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Ester-Linked Crystalline Covalent Organic Frameworks

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ABSTRACT: Ester-linked, crystalline, porous, covalent organic frameworks (COFs) have been synthesized and structurally characterized. Transesterification reactions between di-topic 2-pyridinyl aromatic carboxylates and tri- or tetra-topic phenols gave the corresponding ester-linked COFs. They crystallize as 2D structures in kgm (COF-119) and hcb (COF-120, 121, 122) topologies with surface areas of up to 2,092 m²/g. Notably, crystalline COF-122 comprises edges spanning over 10 phenylene units; an aspect had only been achieved in metal–organic frameworks. This work expands the scope of reticular chemistry to include for the first time crystalline ester-linked COFs, related to common polyesters.

Ester is one of the most common functionalities in organic chemistry; however, it is yet to be reported as a linkage in covalent organic frameworks (COFs).1,2 Despite the ubiquity of polyester materials,3 their porous, crystalline, cross-linked counterparts are undeveloped (Figure 1). In contrast to ester molecules or polyesters, developing synthetic method for ester-linked COFs is considered more challenging as it requires the simultaneous process of carrying out the esterification reactions and framework crystallization.

New linkage development is essential to expanding the scope of reticular chemistry and it has been one of the major research directions in this area. While imine and its related linkages remain the most studied,2 significant advances in expanding the scope of direct COF crystallization have been made in recent years. For example, linkages considered less reversible such as olefin4 and dioxin5 have been developed. Incorporating sp² carbon has also been possible in the form of the aminal linkage.6 We expect that the ‘crystallization problem’ regarding the ester linkage can also be addressed by the proper combination of building units and reaction conditions. Here, we report the successful reticulation of ester-linked COFs as crystalline, porous structures.

We selected tetrakis(4-hydroxyphenyl)ethylene (THPE) along with various terephthalic acid derivatives for COF synthesis. Di(pyridin-2-yl) terephthalate (DPT) was found to be a suitable starting material in reactions leading to a...
highly crystalline product termed COF-119, [(THPE)(DPT)]$_3$ester (Figure 2). The reaction was carried out in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and dioxane at 150 °C in a sealed tube for 3 days. The product was insoluble in common organic solvents such as N,N-dimethylformamide, methanol, and acetone. On the other hand, no highly crystalline COF was obtained when terephthalic acid, terephthaloyl chloride, diphenyl terephthalate, or dimethyl terephthalate was used instead of DPT. This is likely because these starting materials are either too inert or too reactive to allow for a modulated crystallization process. The crystallinity of COF-119 was assessed by a powder X-ray diffraction (PXRD) study (Figure 3a). Remarkably, 15 diffraction peaks were observed with a laboratory X-ray source, far more than those from the more well-developed imine-linked or boronate ester-linked COFs with otherwise identical building units. The structure was modeled with kgm topology in $P\overline{3}$ space group (No. 147), and the unit cell parameters were further refined from the PXRD pattern through Pawley fitting. The layers are stacked in an eclipsed mode and the unit cell parameters ($a = b = 37.48$ Å and $c = 4.95$ Å) were obtained with good agreement factors ($R_p = 3.37\%$, $R_{wp} = 4.51\%$). Porosity was characterized by measuring the nitrogen sorption isotherm of the activated sample at 77 K (Figure 3b). The distinct step

![Figure 3. (a) PXRD pattern of COF-119 from a laboratory source of X-ray (Cu Kα). (b) N$_2$ sorption isotherm for COF-119 at 77 K.](image)

