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Synthesis of three-dimensional covalent - organic frameworks through a symmetry reduction strategy

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Abstract: Developing three-dimensional (3D) covalent organic frameworks (COFs) is crucial for numerous applications. However, conventional design approaches using regular building blocks limit the structural diversity of COFs. In this study, we design and synthesize two 3D COFs, JUC-644 and JUC-645, employing a strategy based on 8-connected (8-c) building blocks with reduced symmetry. Using continuous rotation electron diffraction and high-resolution transmission electron microscopy, their structures were solved and revealed a unique linkage with double chain structure, a phenomenon previously unreported in COFs. We deconstruct these structures into unprecedented [4+3(+2)]-c nets, discovering and defining six topologies. Furthermore, JUC-644 demonstrates high adsorption capabilities for C₃H₈ and *n*-C₄H₁₀ (11.28 and 10.45 mmol g⁻¹ at 298 K and 1 bar, respectively), surpassing most known porous materials, with significant selectivity for C₃H₈/C₂H₆ and *n*-C₄H₁₀/C₂H₆. This approach opens new avenues for designing intricate architectures and enhances COFs' potential in C₂H₆ recovery from natural gas liquids.

Covalent organic frameworks (COFs) represent a class of crystalline porous materials composed of covalently bonded organic building blocks, which assemble into two-dimensional (2D) or three-dimensional (3D) reticular structures. In the context of topological analysis, these building blocks can be abstracted to vertices and edges, as documented in early studies¹⁻⁵. 2D COFs are characterized by covalent networks extending within 2D layers, resulting in a limited number of predictable and analyzable topologies that are relatively easier to investigate⁶⁻¹¹. On the other hand, 3D COFs offer an extensive range of topological possibilities due to the diverse methods of connection they involve, leading to the formation of pores with varying types and sizes. The pioneering work conducted by Yaghi's research group in 2007² initiated the construction of 3D COFs exhibiting various topological features, a milestone that has been followed by the accomplishment of numerous successful efforts¹²⁻¹⁶. The distinct porous structure of 3D COFs determines their primary applications, with their respective topologies playing a crucial role in this regard.

As the topological structure of 3D COFs depends on the coordination number and geometrical symmetry of their organic building blocks, rational design of these building blocks is an effective way to create 3D COFs with a particular or novel topology. So far, traditional tetrahedral nodes have been the most prevalent choice for constructing 3D networks (Figure 1a, see Supplementary Fig. 1 for details)^{12,17,18}. The success in obtaining 3D COFs with zeolite **crb** topology (ZOF) and newfound **ljh** topology are typical cases of designing topology via adjusting bond angles or steric hindrance of conventional building blocks composed of single organic molecules^{19,20}. Another more sophisticated method to enrich the connective environment of topological vertices in COFs is to combine several building subunits into a building block.

According to this method, building blocks are created by connecting each vertex of a central planar (triangular, rectangular, or square) building subunit to an outer triangular building subunit perpendicular to its plane, forming a prismatic building block in D_{nh} ($n=2, 3, 4$) or O_h point groups. Up till now, 6-connected (6-c) triangular prismatic building blocks and 8-connected (8-c) cubic or cuboid building blocks have been constructed in this way, forming highly connected 3D COFs with different topologies (Figure 1b,c and see Supplementary Fig. 1 for details). However, these topologies are still limited in types and relatively predictable because all of the current building blocks of COFs are based on planar polygons, regular polyhedrons, or triangular prisms with relatively rigid structures and low degrees of configurational freedom. It is worth mentioning that for such COFs, topologies are discovered mainly by adopting linkers with different configurations and simply changing building blocks with the same connective polyhedron can hardly produce different topologies. For instance, all of the reported [8(+2)]-c COFs are in **bcu** or its derived nets²¹⁻²⁴, and all of the reported [8+4]-c COFs are in **flu**, **scu** or **tty** topologies²⁵⁻²⁸.

Despite the efforts of topological design, subject to the limited configurational and coordinative variety of the building blocks, the topological variety of COFs is significantly lower than that of metal-organic frameworks (MOFs). A typical example is that building blocks of MOFs may occasionally be connected by multiple links²⁹. For instance, in **snf** and **fqr** topologies, every metal cluster is linked to the six nearest clusters by 12 or 10 linkers, which means partial or all of the clusters are “double-linked”³⁰⁻³². Additionally, by reducing the connectivity of vertices, it is found to be an effective approach to create chemical robust MOFs with rare mesoporous cages³³. In contrast, among all the reported COFs synthesized via bottom-up or self-assembly strategies, neighboring building blocks are connected by single linkers, and the phenomenon of

multiple links connecting adjacent building blocks or the reduction in connectivity has not been previously reported in COF structures. Designing and combining building blocks in various geometric configurations opens opportunities for the generation of novel 3D COFs, but remains a great challenge.

Here, we present a synthetic strategy based on building blocks with reduced symmetry, resulting in two unique 3D COFs designated as JUC-644 and JUC-645 (JUC refers to Jilin University China). Their structures were determined using continuous rotation electron diffraction (cRED) technique assisted by high-resolution transmission electron microscope (HRTEM) images. Remarkably, the 8-c building blocks in these structures exhibit an unexpected coordination of six, leading to the formation of unconventional "double links". This is the reported occurrence of such a phenomenon in COF structures (Figure 1d,e). Therefore, to describe the topology precisely, the framework should be deconstructed by splitting the 8-c building block into one 4-c vertex and four 3-c vertices, unveiling an unprecedented [4+3(+2)]-c (Figure 1f) topology denoted as **jca** and **jcd** (**jca** and **jcd** stand for Jilin University China-a and -d, similar for the other topologies) instead of the traditional [8(+2)]-c or [6(+2)]-c topology. Four other topologies are further defined based on the two COFs. JUC-644, in particular, demonstrates a high adsorption capacity for C₃H₈ and *n*-C₄H₁₀, reaching a value of 11.28 mmol g⁻¹ and 10.45 mmol g⁻¹ at 298 K and 1 bar respectively, which surpasses those of most known porous materials. To further explore its applicability, JUC-644 was subjected to breakthrough experiments for C₂H₆ recovery from simulated natural gas liquids (NGLs), where it exhibited excellent selectivity in terms of C₃H₈/C₂H₆ and *n*-C₄H₁₀/C₂H₆ ratios.

