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Three-Dimensional Triptycene-Based Covalent Organic Frameworks with ceq or acs Topology

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Supporting Information Placeholder

ABSTRACT: The growth of three-dimensional covalent organic frameworks (3D COFs) with new topologies has still been considered a great challenge due to limited high-connectivity building units. Here we report the design and synthesis of novel 3D triptycene-based COFs, termed JUC-568 and JUC-569, in the light of the deliberate symmetry-guided design principle. By combining a triangular prism (6-connected) node with a planar triangle (3-connected) or another triangular prism node, the targeted COFs adopt unreported **ceq** or non-interpenetrated **acs** topology, respectively. Both materials also show permanent porosity and impressive performance in the adsorption of CO_2 (~ 98 cm^3/g at 273 K and 1 bar) and CH_4 (~ 48 cm^3/g at 273 K and 1 bar), and especially in H_2 storage (up to 274 cm^3/g or 2.45 wt% at 77 K and 1 bar), which is highest among all porous organic materials reported to date. Thus, this research provides a promising strategy for diversifying 3D COFs based on complicated building blocks and promotes their potential applications in energy storage and environment-related fields.

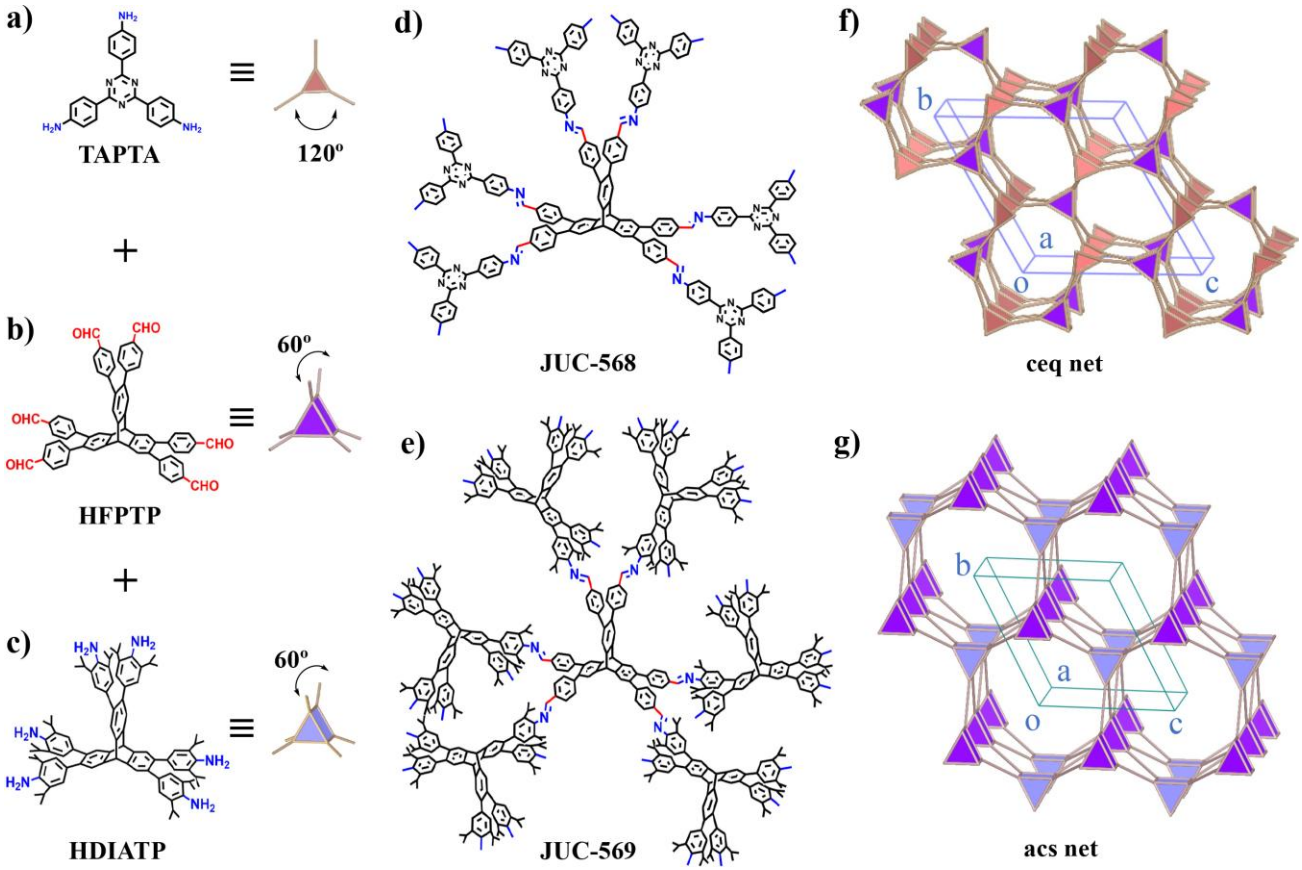
Covalent organic frameworks (COFs), an emerging family of crystalline porous polymers, are assembled from organic reactants by reversible covalent bonds.[1-5] Due to high surface areas, modular natures, and good thermal/chemical stabilities, COF materials have attracted considerable attention in gas storage/separation,[6-9] organic electronics,[10-14] heterogeneous catalysis,[15-20] and some other fields.[21-25] Over the past decade, most the reports were focused on conjugated two-dimensional (2D) sheets, in which the abundant building blocks allowed to establish well developed synthetic strategies.[5] By contrast, three-dimensional (3D) COFs are still less studied due to the scant availability of appropriate molecular building units and relatively complex structure determination.[4] Up till now, only very limited topologies in 3D COFs have been reported,[26-34] such as **dia**, **ctn,** and **bor**. Moreover, almost all know 3D COFs were constructed by using tetrahedral (4-connected) building blocks, including the derivatives of tetraphenylmethane, tetraphenylsilane, and adamantane, which has greatly confined the structural diversities and functionalization of 3D COFs.

