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Entanglement of Square Nets in Covalent Organic Framework

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ABSTRACT: Two entangled 2D square COFs have been synthesized from 4,4',4'',4'''-(9,9'-spirobi[fluorene]-2,2',7,7'-tetrayl)-tetrabenzaldehyde (SFTB) and *p*-phenylenediamine (PPA) and benzidine (BZD) to form COF-38, [(SFTB)(PPA)₂]_{imine} and its isorecticular form COF-39, [(SFTB)(BZD)₂]_{imine}. We also report the single crystal electron diffraction structure of COF-39 and find that it is composed of mutually entangled 2D square nets (**sql**). These COFs represent the first examples of entangled 2D COF structures, which as we illustrate were made possible by our strategy of using the distorted tetrahedral SFTB building unit. SFTB overcomes the propensity of 2D COFs to stack through π - π stacking and allows for entanglements to form. This work adds significantly to the design principles of COFs.

Covalent organic frameworks (COFs) are a class of extended structures formed by linking organic building units through strong covalent bonds.¹⁻⁹ 2D COFs are often constructed by the combination of planar linking units facilitated by π - π stacking.^{3,5,9} For 3D COFs, the vast majority uses non-planar

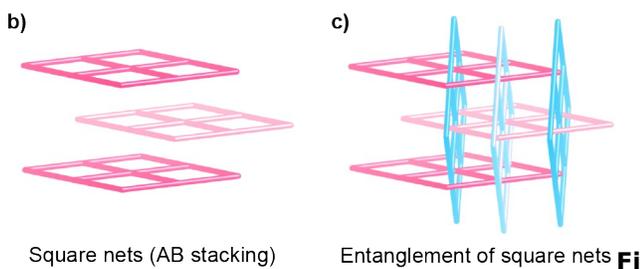
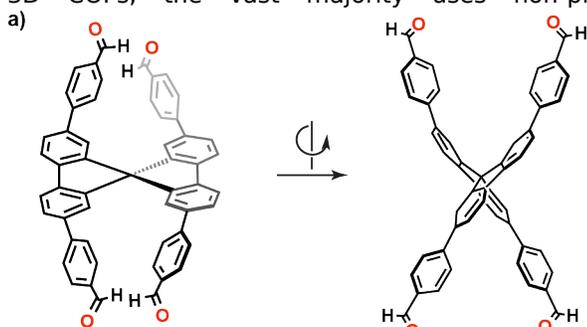


Figure 1. (a) Chemical structure of 4,4',4'',4'''-(9,9'-

spirobi[fluorene]-2,2',7,7'-tetrayl)-tetrabenzaldehyde (SFTB). Illustration of (b) AB stacked square nets and (c) entanglement of square nets.

units¹⁰⁻¹² to produce mainly **bor**,¹³ **ctn**,¹³ **dia**,¹⁴ **pts**,¹⁵ **lon**,¹⁶ **acs**,¹⁷ **bcu**,¹⁸ **stp**,¹⁹ **ljh**,²⁰ and **ceq**²¹ topologies. Although entanglements are well-known for 3D COFs,^{15-17,22,23} they remain unknown for 2D COFs. The persistence of this state of affairs is likely due to the fact that the formation of 2D COFs has relied entirely on choosing planar building blocks and deploying π - π stacking as means of organizing and ultimately crystallizing the material.²⁴⁻²⁶ In this report, we show how a distorted tetrahedral building block could be used to prevent π - π stacking and allow for 2D COF entanglements to form, and therefore increase the dimensionality of COFs from 2D to 3D.

Our strategy is based on using (4,4',4'',4'''-(9,9'-spirobi[fluorene]-2,2',7,7'-tetrayl)-tetrabenzaldehyde, SFTB, Figure 1a) as a building unit. Although the central carbon atom is tetrahedral, the overall geometry of the unit is a distorted tetrahedron as determined by the arrangement that the aldehyde functionalities make with respect to each other. This unit when reticulated with linear linkers was expected to form a square net (Figure 1b). We also recognized that the distorted tetrahedral units, SFTB, should minimize π - π interactions and

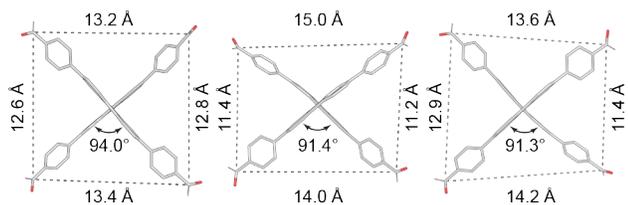


Figure 2. Single crystal structure of SFTB showed three independent as-symmetric units with different edge lengths and dihedral angles.