Results and discussion

Structural design

In contrast to conventional approaches that rely on high-symmetry building blocks, our strategy introduces building blocks with reduced symmetry by combining multiple organic subunits, wherein at least one subunit assumes a 3D coordination environment (Figure 1d-g, and Supplementary Fig. 2 for details). Compared to reported building blocks, these designed building blocks will exhibit different and mostly symmetry-reduced point groups. As an initial implementation of this strategy, we assemble four 3-c triangular outer subunits (C_{2v} symmetry) with a 4-c 3D twisted tetrahedral central subunit (D_{2d} symmetry), resulting in an unconventional 8-c building blocks with D_{2d} symmetry and high degrees of configurational flexibility. In line with this concept, we design two unique building blocks, namely 3,3',5,5'-tetra[(3'',5''-diformylphenyl)-bimesitylene (TDFBM,) and 3,3',5,5'-tetra[(3'',5''-diformylphenyl)-tetraoxomethyl biphenyl (TDFTM, Figure 2). In these designs, the bimesityl and the tetraoxomethyl biphenyl groups naturally serve as twisted tetrahedral central subunits respectively, while the (3',5'-diformylphenyl) groups act as triangular outer subunits (See Supplementary Fig. 2 for details). Using the Gaussian 09 software package³⁴, we performed potential energy scans of these building blocks with reduced symmetry (See Supplementary Fig. 3 for details). Notably, due to the variations of the most stable conformations and the ease of dihedral angle changes, the topologies constructed from these D_{2d} building blocks are inherently unpredictable and have likely not been reported in prior literature. These distinctive 8-c building blocks are subsequently condensed with *p*-phenylenediamine (PDA, Figure 2) as a linear linker to construct two 3D COFs,

namely JUC-644 and JUC-645 (Figure 2), possessing unique structural characteristics and topologies.

Synthesis and characterization

Typically, these building blocks (PDA + TDFBM/TDFTM) were dispersed in 1,4-dioxane in the presence of acetic acid and were then heated under different reaction conditions to build JUC-644 and JUC-645, respectively (see Section S2 for details). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) revealed the cuboid shapes for JUC-644 and JUC-645 particles (Figure 3a,d and Supplementary Figs. 4-7). The Fourier transform infrared (FT-IR) spectra showed the appearance of new C=N stretching bands (1624 cm^{-1} for JUC-644 and 1622 cm^{-1} for JUC-645) and the disappearance of C=O (1706 cm^{-1} for TDFBM and 1708 cm^{-1} for TDFTM) and N-H (3324 cm^{-1} for PDA) stretching bands, manifesting the successful polymerization of aldehyde and amine (Supplementary Figs. 8 and 9). In addition, the peaks at 158 ppm for JUC-644 and 156 ppm for JUC-645 in the solid-state ^{13}C cross-polarization magic-angle-spinning (CP/MAS) nuclear magnetic resonance (NMR) showed the presence of carbons from the imine groups (Supplementary Figs. 10 and 11). The thermogravimetric analysis (TGA, Supplementary Figs. 12 and 13) and powder X-ray diffraction (PXRD) patterns (Supplementary Figs. 14-17) revealed that both 3D COFs were stable under high temperatures ($>400\text{ }^{\circ}\text{C}$) and in various organic solvents and acid/base aqueous solutions. The PXRD patterns of JUC-644 and JUC-645 indicate that a crystalline phase has been formed (Supplementary Figs. 18 and 20).

Structural determination

According to PXRD patterns and electronic micrographs taken by SEM and TEM, JUC-644 and JUC-645 exhibit significantly high crystallinity. Therefore, both structures were determined mainly by the cRED technique. For JUC-644 with relatively better crystallinity, sixteen individual datasets with a resolution up to 1.5 Å were collected at 99 K and the 3D reciprocal space was preliminarily reconstructed using the software *REDp*³⁵. The unit cell of JUC-644 was firstly determined by cRED data (Figure 3c) and the reflection conditions were determined as $0kl: l=2n$; $h0l: l=2n$; $hk0: h=2n$ from the 2D slices cut from the 3D reciprocal lattice, supporting the inference that space group should be *Pcca*. The unit cell ($a = 31.669(6)$ Å, $b = 17.376(3)$ Å, $c = 25.285(4)$ Å, $\alpha = \beta = \gamma = 90^\circ$) and space group was confirmed by Pawley Refinement of PXRD data with software *TOPAS 5*³⁶ with R_{wp} of 5.71% and R_p of 4.13%. The cRED datasets were then processed using *X-ray Detector Software (XDS)*³⁷ and six sets of them were merged by the Python program package *edtools*³⁸ to improve the data completeness. Finally, we obtained a *.hkl peaks list, and fractional coordinates of all non-hydrogen atoms were determined with the software *SHELXT*³⁹. This is the highest reported resolution of cRED data for successful structural determination using the *ab initio* methods. The final crystal structure model was obtained by the Rietveld refinement with *TOPAS 5*, with R_{wp} of 7.56% and R_p of 5.76% (Figure 3b, Supplementary Fig. 19, and see Supplementary Tables 1 and 2 for details). The topological structure of JUC-644 is very characteristic with a 2-fold interpenetrated net, which will be discussed in detail below.

