Entanglement of Square Nets in Covalent Organic Frameworks

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Two entangled 2D square covalent organic frameworks (COFs) have been synthesized from 4,4′,4″-(9,9′-spiropi[fluorene]-2,2′,7,7′-tetracyl)-tetrabenzenaldehyde (SFTB) and p-phenylenediamine (PPA) and benzidine (BZD) to form COF-38, [(SFTB)(PPA)2]Junit and its isoreticular form COF-39, [(SFTB)(BZD)2]Junit. 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 entanglements to form. This work significantly adds to the design principles of COFs.
and elucidated its crystal structure. Therefore, we will discuss the synthesis and characterizations of COF-39 in the following content, whereas the synthesis and characterizations of isoreticular 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). The 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 carbon. The edge lengths were in the range between 11.2 and 15.0 Å. The average dihedral angle of two spirobifluorene rings was 92.2°. The ratio of the rectangle sides in the SFTB linker was ∼1.2, indicating its distorted tetrahedral geometry. The rectangular rather than tetrahedral shape of SFTB 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 days. 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 νC=O = 1625 cm⁻¹ and the consumption of aldehyde starting material because there was no identifiable νC=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 NMR spectroscopy (SI, Section S5), where the characteristic C=N imine resonances at 160 ppm were observed. Additionally, the disappearance of resonances above 190 ppm indicated that SFTB was fully converted into COF-39 by the imine condensation reaction.

The solution-state NMR analysis of acidic-digested COF-39 showed a stochiometric ratio of 1:2 of SFTB/BZD, indicating that there were minimal defects in the COF-39 structure (SI, Section S5). The CHN analysis of COF-39 corresponded to a reticular formula of [(SFTB)(BZD)2]imine (calcd for C77H48N4O18: 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%). These data agreed with the FT-IR spectroscopy and the TGA profile. The thermal stability of COF-39 was studied by TGA measured under a N2 atmosphere, and the onset of the thermal decomposition of COF-39 was found to be at 201 °C (SI, Section S6).

The SEM micrographs of COF-39 showed a homogeneous morphology of 1 μm prism-shaped crystals (Figure 4a) formed by a 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, Section S8). Because of its high crystallinity, COF-39 exhibited a PXRD pattern with sharp peaks and low background (Figure S). 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 the tetragonal Bravais lattice with a space group of P4212. The SEM micrographs of COF-39 clearly showed three independent as-symmetric units with different edge lengths and dihedral angles.

Figure 2. Single-crystal structure of SFTB showing three independent as-symmetric units with different edge lengths and dihedral angles.
Figure 3. Strategy of constructing 3D COFs through the entanglement of squares. (a) 4,4',4''-(9,9'-Spirobi[fluorene]-2,2',7,7'-tetranyl)-tetramaldehyde (SFTB) reacts with \( p \)-phenylenediamine (PPA) and benzidine (BZD) to form COF-38 and COF-39, respectively. (b) Entanglement of squares in COF-39. (c) Overall 3D structure shows 1D square channels in COF-39.
final 3D framework adopting sql-c* as the topology with the 1D square channel along the [001] direction (Figure 3c). From a topological perspective, COF-39 can also be classified based on the degree of catenation of 1/1 in a diagonal/diagonal fashion. The crystal structure of COF-39 is completely different from that claimed to be a 3D COF with seven-fold di topology reported by Liu and coworkers, even though similar building units were used. It should be noted that the flexible and distorted tetrahedral units may act as an internal driving force to the entanglement formation. The detailed mechanism of the entanglement should be addressed in future studies.

High-resolution TEM (HRTEM) images 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 both [001] and [111] showed good agreement (Figure 4e and SI, Section S8).

The permanent porosity of COF-39 was studied using N₂ sorption analysis at 77 K. Similar to entangled 3D COFs, COF-39 exhibited a Type I isotherm with a Brunauer–Emmett–Teller surface area of 813 m² g⁻¹ (SI, Section S9). The Type I isotherm of COF-39 was likely attributed to the presence of water guest molecules, the structural flexibility, or the slight slipping of the layers from each other.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c13468.

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)

Accession Codes
CCDC 2097659 and 2131421–2131422 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336033.

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