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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_v) was identified for direct air capture (DAC) based on a phase change mechanism. HC_x-N_v 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 CO_2 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 (SO_4^{2-} , OAC⁻, and NO_3^{-}). 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_v-N_v) 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.

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-

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, postcombustion 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

^{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.

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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 valueadded products. Literature research has indicated that high value-added substances, such as organic carbonates, 13 chemoenzymatic 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 ~10 000 m² g⁻¹. They have been widely used in gas adsorption, 9 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 CO_2 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 $[HC_4-N_2-CO_2]^{2-}$, $[HC_6-N_3-CO_2]^{3-}$ and $[HC_{10}-N_4-$ CO₂]⁴⁻ under room temperature and pressure without any catalyst.²⁸ As $[HC_4-N_2-CO_2]^{2-}$, $[HC_6-N_3-CO_2]^{3-}$ and $[HC_{10}-N_4-$ 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 CO₂derived 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 CO_2 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 \dagger). 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

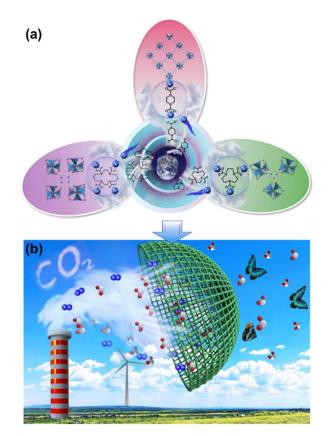


Fig. 1 Schematic diagram of synthetic MOFs and membrane separation. (a) Schematic diagram of the process for MOF synthesis from Zn clusters and various nitrogen-rich heterocycles by introducing CO₂ at room temperature and atmospheric pressure via a one-pot method. (b) Membrane separation diagram for 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 CO_2 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 $HC_x-N_y-CO_2(-Zn)$

In addition to the discovery of HC_x - N_v 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 $HC_x-N_y-CO_2-Zn$ MOFs powders were prepared by means of in situ synthesis via a onepot approach utilizing CO2 at 25 °C. Introducing CO2 into a mixed solution of $Zn(OAc)_2 \cdot 2H_2O$, 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 $HC_x-N_y-CO_2(-Zn)$

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_v-CO₂ arise from different ring sizes and numbers of the secondary amine groups in HC_x-N_y . HC_4- N₂-CO₂ exhibits an evenly distributed and regular ribbon-like morphology with a width of \sim 1 μ m (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 \sim 4 μm (Fig. 2e and f). Besides, HC₁₀-N₄ has an interesting needle-like morphology at the macro scale (Fig. S10a†). Under FESEM, HC_{10} - N_4 appears to have a rod shape of \sim 200 μm length and

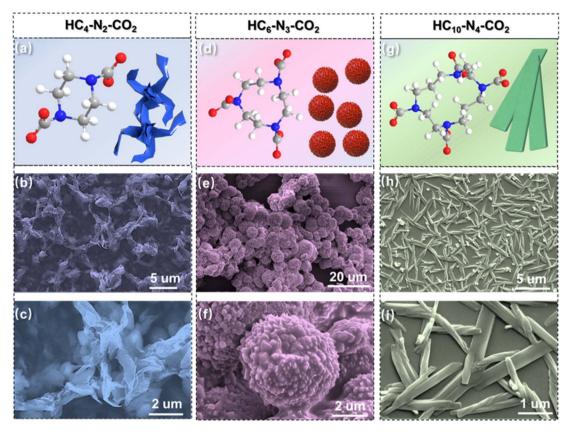


Fig. 2 Molecular structure and morphology of $HC_x - N_y - CO_2$: $(a-c) HC_4 - N_2 - CO_2$, $(d-f) HC_6 - N_3 - CO_2$, and $(g-i) HC_{10} - N_4 - CO_2$. All the ball and stick model states of $HC_x - N_y - CO_2$ are in the lowest energy states optimized through Chemdraw 3D. Different colored spheres represent different atoms, where blue is N, gray is C, and red is O.

