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Communication

Reticulating 1D Ribbons into 2D Covalent Organic Frameworks by Imine and Imide Linkages

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ABSTRACT: The design and synthesis of 2D and 3D crystalline covalent organic frameworks (COFs) from macromolecular and even infinite building units is largely undeveloped. Here, we report a strategy to link molecules and 1D ribbons into 2D crystalline frameworks. Triangular, tris(4-aminophenyl)amine (TAA), and square, 1,3,6,8-tetrakis(*p*-formylphenyl)pyrene (TFPPy), organic building units are joined substoichiometrically by imine linkages to produce 1D ribbons, termed COF-76, bearing free amines, which are then used to link the ribbons into 2D frameworks COF-77 and COF-78. In addition to this stepwise approach, we also demonstrate an *in situ* synthesis of these COFs. We believe our ability to link infinite building blocks, such as the ribbons of COF-76, into higher dimensionality COFs, paves the way to covalent frameworks composed of hierachical chemical structures.

Reticular chemistry of covalent organic frameworks (COFs) is concerned with covalently linking discrete molecular building blocks into extended, crystalline structures.[1−5] The reticular chemistry database features a vast number of theoretically accessible structures starting from small molecule organic building units,[6,7] but the design and synthesis of frameworks from large and even infinite building blocks remains a major challenge.[8,9] The main reason lies in the difficulty in retaining control over solubility and crystallinity during the synthesis.[10−12]

Inspired by the precise control with which nature links small molecules into 1D strands and directs their assembly into more complex 2D and 3D structures, we envisioned linking[13−16] of molecular building units into covalent organic ribbons and *crystalline* frameworks. This requires formation of 1D ribbons bearing reactive functional groups on their backbone for reticulating them into 2D frameworks.

The current strategy to introduce reactive functional groups on the backbone of COFs relies on postsynthetic deprotection of reactive groups.[17−20] Postsynthetic modifications, however, often come at the cost of a loss in crystallinity and porosity.[21,22] Recently, a second protecting group-free strategy has been introduced, which relies on linking molecular building units substoichiometrically. As a result, extended frameworks with periodically uncondensed, "frustrated", functionalities can be targeted.[23−25]

Here, we build on the latter strategy by reacting squares and triangles in a 1:2 substoichiometric ratio to synthesize 1D ribbons having unreacted, frustrated amine-functional groups on the backbone (Figure 1). These amine groups are then used to link the 1D ribbons by imine and imide chemistry into 2D COFs. In addition to this stepwise approach, we report an *in situ* synthesis of these hierarchically composed crystalline 2D frameworks starting from three discrete small molecules. Figure 1 illustrates both synthetic routes.

Specifically, we reacted the four-coordinate 1,3,6,8-tetrakis(*p*-formylphenyl)pyrene (TFPPy) with the three-coordinate tris(4-aminophenyl)amine (TAA) to form 1D ribbons {COF-76, $[(\mathrm{TFPPy})(\mathrm{TAA})_2]_{imine}$}. COF-76 was further reticulated by using either benzene-1,4-dialdehyde (BDA) to form COF-77 $\{(\mathrm{TFPPy})(\mathrm{TAA})_2(\mathrm{BDA})_{imine}\}$ or pyromellitic dianhydride (PMDA) to yield COF-78 $\{(\mathrm{TFPPy})(\mathrm{TAA})_2(\mathrm{PMDA})_{imine,imide}\}$.

COF-76 was synthesized by reacting TFPPy with TAA in a 1:2 stoichiometric ratio under solvothermal conditions with the addition of trifluoroacetic acid (TFA) in nitrobenzene/mesitylene (3:1; 3 d at 85 °C). The addition of the modulator[12] *p*-toluidine (20 equiv) was key in obtaining the product in high crystallinity (see Supporting Information (SI), Section S2). After successful crystallization, the solid was solvent-exchanged with chloroform for 12 h and activated under vacuum at 90 °C for 3 h to ensure complete removal of residual solvent in the pores. COF-76 was subsequently characterized by Fourier-transform infrared (FT-IR) and nuclear magnetic resonance (NMR) spectroscopies as well as thermogravimetric (TGA) and elemental analysis (EA).

