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Three-Dimensional Triptycene-Functionalized Covalent Organic Frameworks with hea Topology for Hydrogen Adsorption

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Supporting Information Placeholder

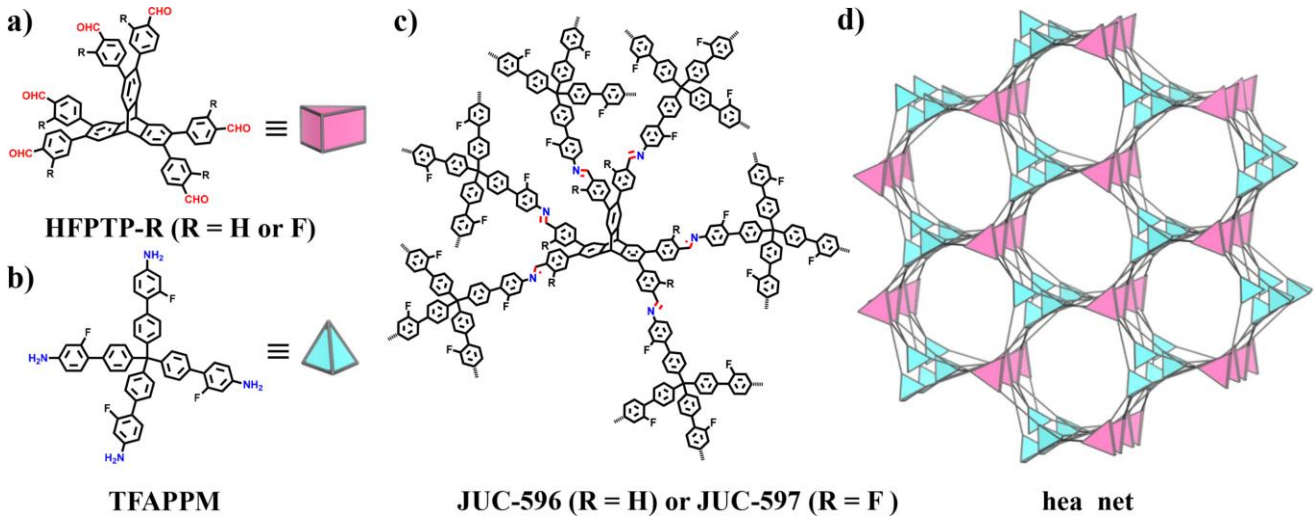
ABSTRACT: Owing to the confined building blocks and difficulty in structural identification, it remains a tremendous challenge to directionally design and synthesize three-dimensional covalent organic frameworks (3D COFs) with predetermined topologies. Herein, we report the first two cases of 3D COFs with the **hea** topology, termed JUC-596 and JUC-597, by using the combination of tetrahedral and triangular prism building units. Due to the presence of triptycene functional group, JUC-596 exhibits an exceptional performance in the H_2 adsorption up to 356 cm^3/g (or 3.18 wt%) at 77 K and 1 bar, which is higher than previous benchmarks from porous materials reported so far, including porous carbon, metal-organic frameworks, amorphous porous polymers, and other COFs. Furthermore, the strong interaction between H_2 and COF materials is validated through the DFT theoretical calculation. This work represents a triumphant example of rational design of functional COFs based on a reticular chemistry guide and demonstrates its promising application in clean energy storage.

Covalent organic frameworks (COFs), [1-4] an emerging class of crystalline porous polymers, are composed of organic reactants and connected by covalent bonds. Since the pioneering study of Yaghi in 2005,[1] these materials have attracted considerable attention due to their relatively defined structure, low density, high specific surface area, and stability.[5-7] According to the connectivity and symmetry of monomers, COFs are mainly divided into two-dimensional (2D) structures with π-π stacking layers and straight channels and three-dimensional (3D) networks with interconnected porous structures.[8-10] Up to now, the preparations of 2D COFs have been well established owing to the multifarious building units, such as [3 + 3], [4 + 4], and [6 + 2].[11-13] On the contrary, the development of 3D architectures is relatively slow, and the primary reasons are as follows: (1) limited building blocks and reversible bound types lead to structural simplification, (2) the formation of high-quality single crystals is difficult due to relatively low reversibility, and (3) the characterization technique analysis is restricted, and thus the structures are hard to determine.[14-17] At the same time, it is essential to develop 3D COFs because of the irreplaceable advantages in higher surface areas and pore volume and more available active sites than 2D counterparts.

