

# Three-Dimensional Large-Pore Covalent Organic Framework with **stp** Topology

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*Supporting Information Placeholder*

**ABSTRACT:** Three-dimensional (3D) covalent organic frameworks (COFs) are excellent porous crystalline polymers for numerous applications, but their building units and topological nets have been limited. Herein we report the first 3D large-pore COF with **stp** topology constructed with a 6-connected triptycene-based monomer. The new COF (termed JUC-564) has high surface area (up to 3300 m<sup>2</sup> g<sup>-1</sup>), the largest pore (43 Å) among 3D COFs, and record-breaking low density in crystalline materials (0.108 g cm<sup>-3</sup>). The large pore size of JUC-564 is confirmed by the incorporation of a large protein. This study expands the structural varieties of 3D COFs as well as their applications for adsorption and separation of large biological molecules.

Covalent organic frameworks (COFs),<sup>1-5</sup> a remarkable class of organic porous crystalline materials with high surface areas and promising stabilities, have attracted wide interests in varied fields including gas adsorption and separation,<sup>6-9</sup> catalysis,<sup>10-15</sup> optoelectronics,<sup>16-20</sup> and some others.<sup>21-26</sup> Over the past decade, most researches have been focused on two-dimensional (2D) COFs with eclipsed AA stacking modes.<sup>1-4</sup> Three-dimensional (3D) COFs are considered as ideal platforms for abundant uses because of their interconnected channels, superior surface areas, and fully exposed active sites.<sup>27-36</sup> However, only few topologies are available for 3D COFs so far, such as **ctn**, **bor**, **dia**, and **pts**, and almost all of them are based on tetrahedral building blocks, which have extremely limited the structural diversities of 3D COFs.<sup>5</sup> Interestingly, Wang, Feng and co-workers synthesized the first 3D anionic COFs with **rra** topology, CD-COFs, in which each boron atom is joined to four  $\gamma$ -cyclodextrin struts, and each  $\gamma$ -cyclodextrin is connected to eight boron atoms.<sup>37</sup> Thomas, Roeser and co-workers have recently demonstrated a novel 3D anionic silicate COF adopting a two-fold interpenetrated **srs-c** topology by reticulating dianionic hexacoordinate [SiO<sub>6</sub>]<sup>2-</sup> nodes with 3-connected triphenylene building blocks.<sup>38</sup> In principle, the employment of new building units, such as 6-connected monomer with *D*<sub>3h</sub> geometry, can establish novel architectures in 3D COFs; however, its realization has remained an enormous challenge.

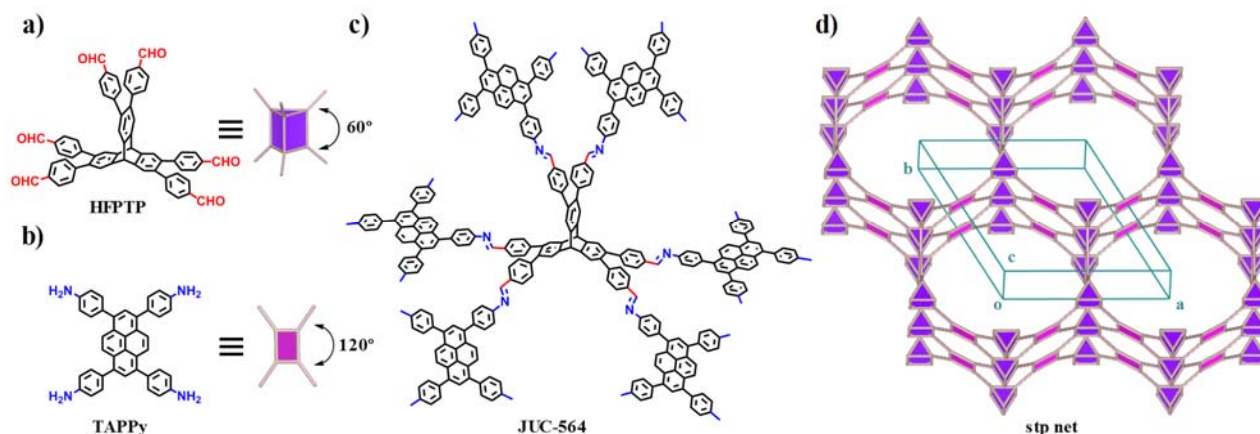
Herein, we for the first time reported a 3D triptycene-based COF with large pores and **stp** topology. This novel COF, termed JUC-564 (JUC = Jilin University China), was constructed from a stereoscopic 6-connected triptycene-based building unit,

2,3,6,7,14,15-hexa(4'-formylphenyl)triptycene (HFPTP). As a result, JUC-564 showed high surface area (> 3300 m<sup>2</sup> g<sup>-1</sup>), the largest pore (43 Å) among 3D COFs, and the lowest density among all crystalline materials (0.108 g cm<sup>-3</sup>). Moreover, due to the presence of large pores, JUC-564 showed a favorable adsorption of a large protein with suitable dimensions.

