldicarboxylate [Mg<sub>2</sub>(dobpdc)], was functionalized with *N,N'*-dimethylethylenediamine (mmen) to afford mmen-Mg<sub>2</sub>(dobpdc) (Fig. 2b).<sup>23</sup> After pore activation, its CO<sub>2</sub> adsorption capacity at 25 °C and 0.39 mbar, conditions simulating ambient air, was 2.0 mmol g<sup>-1</sup>, 15 times higher than measured for Mg<sub>2</sub>(dobpdc) under the same conditions. The isosteric heat of adsorption for mmen-Mg<sub>2</sub>(dobpdc) is -71 kJ mol<sup>-1</sup>, consistent with a chemisorption mechanism involving amine reaction with CO<sub>2</sub> to form carbamate, which was confirmed by *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The CO<sub>2</sub> cyclic capacity measured using dry air was 1 mmol g<sup>-1</sup>, which was maintained after 10 consecutive adsorption/desorption cycles. Regeneration of this MOF sorbent involved heating at 150 °C under nitrogen for 30 min.

This MOF adsorbent exhibits step-shaped isotherms, allowing for a relatively large working capacity with only a small increase in temperature. In direct contrast, classical adsorbents, including most amine-functionalized solids, exhibit Langmuir-type isotherms requiring high desorption temperatures to achieve large working capacities. Spectroscopic and diffraction measurements indicated a mechanism of CO<sub>2</sub> uptake involving cooperative insertion of CO<sub>2</sub> into the metal-amine bonds, resulting in a carbamate group coordinated to the metal center, and further stabilized by hydrogen bonding to an ammonium group formed by proton transfer from the carbamic acid to the free pendent amine group from an adjacent mmen.<sup>24</sup> This cooperative mechanism leading to the formation of one-dimensional ammonium carbamate chains explains the sudden uptake of large amounts of CO<sub>2</sub> and the unusual step-shaped isotherms. The ammonium-carbamate hydrogen bonding may also facilitate the proton transfer during the regeneration of these sorbents, which only require about 2.2–2.3 MJ kg<sup>-1</sup> CO<sub>2</sub>, as measured by differential scanning calorimetry (DSC).

The ethylenediamine-functionalized analogue of Mg<sub>2</sub>(dobpdc), ed-Mg<sub>2</sub>(dobpdc) (Fig. 2c), showed a significant CO<sub>2</sub> uptake of 2.83 mmol g<sup>-1</sup> at 0.39 mbar and 25 °C.<sup>25</sup> A chemisorption mechanism consisting of carbamic acid formation by reaction of the free amine groups with CO<sub>2</sub> was proposed based on *in situ* IR measurements, which is consistent with the estimated stoichiometry of 0.83 moles CO<sub>2</sub> per moles of ED, and the relatively low isosteric heat of adsorption of about -50 kJ mol<sup>-1</sup>. CO<sub>2</sub> desorption required heating at 150 °C for 2 h under air purge.

Further increase in the CO<sub>2</sub> capacity was possible by functionalizing Mg/dobdc with the shortest possible diamine, hydrazine (H<sub>2</sub>NNH<sub>2</sub>) (Fig. 2d).<sup>26</sup> The ultrahigh concentration of amine groups in this sorbent, coupled with their ability to form carbamic acid by reaction with CO<sub>2</sub>, led to the unprecedented CO<sub>2</sub> capacity of 3.89 mmol g<sup>-1</sup> at the atmospheric CO<sub>2</sub> concentration of 0.4 mbar and 25 °C. The formation of carbamic acid was confirmed by *in situ* IR and <sup>13</sup>C NMR spectroscopies, and the measured isosteric heat of adsorption of -90 kJ mol<sup>-1</sup> confirmed the chemisorption of CO<sub>2</sub>. The regeneration energy determined by DSC is 3.02 MJ kg<sup>-1</sup> CO<sub>2</sub>. Regeneration of the sorbent was done by heating at 130 °C under nitrogen flow. The



**Fig. 2** Amine-functionalized MOFs for DAC by chemisorption. (a) Crystal structure of ed-Mg/dobdc. Reproduced with permission from ref. 22. Copyright (2012) American Chemical Society. (b) Crystal structure of mmen-Mg<sub>2</sub>(dobpdc) showing the CO<sub>2</sub> binding by pendent amine groups. Reproduced with permission from ref. 23. Copyright (2012) American Chemical Society. (c) Crystal structure of ed-Mg<sub>2</sub>(dobpdc). Reproduced with permission from ref. 25. Copyright (2014) Royal Society of Chemistry. (d) Crystal structure of H<sub>2</sub>NNH<sub>2</sub>-Mg/dobdc. Reproduced with permission from ref. 26. Copyright (2016) Royal Society of Chemistry.





DAC performance of this sorbent was minimally impacted by the presence of humidity.

Despite their favorable structural and thermodynamic features, amine-functionalized MOFs with stepped isotherms like  $\text{ed-Mg}_2(\text{dobpdc})$  and  $\text{mmen-Mg}_2(\text{dobpdc})$  were found to have some kinetic limitations under DAC conditions. Specifically, the kinetics of  $\text{CO}_2$  adsorption at concentrations of 400 ppm were measured from breakthrough experiments and characterized through an Avrami model, with the mass transfer rate limited by the cooperative insertion of  $\text{CO}_2$ . Notably, the shape of the isotherm and the kinetic factors severely diminish the  $\text{CO}_2$  capture fraction at low concentrations, reducing the viability of these MOF sorbents for practical DAC applications.<sup>27</sup> Nevertheless, the MOFs' structural tunability allows for optimization of  $\text{CO}_2$  adsorption under DAC conditions. For example, small modifications of the appended diamine in  $\text{Mg}_2(\text{dobpdc})$  led to shifts in the threshold pressure for  $\text{CO}_2$  adsorption by over 4 orders of magnitude.<sup>28</sup> Furthermore, it was demonstrated that the adsorption kinetics can also be improved through selection of appropriate diamines that lead to faster  $\text{CO}_2$  adsorption under DAC conditions.<sup>29</sup> Replacing the appended diamines with tetraamines led to more stable MOFs that can cooperatively capture  $\text{CO}_2$  from humid air, and can be regenerated with steam.<sup>30</sup>