To date, the building blocks of 3D COFs dominantly incorporate the derivatives of tetraphenylmethane, tetraphenylsilane, adamantine, and twisting monomers, which are on the basis of the tetrahedral (4-connected, T_d) geometry.[18-20] Because of these confined building units, there are only limited topologies of 3D COFs reported, such as **dia**, **ctn**, **bor**, and **pts.**[21-29] Recently, a few successful attempts about obtaining higher valency (> 4 points of extension) have been established. For instance, Cooper et al. reported a 3D cage-based COF with a twofold interpenetrated **acs** topology, which was constructed by an organic cage molecule as a 6-connected node.[30] It is worth mentioning that Yaghi and coworkers designed a series of organic BPA linkers based on boron and phosphorus, which self-condensed into cubic (8-connected) units and polycubane COFs with the **bcu** topology.[31] By employing triptycene moieties as triangular prism (6-connected, D_{3h}) nodes, our group also developed 3D skeletons with different topologies, such as JUC-564 with **stp** topology,[32] JUC-568 with non-interpenetrated **ceq** topology,[33] and JUC-569 with non-interpenetrated **acs** topology.[33] Although there are some successful examples above, this is in stark contrast to more than 2000 three-periodic structures and rich nodes with up to 24 points of extension in the database of Reticular Chemistry Structure Resource (RCSR).[34] In addition, limited structures also restricted the wide use of COF materials because the properties are determined by their structures. Hence, to expand the structural diversity of 3D COFs is urgent but still remains a great challenge.

Herein, we successfully design and synthesize two novel 3D COFs, termed JUC-596 and JUC-597 (JUC = Jilin University China), based on a derivative of tetraphenylmethane

Scheme 1. A strategy for constructing JUC-596 and JUC-597 with hea topology[a]



[a]Molecular structures of HFPTP-R (R = H or F), a) as a 6-connected 3D-D_{3h} building block and TFAPPM (b) as a synergistic 4-connected 3D-T_d monomer. Two novel 3D COFs, JUC-596 and JUC-597 (c), constructed from the condensation reaction of HFPTP-R and TFAPPM. An extended **hea** net (d) for both COFs.

and triptycene-based monomers with different substituents. With the combination of tetrahedral and triangular prism building units, both products are proved to have the **hea** topology, which is the first case in 3D COFs. Remarkably, because of the existence of triptycene functional moiety, JUC-596 shows an excellent behavior in the H_2 uptake as high as 356 cm^3/g (or 3.18 wt%) at 77 K and 1 bar, which is superior to those of reported porous materials, such as porous carbon, metal-organic frameworks (MOFs), porous polymers, and other COFs. Furthermore, a theoretical study based on the DFT calculation reveals the strong interaction between H_2 and COF frameworks, resulting in an extremely high H_2 adsorption.

A strategy to deal with the problem in the construction of 3D novel COFs has been guided by reticular chemistry based on the topology structures and selection of building units.[35] In principle, the combination of both robust building blocks, tetrahedral (4-connected) and triangular prism (6-connected) monomers, will be beneficial to explore the structural diversity of 3D COFs. However, this branch is still not investigated. To achieve this strategy, two triptycene ramifications, 2,3,6,7,14,15-hexa(4′-formylphenyl) triptycene (HFPTP-H) and 2,3,6,7,14,15-hexa(3′-fluorine-4′-formylphenyl) triptycene (HFPTP-F) were designed as desired 3D-D_{3h} trigonal prismatic arrangements (Scheme 1a), and simultaneously tetra [(2-fluoro-4-aminophenyl) phenyl] methane (TFAPPM, Scheme 1b) as a tetrahedral 3D-T_d configuration was chosen. Thus, the condensation of TFAPPM with HFPTP-H or HFPTP-F leads to two expanded [6 + 4] connected frameworks, JUC-596 and JUC-597, respectively (Scheme 1c). Although such configuration makes them prospective candidates to construct several 3D topologies, such as **fsi**, and **tpt** (Figure S1), these obtained materials tend to be a **hea** network according to the similar bond angle (~ 60°) of the triptycene derivatives between the monomer and final product (Scheme 1 d).

