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Heterocycles for direct air capture and MOFs prepared from CO₂ utilization†

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The technology for carbon capture, utilization, and storage (CCUS) has drawn global attention because of the rapid climate changes. Herein, a series of nitrogen-rich heterocycles (HC_x-N_y) was identified for direct air capture (DAC) based on a phase change mechanism. HC_x-N_y possessed a CO₂ removal efficiency of up to 99% under continuous CO₂ flow with a concentration of 437 ppm *via* spontaneous CO₂ fixation because it has a high CO₂ sorption capacity of 23.82 mol kg⁻¹. Based on this phenomenon, a green and highly efficient strategy was discovered to utilize CO₂ for different MOF syntheses *via* altering monomers and anions (SO₄²⁻, OAC⁻, and NO₃⁻). Furthermore, we made a novel discovery that anions significantly affect the topological structures and morphologies of MOFs. Hence, from the discovery of nitrogen-rich heterocycles (HC_x-N_y) to direct air carbon capture to the synthesis of high value-added MOFs and then to the construction of high-performance gas separation membranes, this integrated strategy provided significant insights into the development of a comprehensive CCUS technology.

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Introduction

Carbon dioxide is the main contributor to the global greenhouse effect, and its atmospheric levels are increasing through human activities such as anthropogenic emissions into the atmosphere from fossil-fuel-based power plants, cement and steel industries, and automobiles. Thus, the global temperature has risen, and climate catastrophe has been triggered in recent decades, posing a threat to the living systems.^{1–3} According to an authoritative data analysis,⁴ the average decadal growth rates of global carbon emissions were 2.8%, 1.3%, 1.1%, 2.7% and 1.7% for each decade since the 1970s. Global annual emissions increased from 33.3 GtCO₂ in 2020 to 34.9 GtCO₂ in 2021, representing a 4.8% increase. Therefore, it is urgent to reduce CO₂ emissions and establish a carbon-neutral society.⁵ In order to deal with the global CO₂ challenge, countries around the world have made commitments to reduce greenhouse gas emissions according to the Paris Agreement:⁶ (1) the European Union would reduce 40% greenhouse gas emissions by 2030 compared to the base year of 1990, (2) the United States would reduce 26–

28% by 2025 compared to the base year of 2005, (3) Australia and Canada would reduce 26–28% and 30%, respectively, by 2030, and (4) China would achieve the carbon peak by 2030 and carbon neutrality by 2060.

Hence, breakthroughs in innovative carbon capture, utilization, and storage (CCUS) must be advanced. Traditionally, carbon capture can be implemented based on three main technologies, including pre-combustion carbon capture, post-combustion carbon capture, and oxy-combustion.⁷ However, these techniques require stationary CO₂ sources, such as large industrial processes and power plants. Generally, it is easy to capture CO₂ from the flue gas of these plants because of high CO₂ concentrations. In contrast, it is extremely challenging to capture CO₂ from dispersed and mobile sources with low CO₂ concentrations of ~400 ppm, which is a typical CO₂ concentration in the atmosphere. Therefore, developing an advanced technology that can extract CO₂ from ambient air has become necessary and urgent. Such technology has been referred to as “direct air capture” (DAC), first introduced by Lackner *et al.* in 1999.⁸ So far, the trade-off relationship between efficiency and capacity in DAC has hindered its further development for practical applications. The ideal materials to mitigate greenhouse gases directly from the atmosphere must satisfy the following characteristics (1) operatable at room temperature and near ambient conditions, (2) effective in all humidity conditions to maintain high CO₂ capture performance.

Currently, many technologies to capture CO₂ have been developed, such as energy-saving gas separation membranes,⁹ eco-friendly CO₂ adsorbents,^{10,11} and high-efficiency photocatalytic or electrocatalytic reduction.¹² Although these

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approaches can effectively capture CO₂, they have disadvantages. Membrane separation technology has a trade-off relationship between CO₂ permeability and selectivity, which is always the bottleneck impeding the development of advanced membranes. Adsorption technology makes it difficult to regenerate CO₂, which is often accompanied by high energy consumption. Photoelectric catalysis has the disadvantages of requiring special equipment, instability of catalysts, unique reaction conditions and inadequate reaction efficiency, which makes it difficult for large-scale practical applications. In addition to overcoming the above bottlenecks and capturing CO₂ at high efficiency, the practical applications of CCUS must utilize the captured CO₂ as a starting material for high value-added products. Literature research has indicated that high value-added substances, such as organic carbonates,¹³ chemo-enzymatic starch,¹⁴ and long-chain compounds (glucose and fatty acids),¹⁵ have been unbelievably synthesized by utilizing CO₂ as the raw material, which are the milestones of great significance to advance R&D for CCUS. The syntheses of the above products inevitably involved lengthy processes, special catalysts, and complicated reaction conditions due to the inert nature of CO₂. Up to now, the preparation of high value-added MOFs using CO₂ as the starting material in mild conditions is still very difficult and rarely reported.

MOFs, composed of metal clusters with polydentate (≥ 2) organic ligands containing O, N or P groups, are usually made by the self-assembly of coordination bonds under certain conditions to form 0D, 1D, 2D, or 3D porous skeleton materials, which are one of the most advanced porous crystal materials in the 21st century.^{16,17} Compared with traditional porous materials (zeolite and activated carbon), MOFs have numerous merits, such as variable secondary building units (SBUs), adjustable length and functional ligand, controllable pore size and high specific surface area varying from 1000 to $\sim 10\,000\text{ m}^2\text{ g}^{-1}$.¹⁸ They have been widely used in gas adsorption,¹⁹ separation,²⁰ sensing,²¹ catalysis²² and other fields.²³ Inspired by these merits and a broad range of applications, a variety of strategies have been designed to prepare MOFs, including solvothermal synthesis,²⁴ microwave synthesis,²⁵ ultrasonic synthesis²⁶ and other synthetic approaches.²⁷ Nevertheless, most of the methods have the shortcomings of high energy consumption, long reaction time, low yield, and the demand for harmful solvents and specific equipment, which violates the principle of low energy consumption, green sustainable development and large-scale production. Adaptation to the above criteria is necessary for the sustainable development of human society and the large-scale preparation of MOFs.

To achieve the double objectives of discovering superior materials for high-efficiency DAC from air and constructing high-value MOFs from the captured CO₂ for gas separation, high geometric symmetry and various sizes of heterocycle HC_x-N_y with different nitrogen-rich contents (*i.e.*, as capture sites) were selected for preliminary investigation in this study where “H” stands for heterocycle, “C_x” and “N_y” stand for the numbers of carbon atoms and nitrogen atoms in the heterocycle, respectively. Our preliminary results have indicated that HC_x-N_y are promising materials for DAC because they have extremely

high absorption rates and capacities with unprecedented states *via* the phase change process. In addition, benefiting from their high activity and symmetry of geometry, HC_x-N_y was further selected as precursors for the CO₂-derived linkers because they were able to react with two, three or four CO₂ molecules to produce the di-carbamate, tri-carbamate and tetra-carbamate salts of [HC₄-N₂-CO₂]²⁻, [HC₆-N₃-CO₂]³⁻ and [HC₁₀-N₄-CO₂]⁴⁻ under room temperature and pressure without any catalyst.²⁸ As [HC₄-N₂-CO₂]²⁻, [HC₆-N₃-CO₂]³⁻ and [HC₁₀-N₄-CO₂]⁴⁻ have two, three and four coordination sites located at six-, nine-, and fourteen-membered rings that own polydentate ligands, and they also define the bridging orientation of the metal clusters. Based on the coordination design criteria of MOFs, it is extremely crucial to select polydentate ligands and metal clusters for perfect porous crystal frameworks. Considering the conditions for ligand preparation and the formation environment for MOFs, a zinc salt was selected to form metal clusters at room temperature. To the best of our knowledge, in the literature, the reactions of HC₆-N₃ and HC₁₀-N₄ with CO₂ or with metal clusters to form MOFs have not been reported. Furthermore, for the first time, we were able to use the CO₂-derived ligands to coordinate with the same metal clusters but different anions (SO₄²⁻, NO₃⁻, and OAc⁻) to synthesize MOFs of diverse morphologies. In order to explore the superiority of nitrogen-rich MOFs, the obtained MOFs were introduced into PIM-1 to optimize the pore characteristics (such as reducing micropore sizes and narrowing PSD) of membranes to construct CO₂ channels and significantly enhance the separation performance. Introducing our new MOFs in MMMs may synergistically break the permeability selectivity trade-off limit and surpass the conventional upper bound.