 ${\sim}20~\mu m$ width (Fig. S10b–S10e†). After the CO $_2$ reaction, the lamellar HC $_{10}$ –N $_4$ –CO $_2$ is obtained with an average length of ${\sim}3~\mu m$ and width of ${\sim}400~nm$ (Fig. 2h and i). To our knowledge, the fantastic ribbon-like HC $_4$ –N $_2$ –CO $_2$, lychee-like HC $_6$ –N $_3$ –CO $_2$, and lamellar-like HC $_{10}$ –N $_4$ –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 HC_x-N_y-CO₂

Considering the interesting morphological changes from HC_x – N_y to HC_x – N_y – CO_2 , a possible mechanism is proposed based on our experimental results and the previous literature. 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 HC_x – N_y has been changed into a solid HC_x – N_y – CO_2 based on the reaction of $[R^1R^2NH(l) + CO_2(g) \rightarrow R^1R^2N$ –COOH(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 HC_x – 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 HC_x-N_y as a strong Lewis base in organic solvents to provide sufficient active sites to electrophilic CO2 at the molecular level. In the second stage, the electron-rich secondary amine of HC_x-N_v (i.e., strong nucleophile) reacts quickly with CO2 molecules to form the monocarbamate (i.e., the formation of a heterogeneous phase). The reaction is rapid within a few seconds because the strong nucleophile attack of HC_x - N_y and the formation of a solid phase promote the reaction in a forward direction. In the third stage, more CO2 is reacted with mono-carbamate to form dicarbamate, tri-carbamate or tetra-carbamate (i.e., the formation of a more heterogeneous phase). This stage is the ratedetermining step due to the complex environments of CO2 reaction, steric hindrance and changes in the electronic structure.35 As an example, Fig. S11† exhibits the digital pictures of the reaction process between HC6-N3 and CO2 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 HC_4 – N_2 reacted quickly with two electrophilic

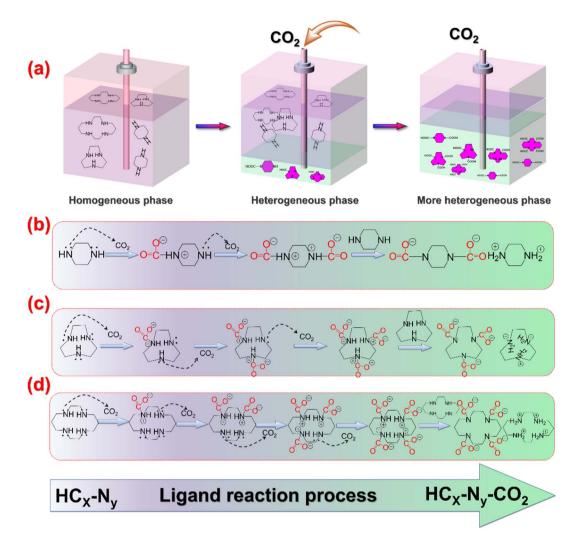


Fig. 3 Formation mechanism of $HC_x - N_y - CO_2$. (a) Model process diagram to form $HC_x - N_y - CO_2$ including mainly three stages (homogeneous phase, heterogeneous phase, and more heterogeneous phase). Mechanisms of ligand formation for MOFs between electrophilic CO₂ and nucleophilic starting materials. (b) HC_4-N_2 . (c) HC_6-N_3 . (d) $HC_{10}-N_4$.

CO₂ 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 HC₆-N₃ or HC₁₀-N₄ reacted with three or four CO₂ molecules, respectively, to form tri-carbamate or tetra-carbamate (Fig. 3c and d). In addition, as depicted in Table S2,† HC_x-N_y has a very high nitrogen content; for instance, 1 equivalent HC₄-N₂, HC₆-N₃, and HC₁₀-N₄ 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 CO2 adsorbents at present, which plays an important role in the adsorption of CO2 with a high speed and capacity. Moreover, according to theoretical calculations, 1 equivalent HC₄-N₂ absorbs 1.048 equivalent CO₂, 1 equivalent HC₆-N₃ absorbs 1.0476 equivalent CO₂, and 1 equivalent HC₁₀-N₄ absorbs 0.898 equivalent CO2. 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 HC_r-N_ν-CO₂ 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 HC₄-N₂-CO₂-ZnSO₄