HRTEM imaging is crucial for elucidating the structural details of COFs, providing precise insights into their atomic arrangements^{40,41}. We used the cRED technique and HRTEM to determine the structure of JUC-645. Twelve individual datasets with a resolution up to 3.0 Å were collected at 99 K and the 3D reciprocal space was preliminarily reconstructed. A unit cell of JUC-

645 was determined by cRED data (Figure 3f) and the reflection conditions were determined as $hkl: h+k=2n, k+l=2n, h+l=2n; 0kl: k+l=4n; h0l: h+l=4n; hk0: h+k=4n$ from the 2D slices cut from the 3D reciprocal lattice, supporting the inference that space group should be $Fddd$. The unit cell ($a = 17.853(5) \text{ \AA}, b = 48.636(8) \text{ \AA}, c = 66.169(14) \text{ \AA}, \alpha = \beta = \gamma = 90^\circ$) and space group was confirmed by Pawley Refinement of PXRD data with software *TOPAS 5*³⁶ with R_{wp} of 2.99% and R_p of 2.09%. Limited by the low resolution, no useful information can be directly solved from the cRED data, and a structure model is then constructed according to the space group symmetry. Since the cell volume of JUC-645 ($\sim 57454 \text{ \AA}^3$) is about 4 times that of JUC-644 ($\sim 13913 \text{ \AA}^3$) and their building blocks share similar configurations, there should be 16 8-c building blocks in each unit cell of JUC-645. Further symmetry analysis shows that the geometric center of 8-c building blocks can only be located in $16f$ or $16g$ Wyckoff positions of $Fddd$ space group. The centroid positions are preliminarily determined by simulated annealing against PXRD data and distances between centroids are then calculated and compared with that of JUC-644 to complete the model structures⁴². Finally, an initial structural model with centroids located at $16g$ Wyckoff position with $z=0.35$ is chemically reasonable and fits well with the PXRD patterns (Please refer to Supplementary Section 9 for details of structural determination). The final crystal structure model was obtained by the Rietveld refinement with *TOPAS 5*, with R_{wp} of 6.77% and R_p of 5.24% (Figure 3e, Supplementary Fig. 21, and see Supplementary Tables 3 and 4 for details). The topological structure of JUC-645 is very characteristic with a 2-fold interpenetrated net, which will be discussed in detail below. HRTEM images were taken and imposed in $p1$ and cmm plane group symmetry using *CRISP* software, and the comparison of the resulting images with the projections of the 2-fold interpenetrated model along $[\bar{1}10]$ direction yielded an excellent

alignment in observed directions, confirming the accuracy of the structural interpretation (Figures 3g-l and Supplementary Figs. 22-24).

Notably, both 3D COFs displayed double chain structures, an extremely uncommon occurrence in COF structures⁴⁴. The dual chains of JUC-644 and JUC-645 are generated by the alignment of adjacent 8-c building blocks with two PDA linkers along the *b*-axis and *a*-axis for each cell (Figure 4a-d and Supplementary Fig. 25 and 26), forming the porous structure along other directions. This phenomenon has a great influence on the topological analysis which will be discussed in detail in the next section.

Another interesting fact about these COFs is that for each structure, the non-penetrated single chain is in the *Pba2* or *Fdd2* space group, non-centrosymmetric *translationengleiche* subgroup of *Pcca* (*Pbab*) or *Fddd* in *mm2* Laue group by removing the *c*-glide or *d*-glide perpendicular to [010] or [001] directions for each respectively. This is because the interpenetration is completed by inversion rather than simply translation to form the center of symmetry in both structures (Figure 4e,f), which means both COFs are in the **IIa** class of interpenetration⁴⁵. This is similar to the interpenetration mode in the ZOF structure, in which two **crb** nets are interpenetrated by 90° rotation¹⁹. Both COFs are in centrosymmetric space groups because the chains appear in pairs in both structures and the whole frameworks are racemic.

Topological analysis

Although the structures of both COFs have been determined, their topologies cannot be defined easily. According to traditional topological analysis methods, the whole building block in COFs is always regarded as a vertex. For instance, when examining a reported COF structure based on 6-c

triangular prismatic nodes in D_{3h} symmetry connected with 2-c linear linkers, it can be classified into **acs** or other [6+2]-c nets. In analyzing this structure, whether the 6-c building block is considered as (3+3)-c or in its entirety does not alter the depiction of the overall structure as **acs** net⁴⁶ (See Supplementary Fig. 27a for details). Similarly, for any reported 3D COF based on 8-c building blocks characterized by D_{4h} or D_{2h} symmetry, the **bcu** net arises through linear linkers, which will not be described clearly by regarding the 8-c building block as (4+3)-c²² (See Supplementary Fig. 27b for details). As a result, dividing the building blocks into multiple topological vertices is unnecessary for reported COF structures. However, under this deconstruction method, the JUC-644 structure is surprisingly in a [6(+2)]-c **pcu**-like topology: every 8-c building block is connected with 6 neighbors along 3 mutually orthogonal directions and there are 2 PDA linkers between neighboring building blocks along the direction parallel to the chains and 1 PDA along the other directions (Figure 5c). Similarly, the JUC-645 structure is in a [6(+2)]-c **bsn**-like topology: every 8-c building block is connected with 6 neighbors along 3 directions and there are 2 PDA linkers between neighboring building blocks along the direction parallel to the chains, and 1 PDA along the other directions (Figure 5f). This implies that adjacent building blocks are connected by multiple links, forming the double chains structure mentioned above, which is unreported in all known 3D COF structures. Keeping considering the topology as a [6(+2)]-c **pcu** or **bsn** net is unreasonable because the “double links” parts are oversimplified to 1D and unable to accurately describe the porous and chain structures generated by the multiple links (Supplementary Fig. 28). As a result, this is a subversive counter-example of the traditional topological analysis method of COFs, indicating that the entire building block cannot always be taken as a single topology vertex.

