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Robust 3D cage-like ultramicroporous network structure with high gas uptake capacities

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Abstract: We report a three-dimensional (3D) cage-like organic network (3D-CON) structure synthesized via the straightforward condensation of building blocks designed with gas adsorption properties. The 3D-CON can be prepared using an easy but powerful route, which is essential for commercial scale-up. The resulting fused aromatic 3D-CON exhibited a high Brunauer-Emmett-Teller (BET) specific surface area of up to 2247 m² g⁻¹. More importantly, the 3D-CON displayed outstanding low pressure hydrogen (H₂, 2.64 wt%, 1.0 bar and 77 K), methane (CH₄, 2.4 wt%, 1.0 bar and 273 K) and carbon dioxide (CO₂, 26.7 wt%, 1.0 bar and 273 K) uptake with a high isosteric heat of adsorption (H₂, 8.10 kJ mol⁻¹; CH₄, 18.72 kJ mol⁻¹; CO₂, 31.87 kJ mol⁻¹). These values are among the best reported for organic networks with high thermal stability (~600 °C).

With the growing consumption of fossil fuels and demand for clean energy, worldwide environmental problems and gas storage needs have become increasingly important^[1]. Organic porous materials (OPMs) are considered fundamentally valuable for capturing carbon dioxide $(CO_2)^{[2]}$ and the safe storage of clean energy resources^[1b] as well as explosive industrial gases (e.g., methane, $CH_4)^{[3]}$. Among clean energy sources, hydrogen (H₂) has long been regarded as one of the best alternatives to replace fossil fuels. It outperforms the others, because it possesses the highest heat of combustion, and water is the only by-product after combustion^[4].

Recent efforts have been undertaken to improve the design of porous materials and develop processes which result in intrinsic porosities, with the goal of enhancing H₂ and CH₄ storage, and CO₂ capture^[5]. A notable area of progress in porous materials research has been the evolution of porous high crystallinity metal-organic frameworks (MOFs), which are constructed from metal ions and organic linkers using reticular chemistry^[6]. Many of these interesting materials have been reported to have the highest surface area and gas uptake capacity among all porous materials^[6b, 7]. However, despite their huge flexibility in design and diversity of structure, MOFs inevitably contain a considerable amount of metal centers and relatively weak coordination bonds, which can badly hamper their applications^[8]. The poor stability problems might be resolved by substituting susceptible chemical coordination bonds with stronger covalent bonds, as has been demonstrated using covalent organic frameworks (COFs) and porous polymeric materials (PPMs)^[5a, 9]. OPMs (COFs and PPMs) are constructed from lightweight building blocks with strong covalent bonding, and have attracted a great amount of scientific and technological curiosity, while achieving critical importance in many applications such as gas storage, catalysis and gas separation^[5a, 9a]. These OPMs generally possess stable and perpetual porosity, synthetic diversity, low mass densities and physiochemical stability, which makes them immensely competitive in gas storage applications^[10]. Further vigorous and intensive efforts are underway to produce OPMs with higher surface areas via different

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strategies^[5a]. To fabricate stable OPMs, it is typically necessary to apply rigid building blocks (repeating units) that prevent the collapse of the framework and fill the volume space in a more periodic manner. OPM rigidity is usually created by fusing repeating aromatic units. However, while significant progress has been made in developing robust OPMs^[11], a better understanding of methods for fabricating rigid structures with permanent pores using light elements is still highly desired.

In the pursuit of high performance OPMs, we employed a strategy based on insights about the C₂N structure^[12], to realize a uniformly microporous robust three-dimensional (3D) cage-like organic network (CON) structure by the condensation of triptycene-based hexamine (THA)^[13] and hexaketocyclohexane (HKH) octahydrate (**Figure 1; S1, S2**;). The resulting 3D-CON has a high Brunauer-Emmett-Teller (BET) specific surface area as well as good thermal and physiochemical stability. In addition to its exceptional surface area, the as-produced 3D-CON outperformed highly porous MOFs in thermal and hydrothermal stability, and demonstrated great potential for H₂ and CH₄ storage as well as CO₂ capture.