The FT-IR spectrum of COF-76 shows the absence of residual aldehyde groups ($\nu_{C=O}$ = 1692 cm^{-1}) present in the starting material (TFPPy). Additionally, the formation of the imine functionality was supported by the appearance of the imine stretch at $\nu_{C=N}$ = 1628 cm^{-1} (see SI, Section S3). Importantly, the FT-IR traces substantiated the presence of free amine functionalities (ν_{N-H} = 3352 cm^{-1}). Further structural insight was gained by ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR spectroscopy. The resonance at 162.4 ppm, stemming from the imine-carbon, is indicative of successful imine formation. Also, the resonance at 146.0 ppm corresponds to the α-carbon of the amino phenyl group (see SI,

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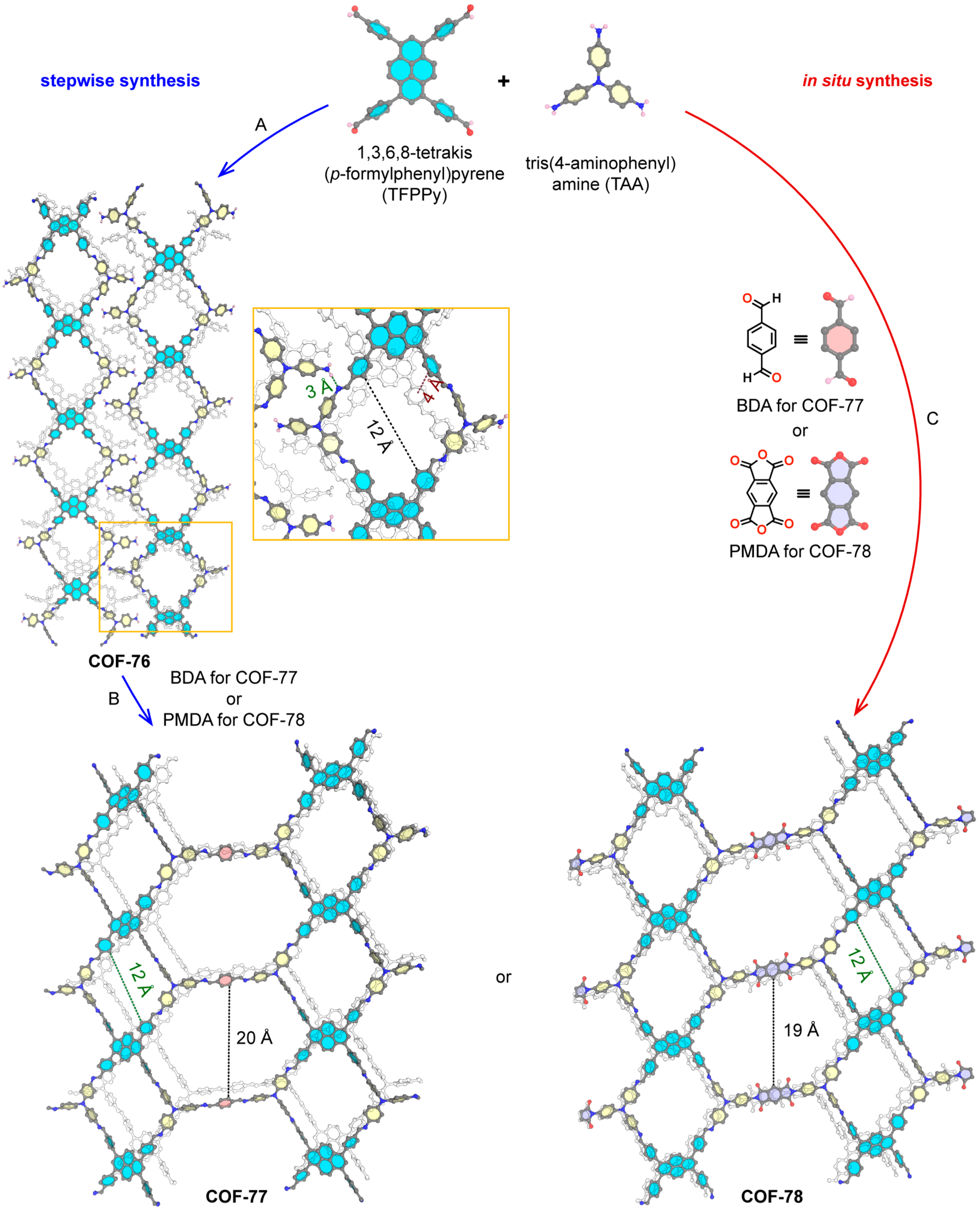