To precisely describe the topology of JUC-644 and JUC-645, following the minimal transitivity principle, we divided the 8-c building block into a 4-c vertex located in the center of the tetrahedron and four 3-c vertices in the center of the benzene ring of 3',5'-diformylphenyl group (Figure 5a). In other words, the structures are deconstructed to a [4+3(+2)]-c net according to the position of the subunits rather than a [6(+2)]-c net according to the whole building block (Figure 5b-g and Supplementary Fig. 29). The deconstruction process was completed using the software *Material Studio*⁴² manually and using software *ToposPro*⁴⁷ by automatically clustering, and both resulting topologies were analyzed and proven to be different based on vertex symbols and different orders of coordination numbers (See Supplementary Table 5 and 6 for details). The result topologies were further analyzed by program *Systre*⁴⁸, showing the highest space group symmetry of the topology is in *Pban* (No.50) and *Fddd* (No.70). The two topologies are not included in the Reticular Chemistry Structure Resource (RCSR) database⁴⁹ or Topological Types Database (TTD)⁵⁰, which means it is two completely unprecedented topologies. The topologies corresponding to JUC-644 and JUC-645 are named **jca** and **jcd** in RCSR style, respectively.

Another intriguing aspect of the topologies is that the projection patterns for **jca** along [110] and $[\bar{1}10]$ directions are identical (Supplementary Fig. 30a,b), suggesting the structure has a good chance of being related to tetragonal symmetry. In order to construct tetragonal symmetry, the cell parameters were set to be $a=b$ to make a tetragonal cell, and 3-c vertices' fractional coordinates were set to be $x=y$ to make them on the diagonal of the xOy plane. The resulting vertex-only structure is obviously in tetragonal symmetry, but the chain edges along the c -axis break the $C4$ axis of rotation. A tetragonal [4+4]-c topology in space group *P4/nbm* (No.125, a minimal *translationengleiche* supergroup of *Pban*) can be accordingly defined by completing the edges

along the c axis, which is also an unprecedented topology (namely **jcb** net, See Supplementary Fig. 31 and Table 7 for details). For **jcd** topology, the projection patterns along $[011]$ and $[0\bar{1}1]$ are also identical (Supplementary Fig. 30c,d) and another unprecedented tetragonal $[4+4]$ -c topology in $I4_1/amd$ (No. 141, a minimal *translationengleiche* supergroup of $Pban$) can be generated by setting cell parameters to $b=c$, adjusting the 3-c vertices' coordinates correspondingly and completing the edges (namely **jce** net, See Supplementary Fig. 32 and Table 8 for details). The relationship between the **jcb/jca** or **jce/jcd** is similar to that between **pcu/cds** (Supplementary Figs. 33, 34, and 37). Deleting part of edges along specific directions would reduce the topological symmetry.

Derived topologies in 4-c structures can be defined by dividing a 4-c vertex into two 3-c vertices. For instance, **dmd**, **dmg**, **dmh**, **sur**, **tfi** and **tfk** are derived from **pts** by splitting tetragonal or square vertices along different directions. The twisted tetrahedral vertex in JUC-644 and JUC-645 can be split into two triangular vertices defined in the center of the mesitylene or tetraoxomethyl benzene ring, forming two $[3+3]$ -c topology denoted as **jcc** and **jcf** respectively (See Supplementary Table 9, 10 for details). They are the fifth and sixth topologies discovered in this work (Figure 5h, i, Supplementary Figs. 35-37). According to the equilibrium placement generated from the Systre program, the 4-c vertices of **jca/jcd** are located on $2a/8d$ Wyckoff positions of $Pcca/Fddd$ space group, whose symmetry is $2\ 2\ 2$, and the separated 3-c vertices of **jcc/jcf** are split along one of these C_2 axes. As a result, the space group symmetry are not broken by this separation, and the highest space groups of **jcc** and **jcf** are still $Pban$ and $Fddd$. Comparison of **jca~jcf** with other similar topologies in the *RCSR* database⁴⁹ is detailed in Supplementary Table 11 and Figs. 38-40.

With the success of structural determination and topological analysis, it remains an interesting topic that these COFs are synthesized from monomers in similar configurations but are in different topologies and space groups. Up to tenth order coordination numbers for six topologies are analyzed and compared carefully for this problem and the results are shown in Supplementary Table 12. The results show that the 1st ~5th order of coordination for **jca/jcd** and **jcb/jce** and 1st~6th order of coordination for **jcc/jcf** (this is because each 4-c vertex is separated into two 3-c vertices in **jcc** and **jcf**) are surprisingly the same while higher ordered coordination numbers are different. This means both structures are actually in similar short-range environments while the long-term translations are different because of the slight difference in steric hindrance and dihedral angles of two 8-c monomers.

The discovery of six topologies indicates the success of our synthetic strategy. Notably, the numbers of vertices in all the six topologies are not inversely proportional to their connected numbers but are determined by the design of 8-c building blocks. This means the quantity ratio of topological vertices in COF structures can be defined manually by controlling the central and outer subunits ratio. For the D_{2d} 8-c building block itself reported in this article, more COFs in different topologies may be designed by adjusting subunits' orientation and steric hindrances, and by connecting the building blocks to linkers with various configurations and coordination numbers. In JUC-644 and JUC-645, an 8-c building block is formed by combining four 3-c outer subunits with a 4-c twisted tetrahedral central unit. This configuration gives rise to two [4+3(+2)]-c topologies through linear connectivity. Notably, the connectivity in the **jca** and **jcd** topologies is quite distinctive, as the ratio of 4-c to 3-c is directly determined by the building block itself. This unique ratio also contributes to the formation of these exceptional connectivity structures.

Furthermore, topologies can be designed and discovered not only by altering the geometry of central or outer subunits to shapes such as tetrahedrons, pyramids, and prisms but also by exploring more complex shapes (Supplementary Fig. 41). This approach allows for a significant expansion of potential structural diversity and COFs designed in this method are in good chance to exhibit in unreported topologies. The conditions for possible topologies are discussed in Supplementary Section 11 and some possible topologies for COFs built from more complicated building blocks are shown in Supplementary Fig. 42. For instance, in the [4+3+3]-c topology (**tfy**), the 4-c:3-c:3-c ratio is 3:12:8, and for the [6+3+6]-c topology (**ceq**), vertices corresponding to 6-c central subunit, 3-c outer subunit and 6-c linkers are in 1:6:2 ratios. Additionally, building blocks can be composed of multiple central subunits combined with various types of outer subunits, further increasing the range of possible topologies.