Inspired by the innovative syntheses of MOF-5,32 MOF- $38(Zn_3(btc)_2)^{33}$ and $Zn_2(TPOM)(btc)_2$ (ref. 34) made of terephthalic acid (1,4-H₂bdc), trimesic acid (1,3,5-H₃btc), benzene-1,2,4,5-tetracarboxylic acid (1,2,4,5-H₄btc) and Zn clusters, $HC_4-N_2-CO_2$, $HC_6-N_3-CO_2$ and $HC_{10}-N_4-CO_2$ ligands were used to form MOFs with zinc clusters. In terms of HC₄-N₂-CO₂-ZnSO₄, a charming micron flowery sphere (like hydrangea) with a diameter of \sim 3 µm was prepared by in situ synthesis of HC₄-N₂ and ZnSO₄ with CO₂ involved via self-assembly of the nanosheets with a thickness of \sim 100 nm (Fig. 4b-d and S12†). Ultimately, field emission transmission electron microscopy

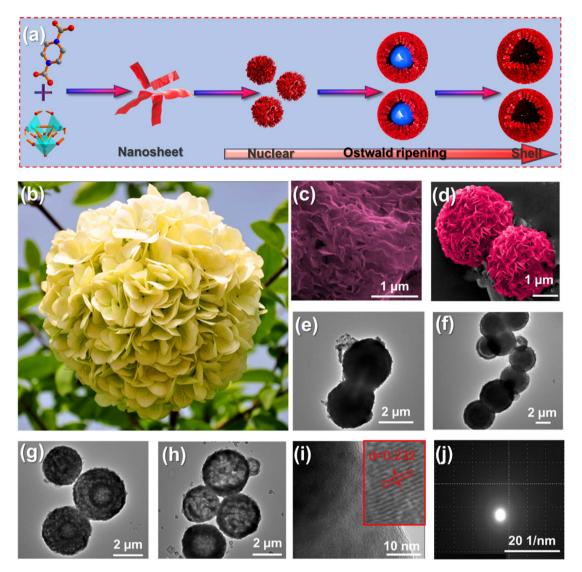


Fig. 4 Formation process of hollow flower-like $HC_4-N_2-CO_2-ZnSO_4$. (a) Model diagram of hollow flower formation according to an inside-out Ostwald ripening process. (b) A digital picture of hydrangea. (c and d) FESEM images. FESEM images were colored red for visual effect. (e-h) Low-magnification TEM images. (i) HR-FETEM image. (j) SAED pattern of $HC_4-N_2-CO_2-ZnSO_4$.

(FETEM) undoubtedly corroborated that HC₄-N₂-CO₂-ZnSO₄ 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 HC₄-N₂-CO₂-ZnSO₄ was formed through the reaction among CO₂, HC₄-N₂ and ZnSO₄ (Fig. 4c). (II) The lamellar HC₄-N₂-CO₂-ZnSO₄ 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 $HC_4-N_2-CO_2-ZnSO_4$ 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 $HC_4-N_2-CO_2-ZnSO_4$ (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 HC₄–N₂–CO₂–ZnSO₄ 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 CO2 to prepare MOFs particles with hollow flower-like structures through a simple room temperature strategy appears more innovative and conducive to CO₂ conversion and environmental protection.

Effect of anions (OAC⁻, SO₄²⁻, NO₃⁻) 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 (SO₄²⁻) with acetate (OAC⁻), a high aspect ratio laminar HC₄-N₂-CO₂-Zn(OAC)₂ was obtained, which had an even size of \sim 2.5 µm length, \sim 400 nm width and ~80 nm thickness (Fig. 5f and f1). A further modification of anions by nitrate (NO₃⁻) resulted in HC₄-N₂-CO₂-Zn(NO₃)₂ with an entirely different morphology of tremellar shape via the bending and folding of a large layer of \sim 10 nm thickness (Fig. 5g and g1). The above results illustrate that the introduction of distinct anions (SO₄²⁻, OAC⁻, NO₃⁻) 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 (SO42-, OAC-, NO3-) 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 metalcontaining 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 (SO₄²⁻, OAC⁻, NO₃⁻) resulting in dissimilar MOFs morphologies, HC₆-N₃-CO₂-Zn and HC₁₀-N₄-CO₂-Zn were also prepared from the same Zn clusters with different anions (NO₃⁻, OAC⁻). Firstly, the influence of OAC⁻ and NO₃⁻ anions on the formation of MOFs prepared from HC₆-N₃, CO₂ and Zn clusters was studied via a similar approach. According to Fig. 5h and h1, the blocky-like HC₆-N₃-CO₂-Zn(OAC)₂, which had a proportion of \sim 2 µm length and \sim 1 µm width, was obtained in the presence of OAC⁻, whereas stick-like HC₆N₃-CO₂-Zn(NO₃)₂ with a size of \sim 0.98 µm length and \sim 68 nm width was acquired with the participation of NO₃⁻ (Fig. 5i and i1). Similarly, a large layer of HC₁₀-N₄-CO₂-Zn(OAC)₂ with a thickness of ~100 nm