Structural identification is one of major roadblocks for developing 3D frameworks with new topologies. Different from other crystalline porous materials, such as aluminosilicate molecular sieves<sup>39</sup> and metal-organic frameworks (MOFs),<sup>40,41</sup> single crystals are not common in COFs and their crystal structures are mostly obtained through powder X-ray diffraction (PXRD) patterns along with structural simulation. Usually, more than one possible topology is available for combinations of multiple building block geometries. After investigating RCSR database carefully, we fortunately found that only definite **stp** topology is available for [6 + 4] (3D-*D*<sub>3h</sub> + 2D-*D*<sub>2h</sub>) nets (Scheme 1), facilitating the structural determination of the target products.<sup>42</sup> To implement this strategy, we firstly designed a 6-connected 3D-*D*<sub>3h</sub> building block, HFPTP, based on a triptycene moiety with a link angle of 60° (Scheme 1a). Condensation of HFPTP and a synergistic 4-connected 2D-*D*<sub>2h</sub> monomer with a link angle of 120° (1,3,6,8-tetra(4-aminophenyl)pyrene, TAPPy, Scheme 1b) leads to an expanded [6 + 4] connected network (JUC-564, Scheme 1c and 1d). To the best of our knowledge, JUC-564 represents the first COF with a 6-connected 3D-*D*<sub>3h</sub> building block and a **stp** net.

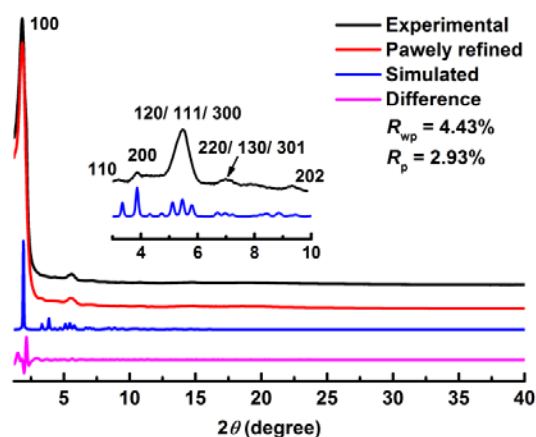
The synthesis of JUC-564 was carried out through traditional solvothermal approach by suspending HFPTP and TAPPy in a mixed solvent of mesitylene and dioxane with the presence of 6 M acetic acid followed by heating at 120 °C for 3 days. Complementary methods have been employed for detailed structural determination and characterization. Scanning electron microscopy (SEM, Figure S1) and transmission electron microscopy (TEM, Figure S2) images revealed isometric microcrystals. Fourier transform infrared (FT-IR) spectrum exhibited a new adsorption corresponding to the characteristic of the C=N bond at 1628 cm<sup>-1</sup>. The concomitant reducing of the C=O stretching (1700 cm<sup>-1</sup> for HFPTP) and N-H stretching (3312 cm<sup>-1</sup>

**Scheme 1. Strategy for constructing JUC-564 with stp topology<sup>a</sup>**



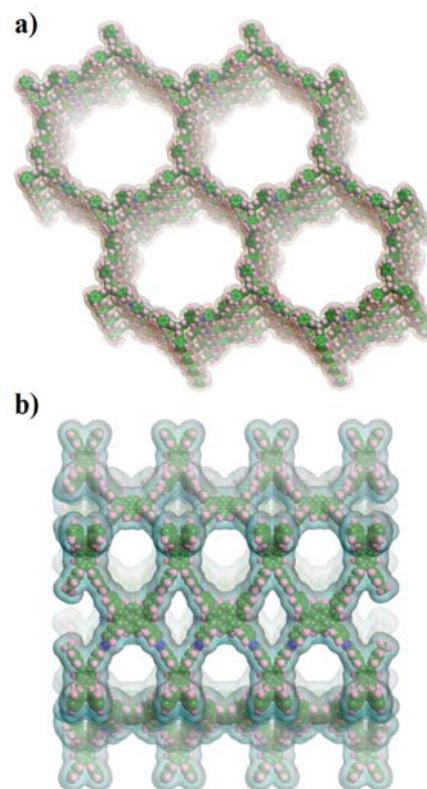
<sup>a</sup>Molecular structures of HFPTP (a) as a 6-connected 3D- $D_{3h}$  core building block and TAPPy (b) as a synergistic 4-connected 2D- $D_{2h}$  monomer. A novel 3D COF, JUC-564 (c), constructed from the condensation reaction of HFPTP and TAPPy. A expanded **stp** net (d) for JUC-564.