Conclusion

In conclusion, we have successfully designed and synthesized two 3D COFs, JUC-644 and JUC-645, by connecting two 8-c organic building blocks in D_{2d} symmetry via linear PDA linkers. Both COFs were determined using the cRED technique and Rietveld refinement combined with HRTEM images. JUC-644 was solved from cRED datasets with a resolution up to 1.5 Å, which is the highest reported resolution of cRED data for successful structural determination using the *ab initio* methods. Notably, these COFs exhibit intricate structures featuring interpenetration through inversions resulting in a center of symmetry and rare double chain linkages, representing a significant advancement in COF structures. To precisely describe their topologies, we develop a strategy for topological analysis. The framework structures can be deconstructed by splitting the

8-c building block into one 4-c vertex and four 3-c vertices and identified as an unprecedented [4+3(+2)]-c nets (**jca** and **jcd**) instead of the traditional [8(+2)]-c or [6(+2)]-c nets. Additionally, through manual symmetry improvement to the tetragonal system, we defined a [4+4]-c topologies (**jcb** and **jce**) in $P4/nbm$ and $I4_1/amd$ space groups and a [3+3]-c topologies (**jcc** and **jcf**) in $Pban$ and $Fddd$ space groups, all of which are not also found in the RSCR or ToposPro database. This research reveals the complexity of COF structures and highlights the importance of cRED for accurate structural determination during COF topology analysis. Furthermore, JUC-644 exhibits high adsorption capacities for C_3H_8 and $n-C_4H_{10}$, reaching 11.28 and 10.45 mmol g^{-1} at 298 K and 1 bar respectively, which surpasses the adsorption performance of most known porous materials. Notably, some activated carbons exhibit higher adsorption capacities for light hydrocarbons. Consequently, developing 3D functionalized COFs with strong adsorption sites remains a challenge to achieve superior adsorption performance. Breakthrough experiments also demonstrate the excellent C_3H_8/C_2H_6 and $n-C_4H_{10}/C_2H_6$ selectivity for JUC-644. Therefore, this strategy for incorporating building blocks with reduced symmetry in 3D COFs offers a promising path for designing complex COF structures. At the same time, the success of these materials in gas separation underscores the potential for C_2H_6 recovery from NGLs.

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Author contributions

Q.F., H.L., and J.L.S. were responsible for the overall project design, direction, and supervision. J.C. and H.Z. conducted the synthesis and characterization of all samples. Z.Z., S.Z., and J.L.S. collected and analyzed the cRED data and topology structure. J.C., Z.Z., H.Z., and H.L. finalized the PXRD refinement and structure analyses. J.C., H.Z., and H.L. conducted the alkane sorption tests and breakthrough experiments. J.Q.S. and F.C. performed DFT calculations and assisted with the TGA and FT-IR tests. C.J. assisted with the calculation of Q_{st} and IAST for alkane sorption. Z.W. captured HRTEM images. All authors contributed to the discussion of results and manuscript writing.

Competing interests

The authors declare no competing interests.

Figure Captions

Figure 1. Schematic illustration of 3D COFs based on different strategies. a-c, The traditional high-symmetry strategy. The [4(+2)] and [4+3] connectivity patterns using 4-connected 3D- T_d building blocks (a). The [6(+2)] and [6+4] connectivity patterns using 6-connected 3D- D_{3h} building blocks (b). The [8(+2)] and [8+4] connectivity patterns using 8-connected 3D- O_h (D_{4h} ,

D_{2h}) building blocks (c, and please refer to Supplementary Fig. 1 for additional connectivity patterns in 3D COFs). **d-g**, A symmetry-reduction strategy for the design and synthesis of 3D COFs. This strategy is exemplified by the designed and synthesized 8-connected building block with D_{2d} symmetry assembly from 4- and 3-connected building subunits (d). The 6-connected mode for each polyhedron when considering the entire building block as a vertex (e), in which there are unique “double links” connectivity (f). A remarkable [4+3(+2)] connectivity pattern when dividing the polyhedron into a 4-c vertex and four 3-c vertices (g).

Figure 2. Schematic Representation for the synthesis of JUC-644 and JUC-645. Chemical structures of the 8-connected D_{2d} building blocks TDFBM and TDFTM, which are formed by the reaction of four 3-c units and one 4-c unit (R_1 is a tetramethyl- 1,3,2- dioxaborolan- 2- yl and R_2 is an iodo). Condensation of TDFBM or TDFTM with the linear linker PDA affords the 3D COFs, JUC-644 and JUC-645 respectively. The lower part of the figure shows a simplified [4+3(+2)] connectivity of JUC-644 or JUC-645 along with their structures.

Figure 3. Structural characterization of JUC-644 and JUC-645. a,b, SEM image (a) and PXRD patterns (b) of JUC-644. c, three-dimensional reciprocal space reconstructed from cRED data and the $0kl$, $h0l$, $hk0$ slices extracted from the 3D reciprocal space of JUC-644 (from left to right). The reflection condition can be determined as $0kl: l=2n$; $h0l: l=2n$; $hk0: h=2n$. d,e, SEM image (d) and PXRD patterns (e) of JUC-645. f, three-dimensional reciprocal space reconstructed from cRED data and the $0kl$, $h0l$, $hk0$ slices extracted from the 3D reciprocal space of JUC-645 (from left to right). The reflection condition can be determined as $hkl: h+k=2n$, $k+l=2n$, $h+l=2n$; $0kl: k+l=4n$; $h0l: h+l=4n$; $hk0: h+k=4n$. g-i, The HRTEM image with resolution of 3.5 Å of $[\bar{1}10]$

orientation of JUC-645 (**g**). Part of the HRTEM image imposed in translation symmetry in $p1$ plane group (**h**). The $cm\bar{m}$ plane group symmetry imposed to the HRTEM image (**i**) and projection of the crystal structure of JUC-645 along the $[\bar{1}10]$ orientation (**j**). The FFT (**k**) with a resolution of 3.5 Å and SAED patterns (**l**) for the same area. The systematic absence is: $hhl: h+l=2n; 00l: l=4n$. Some of the $00l: l=4n+2$ diffractions are observed because of dynamical effect.