Results and discussion

Visible DAC capacity

Visible proof of HC_x-N_y for DAC at an ultralow CO₂ concentration is extremely important (Fig. 1). To investigate its capture performance, various other advanced materials were also examined and compared by studying their CO₂ absorbing capacities from (1) the CO₂ exhaled by a human body with a maximum CO₂ concentration of 2–5% and (2) the atmosphere containing 408 ppm CO₂ (Fig. S1†). As exhibited in Fig. S2a, b and Video S1,† once the exhaled CO₂ was in contact with HC₄-N₂ or HC₆-N₃ molecules, white precipitates HC₄-N₂-CO₂ or HC₆-N₃-CO₂ were formed immediately with an absorption duration of <5 s for HC₆-N₃, showing a high affinity and excellent absorption rate toward CO₂. This characteristic is essential for a material suitable for DAC. In contrast, experimental difficulties were significantly increased by using HC₆-N₃ in the air capture equipment to capture CO₂ in the atmosphere (Fig. S2c†). However, by injecting air into the HC₆-N₃ solution, a small amount of white precipitate was also generated, indicating successful CO₂ capture at an ultralow concentration, as demonstrated in Fig. S2d.† Analyses by field emission scanning electron microscopy (FESEM) indicated that the microscopic morphology of the white precipitate was circular vesicles, with size in the range of 0.2–1.2 nm (Fig. S3†). For quantitative



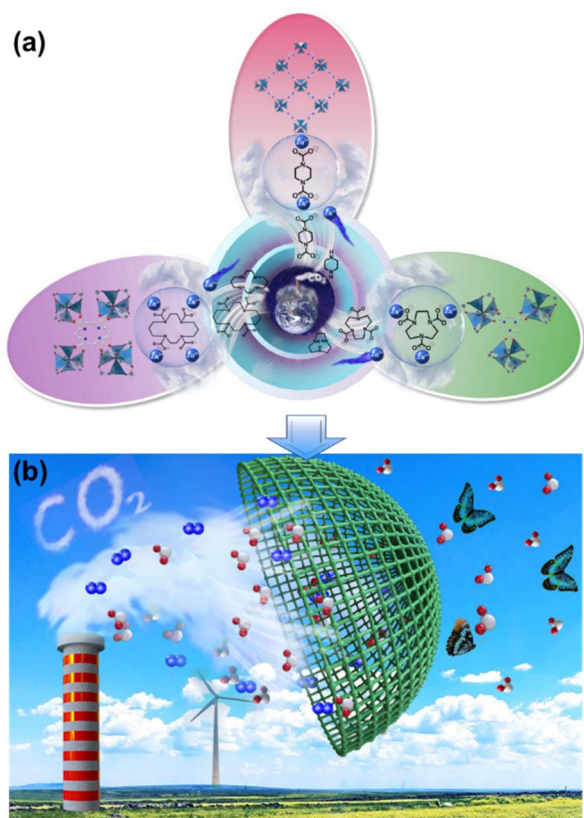


Fig. 1 Schematic diagram of synthetic MOFs and membrane separation. (a) Schematic diagram of the process for MOF synthesis from Zn clusters and various nitrogen-rich heterocycles by introducing CO₂ at room temperature and atmospheric pressure via a one-pot method. (b) Membrane separation diagram for CO₂/N₂ separation.

analyses of the removal efficiency under ultralow CO₂ concentrations, a CO₂ testing system was set up, including an air source, absorption reactor and detection system, as shown in Fig. S2e and S4.† An air source comprising 437 ppm CO₂ was injected into the homogeneous reaction system consisting of HC_x-N_y and acetonitrile (MeCN). After the DAC process, the downstream gas entered a nondispersive infrared meter to analyze the CO₂ concentration. HC₄-N₂ showed the best removal efficiency of more than 90% from the ultralow CO₂ stream within 12 hours because its electron-rich characteristics facilitated the reaction with CO₂. Thus, it has far better CO₂ capture capability than conventional CO₂ absorbers (MEA and KOH). (Fig. S1f, S5 and Video S2†). These results are quite encouraging because the newly discovered HC_x-N_y materials display the superior capability to reduce the CO₂ concentration in the atmosphere, and a carbon-neutral society can therefore be potentially achieved in the near future.

Table S1† summarizes a comparison of CO₂ absorption capacity between HC_x-N_y and other high-performance adsorbents, such as MOFs, zeolites, ionic liquids, amine-decorated mesoporous solids, aza-fused π -conjugated networks and amine solution adsorbents reported in the state-of-the-art literature. The CO₂ absorption capacities of HC_x-N_y are 2 to 8 times higher than those of MEA, MOFs, and bipy-CTF500. To

the best of our knowledge, it is one of the best materials in terms of CO₂ absorption capacity.

Fabrication of HC_x-N_y-CO₂(-Zn)

In addition to the discovery of HC_x-N_y for DAC, the preparation of MOFs from CO₂ is also a focus of this work. The synthetic process of MOFs is shown in Fig. 1a. The HC_x-N_y-CO₂-Zn MOFs powders were prepared by means of *in situ* synthesis via a one-pot approach utilizing CO₂ at 25 °C. Introducing CO₂ into a mixed solution of Zn(OAc)₂·2H₂O, HC_x-N_y in *N,N*-dimethylformamide (DMF) and 2-propanol (IPA) or MeCN led to the formation of a white product at different reaction durations in a homemade device (Fig. S6†). Although HC_x-N_y emerged to be highly symmetrical and similar structures, discrepancies in their ring sizes led to slightly different reaction times and conditions for better crystal growth (Fig. S7–S9†). Distinguishing from the one-step syntheses of HC₄-N₂-CO₂-Zn and HC₆-N₃-CO₂-Zn, HC₁₀-N₄-CO₂-Zn was prepared by first synthesizing HC₁₀-N₄-CO₂ and then further dissolved in an IPA solvent and reacted with Zn²⁺ for a period of time to obtain crystal MOFs at 80 °C (Fig. S9†).

Afterwards, the MOFs would be used to prepare the membrane for gas separation (Fig. 1b).

Characterizations of HC_x-N_y-CO₂(-Zn)

Based on Fig. 2a, d and g, the configurations of ball-and-stick models of HC₄-N₂-CO₂, HC₆-N₃-CO₂ and HC₁₀-N₄-CO₂ in the lowest energy states indicate that the noncoplanar carbon atoms are able to wiggle, which endows the frameworks with flexibility. The flexible HC₄-N₂-CO₂ ligands can construct flexible MOFs by reacting with SBUs. Flexible MOFs represent a particular subgroup within the class of hybrid materials, namely, the third-generation compounds or soft porous crystals.²⁹ Compared with conventional MOFs, flexible MOFs have been widely used to construct stimulus-responsive MOFs due to their excellent attributes of variable structures, such as unique responses from guest molecules, light, temperature, electrical fields, and pressure. Therefore, MOFs with excellent properties possess broad prospects as smart materials.

Before synthesizing MOFs, the reactions between HC₄-N₂, HC₆-N₃, HC₁₀-N₄ and CO₂ were firstly conducted at room temperature and the morphologies of the resultant ligands (*i.e.*, HC₄-N₂-CO₂, HC₆-N₃-CO₂ and HC₁₀-N₄-CO₂) were examined and compared. As illustrated in Fig. 3, the variational morphologies of HC_x-N_y-CO₂ arise from different ring sizes and numbers of the secondary amine groups in HC_x-N_y. HC₄-N₂-CO₂ exhibits an evenly distributed and regular ribbon-like morphology with a width of ~ 1 μm (Fig. 2b and c). In contrast, HC₆-N₃ is so deliquescent in air that it is difficult to obtain its microscopic morphology under FESEM. However, the resultant HC₆-N₃-CO₂ shows excellent stability in air and has an intriguing lychee-like morphology accompanied by some small bumps on the surface, which have a radius of ~ 4 μm (Fig. 2e and f). Besides, HC₁₀-N₄ has an interesting needle-like morphology at the macro scale (Fig. S10a†). Under FESEM, HC₁₀-N₄ appears to have a rod shape of ~ 200 μm length and



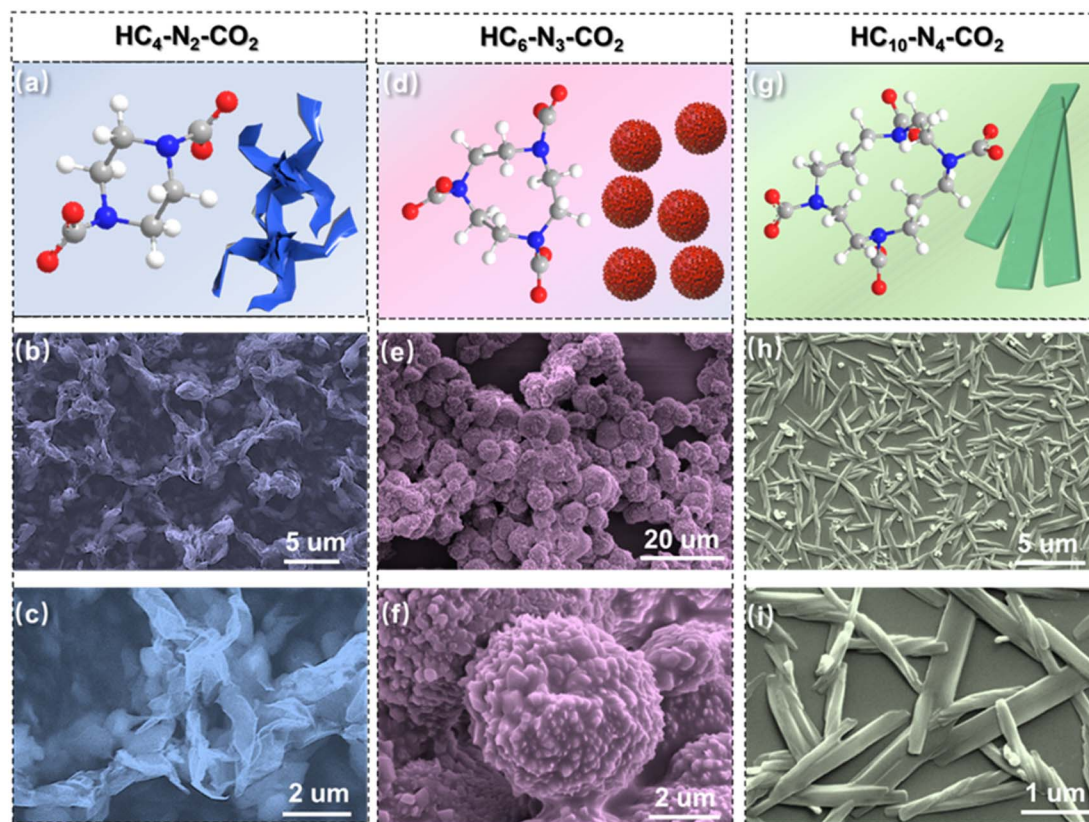


Fig. 2 Molecular structure and morphology of $\text{HC}_x\text{-N}_y\text{-CO}_2$: (a–c) $\text{HC}_4\text{-N}_2\text{-CO}_2$, (d–f) $\text{HC}_6\text{-N}_3\text{-CO}_2$, and (g–i) $\text{HC}_{10}\text{-N}_4\text{-CO}_2$. All the ball and stick model states of $\text{HC}_x\text{-N}_y\text{-CO}_2$ are in the lowest energy states optimized through Chemdraw 3D. Different colored spheres represent different atoms, where blue is N, gray is C, and red is O.