Despite the above issues, 3D COFs are considered a remarkable platform for practical applications due to their unique features,[4] e.g., inter-connective porous structures, high specific surface areas, and easily accessible active sites. In principle, the employment of high-connectivity building units, such as triangular prism (6-connected) monomers, can set up new architectures in 3D COFs, proved by several cases that appeared recently. For example, we synthesized the first 3D large-pore COF, JUC-564, with **stp** topology constructed from a triptycene-based triangular prism monomer, which has the largest pore (43 Å) among 3D COFs and record-breaking low density (0.108 g cm^{-3}) in porous crystalline materials to date.[35] Subsequently, Cooper and coworkers also reported the first cage-based 3D COF, 3D-CageCOF-1, which is fabricated by an organic cage molecule as a triangular prism node and adopts a 2-fold interpenetrated **acs** topology.[36] It must be noted, however, that except for a few successful examples, 3D COFs based on high-connectivity monomers remain largely unexplored.

Herein we report the design and synthesis of new 3D COFs, termed JUC-568 and JUC-569 (JUC = Jilin University China), based on triptycene derivatives with a triangular prism node. By combining the triptycene-based monomer with a planar triangle (3-connected) node, JUC-568 shows a **ceq** topology. Besides, from the assembly of two similar triangular prism building units, JUC-569 adopts a non-interpenetrated **acs** topology. To the best of our knowledge, this study represents the first example of COFs with **ceq** or non-interpenetrated **acs** topology, which effectively promotes the structural varieties of 3D COFs. More importantly, owing to the high crystallinity and permanent porosity, these triptycene-based COFs demonstrate an impressive performance in the capture of CO_2 (~ 98 cm^3/g at 273 K and 1 bar) and CH_4 (~ 48 cm^3/g at 273 K and 1 bar), and particularly in H_2 adsorption (up to 274 cm^3/g at 77 K and 1 bar), which is higher than those from all porous organic materials reported so far.

Our strategy for preparing 3D COFs with new topologies is based on the considered symmetry-guided design principle. A triptycene derivative, 2,3,6,7,14,15-hexa(4′-formylphenyl)

Scheme 1. Schematic representation of the strategy for preparing 3D triptycene-based COFs[a]



[a]Molecular structures of TAPTA (a) as a planar triangle (3-connected) node as well as HFPTP (b) and HDIATP (c) as triangular prism nodes (6-connected) building units. Two 3D triptycene-based COFs, denoted as JUC-568 (d) and JUC-569 (e), are constructed by the condensation reaction of HFPTP and TAPTA or HDIATP. An expanded [6 + 3] connected network (**ceq** topology) in JUC-568 (f), and an expanded [6 + 6] connected network (**acs** topology) in JUC-569 (g).

triptycene (HFPTP, Figure 1b), can perfectly act as a highly symmetrical triangular prism node. After analyzing the Reticular Chemistry Structure Resource (RCSR) database,[37] we found that only one possible topology (**acs**) is available for such a 6-connected nod. At the same time, there are multiple feasible topologies for the combination of 6-connected and 3-connected build units, such as **ceq**, **sab** and **dag**. Therefore, the condensation of HFPTP and a planar triangle (3-connected) monomer, 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (TAPTA, Figure 1a), leads to an expanded [6 + 3] connected network (JUC-568, Figure 1d). Considering their link angles (60º for HFPTP and 120º for TAPTA), the targeted material is more likely to form the **ceq** topology (Figure 1f). Furthermore, to construct a pure 6-connected framework, another triangular prism monomer, 2,3,6,7,14,15-hexa(3′,5′-diisopropyl-4′-amino) triptycene (HDIATP, Figure 1c) was also designed. JUC-569 (Figure 1e) can be obtained from the combination of two triangular prism monomers, HFPTP and HDIATP, with the same 6-connected node and link angle of 120º, which tends to a non-interpenetrated **acs** topology (Figure 1g).