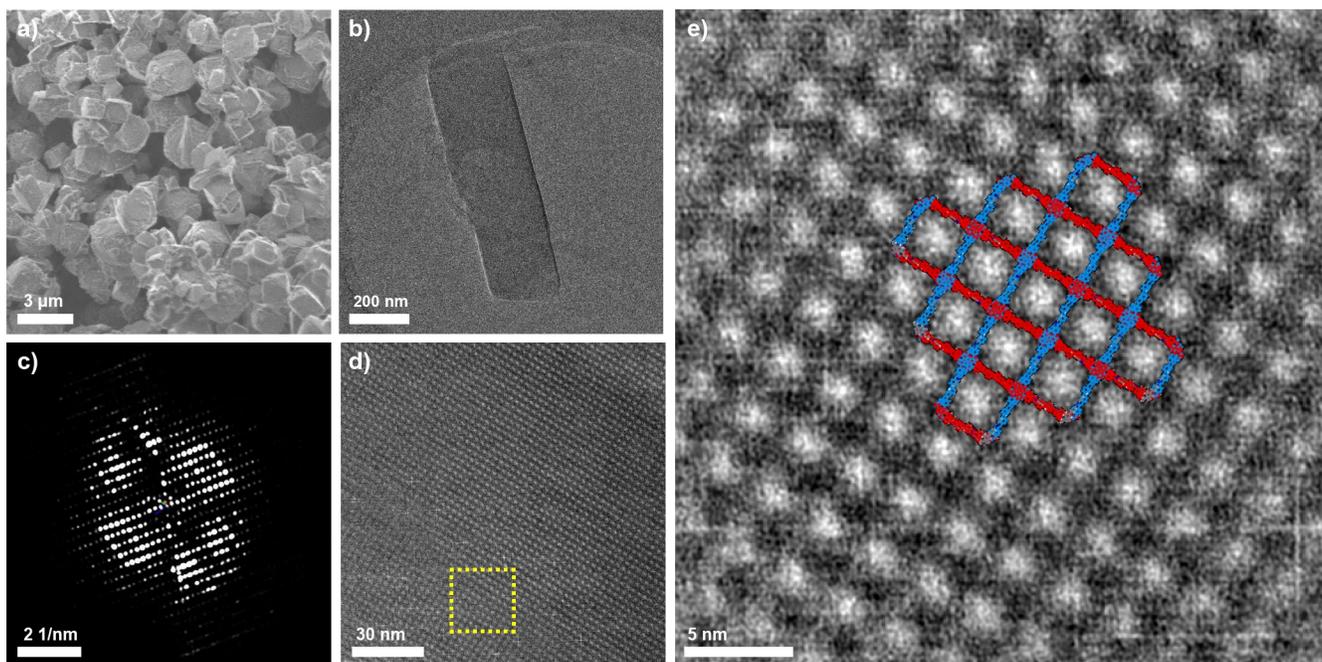


Figure 4. Electron microscopy data of COF-39. (a) Scanning electron microscopy (SEM) image of COF-39 presented the conglomerate of prism-shaped crystals. (b) Corresponding single crystal used for 3D ED data collection. (c) 2D projections of the 3D reciprocal lattice of COF-39 reconstructed from 3D ED data. (d) Average background subtraction filter (ABSF) high-resolution TEM (HRTEM) image of COF-39 taken along [001] direction. (e) Magnified view of the highlighted area of (d) overlaid with a structure model showed good agreement along [001].

therefore encourage the formation of square entanglements rather than the usual stacking of layers. We have successfully implemented this strategy by condensation of SFTB and *p*-phenylenediamine (PPA) or benzidine (BZD) to make 3D COFs (COF-38, [(SFTB)(PPA)₂]_{imine} and COF-39, [(SFTB)(BZD)₂]_{imine}, respectively) composed of entanglement of 2D nets (Figure 1c). We believe that our strategy widens the scope of possible COF structures where COF-38 and COF-39 are the first examples of entangled 2D COFs of any topology. It is worth mentioning that exhaustive efforts were undertaken to grow large crystals for COF-38 but only sub-microcrystals were obtained. However, we successfully synthesized highly crystalline COF-39 sample for electron microscopy analysis and elucidated its crystal structure. Therefore, we will discuss the synthesis and characterizations of COF-39 in the following content while the synthesis and characterizations of isorecticular COF-38 are detailed in the supporting information (SI).

We synthesized SFTB using a slightly modified literature procedure and successfully crystallized this linker (SI, Section S2). We also determined the single crystal X-ray structure of SFTB and found that it has a distorted tetrahedral geometry (SI, Section S3). Single crystal structure of SFTB (Figure 2) clearly showed three independent as-symmetric units with different edge lengths measured counterclockwise from the aldehyde carbon to the adjacent one. The edge lengths were in the range between 11.2 Å and 15.0 Å. The average dihedral angle of two spirobi[fluorene] rings was 92.2°. The ratio of the rectangle sides in SFTB linker was around 1.2, indicating its distorted tetrahedral geometry. The rectangular rather than square SFTB

shape played a role in producing the staggered COF framework and enhancing the flexibility of the extended structure (Figure 1b). SFTB was then reacted with linear amine-functionalized linkers PPA and BZD to form two 2D entangled COFs, namely COF-38 and COF-39, respectively (Figure 3a).