for TAPPy) confirmed the transformation of aldehyde and amine groups (Figure S3). The solid-state  $^{13}\text{C}$  cross-polarization magic-angle-spinning (CP/MAS) NMR spectroscopy further verified the presence of imine groups by the peak at 157 ppm (Figure S4). High thermal stability ( $\sim 450^\circ\text{C}$ ) was observed by thermogravimetric analysis (TGA, Figure S5).



**Figure 1.** PXRD pattern of JUC-564.

The crystal structure was resolved by PXRD measurements in conjunction with structural simulations (Figure 1). After a geometrical energy minimization of JUC-564 by the Materials Studio software package on the basis of **stp** net,<sup>43</sup> the simulated PXRD pattern was in good agreement with the experimental one. Furthermore, the full profile pattern matching (Pawley) refinement was conducted based on experimental peaks at  $1.93, 3.34, 3.87, 5.47, 6.96,$  and  $9.46^\circ$  corresponding to (100), (110), (200), (120) (or (111) and (300)), 220 (or (130) and (301)) and (202) Bragg peaks of space group  $P6/m$  (No. 175). The refinement results can match well with the observed ones with negligible difference and good agreement factors ( $R_p = 2.93\%$  and  $\omega R_p = 4.43\%$ ). The refinement results yield a unit cell with parameters of  $a = b = 52.8112 \text{ \AA}$ ,  $c = 20.4914 \text{ \AA}$ ,  $\alpha = \beta = 90^\circ$ , and  $\gamma = 120^\circ$ , which are very similar to those of suggested model ( $a = b = 52.7911 \text{ \AA}$ ,  $c =$

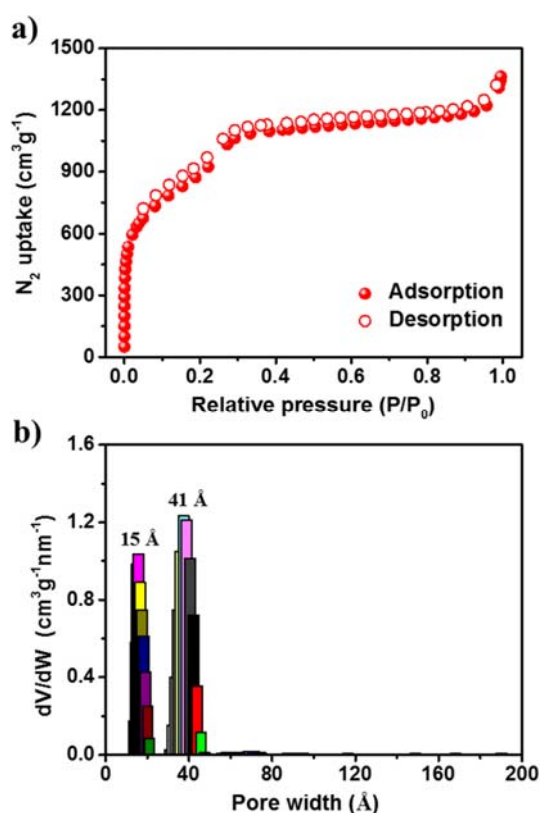


**Figure 2.** Extended structure of JUC-564 viewed along  $c$  axis (a) and  $a$  or  $b$  axis (b). C, green; H, pink; N, blue.