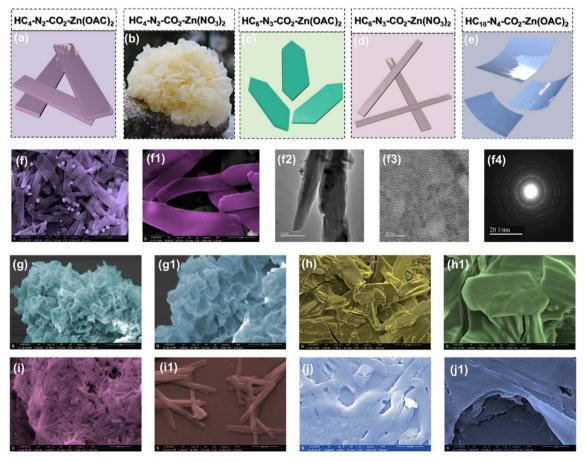


Fig. 5 MOF morphologies analyses. (a-e) Models of different MOF morphologies. (f and f1) FESEM of high aspect ratio laminar $HC_4-N_2-CO_2 Zn(OAC)_2$. (f2 and f3) HR-FETEM image. (f4) SAED pattern of $HC_4-N_2-CO_2-Zn(NO_3)_2$. (g and g1) Tremella-shape $HC_4-N_2-CO_2-Zn(NO_3)_2$. (h and h1) Blocky structure $HC_6-N_3-CO_2-Zn(OAC)_2$. (i and i1) Stick-like $HC_6-N_3-CO_2-Zn(NO_3)_2$. (j and j1) Large layer $HC_{10}-N_4-CO_2-Zn(OAC)_2$. All FESEM images were colored for visual effect.

was acquired from HC_{10} – N_4 – 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 HC_x – N_y – CO_2 –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 HC_4 – 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 HC_4 – N_2 – CO_2 – $ZnSO_4$ are at 13.2, 14.5, 18.1, 20.5 and 30.1°, which are completely different from those of HC_4 – N_2 – CO_2 – $Zn(OAC)_2$, further demonstrating the influence of different anions (SO_4 ² and OAC⁻) on crystal structures. For HC_6 – N_3 – CO_2 – $Zn(OAC)_2$, 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 HC_6 – N_3 – CO_2 –

 $Zn(OAC)_2$ (Fig. 6b). The diffraction peak at 9.9° is its main peak. Regarding HC_{10} – N_4 – CO_2 – $Zn(OAC)_2$, the characteristic X-ray diffraction peaks at 8.9, 9.9, 10.8 and 15.8° are attributed to the crystalline structure of HC_{10} – N_4 – CO_2 – $Zn(OAC)_2$ (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. HC_4 – N_2 – CO_2 – $Zn(OAC)_2$, HC_6 – N_3 – CO_2 – $Zn(NO_3)_2$, and HC_{10} – N_4 – CO_2 – $Zn(OAC)_2$ have specific surface areas of 575, 456, and 127 m² 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 $HC_x-N_y-CO_2-Zn(OAC)_2$ MOFs

The formation of functional groups based on carbamate has been widely studied in the field of CO₂ absorption. ^{47,48} The C-N