The syntheses of both COFs were carried out by the imine formation reaction of HFPTP-R and TFAPPM in a 5:5:1 (v/v/v) mixture of mesitylene/1,4-dioxane/acetic acid at 120 °C for 3 days. Scanning electron microscopy (SEM) images illustrated isometric microcrystals for both COFs (Figure 1a and 1b). The FT-IR spectra demonstrated the appearance of new C=N peaks (JUC-596 at 1629 cm^{-1} and JUC-597 at 1632 cm^{-1}) and the disappearance of C=O (JUC-596 at 1700 cm^{-1} and JUC-597 at 1693 cm^{-1}) and N-H (at ~3390 cm^{-1}) stretching vibration bands, manifesting the successful polymerization of aldehyde and amine (Figures S2 and S3). The ^{13}C cross-polarization/magic-angle-spinning (CP/MAS) NMR spectra further certified the formation of carbons from characteristic imine groups (159 ppm for JUC-596 and 160 ppm for JUC-597, Figures S4 and S5). In addition, thermal gravimetric analysis (TGA) uncovered that both COFs could be steady up to approximately 400 °C (Figures S6 and S7).

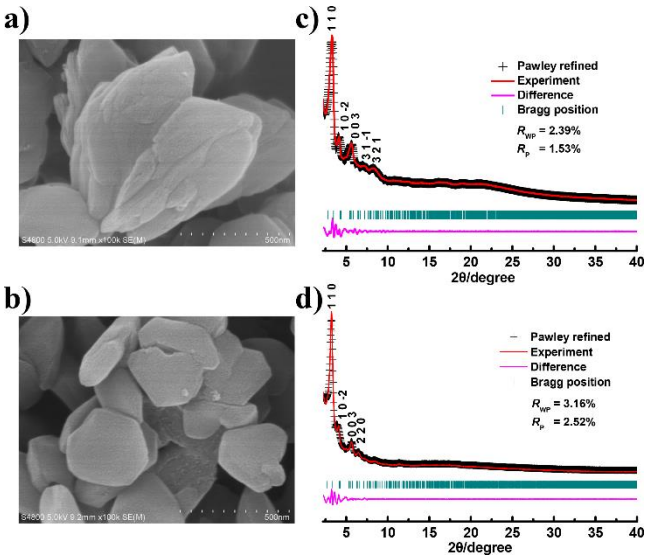


Figure 1. SEM images of JUC-596 (a) and JUC-597 (b), and PXRD patterns of JUC-596 (c) and JUC-597 (d).

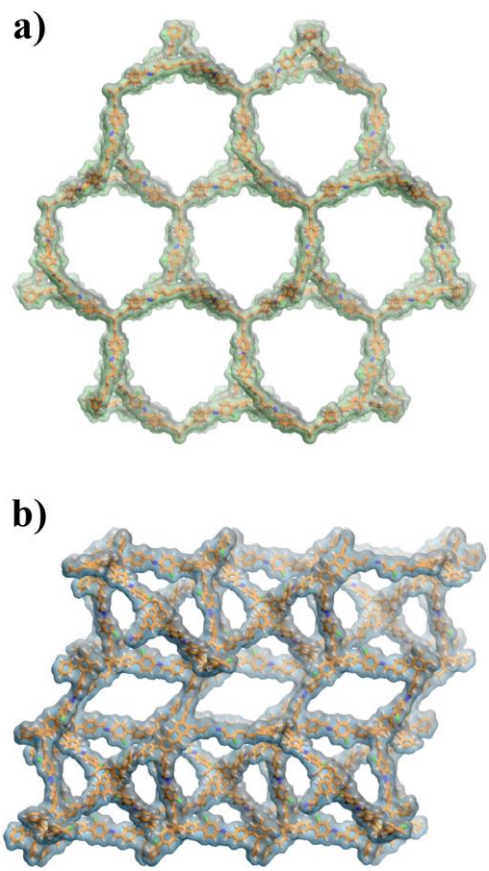


Figure 2. Expanded structure of JUC-596 observed along *c* axis (a) and *a* or *b* axis (b). C, yellow; H, white; F, green, N, blue.

