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Nitrogen-rich porous organic cages with high acetylene storage and separation performance†

Searching for porous materials that can safely store and efficiently separate acetylene (C_2H_2), a commonly used petrochemical feedstock with highly explosive properties, is a pressing and significant task. Nitrogenrich porous materials have garnered substantial attention for their ability to interact strongly with acidic C_2H_2 . Herein, we report two novel nitrogen-rich porous organic cages (POCs), namely CPOC-107 and CPOC-203, constructed from the same bowl-shaped tetraformylcalix[4]resorcinarene but different nitrogen-rich imidazolium-based diamine synthons. X-ray crystallographic analysis reveals that CPOC-107 adopts a [2 + 4] lantern-shaped structure, whereas CPOC-203 takes on a [3 + 6] triangular prism shape. Moreover, the cages exhibit large cavity volumes of up to 787 Å³ and high specific surface areas of up to 1202 m² g⁻¹. Owing to their high surface areas and high nitrogen content, both cages exhibit impressive C_2H_2 adsorption capabilities. Specifically, CPOC-107 achieves a remarkable C_2H_2 uptake value of up to 146 cm³ g⁻¹ at 298 K and 1 atm, the highest among those reported for all porous organic materials to date. Moreover, experimental breakthrough tests have confirmed the effective separation of C_2H_2/CO_2 mixtures using the CPOC-107 adsorbent.

Introduction

Acetylene (C₂H₂) is a crucial petrochemical material used in the production of industrial products involving polyurethane, polyester plastics, synthetic rubber, and so on.1,2 However, storing C₂H₂ safely remains challenging due to its flammability and explosive nature when subjected to pressures above 2 atm at room temperature.3 Moreover, C2H2 is usually produced from fractionation and oil cracking, which always involve a small amount of carbon dioxide (CO₂). Therefore, the discrimination of CO2 to afford high-purity C2H2 is critical to high-level safety for various industrial applications.4 Traditional methods to separate C₂H₂/CO₂ mixtures, such as solvent extraction and cryogenic distillations, not only suffer from high energyconsuming and environment-unfriendly problems but also possess the risk of introducing secondary by-products. Consequently, it is of great importance and urgency to seek better materials for safer storage of C₂H₂ and high-efficiency and lowenergy technologies to realize C₂H₂/CO₂ separation.

In recent years, adsorption and separation technologies based on porous materials have shown promise in addressing C₂H₂ storage and separation problems.⁵⁻⁷ In this region, porous metal-organic frameworks (MOFs) have rapidly developed.8,9 For instances, FJI-H8 and SNNU-98, reported by Hong and Zhai groups, respectively, have realized gravimetric C2H2 uptake values more than 220 cm³ g⁻¹ under ambient conditions. 10,11 Furthermore, SNNU-45, a MOF prepared by the Zhai group, has demonstrated the separation of C₂H₂/CO₂ with breakthrough time up to 80 min g⁻¹. In contrast, the development of porous organic materials (POMs) for C₂H₂ storage and separation is markedly slower than that of MOFs. To the best of our knowledge, POMs' C₂H₂ uptake values are generally less than 100 m² g⁻¹ under ambient conditions, and their ability to separate C₂H₂/CO₂ mixtures via actual breakthrough experiments is also underexplored.13 Therefore, it is crucial to increase their C2H2 adsorption capacity and explore their C₂H₂ purification ability to promote the development of POMs in this field.

Porous organic cages (POCs) are an emerging class of low-density crystalline POMs, which are held together from discrete (zero-dimensional; 0D) covalent-bonded macromole-cules with permanent intrinsic cavities (0D framework) *via* weak intermolecular interactions. ¹⁴⁻¹⁶ Since their inception in 2009 from Cooper's group, ¹⁷ research on the design and synthesis of different linkages, shapes, topologies, sizes, and functions of POCs has attracted much attention from chemists and materials scientists. ¹⁸⁻³³ Our group focuses on using concave-shaped calix[4]resorcinarene (C4RA) as synthons in construction of