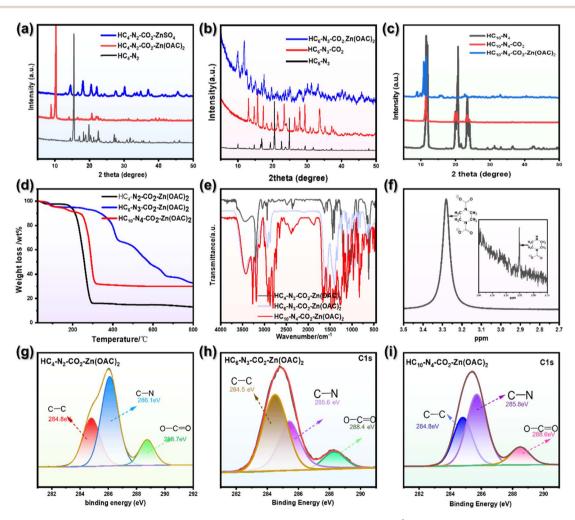


Fig. 6 Property analyses of $HC_x-N_y-CO_2-Zn$. (a) Comparison of PXRD patterns ($\lambda_{Cu}=1.5406$ Å) of HC_4-N_2 , $HC_4-N_2-CO_2-ZnSO_4/Zn(OAC)_2$. (b) $HC_6-N_3-CO_2$, $HC_6-N_3-CO_2-Zn(OAC)_2$. (c) $HC_{10}-N_4$, $HC_{10}-N_4-CO_2$, $HC_{10}-N_4-CO_2-Zn(OAC)_2$. (d) TGA analysis of $HC_x-N_y-CO_2-Zn(OAC)_2$ under N_2 atmosphere. (e) FT-IR characterization of $HC_x-N_y-CO_2-Zn(OAC)_2$. (f) N_2 H NMR spectrum of N_2 Spectra of C 1s in N_2 In N_3 Spectra of C 1s in N_3 In N_3 Spectra of N_3 Spe

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 $HC_x-N_y-CO_2-Zn(OAC)_2$ 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 HC₄- N_2 –CO $_2$ –Zn(OAC) $_2$, 352 °C for HC $_6$ –N $_3$ –CO $_2$ –Zn(OAC) $_2$, and 252 ° C for HC₁₀-N₄-CO₂-Zn(OAC)₂. Compared with HC₄-N₂-CO₂, ⁵⁰ the thermal stability of all MOFs was enhanced, and HC6-N3-CO₂-Zn(OAC)₂ displayed the highest thermal stability in all MOFs.

Chemical component analyses

The Fourier transform infrared spectrum (FT-IR) of HC_x-N_y- CO₂-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 μ_4 -O-Zn of the $[Zn_4O(CO_2)_6]$ clusters,⁵¹ confirming the formation of $Zn_4O(CO_2)_6$. 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 CO2 is successfully involved in the reaction. To monitor the HC_x-N_y-CO₂ formation from HC_x-N_y , the ¹H NMR spectrum of $HC_x-N_y-CO_2-Zn(OAC)_2$ was acquired (Fig. 6f, S16 and S17†). Fig. 6f depicts two peaks at 3.28 and 2.85 ppm caused by CO₂ 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 HC₄-N₂ reacted with CO₂ to form HC₄-N₂-CO₂ dicarbamate, only 0.04% of HC₄-N₂ to form mono-carbamate, and no HC₄-N₂ starting material was found, indicating that HC₄-N₂ had high reactivity, which was consistent with the aforementioned experiments (Fig. S7†). However, as far as HC₆-N₃ and HC₁₀-N₄ are concerned, owing to the excessively long reaction path and steric hindrance, few of them form tricarbamate and tetra-carbamate, while most secondary amine groups react incompletely with CO2 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 HC_4 - N_2 - CO_2 - $Zn(OAC)_2$, HC_6 - N_3 - CO_2 - $Zn(OAC)_2$ and $HC_{10}-N_4-CO_2-Zn(OAC)_2$, 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% CO2 were introduced into the $HC_x-N_y-CO_2-Zn(OAC)_2$ samples, which suggested that ultrahigh levels of CO₂ 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, HC₆-N₃-CO₂-Zn(NO)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 HC6-N3-CO2-Zn(NO)3 with flexible skeleton and nitrogen-rich characteristics may effectively disrupt PIM-1 chain packing and create additional gas transport channels to improve CO2 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',3'-tetramethyl-1,1'-spirobisindane (TTSBI) and 1,4-dicyanotetrafluorobenzene (TFTPN). It had a light yellow color and amorphous morphology (Fig. S20†). HC₆-N₃-CO₂-Zn(NO₃)₂ was dispersed in a PIM-1 solution with a loading of 1 wt% and then cast as polymer membranes with a thickness of \sim 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 HC6-N3-CO2-Zn(NO₃)₂ piled up from the bottom according to the solidification process for HC₆-N₃-CO₂-Zn(NO₃)₂ MMMs (Fig. 7c). This nonaligned, randomly oriented HC₆-N₃-CO₂-Zn(NO₃)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/HC₆-N₃-CO₂-Zn(NO₃)₂ (1%) was additionally confirmed by FTIR and XPS analyses. As shown in Fig. S25 and S26,† thermal degradation of HC₆-N₃-CO₂-Zn(NO₃)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 HC₆-N₃-CO₂-Zn(NO₃)₂ nanoparticles into the PIM-1 matrix because