The condensation reaction between THA and HKH spontaneously results in the irreversible formation of fused aromatic pyrazine rings without the use of an expensive catalyst. The structure of resulting material is highly stable in a practical range of thermal and physiochemical conditions.

Since 3D network structures result in a higher surface area compared to two-dimensional (2D) framework structures, a potential multifunctional candidate (monomer) with 3D topology was deliberately selected to synthesize the 3D-CON in this study. This [3+3] condensation with THA used to form the pyrazine rings has never been previously exploited. Triptycene is considered a promising unit for the synthesis of 3D-CONs with good gas storage performance, because it has a special 'internal free volume' feature^[14]. Moreover, the presence of periodic nitrogen atoms, aromatic phenyl and pyrazine rings in the 3D-CON are very useful for the adsorption and desorption of gases and other metals in the structure.

After completing the condensation reaction between the THA and HKH, a monolithic solid gel-like material was formed, and the reaction solvent (ethylene glycol) around the material was almost clean (Figure 2a, b), suggesting the complete digestion of the starting monomers. The subsequent Soxhlet extraction with water and methanol also confirmed the clean reaction (no monomer residues), with no color removal during the Soxhlet extraction process (Figure 2c). In the ethylene glycol and acetic acid mixture, the material looked black (Figure 2a, b). After the removal of ethylene glycol and acetic acid by washing with water, the material turned bright brown (Figure 2c) and the color remained after freeze drying, with an almost quantitative yield (Figure 2d).

The bright brown color is due to the breaking of aromaticity by a barrelene-like moiety. It is this barrelene-like core in the THA that is responsible for the formation of the stable and high surface area material. Once the condensation between ortho-diamines in the THA and diketones in HKH occurs, a fused aromatic pyrazine ring forms a stable and rigid linker between the THA and HKH units. The resulting





Figure 1. Schematic illustration of robust 3D-CON structure. Triptycene-based hexamine (THA) and hexaketocyclohexane (HKH) in ethylene glycol and acetic acid (3 M) mixture used to form the 3D-CON. The three structures on the right side are from the different view angle.

structure is highly rigid and retains a diamond-like structural stability, and also creates sufficient periodic micropores with greatly increased internal surface areas. In addition, solid-state ¹³C cross-polarization magic angle spinning (CP-MAS) nuclear magnetic resonance (NMR) spectroscopy also revealed that condensation of the starting monomers resulted in the complete transformation to pyrazine-linked fused aromatic rings (Figure 1). The solid-state ¹³C CP-MAS NMR spectrum revealed seven carbon peaks with chemical shifts of 53.5, 113, 124.1, 133.63, 143, 184 and 203 ppm, which can be assigned to the sp^3 bridge carbon (e), aromatic (sp^2) carbons (a, b, c, d, h) and the edge carbonyl (C=O) groups (f, g), respectively (Figure 2e). In order to investigate the long-range structure of the 3D-CON, powder X-ray diffraction (PXRD) and transmission electron microscopy (TEM) were performed. Although the peaks are broad due to the massive molecular size (~∞), the PXRD pattern still revealed some order in the structure (Figure 3a). The 3D-CON material does not exhibit long

range crystallographic ordering, but the locally ordered structure is expected to support a high surface area (*vide infra*).

Thermogravimetric analysis (TGA) revealed that the 3D-CON was thermally stable. When the temperature was raised from 50 to 600 °C, less than 4% weight loss occurred (Figure 3b). The 3D-CON is insoluble in common organic solvents such as DMF, alcohols, acetone and organic acids, even after stirring at ambient condition for a long time (~ month), indicating that the 3D-CON framework possesses high chemical stability. Transmission electron microscopy (TEM) images obtained from the dispersed sample revealed that the texture is sheet-like (Figure S3a), but at high resolution it exhibited uniform micropores (Figure S3b, c). The bulk morphologies of the 3D-CON were visualized with field-emission scanning electron microscopy (FE-SEM). The 3D-CON showed uniform micropores and a clean morphology. Its grain size

varied from tens to hundreds of micrometers, suggesting a fine microporous structure (Figure 3c, d). SEM coupled energy-dispersive spectroscopy (SEM-EDS) (Figure 3e) and SEM elemental mapping were used to corroborate the elemental composition of the 3D-CON. The presence of carbon (C), nitrogen (N) and oxygen (O) was confirmed by elemental mappings of the SEM-EDS analysis (Figure S4). Using different elemental analyses techniques, the chemical composition of the 3D-CON was determined, and the results are summarized in Table S1. The X-ray photoelectron spectroscopy (XPS) technique was used to probe the bonding nature of the 3D-