$\sim 20\ \mu\text{m}$ width (Fig. S10b–S10e[†]). After the CO_2 reaction, the lamellar $\text{HC}_{10}\text{-N}_4\text{-CO}_2$ is obtained with an average length of $\sim 3\ \mu\text{m}$ and width of $\sim 400\ \text{nm}$ (Fig. 2h and i). To our knowledge, the fantastic ribbon-like $\text{HC}_4\text{-N}_2\text{-CO}_2$, lychee-like $\text{HC}_6\text{-N}_3\text{-CO}_2$, and lamellar-like $\text{HC}_{10}\text{-N}_4\text{-CO}_2$ have been prepared successfully for the first time at room temperature. These intriguing ligands would further react with metal clusters to form MOFs by coordination bonds.

Formation mechanism of $\text{HC}_x\text{-N}_y\text{-CO}_2$

Considering the interesting morphological changes from $\text{HC}_x\text{-N}_y$ to $\text{HC}_x\text{-N}_y\text{-CO}_2$, a possible mechanism is proposed based on our experimental results and the previous literature.^{30,31} As manifested in Fig. 3a, the reactions in this system can be divided into three main stages based on the phase change mechanism, in which a liquid $\text{HC}_x\text{-N}_y$ has been changed into a solid $\text{HC}_x\text{-N}_y\text{-CO}_2$ based on the reaction of $[\text{R}^1\text{R}^2\text{NH}(\text{l}) + \text{CO}_2(\text{g}) \rightarrow \text{R}^1\text{R}^2\text{N-COOH}(\text{s})]$. The underlying mechanism of this reaction can be described as follows: The electrophilic nature of the C atom in CO_2 makes it susceptible to being attacked by nucleophilic N from $\text{HC}_x\text{-N}_y$. The secondary amines can act as nucleophiles by directly attacking the free CO_2 to form a zwitterion, which rapidly rearranges into carbamic acid *via* intramolecular proton transfer. The carbamic acid may be converted into a carbamate by transferring the proton to another free

amine (*i.e.*, a Brønsted base). Primarily, a homogeneous phase system is established by dissolving $\text{HC}_x\text{-N}_y$ as a strong Lewis base in organic solvents to provide sufficient active sites to electrophilic CO_2 at the molecular level. In the second stage, the electron-rich secondary amine of $\text{HC}_x\text{-N}_y$ (*i.e.*, strong nucleophile) reacts quickly with CO_2 molecules to form the mono-carbamate (*i.e.*, the formation of a heterogeneous phase). The reaction is rapid within a few seconds because the strong nucleophile attack of $\text{HC}_x\text{-N}_y$ and the formation of a solid phase promote the reaction in a forward direction. In the third stage, more CO_2 is reacted with mono-carbamate to form di-carbamate, tri-carbamate or tetra-carbamate (*i.e.*, the formation of a more heterogeneous phase). This stage is the rate-determining step due to the complex environments of CO_2 reaction, steric hindrance and changes in the electronic structure.³⁵ As an example, Fig. S11[†] exhibits the digital pictures of the reaction process between $\text{HC}_6\text{-N}_3$ and CO_2 at different durations of 0 s, 5 s and 2 h, demonstrating an extremely high reactivity.

Experimentally, the viscosity of the reaction system increased when the reaction proceeded, which further confirmed the reaction progress as more heterogeneous phases were formed. The viscosity result was consistent with the above model mechanism. Specifically, the two nucleophilic secondary amine bonds of $\text{HC}_4\text{-N}_2$ reacted quickly with two electrophilic



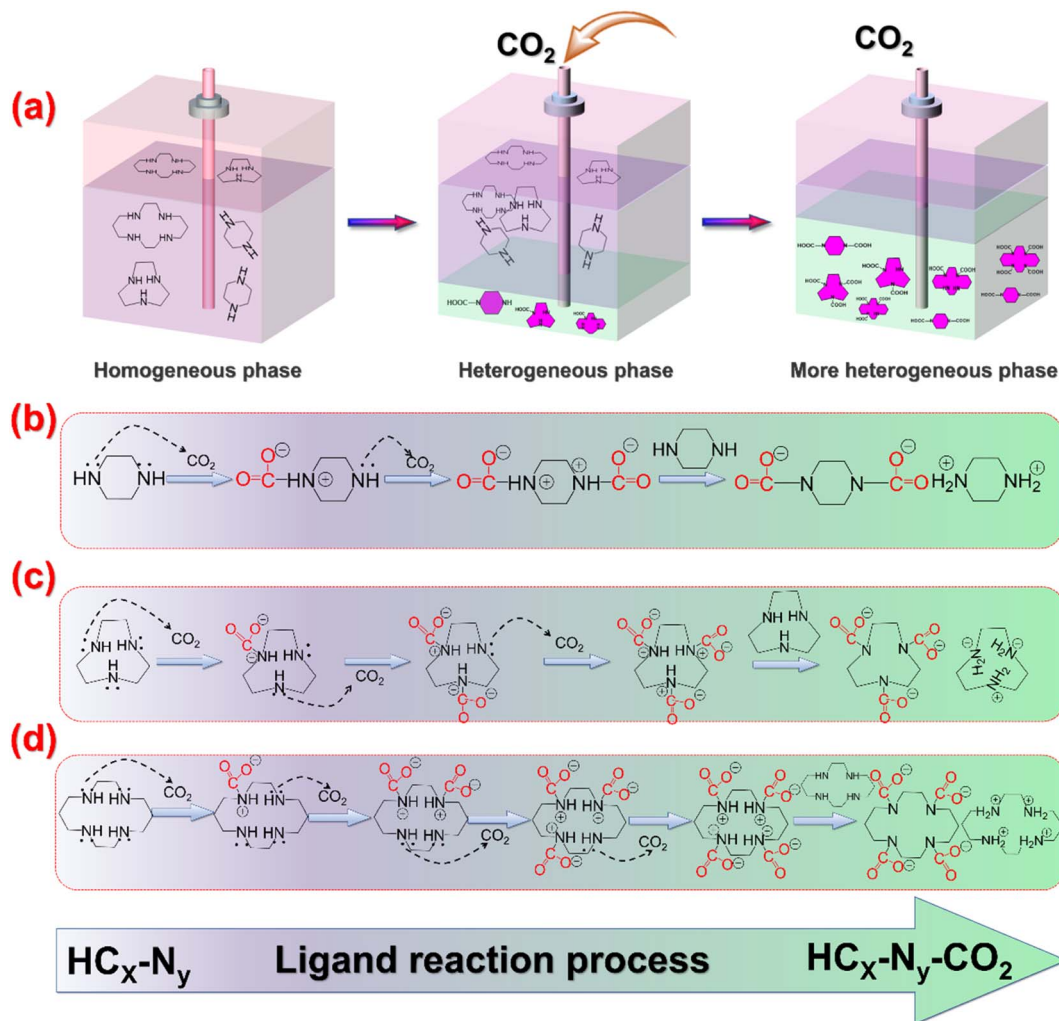


Fig. 3 Formation mechanism of $\text{HC}_x\text{-N}_y\text{-CO}_2$. (a) Model process diagram to form $\text{HC}_x\text{-N}_y\text{-CO}_2$ including mainly three stages (homogeneous phase, heterogeneous phase, and more heterogeneous phase). Mechanisms of ligand formation for MOFs between electrophilic CO_2 and nucleophilic starting materials. (b) $\text{HC}_4\text{-N}_2$. (c) $\text{HC}_6\text{-N}_3$. (d) $\text{HC}_{10}\text{-N}_4$.

CO_2 molecules to form solid di-carbamate (Fig. 3b). Due to the high activity of the secondary amine bonds, the di-carbamate yield was up to 99.96%, according to the quantitative analysis of a liquid nuclear magnetic hydrogen spectrum (Fig. 6f). Following a similar mechanism, electron-rich $\text{HC}_6\text{-N}_3$ or $\text{HC}_{10}\text{-N}_4$ reacted with three or four CO_2 molecules, respectively, to form tri-carbamate or tetra-carbamate (Fig. 3c and d). In addition, as depicted in Table S2,† $\text{HC}_x\text{-N}_y$ has a very high nitrogen content; for instance, 1 equivalent $\text{HC}_4\text{-N}_2$, $\text{HC}_6\text{-N}_3$, and $\text{HC}_{10}\text{-N}_4$ have 0.326, 0.326, and 0.28 equivalent N atoms, respectively. These N contents, as active sites, are higher than those of all advanced CO_2 adsorbents at present, which plays an important role in the adsorption of CO_2 with a high speed and capacity. Moreover, according to theoretical calculations, 1 equivalent $\text{HC}_4\text{-N}_2$ absorbs 1.048 equivalent CO_2 , 1 equivalent $\text{HC}_6\text{-N}_3$ absorbs 1.0476 equivalent CO_2 , and 1 equivalent $\text{HC}_{10}\text{-N}_4$ absorbs 0.898 equivalent CO_2 . However, with the increase in secondary amine bonds, the steric hindrance of the subsequent reaction becomes greater, leading to difficulties in completing

the reaction, which would be confirmed in the subsequent experiments. After the flexible ligands are obtained, these $\text{HC}_x\text{-N}_y\text{-CO}_2$ ligands can be further reversibly deprotonated and coordinated with zinc clusters to synthesize MOFs with different void sizes.