An alternative approach to MOF functionalization with amines is to decorate the pores with  $\text{Zn-OH}$  groups that mimic the active site of carbonic anhydrase. This approach has been recently demonstrated with a  $\text{Zn-benzotriazolate}$  MOF post-synthetically modified to generate nucleophilic  $\text{Zn-OH}$  binding sites for  $\text{CO}_2$  (Fig. 3).<sup>31</sup> After activation by heating at  $100^\circ\text{C}$  under high vacuum, the resulting MOF sorbent exhibited remarkably steep  $\text{CO}_2$  uptake at low pressures, with a  $\text{CO}_2$  capacity of  $2.20\text{ mmol g}^{-1}$  at 0.4 mbar, and an isosteric heat of adsorption of  $-71\text{ kJ mol}^{-1}$ . The enthalpy of binding is consistent with a chemisorption mechanism, which was

confirmed by DRIFTS experiments that revealed the conversion of  $\text{Zn-OH}$  to  $\text{Zn-O}_2\text{COH}$  groups. DFT calculations revealed the formation of hydrogen-bonded bicarbonate dimers that cross-link the  $\text{Zn}$  clusters in the framework. Notably, the  $\text{CO}_2$  cyclic capacity measured over multiple consecutive cycles with simulated air mixtures was somewhat lower (*i.e.*, 5.8 wt%) than the corresponding value measured from the single-component isotherm. Furthermore, this material performed poorly in breakthrough experiments conducted in the presence of humidity. Postsynthetic exchange of  $\text{Zn-OAc}$  groups in the framework with  $\text{Ni-OH}$  resulted in an heterobimetallic analogue with even steeper  $\text{CO}_2$  adsorption isotherm, higher  $\text{CO}_2$  capacity of  $2.7\text{ mmol g}^{-1}$  at 0.4 mbar, and more exothermic heat of adsorption of  $-84\text{ kJ mol}^{-1}$ .<sup>32</sup> DRIFTS experiments and DFT calculations revealed that, unlike in the  $\text{Zn-OH}$  system, the  $\text{Ni-O}_2\text{COH}$  species do not engage in intercluster hydrogen bonding, which could explain its intrinsically higher affinity for  $\text{CO}_2$ . Breakthrough cycling experiments with simulated air yielded a slightly lower  $\text{CO}_2$  cyclic capacity of  $1.93\text{ mmol g}^{-1}$ , though its structure appeared to be stable to repeated cycling with humid gas streams. However, the  $\text{Ni-OH}$  MOF adsorbed more water ( $2.95\text{ mmol H}_2\text{O}$  per g) compared to the  $\text{Zn-OH}$  analogue ( $1.07\text{ mmol H}_2\text{O}$  per g), resulting in an overall decreased DAC performance under humid conditions.

### DAC by crystallization of hydrogen-bonded frameworks

The allure of MOFs comes from their aesthetic porous structures that can be precisely designed and engineered for optimal binding of gas molecules like  $\text{CO}_2$ . Porosity, though, is a high-maintenance functionality. Pore activation is often an elaborate and tedious process. Maintaining an open structure over multiple adsorption/desorption cycles takes effort and energy, as nature abhors vacuum and will do anything to fill those pores with whatever is available in the air. Particularly, water condensation in the pores is a problem for DAC applications, as the energy required to desorb water may be substantial, sometimes exceeding the energy of  $\text{CO}_2$  desorption.<sup>33</sup>

Hydrogen-bonded frameworks (HBFs) offer a viable alternative to MOFs. Like MOFs, the structures of HBFs can be precisely designed and tuned using the principles of crystal engineering. While permanently porous HBFs have recently become a reality,<sup>34</sup> HBF porosity is not actually a prerequisite for DAC. As an alternative approach, the  $\text{CO}_2$  capture can be done in aqueous solutions, as long as the absorption process leads to the formation of stable and insoluble HBF crystals that incorporate  $\text{CO}_2$  in their structures (typically as carbamic acid, carbamate, or carbonate anions). In such cases, the HBF- $\text{CO}_2$  crystals can be simply removed from solution by filtration, followed by  $\text{CO}_2$  desorption from the isolated solids, and recycling of the water-soluble HBFs. Ideally, this strategy combines the benefits of aqueous solvents, such as fast kinetics of  $\text{CO}_2$  absorption, easy scalability, and low cost, with the advantages of crystalline sorbents, such as structural tunability and lower regeneration energies.

A proof of concept for DAC by crystallization of HBFs came from a simple amine system, *m*-xylylenediamine (MXDA).<sup>35</sup> An

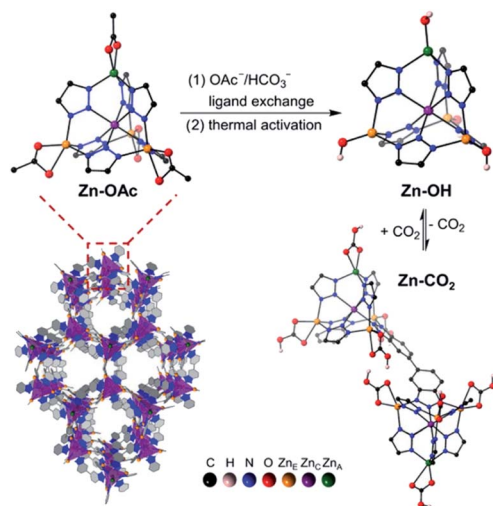


Fig. 3 Crystal structure of a  $\text{Zn-benzotriazolate}$  MOF functionalized with  $\text{Zn-OH}$  binding sites and reaction with  $\text{CO}_2$ . Reproduced with permission from ref. 32. Copyright (2020) American Chemical Society.