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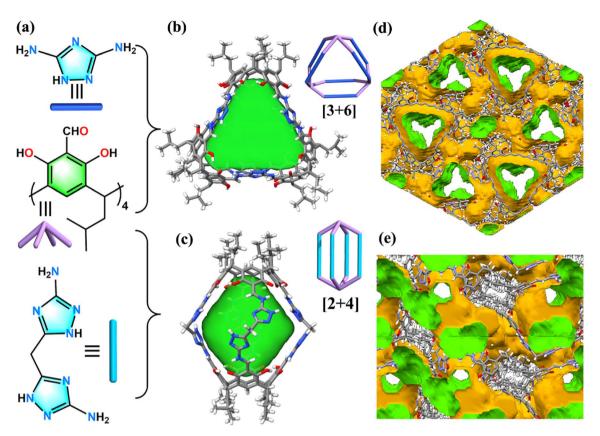


Fig. 1 (a) The chemical structures of organic synthons used for the construction of (b) [3 + 6] CPOC-203 and (c) [2 + 4] CPOC-107 obtained from single-crystal X-ray diffraction and the molecular packing for (d) CPOC-203 and (e) CPOC-107 in the solid state created with Mercury (voids and contact surface in the crystal shown in green and orange, respectively). Carbon is gold, oxygen red, nitrogen blue, and hydrogen white.

novel C4RA-based POCs and their applications.³⁴⁻⁴⁰ In this work, we designed and synthesized two robust nitrogen-rich POCs aiming at efficient storage and separation of C₂H₂, as the basic nitrogen groups have been verified to have strong interaction with acidic C_2H_2 gas. Both the [2 + 4] lantern-shaped cage (CPOC-107) and [3 + 6] triangular prism-shaped cage (CPOC-203) are constructed from the same bowl-shaped tetraformylcalix[4]resorcinarene (C4RACHO) but different nitrogenrich imidazolium-based diamine synthons (Fig. 1a-c and S1-S7†). We found that both materials show high C₂H₂ uptake capacity under ambient conditions (>110 cm³ g⁻¹), and the nitrogen content greatly influences their C₂H₂ uptake capacity and C₂H₂/CO₂ separation ability.

Results and discussion

A mixture of C4RACHO and 3,5-diamino-1,2,4-triazole (DTA) organic synthons with a molar ratio of 1:2 in chlorobenzene and methanol mixture at 80 °C for 24 hours affords red block crystals of CPOC-203. Single crystallographic X-ray determination (SCXRD) suggests that CPOC-203 adopts a triangular prism-shaped cage structure (Fig. 1b), with a [3 + 6] assembly mode that is similar to the previously reported CPOC-201, constructed from C4RACHO and m-phenylenediamine synthons. CPOC-203 crystallizes in the triclinic system with the space group $P\bar{1}$ with Z=2, and its asymmetric unit contains one

full cage molecule as well as a large number of disordered solvate molecules (~46.2% of the unit cell volume), which have been removed by the routine SQUEEZE function of PLATON.41 The central triangular prism core of CPOC-203 comprises three C4RACHO faces and six DTA edges. It has a volume of 787 Å³ and a window diameter of 7.04 Å, as calculated using Voidoo and Pywindow, respectively. 42-44 The cages pack window-towindow in the solid state with the closest distance of \sim 9 Å between neighboring prism faces, forming one-dimensional channels (Fig. 1d).

Then we further increase the nitrogen content in imidazolium-based diamine synthons by using bis(5-amino-1,2,4-triazol-3-yl)methane (BATM). Notably, suitable red block single crystals of CPOC-107 can be obtained by an eightfold Schiff base reaction of C4RACHO (1 equiv.) and BATM (2 equiv.) in dimethyl sulfoxide at 100 °C for 72 hours. SCXRD reveals that **CPOC-107** crystallizes in a triclinic $P\bar{1}$ space group with Z=4, and contains a whole [2 + 4] organic cage in its asymmetric unit, and residual electron density as highly disordered solvent molecules (~45.3% of the unit cell volume), which were removed by SQUEEZE. The structure of CPOC-107 is s a lanternshaped structure with four near rhombic windows (Fig. 1c), featuring two C4RACHO as faces and four BATMs as pillars. The height of the cavity is 15.4 Å which was measured from the center of the C4RACHO face, and its windows can be passed by a sphere with a diameter of about 4.47 Å. Remarkably, CPOC-