Figure 4. Structural analysis of COFs. a,b, Extended structures of 2-fold interpenetrated JUC-644 along the b -axis (**a**) and JUC-645 along the a -axis (**b**). **c,d**, Double chain structure in JUC-644 (**c**) and JUC-645 (**d**). **e,f**, A simplified connectivity pattern of JUC-644 in centrosymmetric $Pcca$ (**e**) and JUC-645 in centrosymmetric $Fddd$ (**f**), forming a symmetric center through interpenetration.

Figure 5. Schematic illustration of the discovery of topologies. a, Chemical structure and schematic representation of the 8-connected building blocks used to construct the 3D-COFs. **b-d**, The $[4+3(+2)]$ -c net of JUC-644 from the topology analysis strategy, where the 8-c building block is divided into one 4-c vertex and four 3-c vertices for a precise topological representation (**b**). Structure of JUC-644 framework with linearized double links (**c**). JUC-644 is based on a traditional topological analysis with a $[6(+2)]$ -c net, where the entire building block is treated as a vertex (**d**). **e-g**, The $[4+3(+2)]$ -c net of JUC-645 from the topology analysis strategy, where the 8-c building block is divided into one 4-c vertex and four 3-c vertices for a precise topological representation (**e**). Structure of JUC-645 framework with linearized double links (**f**). JUC-645 is based on a traditional topological analysis with a $[6(+2)]$ -c net, where the entire building block is treated as a vertex (**g**). **h,i**, Six topological structures ranked in descending order of symmetry. By

adjusting the symmetry and 3-c vertex coordinates, [4+4]-c **jcb** and **jce** nets were discovered. Splitting the 4-c vertex revealed the [3+3]-c **jcc** and **jcf** nets.

Figure 6. Porosity analysis and Adsorption and separation towards various light hydrocarbon molecules of JUC-644 and JUC-645. a,b, N₂ adsorption–desorption isotherm at 77 K (**a** for JUC-644 and **b** for JUC-645), Inset: Pore-size distribution calculated by fitting on the NLDFT model to the adsorption data. **c,d**, C₂H₆, C₃H₈, and *n*-C₄H₁₀ adsorption isotherms at 298 K for JUC-644 (**c**) and JUC-645 (**d**). **e,f**, Comparison of adsorption capacities of representative materials for C₃H₈ (**e**) and *n*-C₄H₁₀ (**f**) at 298 K and 100 Kpa.

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Methods

Synthesis of JUC-644. TDFBM (0.02 mmol, 15.3 mg) and PDA (0.08 mmol, 8.6 mg) were loaded into a Pyrex tube, 1.0 mL 1,4-dioxane, 0.1 mL aniline, and 0.1 mL of acetic acid (6 M) were added. The liquid nitrogen bath was used to freeze the Pyrex tube, which was evacuated to an interior pressure of ca. 19.0 mbar and flame-sealed, decreasing the length by ca. 10.0 cm. The tube was placed in an oven at 120 °C for 7 d after the temperature increased to room temperature. The resulting precipitate was filtered and exhaustively washed with acetone 5 times. The obtained powder was immersed in anhydrous *n*-hexane, and the solvent was exchanged with fresh *n*-hexane several times. The sample was then transferred to a vacuum chamber and evacuated to 20 mTorr under 65 °C. Yield: 18.1 mg, 75.7%. Anal. Calcd: C: 85.38; H: 3.85; N: 10.75. Found: C: 85.86; H: 3.51; N: 10.63. FT-IR (cm⁻¹): 3027, 2920, 2873, 2730, 2579, 2356, 1685, 1618, 1585, 1533, 1503,

1452, 1289, 1245, 1206, 1151, 969, and 827. ^{13}C NMR (ppm): 158, 151, 147, 143, 138, 132, 121, 115, 35, 30, and 18.

Synthesis of JUC-645. TDFTM (0.02 mmol, 15.4 mg) and PDA (0.08 mmol, 8.6 mg) were loaded into a Pyrex tube, 1.0 mL 1,4-dioxane, 0.1 mL aniline, and 0.1 mL of acetic acid (6 M) were added. The liquid nitrogen bath was used to freeze the Pyrex tube, which was evacuated to an interior pressure of ca. 19.0 mbar and flame-sealed, decreasing the whole length by ca. 10.0 cm. The tube was placed in an oven at 120 °C for 7 d after the temperature increased to room temperature. The resulting precipitate was filtered and exhaustively washed with acetone 5 times. The obtained powder was immersed in anhydrous *n*-hexane, and the solvent was exchanged with fresh *n*-hexane several times. The sample was then transferred to a vacuum chamber and evacuated to 20 mTorr under 65 °C. Yield: 17.9 mg, 74.5%. Anal. Calcd: C: 79.27; H: 4.59; N: 10.28; O: 5.86. Found: C: 79.75; H: 4.32; N: 10.37; O: 5.56. FT-IR (cm^{-1}): 3049, 2957, 2865, 2731, 1768, 1622, 1597, 1591, 1499, 1394, 1358, 1290, 1229, 1155, 1095, 966, and 843. ^{13}C NMR (ppm): 156, 153, 151, 147, 139, 131, 126, 120, 115, and 60.