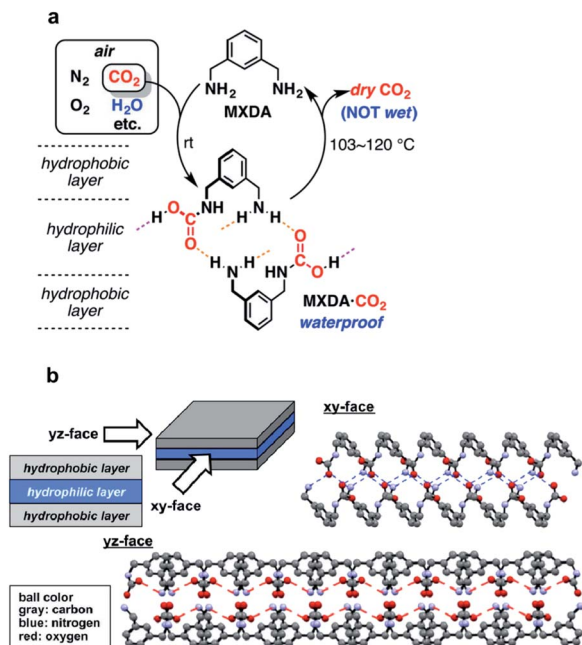


Fig. 4 DAC by crystallization of MXDA. (a) DAC cycle involving atmospheric  $\text{CO}_2$  absorption by an aqueous solution of MXDA. (b) Crystal structure of the carbamic acid formed from the reaction of MXDA with  $\text{CO}_2$ . Reproduced with permission from ref. 35. Copyright (2017) American Chemical Society.

aqueous solution of MXDA left open to air absorbed atmospheric  $\text{CO}_2$  and formed insoluble crystals of  $\text{MXDA} \cdot \text{CO}_2$  (Fig. 4a). X-ray structural analysis revealed a carbamic acid product linked into extensive chains *via*  $\text{NH} \cdots \text{O}$  hydrogen bonds. Additional  $\text{COOH} \cdots \text{NH}_2$  hydrogen bonds crosslink the chains into two-dimensional networks. Finally, the Ph groups pack into hydrophobic layers that sandwich the hydrophilic hydrogen-bonded layers in a reverse lipid bilayer-like structure (Fig. 4b). It was proposed that this crystal packing prevents the water from penetrating into the hydrophilic layers, thereby resulting in low aqueous solubility of  $\text{MXDA} \cdot \text{CO}_2$ . Heating the crystals at 103–120 °C releases the  $\text{CO}_2$  and regenerates MXDA, which can be recycled. The anhydrous nature of this HBF presents a great advantage for a DAC process, in that it avoids

the energy-intensive water evaporation step typically associated with aqueous solvents or hygroscopic sorbents.

The success of the above DAC strategy hinges on the premise that the resulting  $\text{HBF} \cdot \text{CO}_2$  complex has sufficiently low aqueous solubility to drive the  $\text{CO}_2$  absorption and crystallization equilibria in spite of the very low concentration of  $\text{CO}_2$  in the air. However, most amines form products with  $\text{CO}_2$  that are relatively soluble in water; MXDA is more the exception than the rule. Thus, there remains the need to identify design principles for engineering amines or related organic bases that form insoluble carbamic acids or carbamate/(bi)carbonate crystals upon reaction with atmospheric  $\text{CO}_2$ , if this DAC approach is to become more general.

Research at Oak Ridge National Laboratory led recently to development of a new, energy-efficient approach to DAC based on crystallization of hydrogen-bonded bis-iminoguanidinium (BIG) (bi)carbonate salts.<sup>36</sup> BIGs are a new class of anion receptors readily synthesized by imine condensation of aldehydes or ketones with aminoguanidinium salts (Fig. 5).<sup>37–39</sup> BIGs form with oxyanions (*e.g.*, sulfate, carbonate) HBFs of very low aqueous solubilities (on par with  $\text{BaSO}_4$  or  $\text{CaCO}_3$ ), a property that can be exploited for selective separation of these anions by crystallization. The low aqueous solubilities of these salts can be attributed to a number of structural factors: favorable  $\pi$ -stacking of the planar BIG cations, strong charge-assisted hydrogen bonding of the oxyanions by the iminoguanidinium groups, and reduced dehydration penalty of oxyanions, as they crystallize as hydrated clusters.

The prototype glyoxal-bis-iminoguanidine (GBIG), first reported in the chemical literature in 1898 by Johannes Thiele (Fig. 5),<sup>40</sup> provided the proof-of-concept for  $\text{CO}_2$  capture by BIG crystallization. An aqueous solution of GBIG left overnight under a  $\text{CO}_2$  atmosphere led to crystallization of a hydrated GBIG bicarbonate salt. Single-crystal X-ray diffraction analysis (Fig. 6) revealed the formation of centrosymmetric  $(\text{HCO}_3^-)_2$  dimers with  $\text{H} \cdots \text{O}$  contact distances of 1.71 Å (Fig. 6a). Each bicarbonate anion additionally accepts three guanidinium and two water hydrogen bonds (Fig. 6b). The bicarbonate dimers are linked by the water molecules into one-dimensional ladder-shaped clusters (Fig. 6c). On the other hand, the essentially planar  $\text{GBIGH}_2^{2+}$  cations stack along the same direction, with a mean interplanar