107 has a cavity volume of about 744 Å³, the largest among those of all previously reported lantern-shaped CPOCs, with cavity volumes ranging from 358 to 581 Å³.³⁶ The side length of the rhombic windows is about 4.47 Å, which can be passed by a sphere with a diameter of about 4.47 Å. An examination of the **CPOC-107**'s solid-state packing suggested that cage molecules pack *via* weak van der Waals interactions, and there is also a one-dimensional channel in window-to-window mode (Fig. 1e).

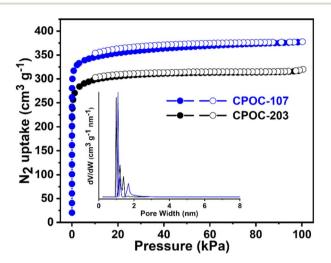


Fig. 2 N_2 gas sorption isotherms at 77 K for CPOC-107 and CPOC-203, inset: the calculated PSD of CPOC-107 and CPOC-203.

The presence of 1D channels in CPOC-107 and CPOC-203 prompts us to study their porosity. Thermal gravimetric analysis measurements showed their stabilities up to about 280 °C (Fig. S7†). Before the gas sorption test, both cages are immersed and exchanged 6 times every 24 hours in MeOH before activating at 100 °C under a high vacuum for 12 hours. Powder X-ray diffraction reveals that after desolvation, no phase change occurs in both materials (Fig. S8 and S9†). N2 gas sorption experiments confirmed their permanent porosity at 77 K (Fig. 2), and both the isotherms of CPOC-107 and CPOC-203 exhibited typical type I adsorption behavior with sharp increases at a pressure below 0.1 P/Po, which reveals their microporous nature. The Brunauer-Emmett-Teller (BET) specific surface areas were 1202 m² g⁻¹ for CPOC-107 and 1132 m² g⁻¹ for CPOC-203, respectively (Fig. S10 and S11†). The nonlocal density functional theory (NLDFT) was used to calculate the pore-size distribution (PSD), and both cages showed microporous cavities with ~1.08 nm for CPOC-107 and \sim 0.98 nm for **CPOC-203** (inset in Fig. 2), which are respectively related to the calculated largest pore diameter of 0.94 and 1.02 nm using Zeo++ software.45

The high surface, together with the presence of a high content of basic nitrogen sites (14.8% for CPOC-203 and 20.1% for CPOC-107) for both cages, further prompts us to use them as solid adsorbents for capturing acidic C_2H_2 gas and separating C_2H_2/CO_2 mixtures. Single-component gas equilibrium sorption isotherms of CPOC-107 and CPOC-203 were recorded at 298 K and pressure up to 1 bar. As shown in Fig. 3a, the saturated

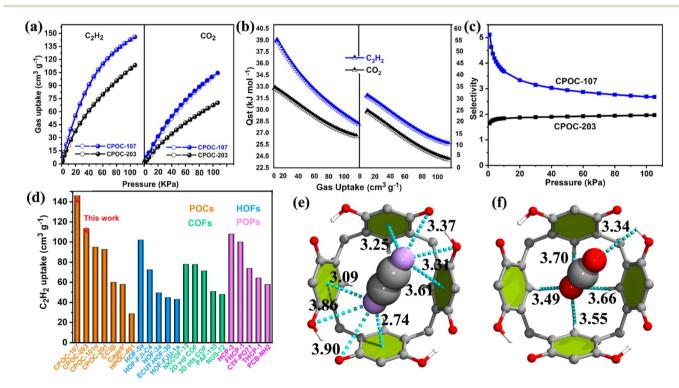


Fig. 3 (a) C_2H_2 and CO_2 sorption isotherms at 298 K; (b) Q_{st} values of C_2H_2 and CO_2 ; (c) the C_2H_2/CO_2 IAST selectivity; (d) comparison of C_2H_2 uptakes with different top-performed POM adsorbents under ambient conditions; (e) C_2H_2 and (f) CO_2 adsorption sites in **CPOC-107** performed in order to understand its C_2H_2/CO_2 separation mechanism. Carbon is gray, oxygen red, and hydrogen lavender. Dashed bonds highlight $H\cdots\pi$ and $H\cdots O$ interactions.