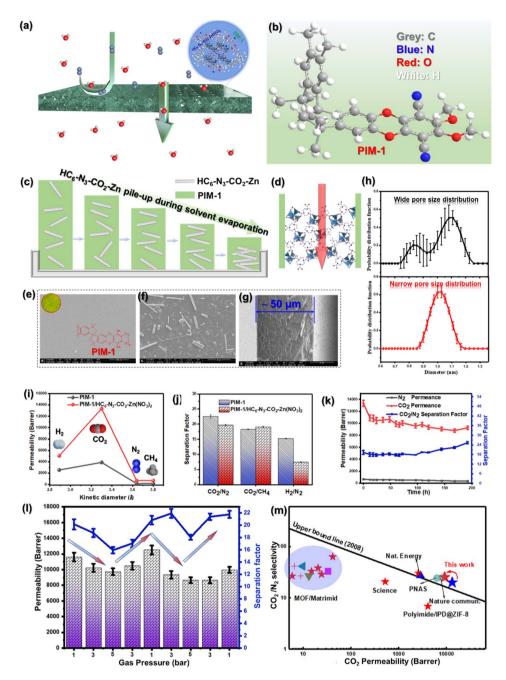


Fig. 7 Mixed matrix membranes for gas separation (a) diagram of gas separation through a membrane. (b) Ladder-like molecular structure of PIM-1 (grey: C, blue: N, red: O, white: H). (c) Illustration of the solidification process of the stick-shaped PIM-1/HC $_6$ -N $_3$ -CO $_2$ -Zn(NO $_3$) $_2$ (1%) membrane. (d) Schematic illustration of gas transport channels through the PIM-1/HC $_6$ -N $_3$ -CO $_2$ -Zn(NO $_3$) $_2$ membrane. (e-g) Top view, bottom view and cross-section of the 1 wt% PIM-1/HC $_6$ -N $_3$ -CO $_2$ -Zn(NO $_3$) $_2$ (1%) membrane. (h) Free volume hole diameters of pure PIM-1 membrane (top) and PIM-1/HC $_6$ -N $_3$ -CO $_2$ -Zn(NO $_3$) $_2$ (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/HC $_6$ -N $_3$ -CO $_2$ -Zn(NO $_3$) $_2$ (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/HC $_6$ -N $_3$ -CO $_2$ -Zn(NO $_3$) $_2$ (1%) membranes for CO $_2$ /N $_2$, CO $_2$ /CH $_4$ and H $_2$ /N $_2$ separations. (k) Long-term tests of 1 wt% PIM-1/HC $_6$ -N $_3$ -CO $_2$ -Zn(NO $_3$) $_2$ (1%) MMMs for CO $_2$ and N $_2$ at 298 K and 2 bar. (l) CO $_2$ permeability and CO $_2$ /N $_2$ separation factor of 1 wt% PIM-1/HC $_6$ -N $_3$ -CO $_2$ -Zn(NO $_3$) $_2$ (1%) MMMs as a function of pressure. (m) A comparison of the Robeson upper bound for CO $_2$ /N $_2$ separation between 1 wt% PIM-1/HC $_6$ -N $_3$ -CO $_2$ -Zn(NO $_3$) $_2$ (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) > H_2 (2.89 Å) > CH_4 (3.76 Å) > N_2 (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/ CH_4) 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 $HC_6-N_3-CO_2-Zn(NO_3)_2$ 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 CO_2/N_2 separation factor by $\approx 20\%$ (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/ $HC_6-N_3-CO_2-Zn(NO_3)_2$ (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 CO_2 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_v , 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 (HCx-Ny-CO2) were obtained based on the phase change mechanism when the nucleophilic HC_x-N_y was in contact with electrophilic CO_2 . 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 $HC_x-N_y-CO_2$ 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.

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