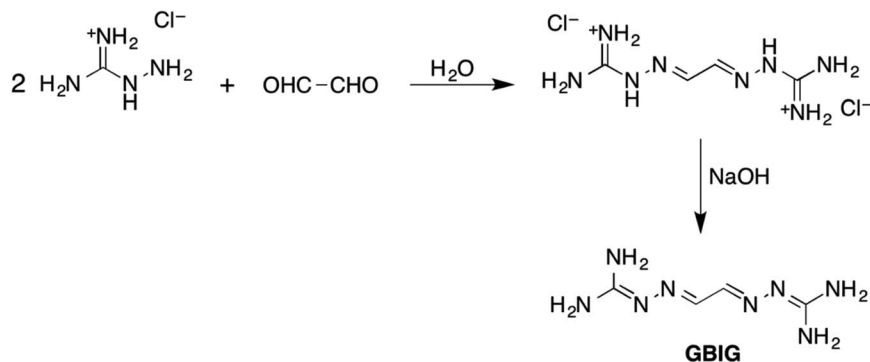
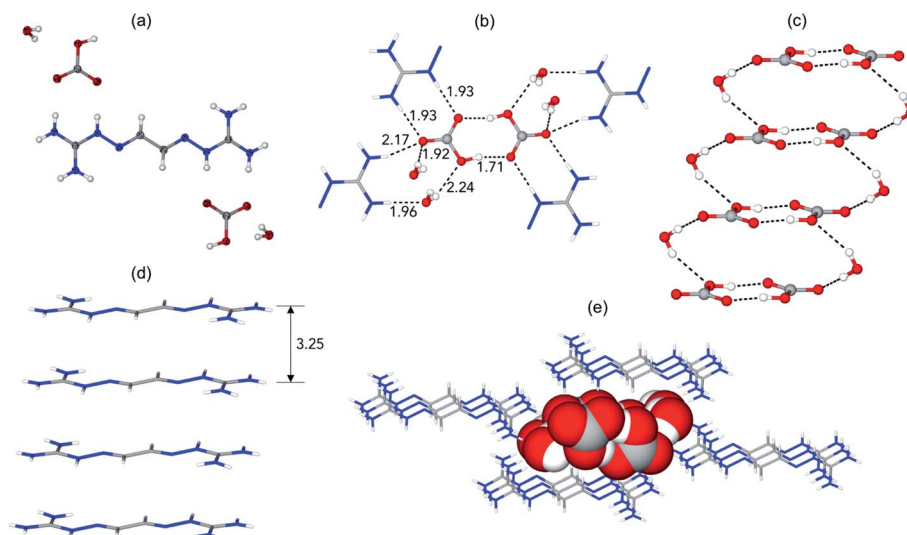


Fig. 5 Synthesis of a BIG exemplified by glyoxal-bis-iminoguanidine (GBIG). Reproduced with permission from ref. 39. Copyright (2020) Royal Society of Chemistry.





**Fig. 6** X-ray crystal structure of GBIG- $\text{HCO}_3^-$ . (a) ORTEP representation, with 50% ellipsoids. (b) Hydrogen bonding of bicarbonate dimers, with contact distances shown in Å. (c) Ladder-shaped hydrogen-bonded  $[(\text{HCO}_3^-)_2(\text{H}_2\text{O})_2]_n$  anionic cluster. (d) Stack of  $\text{GBIGH}_2^{2+}$  cations, with the mean distance between adjacent cations shown in Å. (e) Crystal packing viewed along the crystallographic  $a$  axis, with the cationic stacks (shown as stick models) flanking the anionic cluster (shown as space-filling model). Reproduced with permission from ref. 41. Copyright (2019) Elsevier.

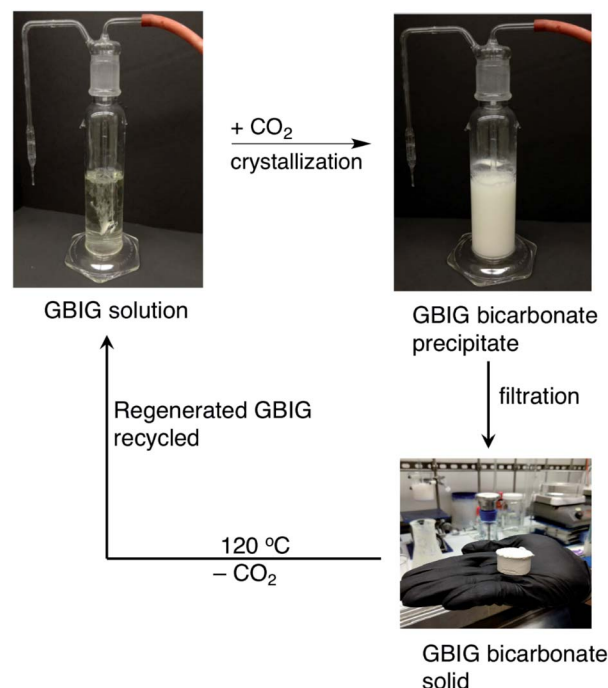
distance of 3.25 Å (Fig. 5d). Finally, the cationic stacks flank the anionic clusters in a close-packed arrangement (Fig. 5e).<sup>41</sup>