The crystalline structures were ascertained via the experimental and simulated powder X-ray diffraction (PXRD). The simulated structures were operated by the Materials Studio software package (Tables S2 and S3).[36] Given the geometry of the monomers, we built up the frameworks of both COFs on the basis of the same non-interpenetrated **hea** net with the *R*32 space group (No. 155) from the RCSR. As can be seen from Figure S8 and S9, the experimental PXRD patterns of both COFs can match well with the calculated ones. Furthermore, a full profile pattern matching from Pawley refinement was conducted. As shown in Figure 1c, JUC-596 revealed dominant peaks at 3.29°, 4.11°, 5.61°, 7.10° and 8.31° corresponding to the (1 1 0), (1 0 -2), (0 0 3), (3 1 -1) and (3 2 1) facets, respectively. An analogical PXRD pattern (Figure 1d) was discovered for JUC-597 with characteristic peaks at 3.21° (1 1 0), 4.07° (1 0 -2), 5.66° (0 0 3) and 6.46° (2 0 0). The refinement results yielded the similar unit cell with parameters of $a = b = 54.328$ Å, $c = 49.246$ Å, $\alpha = \beta = 90°$, and $\gamma = 120°$ for JUC-596 ($a = b = 54.017$ Å, $c = 48.985$ Å, $\alpha = \beta = 90°$, and $\gamma = 120°$ for JUC-597) and good agreement factors (R_p = 1.53% and R_{wp} = 2.39% for JUC-596 as well as R_p = 2.52%, R_{wp} = 3.16% for JUC-597). We also considered the alternative architectures, such as the **fsi** net with the space group of *I*bam and the **tpt** net with the space group of *P*6/mcc. However, these simulated patterns did not meet with the experimental ones (Figures S8 and S9; Tables S4-S7). In light of the above results, both COFs were proposed to have the expected 3D framework with the **hea** topology and two kinds of cavities with the sizes of 1.62 nm along the *a* or *b* axis and 2.62 nm along the *c* axis, respectively (Figures 2 and S10).

In order to evaluate the porosity of JUC-596 and JUC-597, N_2 sorption measurements were conducted at 77 K. As shown in Figure 3, the isotherms of both COFs exhibited a sharp uptake at a low pressure of $P/P_0 < 0.05$, accompanied by a slight inclination in the 0.05-0.2 P/P_0 range, in which the Brunauer-Emmett-Teller (BET) specific surface areas were calculated to be 1934 m^2/g for JUC-596 and 1857 m^2/g for JUC-597, respectively (Figures S10 and S11). Furthermore, the pore size distributions were analyzed with nonlocal density functional theory (NLDFT), giving two dominated pores with sizes of 1.61 and 2.60 nm for JUC-596 and 1.58 and 2.59 nm for JUC-597, which are in accordance with the simulated results of the proposed models. Furthermore, the CH_4 and CO_2 adsorption performance of both materials was also investigated (Figure 4a and 4b). The results indicated that the maximum adsorption amount of JUC-596 was 84 cm^3/g at 273 K and 53 cm^3/g at 298 K for CO_2 as well as 31 cm^3/g at 273 K and 14 cm^3/g at 298 K for CH_4. Similarly, JUC-597 had a slightly lower adsorption capacity of CO_2 (70 cm^3/g at 273 K and 31 cm^3/g at 298 K) and CH_4 (25 cm^3/g at 273 K and 8 cm^3/g at 298 K).