![Figure 4. Synthetic scheme for COF-120 and COF-121, including their powder X-ray diffraction structure models in space-filling style. Color code: H, white; C, gray; and O, red.](image)
between \( P/P_0 = 0.18−0.21 \) results from the mesopore filling of COF-119. The Brunauer–Emmett–Teller (BET) surface area was calculated to be 2,092 m\(^2\)/g. Calculation with the quenched solid density functional theory (QSDFT) based on the carbon model for cylindrical pores yielded pore sizes centered at 29.9 Å and 17.9 Å (Figure S37), comparable to those of the corresponding imine-linked COF (29 Å, 16 Å) based on the same model.\(^{10b,11}\) Conversion of the transesterification reaction was evaluated by Fourier transform infrared (FT-IR), \(^{13}\)C cross-polarization magic angle spinning (CP-MAS) NMR spectroscopies, and elemental analysis (Supporting Information Section S3–5). Consumption of THPE was ascertained by the disappearance of the O-H stretching band in the COF (Figure S6). A blueshift of the ester C=O stretching mode from 1726 cm\(^{-1}\) to 1744 cm\(^{-1}\) was also noted as compared to DPT (Figure S3). On the other hand, a minor difference between the ester \(^{13}\)C chemical shifts of DPT and COF-119 was observed (Figure S18). This is not surprising in light of the similarity between those shifts of DPT and diphenyl terephthalate, which is a close molecular analogue for COF-119. Nevertheless, the chemical shift at 158 ppm of DPT, corresponding to the C2 carbon of the pyridinyl group, is significantly attenuated in the COF. The smaller trigonal pores of COF-120 and COF-119 serve as an additional hurdle for framework deformation and free of noticeable impurities (Section S3, S4). The conversions of the transesterification reactions on the COFs were estimated from residual nitrogen contents to be 95% and 90% for COF-120 and COF-121, respectively (Section S5). The structural models were built and geometrically optimized using the Forceite module in Materials Studio (Section S10). Regarding COF-120 and COF-121, the unit cell parameters \( a \) and \( b \) of fully relaxed models are notably larger than those determined by the experimental X-ray diffraction patterns (Table 1, Entry 1, 2). On the other hand, such discrepancy is less pronounced for COF-119. Smaller experimental \( a \) and \( b \) values are likely due to favorable framework contractions to decrease void spaces within the COFs, which are facilitated by flexible ester linkages.\(^{13}\) As a result, COF-120 and COF-121 are likely to adopt more corrugated hexagonal conformations (Section S7). The smaller trigonal pores of COF-119 serve as an additional hurdle for framework deformation. The ordered stacking between the tetraphenylethylene units may also contribute to the structural rigidity of COF-119.\(^{10b}\) To further elucidate the rigidity difference between these materials, we compared the X-ray diffraction positions of both dry and solvated COFs (Figure S23). In contrast to COF-119, more evident shifts of the diffraction positions towards lower angle were observed for COF-120 and COF-121, indicating framework expansion of these materials in their solvated forms (Table 1, Entry 2, 3).\(^{14}\)

**Table 1. Unit cell parameters \( a = b \) (Å) for ester-linked COFs.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Source</th>
<th>COF-119</th>
<th>COF-120</th>
<th>COF-121</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Relaxed Model</td>
<td>37.70</td>
<td>37.02</td>
<td>44.16</td>
</tr>
<tr>
<td>2</td>
<td>WAXS(^{[a]})</td>
<td>37.55</td>
<td>34.36</td>
<td>41.34</td>
</tr>
<tr>
<td>3</td>
<td>WAXS (CH(_3)CN)(^{[a]})</td>
<td>37.16</td>
<td>35.99</td>
<td>43.02</td>
</tr>
</tbody>
</table>

\[^{[a]}\] Wide-angle X-ray scattering (WAXS). Samples were measured in capillary tubes with synchrotron X-ray. Unit cell parameters \( a = b \) here were directly calculated from the (100) diffraction positions.

To further explore the scope of the method, extended di- and tri-topic building units were used to construct a hexagonal COF with the largest pore size to date (Section S2).\(^{15,16}\) Insoluble crystalline product was isolated with an ester conversion of 97% (Section S5). Based on the corresponding WAXS data, a distorted hexagonal structure was modeled, with each edge spanning 10 phenylene units and
2 ester linkages (Figure 6a, b). Nevertheless, stacking mode between the layers is not assigned due to the low crystallinity and porosity (BET surface area: 646 m²/g, Figure S35, S36). Similar to the other ester-linked COFs with hcb topology, COF-122 undergoes unit cell expansion when solvated in acetonitrile, as evidenced by the shift of diffraction positions towards the lower angle (Figure 6c). Further studies are underway to firmly establish the detailed structure of COF-122. These efforts are currently challenged by the flexibility of its structure. However, it is quite remarkable that this COF based on ester linkages can be crystallized with edges containing ten phenylene units; an aspect only achieved in the chemistry of metal-organic frameworks and pointing to the level of progress being achieved in COF chemistry.2e,17

Figure 6. (a) Space filling diagram of one hexagon unit of activated COF-122. Color code: H, white; C, gray; and O, red. (b) WAXS pattern of activated COF-122. (c) Comparison between WAXS patterns of activated and CH₃CN-solvated COF-122.

In summary, we developed the first synthetic method to access crystalline, porous COFs with ester linkages. Trans-esterification reactions between di-topic 2-pyridyl aromatic carboxylates and tri- or tetra-topic phenols provided COFs with kmg and hcb topologies. The difference in topology also resulted in markedly different crystallinity and framework rigidity. This method also led to crystallization of a hexagonal COF with the largest edge length.

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

Methods and additional data (PDF)

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Notes
The authors declare no competing financial interest.

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