The  $\text{CO}_2$  absorption by GBIG consists of the following elementary steps: protonation of GBIG by water to generate  $\text{GBIGH}_2^{2+}$  cations and  $\text{HO}^-$  anions,  $\text{CO}_2$  transport from air into the aqueous solution, reaction of  $\text{CO}_2$  with  $\text{HO}^-$  to generate  $\text{HCO}_3^-$ , and crystallization of  $\text{GBIGH}_2^{2+}$  and  $\text{HCO}_3^-$  ions into  $\text{GBIGH}_2(\text{HCO}_3)_2(\text{H}_2\text{O})_2$ . The reaction enthalpy for the overall  $\text{CO}_2$  capture process is  $-61 \text{ kJ mol}^{-1} \text{ CO}_2$ , close to the lower end of the 60–80  $\text{kJ mol}^{-1}$  range of absorption enthalpies for amine-based sorbents. Heating the crystals at 120 °C under a flow of air in the oven releases the  $\text{CO}_2$  and regenerates GBIG quantitatively, thereby closing the  $\text{CO}_2$ -separation cycle. Experimental and computational investigations provided evidence for a  $\text{CO}_2$  release mechanism consisting of surface-initiated low-barrier proton transfer from the GBIG cations to the bicarbonate anions with the formation of carbonic acid dimers, followed by  $\text{CO}_2$  and  $\text{H}_2\text{O}$  release in the rate-limiting step, with a measured activation energy of  $102 \pm 12 \text{ kJ mol}^{-1}$ .<sup>41</sup>

The  $\text{CO}_2$  capture cycle with GBIG was tested with a flue gas simulant (Fig. 7).<sup>41</sup> A  $\text{CO}_2$  crystallization yield of 89% and quantitative GBIG regeneration were sustained for ten consecutive cycles. The  $\text{CO}_2$  capacity of the isolated carbonate solid, based on its molecular formula, is  $6.1 \text{ mmol g}^{-1}$ . However, this is only a theoretical number that represents the upper limit achievable for the cyclic capacity. The actual working capacity will depend on the exact composition of the initial GBIG solution and other variables selected in the process design. The regeneration energy of GBIG is  $151.5 \text{ kJ mol}^{-1} \text{ CO}_2$ , 24% lower than the regeneration energy of monoethanolamine (MEA), a benchmark industrial  $\text{CO}_2$  solvent for which excessive energy is consumed in heating and vaporization of water.

While GBIG was found to capture  $\text{CO}_2$  from flue gas energy efficiently, it proved inadequate for DAC. Exposure of an

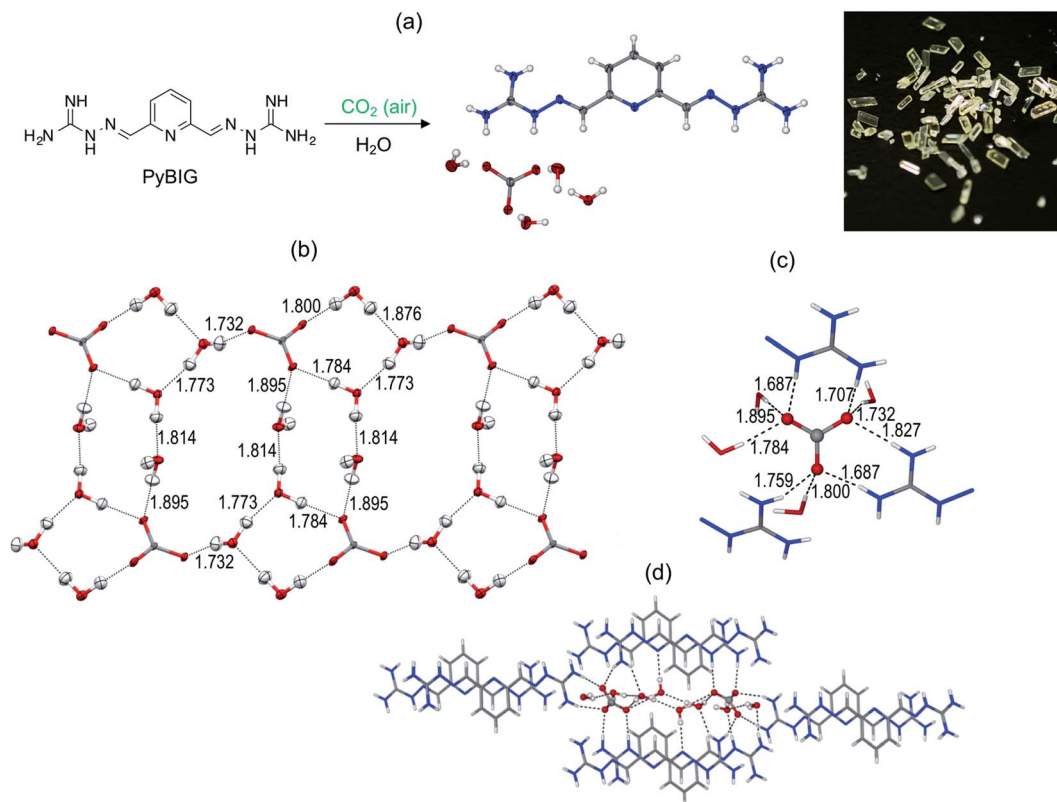
aqueous GBIG solution to air simply led to crystallization of the hydrated free ligand. In direct contrast, 2,6-pyridine-bis(iminoguanidine) (PyBIG), a different analogue from the BIG family, proved effective for DAC.<sup>42</sup> An aqueous solution of



**Fig. 7**  $\text{CO}_2$  separation via GBIG bicarbonate crystallization. A flue gas simulant (12.8%  $\text{CO}_2$ , EPA standard) is bubbled through an aqueous GBIG solution, leading to crystallization of GBIG bicarbonate. The solid is collected by filtration, then heated at 120 °C to release the  $\text{CO}_2$  and regenerate the GBIG sorbent. The filtrate containing the residual GBIG, and the regenerated GBIG solid are recycled.