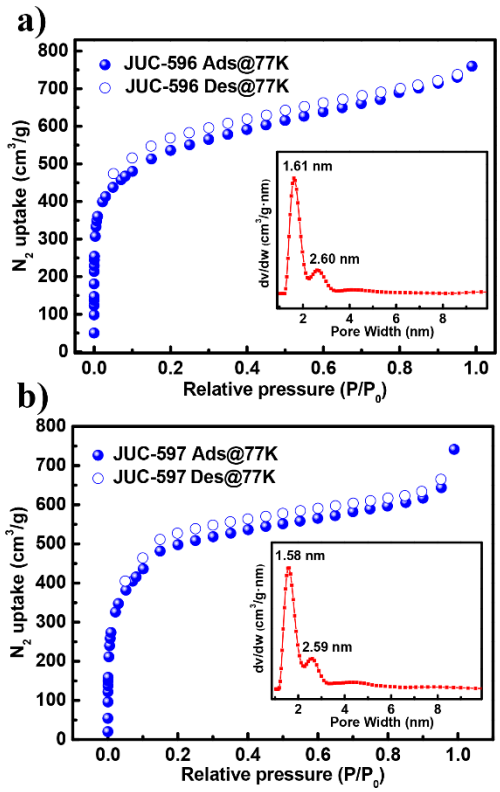


Figure 3. N_2 adsorption-desorption isotherms of JUC-596 (a) and JUC-597 (b) at 77 K. Inset: their pore-size distributions.

It is considered that triptycene and its derivatives can be used as an excellent functional unit for H_2 adsorption.[37]Thus, the H_2 adsorption behavior of both COFs was explored under 1 atm (Figure 4c). Impressively, compared with JUC-597 (155 cm^3/g at 77 K and 105 cm^3/g at 87 K for H_2), JUC-596 showed a remarkable capacity in H_2 adsorption with 356 cm^3/g at 77 K and 224 cm^3/g at 87 K, respectively. Remarkably, the H_2 storage capacity of JUC-596 at 1 bar and 77 K (356 cm^3/g or 3.18 wt%) is higher than those of reported porous materials under approximate test conditions (Figure 5 and Table S1),

such as AC-M (325 cm^3/g or 2.9 wt%),[38] PCN-12 (341 cm^3/g or 3.05 wt%),[39] Trip (*i*-Pr)-PIM (205 cm^3/g or 1.83 wt%),[40] and JUC-568 (274 cm^3/g or 2.45 wt%),[33] owing to the special aspect of functional triptycene group having high fractional free volume and more available sites in the 120° dihedral region and between the extended benzene rings.[41]

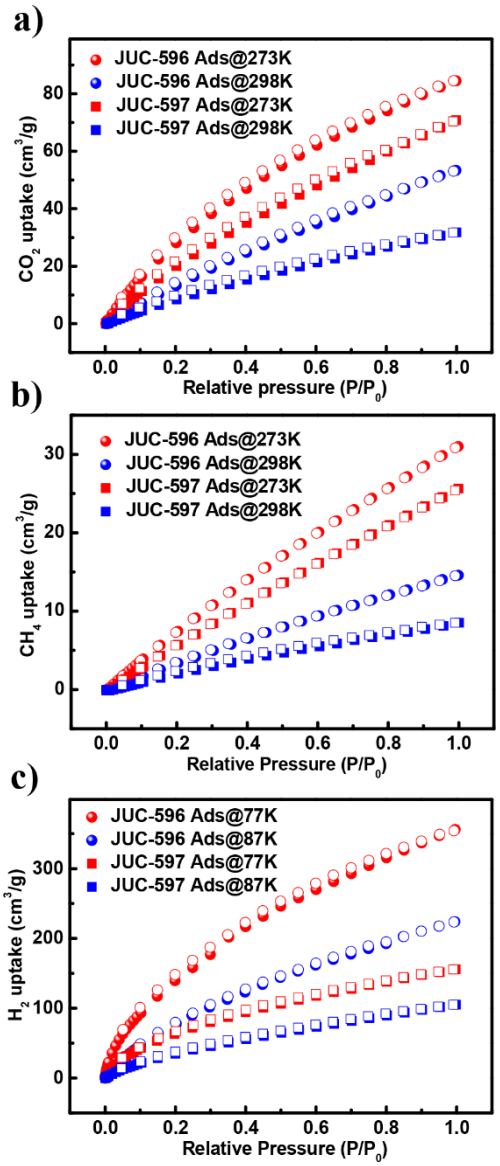


Figure 4. The uptakes of CO_2 (a), CH_4 (b) and H_2 (c) for JUC-596 and JUC-597 measured at different temperatures..