Formation process of the hollow flower-like $\text{HC}_4\text{-N}_2\text{-CO}_2\text{-ZnSO}_4$

Inspired by the innovative syntheses of MOF-5,³² MOF-38($\text{Zn}_3(\text{btc})_2$)³³ and $\text{Zn}_2(\text{TPOM})(\text{btc})_2$ (ref. 34) made of terephthalic acid (1,4- H_2bdc), trimesic acid (1,3,5- H_3btc), benzene-1,2,4,5-tetracarboxylic acid (1,2,4,5- H_4btc) and Zn clusters, $\text{HC}_4\text{-N}_2\text{-CO}_2$, $\text{HC}_6\text{-N}_3\text{-CO}_2$ and $\text{HC}_{10}\text{-N}_4\text{-CO}_2$ ligands were used to form MOFs with zinc clusters. In terms of $\text{HC}_4\text{-N}_2\text{-CO}_2\text{-ZnSO}_4$, a charming micron flowery sphere (like hydrangea) with a diameter of $\sim 3 \mu\text{m}$ was prepared by *in situ* synthesis of $\text{HC}_4\text{-N}_2$ and ZnSO_4 with CO_2 involved *via* self-assembly of the nanosheets with a thickness of $\sim 100 \text{ nm}$ (Fig. 4b–d and S12†). Ultimately, field emission transmission electron microscopy



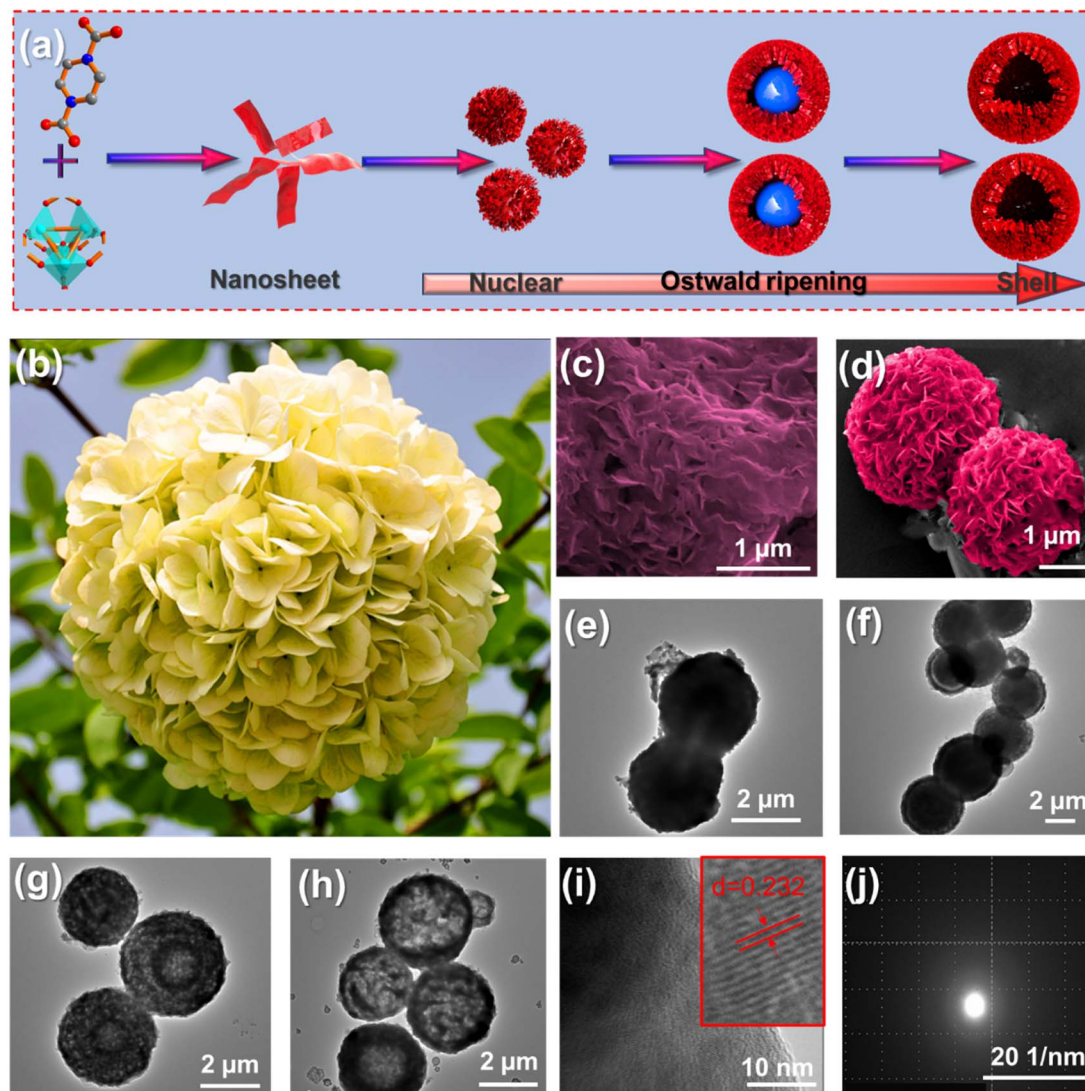


Fig. 4 Formation process of hollow flower-like $\text{HC}_4\text{-N}_2\text{-CO}_2\text{-ZnSO}_4$. (a) Model diagram of hollow flower formation according to an inside-out Ostwald ripening process. (b) A digital picture of hydrangea. (c and d) FESEM images. FESEM images were colored red for visual effect. (e–h) Low-magnification TEM images. (i) HR-FETEM image. (j) SAED pattern of $\text{HC}_4\text{-N}_2\text{-CO}_2\text{-ZnSO}_4$.

(FETEM) undoubtedly corroborated that $\text{HC}_4\text{-N}_2\text{-CO}_2\text{-ZnSO}_4$ had a hollow-shell structure (Fig. 4h). The interesting morphology might result from an inside-out Ostwald ripening process.^{35,36} As illustrated in Fig. 4a, the formation processes of the hollow flower-like structure mainly included the following four stages: (I) lamellar $\text{HC}_4\text{-N}_2\text{-CO}_2\text{-ZnSO}_4$ was formed through the reaction among CO_2 , $\text{HC}_4\text{-N}_2$ and ZnSO_4 (Fig. 4c). (II) The lamellar $\text{HC}_4\text{-N}_2\text{-CO}_2\text{-ZnSO}_4$ self-assembled into dense inner nuclear MOFs (Fig. 4e), but the high surface energy of the inner nuclear led to instability owing to the mismatch defects generated during the initial fast growth process and the higher curvature of the spheres with a smaller radius. (III) The intermediate core-shell structure was formed from dense MOFs to hollow flower-like MOFs in order to reduce the high surface energy. According to Fig. 4f, some small cavities appeared between the core and shell. As MOFs continued to grow, the small cavity gradually became larger, as shown in Fig. 4g. (IV)

Inner crystallites of $\text{HC}_4\text{-N}_2\text{-CO}_2\text{-ZnSO}_4$ migrated from the inner core and self-assembled at the outer walls of the hollow flower to minimize the surface energy of the system. The morphological change was from a small inner core (Fig. 4g) to a hollow flower (Fig. 4h). The high-resolution FETEM (HR-FETEM) image presented lattice fringes of $\text{HC}_4\text{-N}_2\text{-CO}_2\text{-ZnSO}_4$ (Fig. 4i), and a SAED pattern was obtained (Fig. 4j). These analyses revealed that a crystal consisting of hollow flower-like MOFs was acquired successfully.

The existence of interior space in the shell of $\text{HC}_4\text{-N}_2\text{-CO}_2\text{-ZnSO}_4$ particles verifies their unique characteristics, such as confined reaction and low mass transfer resistance, which are essential for subsequent applications, such as catalyzed synthesis,³⁷ sodium-ion batteries,³⁸ and photoelectron catalytic conversion.³⁹ So far, most hollow-shell structure materials must be prepared at high temperatures or by introducing an appropriate template, which is extremely difficult and rare to synthesize



at room temperature. Therefore, utilizing CO_2 to prepare MOFs particles with hollow flower-like structures through a simple room temperature strategy appears more innovative and conducive to CO_2 conversion and environmental protection.