CON. The survey scan spectrum from the 3D-CON indicated the presence of C 1s, N 1s and O 1s without any other elements in the structure (Figure S5a). The peak, which appeared at 398.7 eV, was attributed to the characteristic sp²-hybridized nitrogen atoms in the 3D-CON structure. In the high resolution XPS spectrum, C 1s can be deconvoluted into 284.3, 285.2 and 288.7 eV, which are assignable to sp² C-C and sp² C-N in the aromatic ring, and the minor peak at 288.7 eV is attributed to the C-heteroatoms, e.g., sp² C=O and sp² C-NH₂ at the edges (Figure S5b). The N 1s peak shows one major peak at 398.7 eV for the pyrazine-like nitrogen in the structure (Figure S5c). The presence of the O 1s peak in the 3D-CON can be assigned to trapped moisture and/or oxygen in the pores and residual carbonyl (C=O) groups at the edges (Figure S5d).

The porous properties and surface area of the 3D-CON was investigated by subjecting the framework to nitrogen adsorption-desorption experiments at 77

K. Before the sorption isotherm measurements, the sample was preheated at 150 °C for 12 h under dynamic vacuum. As the sorption isotherm displayed in **Figure 3f**, the 3D-CON isotherm was fully reversible with an extremely steep nitrogen uptake in the low pressure range (0-0.01). This result reflects the permanent microporous nature of the material according to the IUPAC of relative pressure suggests that the pore surface has relatively classification^[15]. The small hysteresis observed over the whole range strong gas binding force. The sharp uptake at very low p/p_o is due to enhanced adsorbent-adsorptive interactions in the ultramicropores, resulting in micropore filling at very low p/p_o . The Brunauer-Emmett-Teller (BET) model was used on the isotherms at a relative p/p_o range (0.005-0.05) to generate the BET surface area. The specific surface area found to be 2247 m² g⁻¹ with a total pore volume of 1.06 cm³ g⁻¹ and an average pore diameter of 1.8 nm.



Figure 2. Digital images and NMR spectrum of 3D-CON. (a) Tilted Pyrex glass ampule showing the clean reaction solvent after completion of the reaction. (b) After draining the reaction solvent from the Pyrex glass ampule. (c) During Soxhlet extraction with water and methanol. (d) After freeze drying at -120 °C for four days under dynamic vacuum. (e) Solid-state ¹³C CP-MAS NMR spectrum.

Pore size distribution obtained using the nonlocal density functional theory (NLDFT), which gives a more closely matching adsorption isotherm, was centered at around 0.55 nm (**inset, Figure 3f**). The BET measurements suggest that the 3D-CON possesses a uniform pore size (narrow pore size distribution), which is well related to the dimensions of the structure. Thus, it is clear that this material has an ordered structure. Given the high specific surface area, microporous nature and narrow pore size distribution of 3D-CON material, the potential gas uptake capacities of small target molecules (H_2 , CH_4 and CO_2) were investigated.

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Figure 3. Structural characterization of the robust 3D-CON structure. (a) Powder X-ray diffraction (PXRD) pattern. (b) TGA curve of the as-prepared sample under nitrogen atmosphere after in situ activation at 150 °C in a TGA instrument, to remove any adsorbed guest molecules, at a ramping rate of 10 °C min⁻¹. (c, d) SEM images at different magnifications. (e) Energy dispersive X-ray spectroscopy (EDS) spectrum with corresponding SEM image, showing elemental contents. (f) Nitrogen adsorption and desorption isotherm at 77 K. The inset is the corresponding pore size distribution from the NLDFT approximation.