**Fig. 8** DAC with PyBIG. (a) Crystallization of hydrated PyBIG carbonate from aqueous PyBIG and atmospheric CO<sub>2</sub>. (b) Extended carbonate–water clusters from the single-crystal neutron diffraction structure, with the hydrogen bond contacts in Å. (c) Carbonate binding site in the crystal, showing the hydrogen bond contacts (Å) from the guanidinium groups and water molecules. (d) Crystal packing consisting of cationic PyBIGH<sub>2</sub><sup>2+</sup> stacks that flank the anionic [CO<sub>3</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>2-</sup> clusters.

PyBIG open to air reacted with atmospheric CO<sub>2</sub> and crystallized as a hydrated carbonate salt with the formula PyBIGH<sub>2</sub>(CO<sub>3</sub>)(H<sub>2</sub>O)<sub>4</sub>. This corresponds to a theoretical CO<sub>2</sub> capacity of 2.6 mmol g<sup>−1</sup>. The crystal-structure analysis by X-ray and neutron diffraction revealed extended one-dimensional carbonate–water clusters and stacked PyBIGH<sub>2</sub><sup>2+</sup> cations (Fig. 8). It appears that the very low aqueous solubility of the PyBIG carbonate salt ( $K_{sp} = 1.0 \times 10^{-9}$ ), on a par with CaCO<sub>3</sub>, drives the overall DAC equilibrium despite the very low concentration of CO<sub>2</sub> in the air. Another favorable factor is the alkalinity of the PyBIG solution (pH ≈ 10), which reacts with the CO<sub>2</sub> from air and generates carbonate anions in sufficient concentration to achieve supersaturation of the PyBIG carbonate salt. A likely structural factor contributing to the low solubility of the PyBIG carbonate salt is the strong hydrogen bonding of the carbonate anions by the guanidinium groups and the water molecules included in the crystals, as found by single-crystal neutron diffraction combined with electron density measurements from high-resolution X-ray diffraction.<sup>43</sup> Heating of the carbonate crystals at 120 °C under a flow of air in the oven releases the CO<sub>2</sub> and regenerates the PyBIG ligand quantitatively, thereby closing the CO<sub>2</sub>-separation cycle. The measured enthalpy of regeneration is 223 kJ mol<sup>−1</sup>, of which 148 kJ mol<sup>−1</sup> (66%) is wasted for water desorption.<sup>44</sup> Thus, crystal engineering of anhydrous BIG carbonate crystals would

greatly improve the efficiency of the DAC process. Another component of the heat of regeneration is the sensible heat of 65 kJ mol<sup>−1</sup> necessary to heat the crystals from ambient temperature to the 120 °C temperature of regeneration. This brings the overall heat of regeneration to 288 kJ mol<sup>−1</sup>.<sup>45</sup>

In order to understand the structural factors determining the DAC chemistry of BIGs, we initiated a systematic structure–properties relationship study, focusing initially on the very basic series of BIG structures resulting from glyoxal (GBIG) and its simple analogs methylglyoxal (MGBIG) and diacetyl (DABIG) (Fig. 9).<sup>10</sup> To a large extent, DAC by BIG crystallization is driven by the solubility difference between the neutral BIG ligand and the corresponding BIG carbonate salt. For GBIG, the solubility ratio between the free ligand and its bicarbonate salt is only 1.6, too small to drive DAC. In principle, the equilibrium DAC reactions could be shifted towards the carbonate solids by engineering BIG crystals with higher solubility and BIG carbonate crystals with lower solubilities. Our study found that relatively minor modifications in the molecular structure of GBIG, *i.e.*, substituting one or two hydrogen atoms with methyl groups, led to dramatic differences in the crystal structures of the corresponding MGBIG and DABIG. This, in turn, led to large increases in their aqueous solubilities, by factors of 96 and 14 relative to GBIG, respectively. One notable difference between the crystal structures of GBIG and those of MGBIG and DABIG is



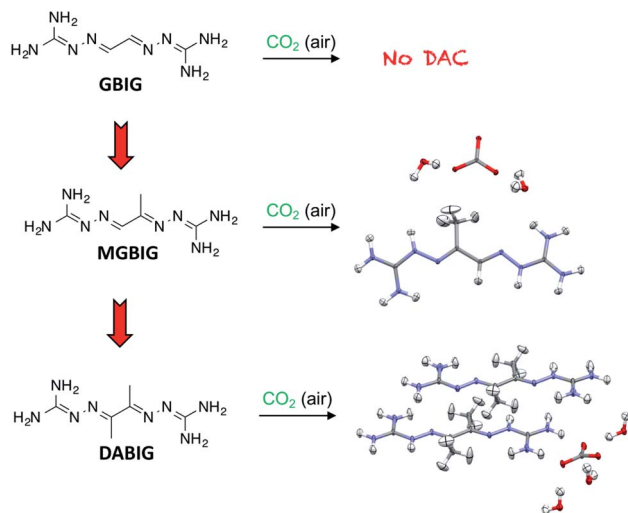


Fig. 9 Dialing in DAC by crystal engineering of BIGs. An aqueous solution of GBIG left open to air led to crystallization of the free ligand, whereas the corresponding solutions of the methylated analogs MGBIG and DABIG led to DAC.

the presence of  $\pi$ -stacking in the former, and the absence of it in the latter, apparently due to increased conformational flexibility and steric hindrance caused by the methyl groups. On the other hand, the crystal structures of the corresponding carbonate salts of MGBIG and DABIG revealed relatively planar BIG cations that are closely stacked in the crystals. Another structural feature that enhances the stability of these carbonate crystals is the inclusion of at least two water molecules per carbonate anion, and the formation of extended carbonate–water clusters. As a result, the aqueous solubilities of the carbonate salts of DABIG and MGBIG are lower than the corresponding solubilities of the neutral ligands by factors of 38

and 72, respectively, thereby providing the thermodynamic driving force required for the DAC reactions.