Effect of anions (OAC^- , SO_4^{2-} , NO_3^-) on MOFs formation

To the best of our knowledge, most research on MOFs has mainly focused on the influence of different types of SBUs⁴⁰ and ligands,⁴¹ but has not explored the influence of anions on MOFs formation. Therefore, the same Zn clusters were employed as the metal source with similar synthesis conditions, but dissimilar anions were used to explore their effects on morphology. By substituting sulfate (SO_4^{2-}) with acetate (OAC^-), a high aspect ratio laminar $\text{HC}_4\text{-N}_2\text{-CO}_2\text{-Zn}(\text{OAC})_2$ was obtained, which had an even size of $\sim 2.5 \mu\text{m}$ length, $\sim 400 \text{ nm}$ width and $\sim 80 \text{ nm}$ thickness (Fig. 5f and f1). A further modification of anions by nitrate (NO_3^-) resulted in $\text{HC}_4\text{-N}_2\text{-CO}_2\text{-Zn}(\text{NO}_3)_2$ with an entirely different morphology of tremella shape *via* the bending and folding of a large layer of $\sim 10 \text{ nm}$ thickness (Fig. 5g and g1). The above results illustrate that the introduction of distinct anions (SO_4^{2-} , OAC^- , NO_3^-) has a significant effect on MOFs morphology because anions can

change the topological type of MOFs due to the template mechanism of anions.^{42–44} Anions (SO_4^{2-} , OAC^- , NO_3^-) as templating agents are used to link together different organic and metal-containing building blocks into assemblies with high selectivity for the templating anions. Meanwhile, due to the differences in the coordination of different anions with metal-containing building blocks, MOFs with different topological configurations were obtained. This phenomenon has rarely been reported in the literature.⁴⁵

To further elucidate the universality of different anions (SO_4^{2-} , OAC^- , NO_3^-) resulting in dissimilar MOFs morphologies, $\text{HC}_6\text{-N}_3\text{-CO}_2\text{-Zn}$ and $\text{HC}_{10}\text{-N}_4\text{-CO}_2\text{-Zn}$ were also prepared from the same Zn clusters with different anions (NO_3^- , OAC^-). Firstly, the influence of OAC^- and NO_3^- anions on the formation of MOFs prepared from $\text{HC}_6\text{-N}_3$, CO_2 and Zn clusters was studied *via* a similar approach. According to Fig. 5h and h1, the blocky-like $\text{HC}_6\text{-N}_3\text{-CO}_2\text{-Zn}(\text{OAC})_2$, which had a proportion of $\sim 2 \mu\text{m}$ length and $\sim 1 \mu\text{m}$ width, was obtained in the presence of OAC^- , whereas stick-like $\text{HC}_6\text{-N}_3\text{-CO}_2\text{-Zn}(\text{NO}_3)_2$ with a size of $\sim 0.98 \mu\text{m}$ length and $\sim 68 \text{ nm}$ width was acquired with the participation of NO_3^- (Fig. 5i and i1). Similarly, a large layer of $\text{HC}_{10}\text{-N}_4\text{-CO}_2\text{-Zn}(\text{OAC})_2$ with a thickness of $\sim 100 \text{ nm}$

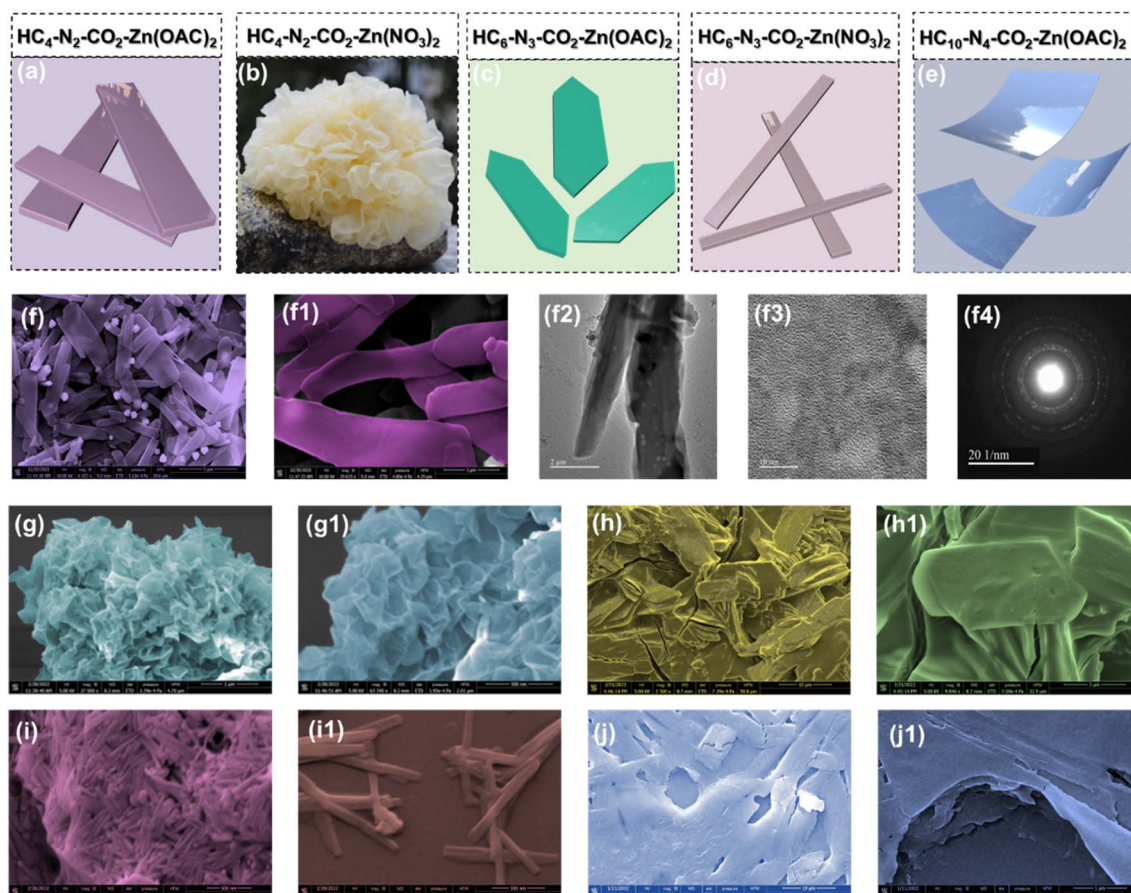


Fig. 5 MOF morphologies analyses. (a–e) Models of different MOF morphologies. (f and f1) FESEM of high aspect ratio laminar $\text{HC}_4\text{-N}_2\text{-CO}_2\text{-Zn}(\text{OAC})_2$. (f2 and f3) HR-FETEM image. (f4) SAED pattern of $\text{HC}_4\text{-N}_2\text{-CO}_2\text{-Zn}(\text{NO}_3)_2$. (g and g1) Tremella-shape $\text{HC}_4\text{-N}_2\text{-CO}_2\text{-Zn}(\text{NO}_3)_2$. (h and h1) Blocky structure $\text{HC}_6\text{-N}_3\text{-CO}_2\text{-Zn}(\text{OAC})_2$. (i and i1) Stick-like $\text{HC}_6\text{-N}_3\text{-CO}_2\text{-Zn}(\text{NO}_3)_2$. (j and j1) Large layer $\text{HC}_{10}\text{-N}_4\text{-CO}_2\text{-Zn}(\text{OAC})_2$. All FESEM images were colored for visual effect.



was acquired from $\text{HC}_{10}\text{-N}_4\text{-CO}_2$, as demonstrated in Fig. 5j and j1, under heating after the reaction. These results reconfirmed that different anions have a crucial influence on the formation of MOFs.

In addition to the microscopic morphology, the structural characteristics of $\text{HC}_x\text{-N}_y\text{-CO}_2\text{-Zn}$ were also analyzed. As shown in Fig. 6a, the XRD pattern indicates that the appearance of new X-ray diffraction peaks at 8.9, 10.2 and 37.9° are attributed to the successful formation of crystals, while the original intrinsic characteristic peaks of $\text{HC}_4\text{-N}_2$ are mainly at 15.5, 18.8, 19.9 and 22.5°. The diffraction peak at 10.2° is the dominant peak of MOFs, which is associated with the (220) crystal plane of MOFs.⁴⁶ The characteristic X-ray diffraction peaks of $\text{HC}_4\text{-N}_2\text{-CO}_2\text{-ZnSO}_4$ are at 13.2, 14.5, 18.1, 20.5 and 30.1°, which are completely different from those of $\text{HC}_4\text{-N}_2\text{-CO}_2\text{-Zn(OAC)}_2$, further demonstrating the influence of different anions (SO_4^{2-} and OAC^-) on crystal structures. For $\text{HC}_6\text{-N}_3\text{-CO}_2\text{-Zn(OAC)}_2$, the X-ray characteristic diffraction peaks located at 9.9, 11.9, 13.9, 15.2 and 16.9° belong to the crystal structure of the stably existing $\text{HC}_6\text{-N}_3\text{-CO}_2\text{-Zn(OAC)}_2$

(Fig. 6b). The diffraction peak at 9.9° is its main peak. Regarding $\text{HC}_{10}\text{-N}_4\text{-CO}_2\text{-Zn(OAC)}_2$, the characteristic X-ray diffraction peaks at 8.9, 9.9, 10.8 and 15.8° are attributed to the crystalline structure of $\text{HC}_{10}\text{-N}_4\text{-CO}_2\text{-Zn(OAC)}_2$ (Fig. 6c), where the diffraction peak at 10.8° is its dominant peak. In addition, we carried out the BET surface areas and pore size analysis of MOFs. $\text{HC}_4\text{-N}_2\text{-CO}_2\text{-Zn(OAC)}_2$, $\text{HC}_6\text{-N}_3\text{-CO}_2\text{-Zn(NO}_3)_2$, and $\text{HC}_{10}\text{-N}_4\text{-CO}_2\text{-Zn(OAC)}_2$ have specific surface areas of 575, 456, and 127 $\text{m}^2 \text{g}^{-1}$, respectively. The pore size of MOF increased with the increase of N heterocycle, which is 0.64, 0.78, 1.02 nm, separately (Fig. S13†). The aperture of MOFs is mainly less than 2 nm (micropore), so we choose the CO_2 isotherm. The temperature of the CO_2 isotherm is 195 K. Horvath-Kawazoe (HK) method was used to test the micropores of MOFs.