C₂H₂ adsorption value under the conditions above is 146 cm³ g⁻¹ for **CPOC-107**, which is higher than that of **CPOC-203**, with a value of 114 cm³ g⁻¹. Both values are higher than those of our previously reported cages with similar structural assemblies. Specifically, the C₂H₂ uptakes for the previously reported lantern-shaped [2 + 4] CPOC-101 to CPOC-104 (nitrogen content < 6.2%) are all less than 95 cm³ g⁻¹;^{38,46} while for the reported similar triangular prism-shaped [3 + 6] CPOC-201 with a nitrogen content of 5.8% the C_2H_2 uptake is only 91 cm³ g⁻¹.38 The discussions above reveal that increasing the nitrogen content in CPOCs can improve their C2H2 uptake ability. Notably, the C_2H_2 uptake value (146 cm³ g⁻¹) of **CPOC-107** is the highest among those reported for all POMs (Fig. 3d), including POCs,47,48 hydrogen-bonded organic frameworks (HOFs),49-52 covalent organic frameworks (COFs)53-56 and porous organic polymers (POPs).57-59

In contrast, under the same conditions, the CO2 absorbed capacities of CPOC-107 and CPOC-203 are only 100 and 70 cm³ g⁻¹ (Fig. 3a), much lower than their C₂H₂ uptake capacities under the same conditions. Such a result reveals that the affinity for C₂H₂ is stronger than that for CO₂ in both cages. In order to quantify the affinity (low-coverage heat of adsorption; Q_{st}) between the cage hosts and the guest gas molecules, their C2H2 and CO2 sorption isotherms at 273 K have also been measured (Fig. S12 \dagger). The $Q_{\rm st}$ values are calculated using adsorption isotherms at 273 and 298 K and fitted by a virial equation (Fig. S13–S16†). The calculated $Q_{\rm st}$ values for C_2H_2 were 39.1 and 34.9 kJ mol⁻¹ for CPOC-107 and CPOC-203, respectively, which are higher than those for CO2 with values of 32.8 and 23.2 kJ mol⁻¹, respectively (Fig. 3b). Such calculated results highly indicate the preferential sorption of C₂H₂ over CO₂ in both cages. Moreover, their gas selectivity values have been calculated using the widely studied ideal adsorbed solution theory (IAST), and the equimolar binary C2H2/CO2 for CPOC-107 is 2.7 at 298 K and 100 kPa, which is much higher than 1.9 for CPOC-203. Moreover, the higher C₂H₂ capacity and C₂H₂/CO₂ selectivity of CPOC-107 suggest that its separation ability for C₂H₂/CO₂ may be better than that of CPOC-203. Therefore, their separation potentials (Δq) are a comprehensive index to evaluate the separation effectiveness of adsorbents based on combining adsorption capacity and selectivity. The calculated Δq value for CPOC-107 is 2.67 mmol g⁻¹, and for CPOC-203 it is 1.30 mmol g⁻¹ (Fig. S17†), consistent with our guess.⁶⁰

Moreover, the detailed dispersion-corrected density functional theory (DFT-D) calculations for CPOC-107 were also carried out by loading CO2 and C2H2 molecules into its crystal structure for further optimization. The lowest-energy binding configurations of the final gas-loaded structures of CPOC-107 were calculated using DFT-D. In the gas-loaded CPOC-107, both C₂H₂ and CO₂ molecules were observed to preferentially reside around C4RA's cavities via weak Waals interactions (Fig. 3e and f). Specifically, for the C₂H₂ molecule, both hydrogen atoms were oriented toward the four C4RA's phenyl rings through H... π interactions at distances ranging from 2.74 to 3.61 Å. In contrast, their two hydrogen tails were observed to interact with the four C4RA's hydroxy groups through H···O interactions at distances ranging from 3.31 to 3.90 Å. For the CO₂ molecule,