Preliminary experiments confirmed both MGBIG and DABIG are effective at DAC. An aqueous solution of DABIG left open to air reacted with CO<sub>2</sub> and yielded a hydrated crystalline carbonate salt with molecular formula (DABIGH<sup>+</sup>)(DABIGH<sub>2</sub><sup>2+</sup>)<sub>0.5</sub>(CO<sub>3</sub><sup>2-</sup>)(H<sub>2</sub>O)<sub>3</sub> (Fig. 9). This corresponds to a theoretical CO<sub>2</sub> capacity of 2.4 mmol g<sup>-1</sup>. The CO<sub>2</sub> and water are released by heating the crystals at 80–120 °C (under nitrogen purging) and the free DABIG ligand is regenerated quantitatively. The total regeneration energy, consisting of reaction enthalpy and sensible heat is 422 kJ mol<sup>-1</sup>. On the other hand, an aqueous solution of MGBIG left open to air reacted with CO<sub>2</sub> and yielded two main crystalline carbonate phases with the formulas (MGBIGH<sup>+</sup>)<sub>2</sub>(CO<sub>3</sub><sup>2-</sup>)(H<sub>2</sub>O)<sub>2</sub> and (MGBIGH<sub>2</sub><sup>2+</sup>)(CO<sub>3</sub><sup>2-</sup>)(H<sub>2</sub>O)<sub>2</sub>. The corresponding theoretical CO<sub>2</sub> capacities are 2.1 and 3.5 mmol g<sup>-1</sup>, respectively. The measured regeneration energies of the two phases are 358 and 323 kJ mol<sup>-1</sup>, respectively, more than twice as large compared to the corresponding value for GBIG (151.5 kJ mol<sup>-1</sup>). Nevertheless, the temperatures of regeneration are very similar for GBIG, MGBIG, and DABIG, in the range of 120 to 160 °C (under a flow of air).<sup>10</sup>

### Outstanding challenges and future opportunities

With its structural precision and the prospect for tuning the CO<sub>2</sub> binding, transport, and release in crystalline frameworks, crystal engineering of MOFs and HBFs offers unique opportunities for DAC. Table 1 summarizes the key properties for some of these materials, relevant to their DAC performance.

Atmospheric CO<sub>2</sub> capture with MOFs can be done *via* either physisorption or chemisorption mechanisms. The former offers the prospect for lower regeneration energies, though that may come at the expense of reduced working capacities and lower

Table 1 Key properties of MOFs and HBFs relevant to DAC

| Sorbent                                    | CO <sub>2</sub> capacity mmol g <sup>-1</sup> | Heat of regeneration kJ mol <sup>-1</sup> | <i>T</i> of regeneration °C | Reference |
|--------------------------------------------|-----------------------------------------------|-------------------------------------------|-----------------------------|-----------|
| <b>MOFs</b>                                |                                               |                                           |                             |           |
| TIFSIX-3-Ni                                | 0.41                                          | 50 <sup>a</sup>                           | 90 <sup>c</sup>             | 19        |
| NbOFFIVE-1-Ni                              | 1.3                                           | 54 <sup>a</sup>                           | 105 <sup>c</sup>            | 20        |
| ed-Mg(dobdc)                               | 1.5                                           | NA                                        | 120 <sup>c</sup>            | 22        |
| mmen-Mg <sub>2</sub> (dobpdc)              | 1                                             | 103 <sup>b</sup>                          | 150 <sup>c</sup>            | 23        |
| ed-Mg <sub>2</sub> (dobpdc)                | 2.83                                          | 50 <sup>a</sup>                           | 150 <sup>d</sup>            | 25        |
| NH <sub>2</sub> NH <sub>2</sub> -Mg(dobdc) | 3.89                                          | 133 <sup>b</sup>                          | 130 <sup>c</sup>            | 26        |
| MOF-Zn-OH                                  | 2.2                                           | 71 <sup>a</sup>                           | 100 <sup>e</sup>            | 31        |
| MOF-Ni-OH                                  | 2.7                                           | 84 <sup>a</sup>                           | 100 <sup>e</sup>            | 32        |
| <b>HBFs</b>                                |                                               |                                           |                             |           |
| MXDA                                       | 5.6 <sup>f</sup>                              | NA                                        | 103–120 <sup>c</sup>        | 35        |
| GBIG                                       | 6.1 <sup>f</sup>                              | 151.5 <sup>b</sup>                        | 120 <sup>d</sup>            | 41 and 46 |
| PyBIG                                      | 2.6 <sup>f</sup>                              | 288 <sup>b</sup>                          | 120 <sup>d</sup>            | 42 and 44 |
| DABIG                                      | 2.4 <sup>f</sup>                              | 422 <sup>b</sup>                          | 80–120 <sup>c</sup>         | 10        |
| MGBIG-1                                    | 2.1 <sup>f</sup>                              | 358 <sup>b</sup>                          | 80–120 <sup>c</sup>         | 10        |
| MGBIG-2                                    | 3.5 <sup>f</sup>                              | 323 <sup>b</sup>                          | 80–120 <sup>c</sup>         | 10        |

<sup>a</sup> Based solely on the *Q*<sub>st</sub> value. <sup>b</sup> Measured by DSC – includes desorption enthalpy and sensible heat. <sup>c</sup> Regenerated under inert gas purging. <sup>d</sup> Regenerated under air flow. <sup>e</sup> Regenerated under vacuum. <sup>f</sup> Capacity calculated from the molecular formula of the crystallized solid.