Thermal stability of $\text{HC}_x\text{-N}_y\text{-CO}_2\text{-Zn(OAC)}_2$ MOFs

The formation of functional groups based on carbamate has been widely studied in the field of CO_2 absorption.^{47,48} The C-N

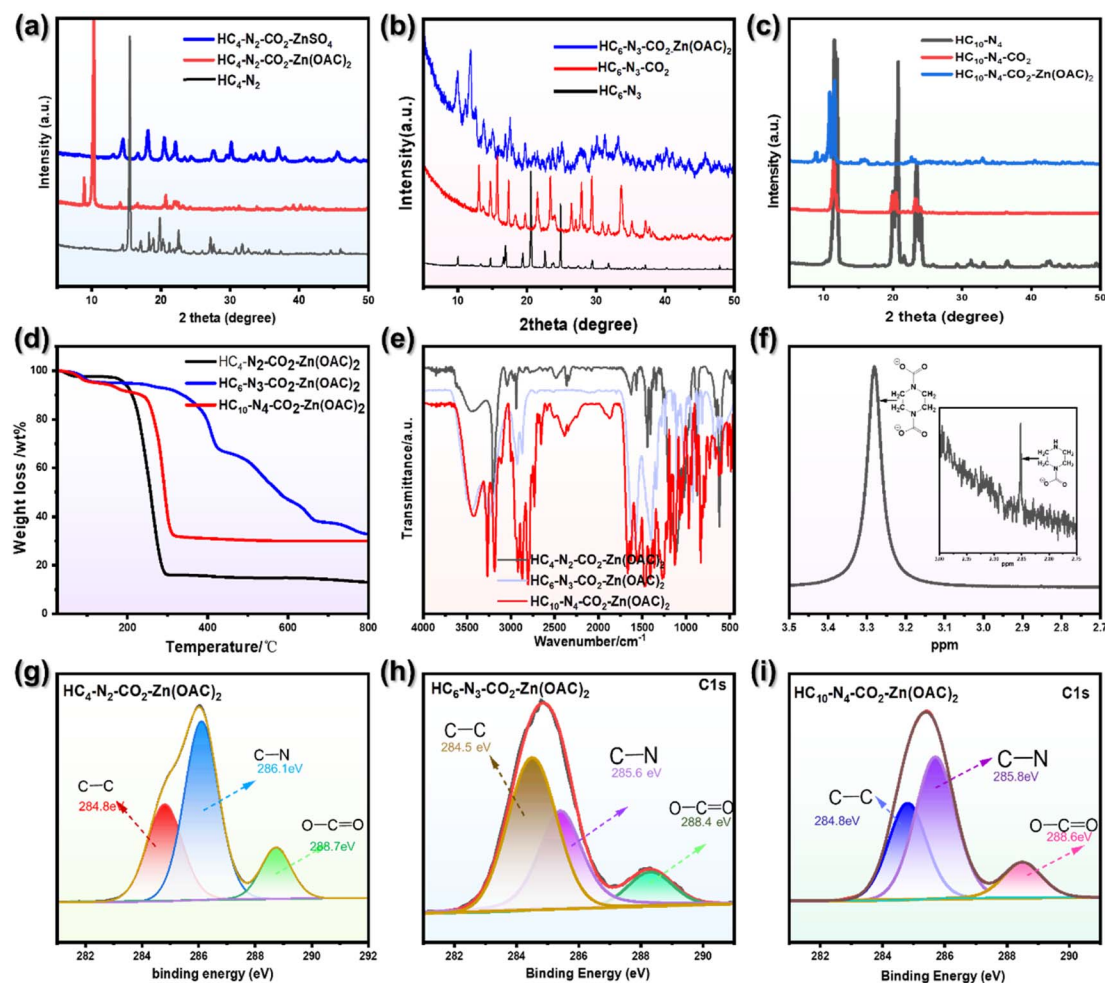


Fig. 6 Property analyses of $\text{HC}_x\text{-N}_y\text{-CO}_2\text{-Zn}$. (a) Comparison of PXRD patterns ($\lambda_{\text{Cu}} = 1.5406 \text{ \AA}$) of $\text{HC}_4\text{-N}_2$, $\text{HC}_4\text{-N}_2\text{-CO}_2\text{-ZnSO}_4/\text{Zn(OAC)}_2$. (b) $\text{HC}_6\text{-N}_3\text{-CO}_2$, $\text{HC}_6\text{-N}_3\text{-CO}_2\text{-Zn(OAC)}_2$. (c) $\text{HC}_{10}\text{-N}_4$, $\text{HC}_{10}\text{-N}_4\text{-CO}_2$, $\text{HC}_{10}\text{-N}_4\text{-CO}_2\text{-Zn(OAC)}_2$. (d) TGA analysis of $\text{HC}_x\text{-N}_y\text{-CO}_2\text{-Zn(OAC)}_2$ under N_2 atmosphere. (e) FT-IR characterization of $\text{HC}_x\text{-N}_y\text{-CO}_2\text{-Zn(OAC)}_2$. (f) ^1H NMR spectrum of $\text{HC}_4\text{-N}_2\text{-CO}_2\text{-Zn(OAC)}_2$. (g-i) The high-resolution XPS spectra of C 1s in $\text{HC}_4\text{-N}_2\text{-CO}_2\text{-Zn(OAC)}_2$. (h) $\text{HC}_6\text{-N}_3\text{-CO}_2\text{-Zn(OAC)}_2$. (i) $\text{HC}_{10}\text{-N}_4\text{-CO}_2\text{-Zn(OAC)}_2$ samples. Property analyses of $\text{HC}_x\text{-N}_y\text{-CO}_2\text{-Zn}$.



bond of carbamate can be formed rapidly and then destroyed immediately at a lower temperature according to a step adsorption model with special characteristics of rapid adsorption and desorption. Therefore, most carbamates are thermodynamically unstable because of weak C–N bonds that result in ready dissociation of carbamate bonds under heating or low pressures.⁴⁹ To interrogate the enhanced thermal stability of carbamate-incorporated MOFs, thermal gravimetric analyses (TGA) of $\text{HC}_x\text{-N}_y\text{-CO}_2\text{-Zn(OAC)}_2$ were performed for a comparative study (Fig. 6d). The mass of all samples decreased slightly between room temperature and 100 °C, which resulted from the trace organic content (IPA, MeCN) or moisture in the samples. The onset temperatures for the weight loss were 202 °C for $\text{HC}_4\text{-N}_2\text{-CO}_2\text{-Zn(OAC)}_2$, 352 °C for $\text{HC}_6\text{-N}_3\text{-CO}_2\text{-Zn(OAC)}_2$, and 252 °C for $\text{HC}_{10}\text{-N}_4\text{-CO}_2\text{-Zn(OAC)}_2$. Compared with $\text{HC}_4\text{-N}_2\text{-CO}_2$,⁵⁰ the thermal stability of all MOFs was enhanced, and $\text{HC}_6\text{-N}_3\text{-CO}_2\text{-Zn(OAC)}_2$ displayed the highest thermal stability in all MOFs.

Chemical component analyses

The Fourier transform infrared spectrum (FT-IR) of $\text{HC}_x\text{-N}_y\text{-CO}_2\text{-Zn(OAC)}_2$ exhibits a characteristic peak at 522–535 cm^{-1} (Fig. 6e, S14 and S15[†]). The peak is in good agreement with the stretching vibration of $\mu_4\text{-O-Zn}$ of the $[\text{Zn}_4\text{O}(\text{CO}_2)_6]$ clusters,⁵¹ confirming the formation of $\text{Zn}_4\text{O}(\text{CO}_2)_6$. The peak at 2360 cm^{-1} is attributed to carbamate.⁵² The infrared peak at 2500–2600 cm^{-1} is derived from the generated quaternary ammonium salt (zwitterion). This indicates that CO_2 is successfully involved in the reaction. To monitor the $\text{HC}_x\text{-N}_y\text{-CO}_2$ formation from $\text{HC}_x\text{-N}_y$, the ^1H NMR spectrum of $\text{HC}_x\text{-N}_y\text{-CO}_2\text{-Zn(OAC)}_2$ was acquired (Fig. 6f, S16 and S17[†]). Fig. 6f depicts two peaks at 3.28 and 2.85 ppm caused by CO_2 absorption in the MOFs, corresponding to mono-carbamate and di-carbamate, respectively.^{53,54} Ultimately, the integral of peak area verified that 99.96% of $\text{HC}_4\text{-N}_2$ reacted with CO_2 to form $\text{HC}_4\text{-N}_2\text{-CO}_2$ di-carbamate, only 0.04% of $\text{HC}_4\text{-N}_2$ to form mono-carbamate, and no $\text{HC}_4\text{-N}_2$ starting material was found, indicating that $\text{HC}_4\text{-N}_2$ had high reactivity, which was consistent with the aforementioned experiments (Fig. S7[†]). However, as far as $\text{HC}_6\text{-N}_3$ and $\text{HC}_{10}\text{-N}_4$ are concerned, owing to the excessively long reaction path and steric hindrance, few of them form tri-carbamate and tetra-carbamate, while most secondary amine groups react incompletely with CO_2 to form mono-carbamate and di-carbamate or tri-carbamate (Fig. S16 and S17[†]). In addition, as illustrated in Fig. 6g–i and S18,[†] XPS analyses further verified the composition of MOFs. By fitting the peaks of the C 1s spectrum, three peaks of binding energies at 288.7, 288.4 and 288.6 eV were assigned to the emerging target group O-C=O of $\text{HC}_4\text{-N}_2\text{-CO}_2\text{-Zn(OAC)}_2$, $\text{HC}_6\text{-N}_3\text{-CO}_2\text{-Zn(OAC)}_2$ and $\text{HC}_{10}\text{-N}_4\text{-CO}_2\text{-Zn(OAC)}_2$, respectively, indicating the successful formation of carbamate.^{55,56} The peak areas of O-C=O calculated by integral quantitative analyses corroborated that 37.04%, 28.412%, and 37.02% CO_2 were introduced into the $\text{HC}_x\text{-N}_y\text{-CO}_2\text{-Zn(OAC)}_2$ samples, which suggested that ultra-high levels of CO_2 were utilized to prepare MOFs. Furthermore, fine Zn 2p, N 1s, and O 1s XPS spectra of different MOFs

samples were analyzed, which showed similar atomic proportions (Fig. S19[†]).