Porosity analysis. The nitrogen (N_2) adsorption and desorption isotherms were performed to determine the porosity of both COFs at 77 K. As illustrated in Figure 6a, b, JUC-644 and JUC-645 exhibit a sharp gas uptake at low pressure ($P/P_0 < 0.1$) demonstrating a typical reversible Type I isotherm, confirming their microporous nature. The semi-log plots highlight the adsorption isotherms at low pressures, indicating the occupation of the micropores within JUC-644 and JUC-645 by N_2 at relatively higher relative pressures (Supplementary Figs. 43 and 44). These two COFs both show microporous cavities and the measured pore sizes are 0.7 nm, 1.0 nm, and 1.0 nm

along the *a*, *b*, and *c* axis for JUC-644 and are 0.95 nm and 1.0 nm along *a* axis for JUC-645 (Supplementary Figs. 47-52). Their theoretical pore size distributions calculated by the nonlocal density functional theory (NLDFT) also revealed micropores with pore sizes of 0.71 and 0.98 nm for JUC-644, and 0.97 nm for JUC-645 along the different axes, perfectly fitting on the proposed models. The pore size data provided support for their 2-fold interpenetrated structures. The Brunauer-Emmett-Teller (BET) surface areas were calculated to be 3117 and 2132 m² g⁻¹ for JUC-644 and JUC-645, using the BETSI method⁵¹ (Supplementary Figs. 45 and 46). For more accurate comparisons, we used Zeo++ software⁵² to calculate the theoretical surface areas of JUC-644 and JUC-645. The results showed that the theoretical surface areas of JUC-644 and JUC-645 were 3250 and 2726 m² g⁻¹ respectively, which are consistent with the experimental values obtained using the BETSI method (JUC-644: 3117 m² g⁻¹ and JUC-645: 2132 m² g⁻¹). These minor differences further confirm the exceptionally high crystallinity of both JUC-644 and JUC-645.

Gas adsorption and separation. The porous structure and high surface area of JUC-644 and JUC-645 provide promising potential for gas adsorption and separation. In this regard, we investigated the adsorption characteristics of JUC-644 and JUC-645 towards various light hydrocarbon molecules. Single-component adsorption isotherms of C₂H₆, C₃H₈, and *n*-C₄H₁₀ on JUC-644 and JUC-645 were measured at three different temperatures: 283 K, 298 K, and 313 K (Figure 6c,d and Supplementary Figs. 53-55). Our results reveal that JUC-644 exhibits higher adsorption capacities for C₂H₆, C₃H₈, and *n*-C₄H₁₀ compared to JUC-645 at 298 K (4.83, 11.28, 10.45 mmol g⁻¹ in JUC-644 and 4.17, 8.37, 8.51 mmol g⁻¹ in JUC-645 respectively), demonstrating the highest C₃H₈ adsorption uptake among known porous materials, surpassing values reported for C₃H₈ in BSF-1 (1.94 mmol g⁻¹)⁵³, PAF-40-Fe (2.58 mmol g⁻¹)⁵⁴, activated

carbon (6.36 mmol g^{-1})⁵⁵ and $\text{g-C}_3\text{N}_4\text{@Zr-BPDC}$ (8.90 mmol g^{-1} , Figure 6e and Supplementary Table 13)⁵⁶. Regarding the $n\text{-C}_4\text{H}_{10}$ adsorption, JUC-644 surpasses that of most reported materials, such as NaX zeolite (1.56 mmol g^{-1})⁵⁷, Zn-BTM (2.01 mmol g^{-1})⁵⁸, and Zn-ZIF-8 (4.69 mmol g^{-1} , Figure 6f and Supplementary Table 14)⁵⁷. Notably, JUC-644's adsorption for $n\text{-C}_4\text{H}_{10}$ ($10.45 \text{ mmol g}^{-1}$) is slightly lower than that of some activated carbon materials with exceptional adsorption capacities, such as BAX-1500 ($11.10 \text{ mmol g}^{-1}$) and Maxsorb III ($12.52 \text{ mmol g}^{-1}$, Figure 6f and Supplementary Table 14)^{59,60}. Compared to JUC-645, the high adsorption capacities of JUC-644 for light hydrocarbon molecules can be attributed to its significantly larger surface area ($3117 \text{ m}^2 \text{ g}^{-1}$ for JUC-644 and $2132 \text{ m}^2 \text{ g}^{-1}$ for JUC-645 respectively) and more accessible adsorption sites. To comprehensively assess the high adsorption capabilities of JUC-644, we conducted adsorption tests on two classic 3D COFs (COF-300¹⁷ and JUC-564⁶¹) at 298 K. Both materials exhibited much lower adsorption capacities for C_2H_6 , C_3H_8 , and $n\text{-C}_4\text{H}_{10}$, with COF-300 showing 1.47 , 5.18 , and 5.35 mmol g^{-1} and JUC-564 showing 2.38 , 4.99 , and 7.38 mmol g^{-1} respectively (Supplementary Figs. 56 and 57). The $n\text{-C}_4\text{H}_{10}$ isotherms of JUC-644 and JUC-645 exhibited a slightly steeper increase compared to C_3H_8 , and both were considerably steeper than the C_2H_6 isotherm. This indicates that the framework affinity of JUC-644 and JUC-645 for guest molecules follows the order of $n\text{-C}_4\text{H}_{10} > \text{C}_3\text{H}_8 > \text{C}_2\text{H}_6$. The affinity sequence of the framework towards these guest molecules is consistent with that observed in porous materials reported, underscoring the reliability of our results. To further substantiate the adsorption performance, we conducted theoretical calculations for JUC-644. The remarkably consistent alignment between simulation results and experimental data further validates the exceptionally high crystallinity and adsorption capability of JUC-644 (Supplementary Fig. 58). The Clausius–Clapeyron equation⁶² is

utilized to calculate the isosteric heat of adsorption (Q_{st}) values for n -C₄H₁₀, C₃H₈, and C₂H₆ at near-zero loading, yielding values of 34.8, 30.7, and 15.2 kJ mol⁻¹, respectively (Supplementary Fig. 59 and Tables 15-17). This outcome aligns with the observed lower uptake and more gradual isotherms for C₂H₆, indicating a high adsorption selectivity for n -C₄H₁₀/C₂H₆ and C₃H₈/C₂H₆. The ideal adsorbed solution theory (IAST) selectivity⁶³ parameter is paramount in assessing materials' adsorption and separation efficiency. Within the 0-100 kPa range, the n -C₄H₁₀/C₂H₆ selectivity of JUC-644 exhibits an increasing trend, while the C₃H₈/C₂H₆ selectivity initially decreases and then increases. The maximum values of the selectivity of n -C₄H₁₀/C₂H₆ and C₃H₈/C₂H₆ at 100 kPa are 79.2 and 10.4, respectively (Supplementary Figs. 60-69 and Tables 18-21).