COF-39 was synthesized solvothermally by reacting the linkers SFTB and BZD in a 1:2 molar ratio in trichlorobenzene with aqueous trifluoroacetic acid as a catalyst (SI, Section S2). The reaction mixture was sealed in a Pyrex tube and heated to 120 °C for 3 d. COF-39, a yellow precipitate formed at the bottom of the tube, was isolated by centrifugation and washed by Soxhlet extraction with anhydrous tetrahydrofuran for 18 h to remove unreacted reactants. The material was then solvent exchanged with supercritical carbon dioxide and was finally activated under dynamic vacuum at room temperature for 1 h and then at 150 °C for 5 h. COF-39 was fully characterized by powder X-ray diffraction (PXRD), Fourier-transform infrared (FT-IR) spectroscopy, solid- and solution-state nuclear magnetic resonance (NMR) spectroscopies, elemental analysis (EA), thermogravimetric analysis (TGA), nitrogen sorption, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) (SI, Sections S2-S9).

The FT-IR spectroscopy indicated the formation of imine linkages of COF-39 at $\nu_{C=N} = 1625 \text{ cm}^{-1}$ and the consumption of aldehyde starting material since there was no identifiable $\nu_{C=O}$ aldehyde stretching vibration at 1695 cm^{-1} remaining (SI, Section S4). Further confirmation of imine-linkage formation in COF-39 was shown by ¹³C cross-polarization magic angle spinning (CP-MAS) NMR spectroscopy (SI, Section S5) where the characteristic C=N imine

resonances at 160 ppm was observed. Additionally, the disappearance of resonances above 190 ppm indicated that SFTB was fully converted into COF-39 by the imine condensation reaction. Analysis by solution-state NMR of acidic-digested COF-39 showing a stoichiometric ratio of 1:2 of SFTB:BZD, indicating there were minimal defects in COF-39 structure (SI, Section S5). CHN analysis of COF-39 corresponded to a reticular formula of $[(\text{SFTB})(\text{BZD})_2]_{\text{imine}}$ (Calcd for $\text{C}_{77}\text{H}_{48}\text{N}_4 \cdot 3\text{H}_2\text{O}$: C, 85.37; H, 5.02; N, 5.17%. Found: C, 85.94; H, 5.23; N, 5.29%; SI, section S2) indicating that all water molecules were not fully removed in COF-39 (ca. 5.0%). This data agreed with the FT-IR spectroscopy and TGA profile. The thermal stability of COF-39 was studied by TGA measured under N_2 atmosphere, and the onset in thermal decomposition of COF-39 was found to be around 480 °C (SI, section S6).

The SEM micrographs of COF-39 showed a homogeneous morphology of 1- μm prism-shaped crystals (Figure 4a) formed by conglomerate of thin and long needle-like crystals (SI, section S7). The homogeneous morphology of COF-39 indicates phase purity, as also shown by TEM analysis (Figure 4b-e, and SI, S8). Due to its high crystallinity, COF-39 exhibited the PXRD pattern with sharp peaks and low background (Figure 5). We were able to index at least 30 peaks from the PXRD pattern of COF-39 (SI, section S8). The indexing result suggested that COF-39 crystallized in Tetragonal Bravais lattice with space group of $I4_1$ or $I4$ which was in line with our hypothesis of having a 3D rather than a 2D COF structure.

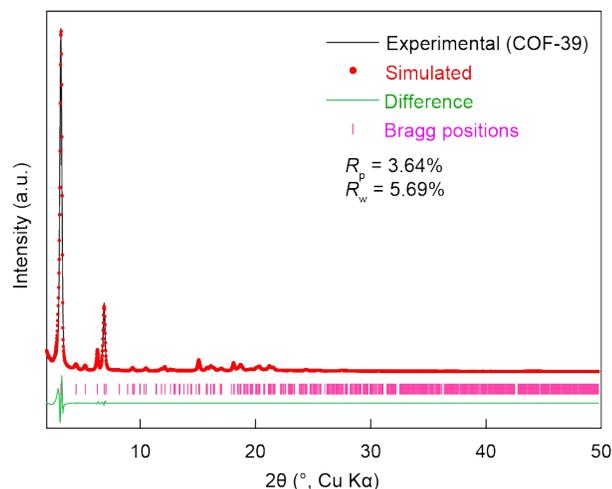


Figure 5. Pawley fitting (red circles) of experimental PXRD patterns (black lines) of activated sample of COF-39.