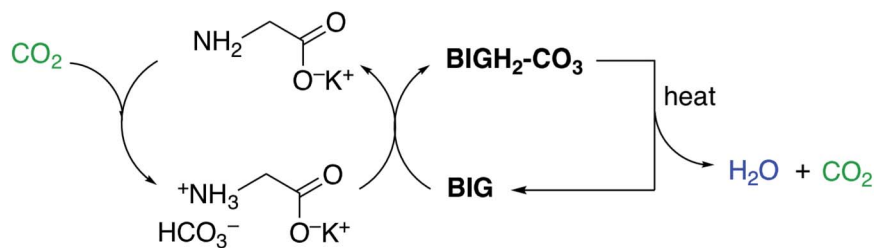


Fig. 10 DAC by CO<sub>2</sub> absorption with aqueous amino acids and carbonate crystallization with BIGs. Reproduced with permission from ref. 45. Copyright (2019) American Chemical Society.

CO<sub>2</sub>/H<sub>2</sub>O selectivities. These limitations can be addressed by functionalizing the MOF pores with amine or M–OH groups that react with CO<sub>2</sub> and convert it into carbamic acid, carbamate, or bicarbonate anions. However, water condensation in the pores can lead to higher regeneration energies and sometimes chemical stability issues. While MOFs tend to have superior working capacities compared to other porous material that are less crystalline, very few MOFs have been tested under realistic DAC conditions, with their reported performances often based solely on single-component CO<sub>2</sub> sorption isotherms. The reported regeneration energies are also typically based on measurement of isosteric heat of reactions from sorption isotherms at low CO<sub>2</sub> loading, without taking into account the sensible heat or the heat required to remove the co-adsorbed water. MOF regeneration is often done by purging with an inert gas, which dilutes the output of CO<sub>2</sub>, thereby requiring additional separation steps before the carbon dioxide is ready to be compressed for storage or utilization.

Crystallization of HBFs presents an alternative approach to DAC that obviates the need for sorbent porosity. The challenge, in this case, is to identify organic bases, such as amines or guanidines, that form crystalline HBFs of low aqueous solubilities with CO<sub>2</sub>. Unfortunately, crystal engineering is still not sophisticated enough to predict solubilities of molecular crystals or organic salts. While advances in computational methods may one day allow for *ab initio* design of crystal structures, aqueous solubilities, and free energies of reactions involved in DAC, structure–properties relationship studies remain for the moment the most reliable approach to developing new crystalline DAC systems. Along this line, one of the priorities is to identify design principles leading to exclusion of water from the BIG carbonate crystals, as water desorption comes with a high enthalpic cost, which can significantly increase the regeneration energy of the DAC process. Alternatively, developing improved desorption processes that avoid water evaporation or recover the energy stored in the water vapor during condensation could make the overall DAC process more energy sustainable. As in the case of MOFs, the CO<sub>2</sub> desorption step has typically been done under inert gas or air, though vacuum- or steam-assisted desorption may be feasible for some HBFs and need to be explored further.

In addition to favorable thermodynamics of CO<sub>2</sub> capture, crystallization, and desorption, fast kinetics for these steps are also critical for a viable DAC system. For instance, crystallization of BIGs with atmospheric CO<sub>2</sub> is thermodynamically driven

by the very low aqueous solubility of the BIG–CO<sub>3</sub> salts, but the rates of CO<sub>2</sub> uptake by the aqueous BIGs are generally too slow, with loading times on the order of days. The rates of CO<sub>2</sub> uptake can be greatly accelerated by combining BIG–CO<sub>3</sub> crystallization with CO<sub>2</sub> absorption by aqueous amino acids or peptides, which work in synergy with BIGs to achieve effective and energy-efficient DAC.<sup>44–46</sup>

As illustrated in Fig. 10, the DAC cycle with amino acids/BIGs comprises the following steps: (i) fast CO<sub>2</sub> absorption by the aqueous amino acid (glycine is shown as a representative example), yielding the corresponding bicarbonate salt (*via* a carbamate intermediate); (ii) crystallization of the carbonate anions with BIG, which regenerates the amino acid; (iii) CO<sub>2</sub> release from the BIG carbonate solid and BIG regeneration.

While crystal engineering may be critical in the initial design of novel crystalline DAC systems, developing a practical and efficient DAC technology also involves equally important chemical engineering aspects, such as process design and optimization, scale up, design, manufacturing, and testing of efficient air–solid or air–liquid contactors, crystallizers, and solid–liquid separators. Optimization of the CO<sub>2</sub> desorption to minimize the required temperature and maximize the purity of the CO<sub>2</sub> is another important aspect. Along this line, purging with inert gas or air should be avoided as much as possible if high purity for the CO<sub>2</sub> product is needed. Instead, vacuum- or steam-aided desorption are preferred, which not only result in high-purity CO<sub>2</sub>, but also lower the regeneration temperatures. Once all components and operations are in place and working synergistically, the economic and environmental feasibility, and the carbon footprint of the ensuing DAC technology needs to be evaluated through rigorous technoeconomic and lifecycle analyses.

Finally, crystalline organic materials are not ready yet for large-scale deployment in DAC applications, as both MOFs and HBFs need to be manufactured at a much larger scale (Mt per year) at a reasonable cost (<\$10 per kg) and tested over tens of thousands of loading/unloading cycles under realistic DAC conditions. Nevertheless, understanding and improving their fundamental DAC chemistry is a critical first step in developing viable DAC technologies, and it is the author's hope that this article will stimulate further research along this direction.

## Author contributions

Conceptualization, funding acquisition, writing – original draft, writing – review & editing, R. C.



## Conflicts of interest

The author is an inventor on a couple of patents on CO<sub>2</sub> capture by crystallization of BIGs<sup>47,48</sup> and seeks to license and commercialize a DAC technology based on this approach.

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