Furthermore, we explored the interaction behavior between H_2 and COF fragments through the DFT theoretical calculation using ORCA program package with the B97-3c method.[42,43] Notably, three specific adsorption sites were found on these triptycene-functionalized COFs. For the triptycene fragment, the dihedral region showed a strong interaction with hydrogen with energy of -1.48 kcal/mol for JUC-596 and -1.46 kcal/mol for JUC-597, respectively (Figure S13). Meanwhile, two adjacent phenyl groups of the triptycene fragment also interactes with hydrogen with energy values of -1.12 kcal/mol for JUC-596 and -0.95 kcal/mol for JUC-597 (Figure S14). In addition, the preferential hydrogen adsorption site for the TFAPPM fragment was on top of the benzene rings joined to the sp^3 carbon, showing an interaction energy of -1.26 kcal/mol (Figure S15). Therefore, compared with JUC-597, the higher storage capacity of H_2 in JUC-596 can be attributed to the high adsorption energy of H_2 based on these specific adsorption sites of both materials. For comparison, we also calculated the interaction energy between H_2 and tetraphenyl methane (TPM) with a tetrahedral geometry, a typical fragment of 3D COFs, such as COF-300 and COF-320. However, only one interaction was observed with an energy of -1.16 kcal/mol, which means that such materials potentially possess a low storage capacity of H_2 (Figure S16).

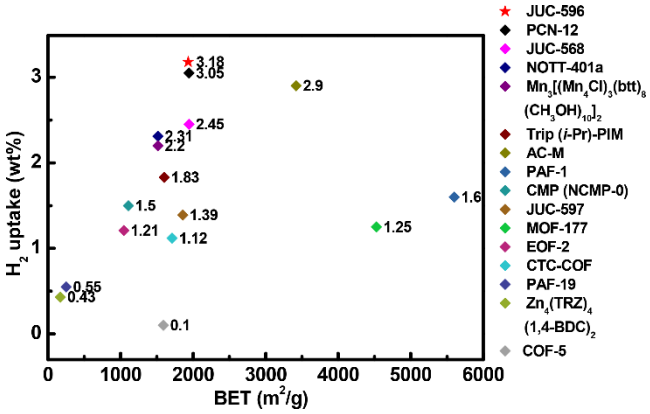


Figure 5. A summary of H_2 adsorption at 1 atm and 77 K versus BET surface area in porous materials reported so far.

In conclusion, two 3D triptycene-based COFs, JUC-596 and JUC-597, were successfully prepared by adopting the association of tetrahedral (TFAPPM) and triangular prism (HFPTP-H or HFPTP-F) building units. Based on these designs, the obtained materials showed a new non-interpenetrated **hea** net in COFs for the first time. Remarkably, JUC-596 displayed a considerable performance in the adsorption of H_2 as high as 3.18 wt% (356 cm^3/g) at 77 K and 1 bar, which is uppermost, comparing with other porous materials published so far, such as porous carbon, MOFs, porous polymers, and COFs. The DFT theoretical calculation further demonstrated the higher H_2 storage capacity of JUC-596 was due to the lower H_2 adsorption energy based on three specific adsorption sites in JUC-596. Therefore, this work broadens the diversities of 3D COF structures guided by reticular chemistry and points that functional COF materials will be a promising candidate for clean energy storage and fuel cell applications.

Supporting Information

Methods and synthetic procedures, FTIR, solid state ^{13}C NMR, TGA, BET plot, DFT theoretical calculations 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

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

Notes

The authors declare no competing financial interests.

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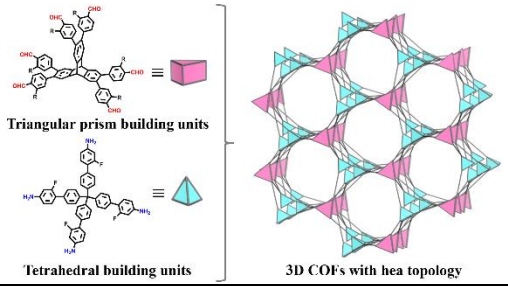
TOC Graphic:


Triangular prism building units
Tetrahedral building units
3D COFs with hea topology