The synthesis of JUC-568 was carried out by the solvothermal reaction of HFPTP (22.0 mg, 0.025 mmol) and TAPTA (17.7 mg, 0.05 mmol) in a mixture of dioxane, mesitylene, and acetic acid, with heating at 120 ºC for 3 days; while JUC-569 was obtained by suspending HFPTP (22.0 mg, 0.025 mmol) and HDIATP (32.3 mg, 0.025 mmol) in a mixture of *o*-dichlorobenzene, *n*-butanol

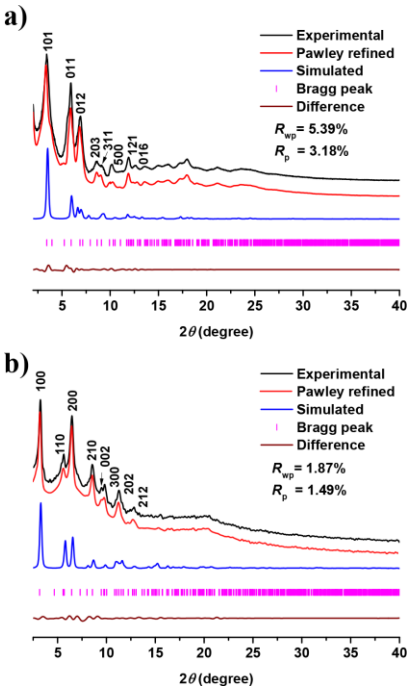


Figure 1. PXRD patterns of JUC-568 (a) and JUC-569 (b).

and acetic acid under 120 ºC for 3 days. The as-synthesized COFs were insoluble in water or common organic solvents, such as hexane, acetone, *N*,*N*-dimethylformamide, ethanol, and tetrahydrofuran. The morphologies of both COFs were characterized by scanning electron microscopy (SEM), which show isometric crystals with an average size of 0.2 μm (Figures S1 and S2). New COFs fourier transform infrared (FT-IR) spectra displayed peaks at 1598 cm^{-1} for JUC-568 and 1625 cm^{-1} for JUC-569, which are characteristic of C=N bond. At the same time, the depletion of peaks ascribed to C=O stretching vibration (1699 cm^{-1} for HFPTP) and N-H stretching vibration (~3323 cm^{-1} for TAPTA and ~3403 cm^{-1} for HDIATP) confirmed that aldehyde and amine groups had been transformed (Figures S3 and S4). Solid-state ^{13}C cross-polarization magic-angle-spinning (CP/MAS) NMR spectroscopy indicated that the presence of carbons from imine groups by the peaks at 158 ppm for JUC-568 and 162 ppm for JUC-569 (Figures S5 and S6). Thermogravimetric analysis (TGA) showed that both COFs had high thermal stability (~ 450 ºC, Figures S7 and S8).

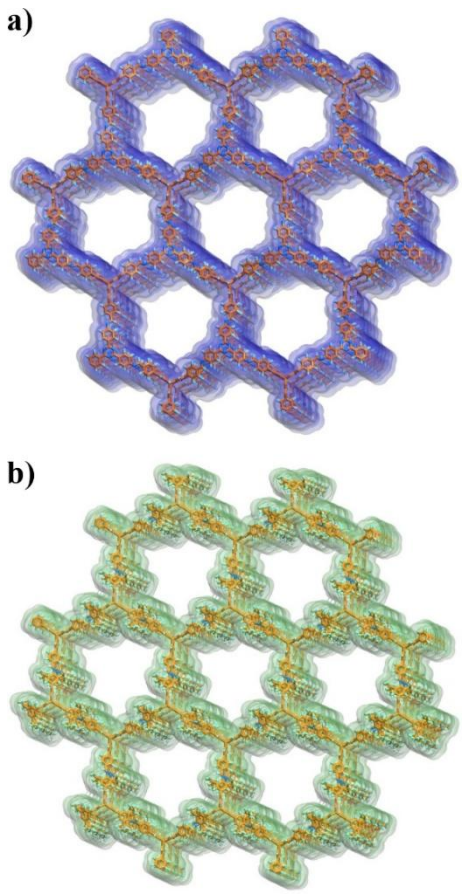


Figure 2. Extended structures of JUC-568 (a) and JUC-569 (b) viewed along *c*-axis.