It has been reported that nitrogen containing microporous frameworks generally perform well as a material for storing small gas molecules^[14b]. The H₂ uptake capacity of the 3D-CON was then explored. The physiosorption storage of H₂ for energy applications is a promising approach to replace conventional fossil energy sources. The standard for on-board H₂ storage systems set by the US Department of Energy (DOE) by the year 2020 is 5.5 wt% and 40 g of H₂ L⁻¹. The H₂ adsorption-desorption isotherm of the 3D-CON was collected at 77 K with pressures up to 1.0 bar (Figure 4a; S6a). The highest H₂ uptake was 2.64 wt% (296.30 cm³ g⁻¹). This value was higher than most OPMs reported recently (Figure 4f; Table S2). This high H₂ uptake capacity can be attributed to the large surface area, which results from the combined effect of the 'internal free volume' of the triptycene-based 3D framework. The absence of hysteresis confirms the reversible physiosorption of H₂. In addition to exhibiting high surface area and stability, the 3D-CON met the DOE 2020 storage target at 77 K and 59 bar (Figure 4d; S7).

As the basic constituent of natural gas, methane (CH₄) is an alternative fuel that is cleaner than petroleum oils due to its lower carbon emissions. CH₄ furnishes more energy because of its higher hydrogen to carbon ratio. Although CH₄ is more abundant and economical than gasoline, for use in automobiles an efficient and secured storage is required. The storage capacity should allow the vehicle to drive more than several hundred kilometers before refueling. To further explore the different aspects that affect the CH₄ uptake in the 3D-CON, CH₄ adsorption assessments were performed at 273 K and 298 K in the low pressure range (**Figure 4b**; **S6b**). As shown in **Figure 4b**, the CH₄ uptake at 1 bar is 2.4 wt% (33.5 cm³ g⁻¹) at 273 K and 1.55 wt% (21.6 cm³ g⁻¹) at 298 K (**Figure S8a**). This CH₄ uptake of 3D-CON is among the best reported values in the literature (**Table S2**).

The discharge of CO_2 due to the combustion of fossil fuels is now considered responsible for abnormal climate change, rising sea levels and an irreversible increase in the acidity of the oceans, resulting in adverse impacts on the sea ecology and environment. These issues have inspired the pursuit of state-of-the-art CO_2 capture technology and materials. The 3D-CON material, with its well-defined microporous structure, holds great potential for CO_2 capture. Testing of the low pressure CO_2 uptake of the 3D-CON was performed, and it exhibited excellent CO_2 uptake at 1.0 bar, with a value of 26.7 wt% (137 cm³ g⁻¹) at 273 K (Figure 4c; S6c) and 17.15 wt% (88 cm³ g⁻¹) at 298 K for CO₂ (Figure S8b). Adsorption and desorption isotherms showed no hysteresis, indicating the CO2 uptake in 3D-CON was a reversible process; the interactions between the 3D-CON and CO2 are weak, and the framework can be regenerated without the application of heat^[16]. Again, the adsorption capacity values for 3D-CON were found to be among the highest compared to most of the OPMs previously reported, and were even competitive with the best reported MOFs under the same conditions (Table S2)[17]. To further understand the interactions and adsorption properties of gases with the 3D-CON, the isosteric heat of adsorption (Qst) for H2, CH4 and CO2 was calculated from the gas adsorption isotherms at two different temperatures by fitting the values into the Clausius-Clapeyron equation^[18]. The Q_{st} for hydrogen was examined by using the H₂ adsorption experiments at 77 and 87 K (inset in Figure 4a; S9). One of the reasons for a lower uptake of H₂ is the weak interaction of H₂ with the adsorbent, due to a lack of binding sites. The 3D-CON displayed a Qst value of 8.10 kJ mol⁻¹ for H₂ adsorption at low H₂ uptake. Then, the Q_{st} value decreased slowly as the hydrogen uptake increased, and reached a value of