For TEM analysis (SI, Section S8), COF-39 was highly dispersed into ethanol and several droplets of the suspension were subsequently dropped onto a carbon-coated copper grid for volatilization under ambient conditions. 3D electron diffraction (3D ED) data of COF-39 were collected to further elucidate the crystal structure.²⁷ A typical 3D ED dataset with a resolution about 1.9 Å is shown in projections (Figure 4c). From the reconstructed 3D reciprocal lattice, a body-centered Tetragonal Bravais lattice was identified (SI, Section S8) and the unit cell

parameters were determined as $a = 39.9 \text{ \AA}$, $c = 19.3 \text{ \AA}$, and $V = 30654.6 \text{ \AA}^3$.

Based on the information obtained from 3D ED, we tried to build the structural model of COF-39 in Materials Studio® 8.0²⁸ using the Tetragonal space group $I4$, $I-4$, and $I4/m$. However, only the structural model built using $I4$ as the space group showed chemically reasonable structure and the simulated PXRD pattern showed great alignment to the experimental one (SI, Section S8). The unit cell parameters were then refined by Pawley fitting against the experimental PXRD pattern: $a = 39.8 \text{ \AA}$, $c = 19.2 \text{ \AA}$, $V = 30413 \text{ \AA}^3$ with very low reliability factors ($R_p = 3.64\%$, $R_w = 5.69\%$; Figure 5). More importantly, the calculated PXRD pattern of the built structure matched well with the experimental data of COF-39 (SI, Section S8).

According to the structural model, 2D **sql** layers (Figure 3a) were formed by stitching together SFTB and BZD, followed by the staggered stacking (AB-stacking form) of these formed layers along the c axis. The edge lengths of SFTB in COF-39 were found to be $8.4 \text{ \AA} \times 16.4 \text{ \AA}$. The rectangle sides ratio was 2.0, larger than that of SFTB alone, indicating the high flexibility of the resulting framework. The dihedral angle of two spirobi[fluorene] rings in COF-39 was 92.5° (SI, Section S8). The wide opening of the rhombic windows within each of the layers and the high flexibility of building units triggered the entanglement of another identical net (Figure 3b). Accordingly, one set of the staggered stacked layers entangled perpendicularly with another identical set to give rise to the final 3D framework adopting **sql-c*** as the topology with 1D square channel along [001] direction (Figure 3c).²⁹ For the topological perspective, COF-39 can also be classified based on degree of catenation of 1/1 with a diagonal/diagonal fashion.²⁴ The crystal structure of COF-39 is completely different from that claimed to be a 3D COF with 7-fold **dia** topology reported by Liu and co-workers,³⁰ even though similar building units were used. It should be noted that the flexible and distorted tetrahedral units may act as internal driving force to the entanglement formation. The detailed mechanism of the entanglement should be addressed in future studies.

High-resolution TEM images (HRTEM) were also taken to further gain insights into the crystal structure of COF-39. Indeed, the overlay of the structural model with the experimentally obtained HRTEM images along [001] and [111] both showed good agreement (Figure 4e, and SI, Section S8).

The permanent porosity of COF-39 was studied using N_2 sorption analysis at 77 K. Similar to entangled 3D COFs,^{16,19} COF-39 exhibited a Type I isotherm with a Brunauer-Emmett-Teller surface area of $813 \text{ m}^2 \text{ g}^{-1}$ (SI, Section S9). The Type I isotherm of COF-39 was likely attributed to the presence of water guest molecules, structural flexibility, and/or slightly slipping of the layers from each other.

ASSOCIATED CONTENT

The supporting information is available free of charge via the Internet at <http://pubs.acs.org>.

Synthesis and characterization details of COF-38 and COF-39 including elemental analysis, Fourier-transform infrared spectroscopy, nuclear magnetic resonance spectra, powder X-ray diffraction analysis data, electron microscopy data, computational modeling, N₂ sorption measurements, and thermogravimetric analysis (PDF).

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Notes

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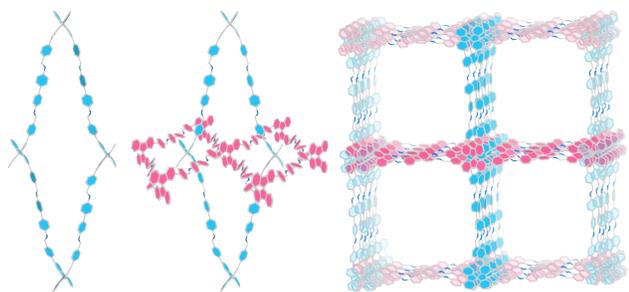
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Table of Content



Square net Entanglement of square nets

COF-39