The crystalline structures of 3D triptycene-based COFs were verified by the powder X-ray diffraction (PXRD) in conjunction with structural simulations (Figure 1). After a geometrical energy minimization by the Materials Studio software package,[38] the unit cell parameters were acquired with a = 49.570 Å, b = 50.541 Å, c = 15.618 Å and $\alpha = \beta = 90°$, $\gamma = 120°$ for JUC-568 based on a **ceq** net, while the unit cell parameters of JUC-569 with a non-interpenetrated **acs** net were $a = b$ = 31.110 Å, c = 18.468 Å and $\alpha = \beta = 90°$, $\gamma = 120°$. Moreover, the experimental PXRD patterns were accomplished by full profile pattern matching (Pawley) refinement. Peaks at 3.43, 5.92, 6.82, 8.65, 9.08, 10.21,11.86 and 12.70° for JUC-568 belong to the (101), (011), (012), (203), (311), (500), (121) and (016) Bragg peaks of the space group *Pm* (No. 6), and peaks at 3.24, 5.61, 6.47, 8.55, 9.48, 9.87, 11.30 and 12.84° for JUC-569 correspond to the (100), (110), (200), (210), (002), (300), (202) and (212) Bragg peaks of the space group *P-6* (No. 174). The calculated results can well match with those experimental ones with good agreement factors (Rp = 3.18% and ωRp = 5.39% for JUC-568; Rp = 1.49% and ωRp = 1.87% for JUC-569). In addition, we also tried alternative structures with different topologies, such as **sab** and **dag** net for JUC-568; however, there was a significant difference between the experimental and simulated PXRDs (Figures S9-11). In consideration of all these results, the obtained COFs were proposed to have the expected networks, **ceq** topology for JUC-568, and **acs** topology for JUC-569. Therefore, both COF materials show microporous cavities with ~1.98 nm for JUC-568 and ~1.94 nm for JUC-569 viewed along the *c*-axis (Figure 2).

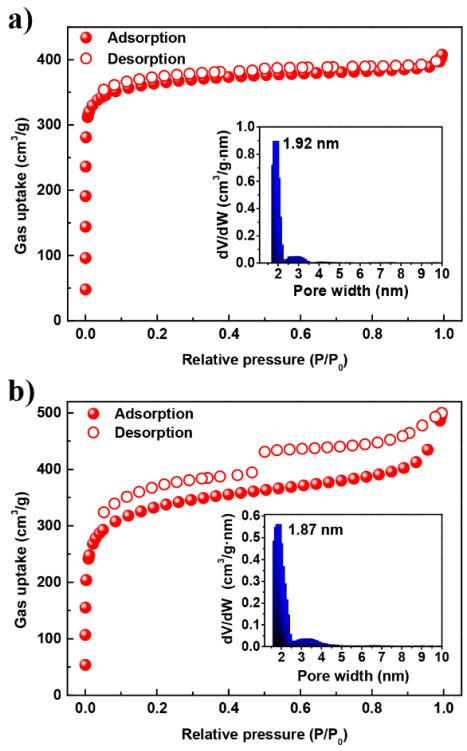


Figure 3. N_2 adsorption-desorption isotherms for JUC-568 (a) and JUC-569 (b) at 77 K. Inserts: corresponding calculated pore-size distribution.

N_2 adsorption measurements determined the permanent porosity and specific surface areas of 3D triptycene-based COFs at 77 K. As can be seen in Figure 3, both COFs showed a sharp increase at low pressure (below 0.1 P/P_0), which reveals their microporous nature. The presence of textural mesopores in JUC-569 led to the isotherm inclination in the 0.8-1.0 P/P_0 range. Slight desorption hysteresis was observed, which is a consequence of the agglomeration of COF crystals.[39] The Brunauer−Emmett−Teller (BET) specific surface areas were 1433 m^2/g for JUC-568 and 1254 m^2/g for JUC-569, respectively (Figures S9-12). The non-local density functional theory (NLDFT) was used to calculate the pore-size distribution, and both COFs showed microporous cavities with ~ 1.92 nm for JUC-568 and ~ 1.87 nm for JUC-569 (inserts in Figure 3), which are in good agreement with the pore sizes pre-

dicted from their crystal structures (~ 1.98 nm for JUC-568 and ~ 1.94 nm for JUC-569).