$20.4794 \text{ \AA}$ ,  $\alpha = \beta = 90^\circ$ , and  $\gamma = 120^\circ$ ). In light of these results, JUC-564 is proposed to have the expected 3D framework with pore sizes of  $14 \text{ \AA}$  along  $a$  or  $b$  axis and  $43 \text{ \AA}$  along  $c$  axis (Figure 2). Notably, benefiting from its highly void framework and light constitutional elements, JUC-564 has a calculated density of  $0.108 \text{ g cm}^{-3}$ , which is the lowest reported for any crystalline material known to date, such as MOFs ( $0.22 \text{ g cm}^{-3}$  for MOF-200,<sup>44</sup>  $0.195 \text{ g cm}^{-3}$  for

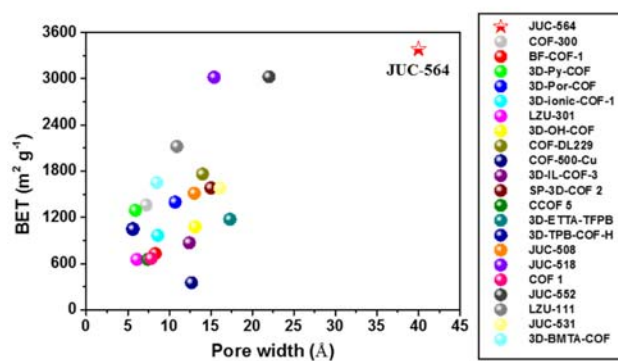
IRMOF-74-XI,<sup>45</sup> and 0.124 g cm<sup>-3</sup> for NU-1301<sup>46</sup>) and COFs (0.19 g cm<sup>-3</sup> for JUC-518,<sup>20</sup> 0.17 g cm<sup>-3</sup> for COF-108,<sup>27</sup> and 0.13 g cm<sup>-3</sup> for DBA-3D-COF<sup>147</sup>).

To investigate the porosity of JUC-564, gas sorption study of N<sub>2</sub> was conducted at 77 K. As shown in Figure 3a, JUC-564 exhibited typical reversible type IV isotherms, which is one of the main characteristics of mesoporous materials. The surface area was calculated to be 3383 m<sup>2</sup> g<sup>-1</sup> using the Brunauer–Emmett–Teller (BET) model (Figure S6). Pore size distribution calculated by nonlocal density functional theory (NLDFT) illustrated two kinds of pores with sizes of 15 Å and 41 Å (Figure 3b), which are in good agreement with those of the proposed structure (14 Å and 43 Å). Remarkably, the largest pore size of JUC-564 (43 Å) is far superior to that of other reported 3D COFs (Table S1), such as 13.5 Å for COF-102,<sup>27</sup> 13.6 Å for DL-COF-1,<sup>33</sup> 15.4 Å for JUC-518,<sup>20</sup> and 28 Å for DBA-3D-COF 1.<sup>47</sup> Furthermore, its BET surface area (3383 m<sup>2</sup> g<sup>-1</sup>) is much higher than that of other 3D imine-based COFs (Figure 4 and Table S2), such as 1360 m<sup>2</sup> g<sup>-1</sup> for COF-300,<sup>48</sup> 1513 m<sup>2</sup> g<sup>-1</sup> for JUC-508,<sup>15</sup> 2020 m<sup>2</sup> g<sup>-1</sup> for LZU-111,<sup>31</sup> and 3023 m<sup>2</sup> g<sup>-1</sup> for JUC-552.<sup>36</sup>



**Figure 3.** (a) N<sub>2</sub> adsorption-desorption isotherm at 77 K and (b) pore-size distribution for JUC-564.

To further define the structure and large channels of JUC-564, incorporation of large biomolecules with suitable dimensions as probes was explored (Figures S7-12). The uptake ability of JUC-564 for myoglobin (Mb, about 21 Å × 35 Å × 44 Å)<sup>49</sup> was confirmed by UV-vis spectrum, which proves the existence of the wide channel (43 Å) in JUC-564. For comparison, no observable adsorption of Mb in the microporous COF-320 took place due to its smaller pore size (~12 Å).



**Figure 4.** A summary of BET surface areas versus pore sizes in 3D imine-based COFs.

In summary, we have developed a large-pore 3D COF with novel **stp** topology utilizing a rare 6-connected *D*<sub>3h</sub> node based on triptycene. JUC-564 exhibited interconnected channel systems with high surface areas (3383 m<sup>2</sup> g<sup>-1</sup>), ultra-large channels (up to 43 Å), record-breaking low density (0.108 g cm<sup>-3</sup>), and positive uptake of a large protein molecule. This work not only opens a door to enrich 3D structures of COFs but also promotes new applications of 3D COFs in adsorption of large biological molecules.

## Supporting Information

Methods and synthetic procedures, SEM, FTIR, solid state <sup>13</sup>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

<sup>§</sup>H.L. and J.D. contributed equally to this work.

### Notes

The authors declare no competing financial interests.

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**TOC Graphic:**