one oxygen atom remained closer to the cage's window through O···H interactions at a distance of 3.34 Å. At the same time, the other one was oriented towards the bottom of C4RA through O···H interactions at distances ranging from 3.49 to 3.70 Å. The calculated static binding energies of C₂H₂ and CO₂ were -38.9 and $-31.1 \text{ kJ mol}^{-1}$, respectively, for **CPOC-107**. These binding energies and the hydrogen-bond number confirmed the stronger host-guest interactions between C2H2 and the cage compared to that of CO2, which is entirely consistent with our experimental observations.

Lab-scale fixed-bed breakthrough experiments have been performed under ambient conditions to make clear the separation performance of C₂H₂/CO₂ by using CPOC-107 and CPOC-203 as adsorbents. An equimolar CO₂/C₂H₂ gas mixture typically flowed over a packed column of the activated samples with a total flow of 2 mL min⁻¹ at 298 K and 1 bar. As shown in Fig. 4a, CO₂ passed through the packed column first to produce

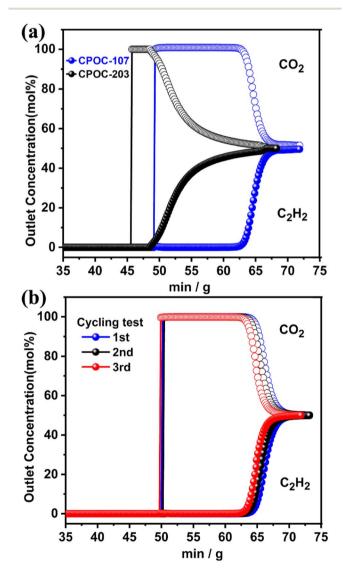


Fig. 4 (a) Experimental breakthrough curves for an equimolar mixture of C₂H₂/CO₂ at 298 K and 1 bar; (b) the recyclability of CPOC-107 under multiple mixed gas column breakthrough tests.

an outflow of pure gas containing no detectable C_2H_2 , and then C_2H_2 eluted following a substantial time-lapse for both CPOC materials. The breakthrough time values of **CPOC-107** and **CPOC-203** are \sim 13 and 5 min g⁻¹, respectively. The longer effective separation time of **CPOC-107** than **CPOC-203** suggested that the C_2H_2/CO_2 separation ability of **CPOC-107** is better than that of **CPOC-203**, consistent with the above-mentioned IAST and Δq results. An ideal separation material should possess recyclability performance to meet practical applications. To evaluate the durability, multiple cycling breakthrough tests for **CPOC-107** have been carried out under the same conditions. As displayed in Fig. 4b, the breakthrough time remains unchanged after three recycling experiments, indicating that **CPOC-107** is an auspicious C_2H_2/CO_2 separation system.

Conclusions

In summary, we presented two novel C4RA-based POCs with high nitrogen content (>14%), including [2 + 4] lantern-shaped CPOC-107 and [3 + 6] triangular prism-shaped CPOC-203. Both cages exhibit high surface areas (>1100 $\rm m^2~g^{-1}$), and high $\rm C_2H_2$ uptake capacity (>110 $\rm cm^3~g^{-1}$) at 298 K and 1 atm. Notably, the nitrogen content of CPOC-107 is up to 20.1%, and thus its $\rm C_2H_2$ uptake capacity under ambient conditions is up to 146 $\rm cm^3~g^{-1}$, which is the highest among those reported for POMs. Moreover, CPOC-107 can also efficiently separate $\rm C_2H_2/CO_2$ with a breakthrough time of 13 min g $^{-1}$. This work suggests that nitrogenrich POCs can be promising materials for safer $\rm C_2H_2$ storage, as well as $\rm C_2H_2$ purification application. Further studies are focusing on design and synthesis of functionalized POCs by introducing specific group sites for improving their gas storage and separation performances.

Conflicts of interest

There are no conflicts to declare.

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