7.25 kJ mol-1 (inset, Figure 4a). This value is at the higher end compared to the reported literature^[5a]. At the same time, the higher Q_{st} value in the low pressure region is indicative of the higher affinity toward 3D-CON, due to the narrow ultramicroporous pore size distribution and robust fused-aromatic framework. The Qst values of the 3D-CON toward CH4 and CO2 were estimated from the adsorption data collected at 273 and 298 K (inset, Figure 4b, c). In the low CH₄ uptake zone, the Q_{st} value (18.72 kJ mol⁻¹) implied a highly reversible (absence of hysteresis) CH₄ attraction toward 3D-CON. A strong binding energy is preferred for storing a large amount of CH₄ at low pressure (inset, Figure 4b). The magnitude of Qst was among the optimum heat of adsorption values reported for CH4 adsorption, allowing both adsorption and desorption to occur at a fast rate, which is desirable for a fuel storage system^[19]. In the low CO₂ uptake zone, the 3D-CON exhibited a large Q_{st} value (31.87 kJ mol⁻¹) implying high CO2 affinity toward the 3D-CON. The reason for the high Qst value observed in the low pressure region may be the strong interactions between CO2 and the 3D-CON, as well as the narrow ultramicroporosity (inset, Figure 4c). Furthermore, the 3D-CON showed a gradual decrease in Qst as a function of the quantity adsorbed. All of the Qst values (H2, CH4, CO2) were among the highest reported values for OPMs, and comparable to MOFs as well^[3a, 20]. The low pressure gas sorption studies showed that the 3D-CON was far from saturation at 1 bar pressure. Thus, to evaluate the high pressure gas uptake capacity, high pressure gas sorption analyses for H₂, CH₄ and CO_2 were also performed (Figure 4d). The H₂ uptake by the 3D-CON at 77 K revealed a gradual increase with pressure, and the H₂ storage at 59 bar reached 5.5 wt% (27.24 mmol g⁻¹) (Figure 4d; S7a) with saturation being reached at 70 bar (5.8 wt%). This exceeds the hydrogen uptake capacities of most OPMs having a similar surface area (Table S2). The high pressure uptake capacity of H₂ at 298 K was investigated (Fig. S10) and found to be 0.23 wt% at 38 bar (Verified high pressure gas adsorption certificate has been appended in the Supplementary Information). The high pressure CH₄ uptake capacity of the 3D-CON at 298 K and 84 bar was found to be 24.5 which is fairly comparable to the best reported values (Table S2). The CO2 storage was quite significant, reaching 70 wt% (15.90 mmol g⁻¹) at 298 K and 35 bar (Figure 4d; S7c). This value exceeds those of

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most reported OPMs (Table S2). The microporosity of the 3D-CON was further confirmed by measuring the argon (Ar) gas adsorption isotherm. Moreover, measuring Ar adsorption at 87 K has some advantages for micropore analysis, because Ar does not have a quadrupole interaction. Figure 4e shows the Ar isotherm measured for 3D-CON, which exhibits a rapid Ar uptake at a very low relative pressure, indicating the typical behavior of permanent microporosity, followed by a very small gradual increase in Ar uptake (P/Po = 0.05-0.9). The steep uptake at very low pressure is due to enhanced interactions in the narrow micropores, a typical type I isotherm, resulting in micropore filling at very low pressure. The pore size distributions were estimated by using NLDFT from the adsorption of the Ar isotherm (inset, Figure 4e), showing that the 3D-CON has only one major peak centered at 2.82 Å. This ultrahigh microporosity could be the reason of its exceptional H₂ uptake at low pressure, which should be associated with the robust fused-aromatic ring-based 3D-CON





structure, suggesting a promising potential for clean energy and environmental applications.

In summary, we have presented the design and synthesis of shape persistent cage-like organic network structure using a rigid shape persistent building block derived from triptycene hexamine. This robust structure is thermally stable, ultramicroporous and display outstanding gas adsorption property. The cage-like organic network structure exhibits a BET surface area up to 2247 m² g⁻¹ and high gas adsorption capacity. Owing to the small pore size distribution and aromatic fused ring system, the cage-like network structure exhibits excellent H₂ uptake of up to 2.64 wt % at 77K and 1.0 bar. Uptake for CO₂ is 26.7 wt % and CH₄ is 2.4 wt % at 273 K and 1.0 bar. This strategy of exploiting the effective condensation reaction to synthesize organic frameworks with high uptake capacity and high physiochemical stabilities hold huge promise for practical applications. CON demonstrates huge advance in the preparation of cage-like porous aromatic frameworks for high gas storage capacity.

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