Density-functional theory (DFT) calculations. To investigate the interaction between gas molecules and the channels, *ab initio* molecular dynamics (AIMD) simulations were carried out using the CP2K software, employing DFT as the computational method^{64,65}. We initially positioned the gas molecules at the center of the channels and simulated their trajectory changes at 298.15 K. As is shown in Supplementary Fig. 70 and the GIF images in attaching files, during the process of simulation, the color of the guest molecules transitioned from blue to white, and then to red (the blue-to-white transition represents the adsorption process of gas molecules from the center of the channels to the channel walls, while the white-to-red transition represents the thermal motion trajectory of the molecules after adsorption within the channels). It can be observed that the white-to-red trajectories of C₂H₆ and C₃H₈ show clear separation, indicating weaker restrictive effects of the COF channels on these two gas molecules. The thermal motion within the channels is relatively facile for these molecules, resulting in faster diffusion. Furthermore, examining the positions of the white-to-red trajectories of C₂H₆ and C₃H₈, it is evident that the white-to-red

trajectory of C_2H_6 is closer to the center of the COF channels, indicating weaker interaction between C_2H_6 and the channels, thus facilitating easier diffusion within the channels (Supplementary Fig. 70a-f). In contrast, the white-to-red trajectory of $n-C_4H_{10}$ largely overlaps, and even partially overlaps with some blue trajectories, suggesting stronger restrictive effects of the COF channels on this molecule (Supplementary Fig. 70g-i). Consequently, the thermal motion and diffusion of $n-C_4H_{10}$ within the channels are relatively restricted, leading to slower diffusion.

Breakthrough experiment. The substantial disparity in adsorption capacities between C_2H_6 and longer alkanes suggests the promising potential of JUC-644 for recovering C_2H_6 from NGLs. The recovery of C_2H_6 from NGLs is a significant source of industrial C_2H_6 , which is a primary raw material for C_2H_4 production^{66,67}. Nevertheless, conventional cryogenic distillation and solvent absorption methods employed for gas separation are characterized by their high energy consumption and detrimental environmental impact. In light of these inherent shortcomings, adsorption separation has emerged as a promising and sustainable alternative, offering energy efficiency and environmental friendliness^{68,69}. A key aspect of this approach lies in developing porous materials possessing exceptional adsorption capacity and separation selectivity^{70,71}. Although MOFs have gained considerable attention in the realm of light hydrocarbon separation⁷²⁻⁷⁴, their practical utilization in this context has been impeded by their relatively lower adsorption capacities for C_3H_8 and $n-C_4H_{10}$ at ambient temperatures, as well as their inadequate stability under humid conditions. Addressing these limitations, JUC-644 stands out as an exceptional porous adsorbent, perfectly suited for ethane recovery from NGLs. We initially tested the separation performance of JUC-644 in C_2H_6/C_3H_8 and $C_2H_6/n-C_4H_{10}$ (1:1, Tfr: 2 mL min⁻¹) mixtures. The results revealed that in the C_2H_6/C_3H_8 mixture, the retention times for C_2H_6 and

C_3H_8 were 73.8 min g^{-1} and 183.6 min g^{-1} (Extended Data Figure 1a and Supplementary Figs. 71 and 72). In the $C_2H_6/n-C_4H_{10}$ mixture, the retention times for C_2H_6 and $n-C_4H_{10}$ were 61.9 min g^{-1} and 220.5 min g^{-1} , respectively (Extended Data Figure 1b and Supplementary Figs. 73 and 74). To validate the practical application of JUC-644 in C_2H_6 recovery from NGL, we also conducted separation tests on a $C_2H_6/C_3H_8/n-C_4H_{10}$ (46:34:20, v/v/v, Tfr: 5 mL min^{-1}) mixture at 298 K. The results demonstrated that C_2H_6 rapidly passed through JUC-644 with a retention time of 29.2 min g^{-1} , while C_3H_8 and $n-C_4H_{10}$ exhibited retention times of 73.8 min g^{-1} and 162.3 min g^{-1} , respectively (Extended Data Figure 1c and Supplementary Figs. 75 and 76). The yield of C_2H_6 (purity >99.99%) was 4.73 mmol g^{-1} . Furthermore, breakthrough experiments were performed under moist conditions (~50% relative humidity). The retention times of C_3H_8 and $n-C_4H_{10}$ remained relatively unchanged (73.1 min g^{-1} and 157.2 min g^{-1} , respectively) in the presence of water (Supplementary Figs. 77 and 78). Additionally, the performance of JUC-644 was verified through five consecutive separation cycles, demonstrating its sustained separation efficiency (Extended Data Figure 1d). Following the separation cycle of JUC-644, we performed SEM, PXRD, and N_2 adsorption-desorption isotherms (Supplementary Figs. 79-81). The findings indicate that the crystallinity and porosity of JUC-644 were preserved after the separation cycle. These results confirm that JUC-644 is a promising material for efficient and environment-friendly recovery of C_2H_6 from NGLs.

Data availability. Crystallographic data for the structures reported in this Article have been deposited at the Cambridge Crystallographic Data Centre, under deposition numbers CCDC 2296805 (JUC-644) and 2353775 (JUC-645). Copies of the data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>. The authors declare that the data supporting the findings

of this study are available within the Article and its Supplementary Information files, or from the corresponding author on reasonable request.