Furthermore, the uptakes of H_2, CH_4 and CO_2 under one aerosphere were studied to expand the potential of 3D triptycene-based COFs in the greenhouse gas capture and energy storage. As shown in Figure 4, JUC-568 had higher adsorption capacity of CO_2 (98 cm^3/g at 273 K and 81 cm^3/g at 298 K), CH_4 (48 cm^3/g at 273 K and 32 cm^3/g at 298 K), and H_2 (274 cm^3/g at 77 K) than JUC-569 (CO_2: 47 cm^3/g at 273 K and 31 cm^3/g at 298 K, CH_4: 19 cm^3/g at 273 K and 11 cm^3/g at 298 K, and H_2: 167 cm^3/g at 77 K). Remarkably, the H_2 storage capacity (274 cm^3/g or 2.45 wt%) of JUC-568 at 1 bar and 77 K is superior to those of porous organic materials (POMs) reported to date (Table S1), such as PPN-3 (1.58 wt%),[40] PAF-1 (1.66 wt%),[41] SPT-CMP1 (1.72 wt%),[42] and DL-COF-1 (2.09 wt%),[43] which can be attributed to the unique shape of triptycene as a rigid, fused-ring skeleton and three-fold symmetry building unit.[44]

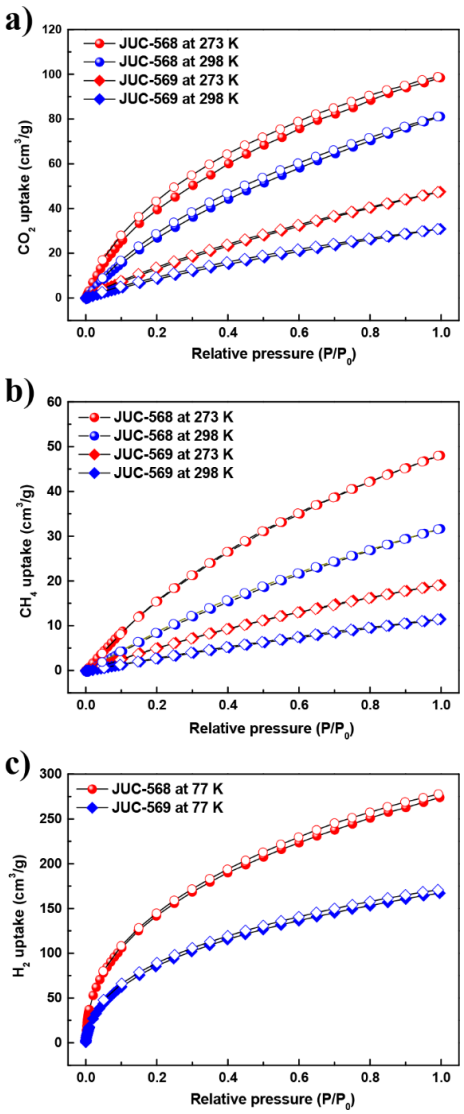


Figure 4. The uptakes of CO_2 (a), CH_4 (b), and H_2 (c) for JUC-568 and JUC-569 measured at different temperatures.

In summary, we have developed two 3D triptycene-based COFs, JUC-568 and JUC-569, with unreported **ceq** or non-interpenetrated **acs** topology, respectively. Noteworthy, JUC-568 possesses the permanent porosity and impressive performance in the uptakes of CO_2 (98 cm^3/g at 273 K and 1 bar) and CH_4 (48 cm^3/g at 273 K and 1 bar), and more importantly in H_2 storage (274 cm^3/g or 2.45 wt% at 77 K and 1 bar), which is highest among porous organic materials reported so far. Thus, this work offers a prospective strategy for constructing 3D COFs from high-connectivity building blocks and facilitates their future applications in energy storage and environment protection.

Supporting Information

Methods and synthetic procedures, SEM, FTIR, solid state ^{13}C NMR, TGA, BET plot, and unit cell parameters. This material is available free of charge via the internet at http://pubs.acs.org.

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Author Contributions

[§]H.L. and F.C. contributed equally to this work.

Notes

The authors declare no competing financial interests.

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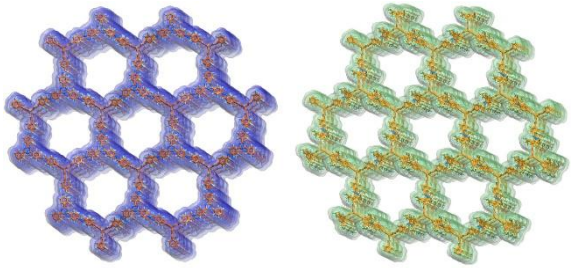
TOC Graphic:



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