Gas separation performance

As an alternative to traditional energy-intensive gas separation approaches, membrane-based gas separation has shown remarkable advantages in terms of low energy consumption, easy operation, eco-friendship, and small footprint. Among various materials, MOFs such as ZIF-8, HZIF-8, UiO-66, and Cu(BDC) have been extensively studied as advanced fillers for constructing functional mixed matrix membranes (MMMs).⁵⁷ The MMMs obtained *via* the combination of MOFs and a polymer matrix are one of the most promising solutions for gas separation (Fig. 7a). To evaluate the performance of our obtained MOFs, $\text{HC}_6\text{-N}_3\text{-CO}_2\text{-Zn(NO}_3)_3$, as a filler, was mixed with PIM-1. As an emerging membrane material first developed by Budd *et al.* in 2004,⁵⁸ PIM-1 with ladder-like structures (Fig. 7b), contortion sites, irregular and kinked chain architecture, interconnected micropores and high specific surface area exhibit ultrahigh gas permeability. However, inefficient packing of PIM-1 chains leads to a non-equilibrium state where molecular relaxation occurs over time, reaching an equilibrium state and causing the losses of fractional free volume and permeability during the physical aging process.⁵⁹ Besides, achieving a desirable match between polymers and MOFs for the development of advanced MMMs is challenging, especially when the emerging highly permeable PIM-1 materials are deployed. New synthetic $\text{HC}_6\text{-N}_3\text{-CO}_2\text{-Zn(NO}_3)_3$ with flexible skeleton and nitrogen-rich characteristics may effectively disrupt PIM-1 chain packing and create additional gas transport channels to improve CO_2 separation performance.

Fig. 7 illustrates the molecular structure of PIM-1, gas separation process, membrane morphology and pore characteristics, as well as separation performance. PIM-1 was synthesized from a polycondensation reaction between 5,5',6,6'-tetrahydroxy-3,3',3'-tetramethyl-1,1'-spirobisindane (TTSBI) and 1,4-dicyanotetrafluorobenzene (TFTPN). It had a light yellow color and amorphous morphology (Fig. S20[†]). $\text{HC}_6\text{-N}_3\text{-CO}_2\text{-Zn(NO}_3)_2$ was dispersed in a PIM-1 solution with a loading of 1 wt% and then cast as polymer membranes with a thickness of ~ 50 μm (Fig. 7g and S21[†]). The resultant MMMs had a smooth top and rough bottom surfaces (Fig. 7e and f, respectively), suggesting that the stick-shaped $\text{HC}_6\text{-N}_3\text{-CO}_2\text{-Zn(NO}_3)_2$ piled up from the bottom according to the solidification process for $\text{HC}_6\text{-N}_3\text{-CO}_2\text{-Zn(NO}_3)_2$ MMMs (Fig. 7c). This nonaligned, randomly oriented $\text{HC}_6\text{-N}_3\text{-CO}_2\text{-Zn(NO}_3)_2$ stick distribution would lead to a selective gas permeation highway to enhance the overall separation performance (Fig. 7d). According to Fig. S22–S24,[†] the chemical composition of PIM-1 and PIM-1/ $\text{HC}_6\text{-N}_3\text{-CO}_2\text{-Zn(NO}_3)_2$ (1%) was additionally confirmed by FTIR and XPS analyses. As shown in Fig. S25 and S26,[†] thermal degradation of $\text{HC}_6\text{-N}_3\text{-CO}_2\text{-Zn(NO}_3)_2$ powders and PIM-1 started at around 302 °C and 490 °C, separately. Above this temperature, a continuous weight loss was observed. Thermal stability was improved with the incorporation of $\text{HC}_6\text{-N}_3\text{-CO}_2\text{-Zn(NO}_3)_2$ nanoparticles into the PIM-1 matrix because



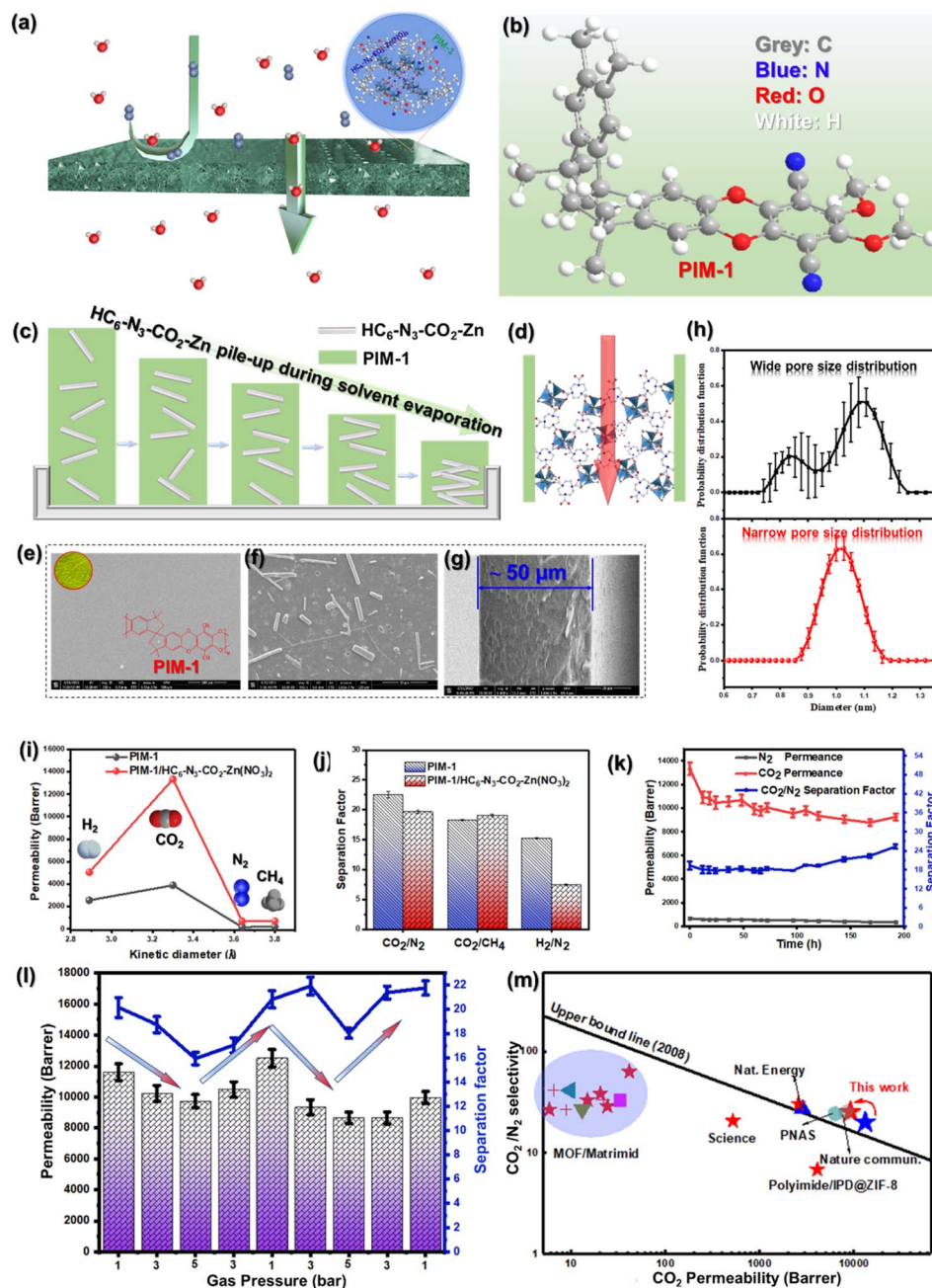


Fig. 7 Mixed matrix membranes for gas separation (a) diagram of gas separation through a membrane. (b) Ladder-like molecular structure of PIM-1 (grey: C, blue: N, red: O, white: H). (c) Illustration of the solidification process of the stick-shaped PIM-1/HC₆-N₃-CO₂-Zn(NO₃)₂ (1%) membrane. (d) Schematic illustration of gas transport channels through the PIM-1/HC₆-N₃-CO₂-Zn(NO₃)₂ membrane. (e–g) Top view, bottom view and cross-section of the 1 wt% PIM-1/HC₆-N₃-CO₂-Zn(NO₃)₂ (1%) membrane. (h) Free volume hole diameters of pure PIM-1 membrane (top) and PIM-1/HC₆-N₃-CO₂-Zn(NO₃)₂ (1%) MMMs (bottom) determined by positron annihilation lifetime distributions (PALS) under vacuum at 298 K. (i) Single-gas separation permeability of PIM-1, PIM-1/HC₆-N₃-CO₂-Zn(NO₃)₂ (1%) membranes as a function of gas kinetic diameter at 298 K and 2 bar. (j) Separation factors of PIM-1 and 1 wt% PIM-1/HC₆-N₃-CO₂-Zn(NO₃)₂ (1%) membranes for CO₂/N₂, CO₂/CH₄ and H₂/N₂ separations. (k) Long-term tests of 1 wt% PIM-1/HC₆-N₃-CO₂-Zn(NO₃)₂ (1%) MMMs for CO₂ and N₂ at 298 K and 2 bar. (l) CO₂ permeability and CO₂/N₂ separation factor of 1 wt% PIM-1/HC₆-N₃-CO₂-Zn(NO₃)₂ (1%) MMMs as a function of pressure. (m) A comparison of the Robeson upper bound for CO₂/N₂ separation between 1 wt% PIM-1/HC₆-N₃-CO₂-Zn(NO₃)₂ (1%) MMMs and literature data. Information on the data points is also given in ESI Table 7.†

the PIM-1/HC₆-N₃-CO₂-Zn(NO₃)₂ (1%) MMMs had a high decomposition temperature than that of PIM-1 pure membrane.

PALS is an advanced technology to probe the pore (or free volume) sizes and PSD of membranes. Fig. 7h, S27, S28 and Table S3† show the pore sizes and PSD measured by PALS under



vacuum at 298 K. Consistent with the previous reports,^{60,61} the PIM-1 membrane had two pores with diameters of 8.3 Å and 10.9 Å. Interestingly, the PIM-1/HC₆-N₃-CO₂-Zn(NO₃)₂ (1%) membrane exhibited a relatively higher intensity for the peak at around 10.1 Å and a narrower PSD than the PIM-1 membrane, possibly due to the effects of hydrogen bonding or coordination between MOFs ligands or metals and PIM-1 skeleton.⁶² Overall, the above results confirmed that the introduction of HC₆-N₃-CO₂-Zn(NO₃)₂ into PIM-1 could effectively tailor the membrane pore characteristics, which was beneficial to enhance the gas transport, as revealed in the following section.

The gas separation performances were studied using a constant volume-variable pressure method *via* a homemade apparatus, including the gas source, membrane modules, vacuum and detecting system (Fig. S29†). The membranes were wrapped with tape for testing (Fig. S31 and S32†). The gas permeability of membranes decreased in the order of CO₂ (kinetic diameter of 3.30 Å) > H₂ (2.89 Å) > CH₄ (3.76 Å) > N₂ (3.64 Å) (Table S4†). For PIM-1 membranes, the gas permeabilities were 2566 (H₂), 3898 (CO₂), 171 (N₂), 210 (CH₄) barrer, respectively (Fig. 7i), and the ideal selectivity of CO₂/N₂ (CO₂/CH₄) was 22 (18). For the PIM-1/HC₆-N₃-CO₂-Zn(NO₃)₂ (1%) MMMs, the gas permeability increased dramatically when HC₆-N₃-CO₂-Zn(NO₃)₂ was loaded, while the ideal selectivity was almost unchanged. The CO₂ permeability dramatically increased from 3898 to 13 343 barrer and the CO₂/N₂ and CO₂/CH₄ selectivity changed from 22 to 20 and 18 to 19 (Fig. 7i, j and Table S5†). Further, we collected more data under different HC₆-N₃-CO₂-Zn(NO₃)₂ loadings (0.5 wt%, 1.5 wt%, 2.0 wt%). With the increase in MOF contents, CO₂ permeability increased significantly from 5509 (0.5 wt%), 14 377 (1.5 wt%) to 16 377 (2.0 wt%), while the selectivity of CO₂/N₂ decreased significantly from 22.2 (0.5 wt%), 17.8 (1.5 wt%) to 16.3 (2.0 wt%) (Fig. S33†). Therefore, 1.0 wt% HC₆-N₃-CO₂-Zn(NO₃)₂ loading MMM had the best performance in terms of selectivity and permeability. The above results indicated that the CO₂ permeability of the MMMs can be significantly increased without much compromise in selectivity, which is conducive to improving the high productivity of the MMMs for practical applications.

Physical aging is a phenomenon where glassy materials relax to a denser configuration with time.⁶³ Therefore, PIM-1 by itself, with abundant pore volume due to the poor chain packing, can be detrimental to its permeability over extended time periods but gains in selectivity *via* reducing the fractional free volume and pore size from a non-equilibrium state to a more energetically favored state.⁶⁴ The addition of HC₆-N₃-CO₂-Zn(NO₃)₂ MOFs to PIM-1 was found to stabilize this aging behavior. The partially unreacted HC₆-N₃ on the surface of HC₆-N₃-CO₂-Zn(NO₃)₂ sticks interacted with the nitrile groups of PIM-1. It not only formed defect-free matrix-filler interfaces with good compatibility but also potentially restricted chain movements of PIM-1 over time. The permeability of CO₂ decreased slightly from 13 343 to 9264 barrer in 192 h, and the selectivity increased from 20.0 to 25.5 (Fig. 7k and Table S6†). Therefore, PIM-1/HC₆-N₃-CO₂-Zn(NO₃)₂ MMMs (1%) have good anti-ageing properties for gas separation.

Since CO₂ would plasticize the membranes at high pressures, it is important to understand the effect of CO₂ pressure on CO₂ permeability and plasticization behavior of PIM-1/HC₆-N₃-CO₂-Zn(NO₃)₂ (1%). The separation performance of PIM-1/HC₆-N₃-CO₂-Zn(NO₃)₂ (1%) was assessed under various feed pressures. As shown in Fig. 7l, both gas permeability and selectivity slightly decreased with increasing feed pressure. Increasing the feed pressure to 5 bar led to a decrease in CO₂ permeability by ≈ 16%, and the permeability slightly decreased after restoring the pressure to the initial pressure, indicating that less plasticization was generated in this pressure range. Meanwhile, increasing the pressure to 5 bar led to a decrease in the CO₂/N₂ separation factor by ≈ 20% (Table S7†). Afterwards, the CO₂ permeability and the CO₂/N₂ selectivity had small changes during pressure cycling, implying that the membrane had good plasticization resistance. Fig. 7m and S34† compare the CO₂/N₂ and CO₂/CH₄ separation performance of PIM-1/HC₆-N₃-CO₂-Zn(NO₃)₂ (1%) and other polymer/MOF MMMs in a Robeson's upper-bound plot.⁵⁷ As expected, the PIM-1/HC₆-N₃-CO₂-Zn(NO₃)₂ (1%) membrane easily surpasses the upper bound and demonstrates significant superiority to various reported polymer/MOFs MMMs (Table S8†). The binary CO₂/N₂ (50/50) mixed-gas performance of PIM-1 and PIM-1/HC₆-N₃-CO₂-Zn(NO₃)₂ (1%) membranes with a feed pressure of 2 bar is shown in Fig. 2. All of the membranes provided a lower CO₂ permeability under mixed feeding gas than single gas under the same conditions, which is caused by the competitive sorption mechanism between CO₂ and N₂. N₂ adsorbed in the membranes reduced the CO₂ transport. The CO₂ permeability of PIM-1, PIM-1/HC₆-N₃-CO₂-Zn(NO₃)₂ (1%) decreased from 3898, 13 343 barrer using a single feeding of CO₂ to 2039, 7377 barrer with upstream charged with 2 bar CO₂/N₂ (50/50) mixed gas, respectively. The CO₂/N₂ selectivity of the PIM-1, PIM-1/HC₆-N₃-CO₂-Zn(NO₃)₂ (1%) membranes decreased from 22 to 19.3 and from 20 to 19.1, separately, after the upstream charged with CO₂/N₂ (50/50) mixed gas as the feeding gas (Fig. S35†).

Conclusion

The nitrogen-rich heterocycles were applied not only for CO₂ capture from the atmosphere but also green utilization for MOFs preparation. For heterocycles HC_x-N_y, the unique merits, such as (i) abundant nucleophilic absorption sites, (ii) high absorption capacity and rate, (iii) symmetrical geometry, and (iv) flexible and variable structure, endow them with a superior DAC capacity. The white precipitates (HC_x-N_y-CO₂) were obtained based on the phase change mechanism when the nucleophilic HC_x-N_y was in contact with electrophilic CO₂. The high CO₂ absorption efficiency of 99% was demonstrated for a long duration of 12 h even under ultralow CO₂ concentration (437 ppm), which shows the practical DAC application. The crystalline carbamate-based MOFs with luxuriant morphologies were prepared from the resultant HC_x-N_y-CO₂ ligands and metal clusters. The incorporation of carbamate-based MOFs into the PIM-1 membrane rearranges the architecture of micropore sizes and pore size distribution, and provides more transport channels for CO₂ separation from flue gas, which



breaks the trade-off limitation between permeability and selectivity, and surpasses the conventional upper bound line. Based on the above work, the novel nitrogen-rich heterocyclic materials show significant promise for direct air carbon capture, high value-added product utilization, high-efficiency CO₂ separation and capture from flue gas, which will accelerate the transition of our world from abundant CO₂ emission to the negative carbon emission and open a boulevard for the future development of CCUS.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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