Figure 1. Synthesis of 1D COF-76, 2D COF-77, and -78 by a stepwise (A and B) and *in situ* method (C). 1,3,6,8-Tetrakis(*p*-formylphenyl)pyrene (TFPPy) and tris(4-aminophenyl)amine (TAA) were reacted in a 1:2 stoichiometric ratio to form COF-76 (A). COF-76 was linked by imine (with benzene-1,4-dialdehyde, BDA) and imide condensation (with pyromellitic dianhydride, PMDA) to form COF-77 and COF-78, respectively (B). COF-77 and COF-78 were formed in one step from TFPPy and TAA with BDA or PMDA (C). Atom sphere colors: C, gray; N, blue; O, red. Hydrogen atoms, except for aldehyde- and amine-hydrogens, omitted for clarity.

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Section S4).[26] Again, no residual aldehyde signals were observed.

Structural elucidation of COF-76 was carried out by powder X-ray diffraction (PXRD), followed by subsequent analysis of the pattern (Figure 2, see SI, Sections S1 and S5). The Charge Flipping[27] method was used to calculate the electron density map (EDM) of COF-76. The structure was then modeled by localizing the TFPPy fragments based on the EDM analysis. The TAA fragments were subsequently linked to the TFPPy units generating the 1D ribbon. The high resolution data, a result of the high crystallinity, enabled the use of the Rietveld refinement[28] to assign the structural parameters of COF-76 leading to the final unit cell parameters (*Ima*2, $a = 48.2495(3)$ Å, $b = 22.3132(2)$ Å, $c = 8.1481(6)$ Å) and converged *R* factors ($R_p = 8.47\%$, $R_{wp} = 11.80\%$; Figure 2 and SI, Section S5).

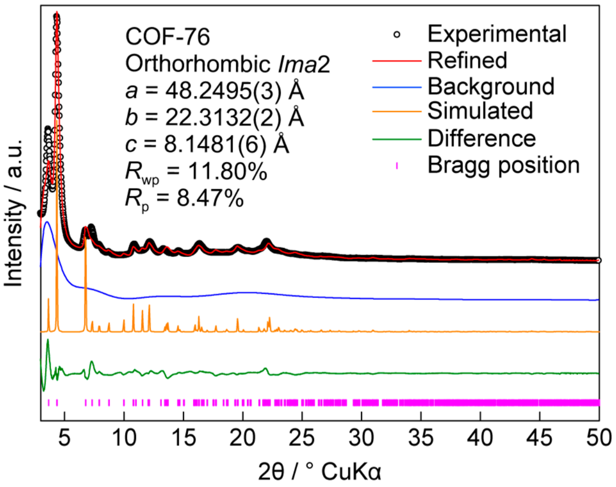

Figure 2. Overlay of the experimental and calculated PXRD traces obtained for COF-76. Rietveld refinement was applied to obtain the converged unit cell parameters.

In this model, the single 1D ribbons are locked into each other, with the free amine group pointing toward the imine linkage (H···N = 3 Å, Figure 1). Along the *c*-axis, the COF-76 strands are stacked onto each other with interlayer distances of $C_{centroid}\cdots C_{centroid} = 4$ Å. COF-76 displays a cylindrical pore with a diameter of 12 Å (C···C distances using van der Waals radii, Figure 1).

The N_2 isotherm of COF-76 measured at 77 K showed a Type I isotherm, indicating permanent porosity and a Brunauer–Emmett–Teller (BET) surface area of 860 $m^2\ g^{-1}$ (see SI, Section S6). The pore size distribution, estimated by density functional theory (DFT) calculation using the cylinder geometry and N_2-cylindrical pores-oxide surface model, was calculated from its N_2 sorption isotherm with a pore diameter of 12 Å, which is in good agreement with the modeled pore size (Figure 1). The experimental pore volume of COF-76, extracted from the N_2 isotherm, amounts to 0.42 $cm^3\ g^{-1}$, which is in good

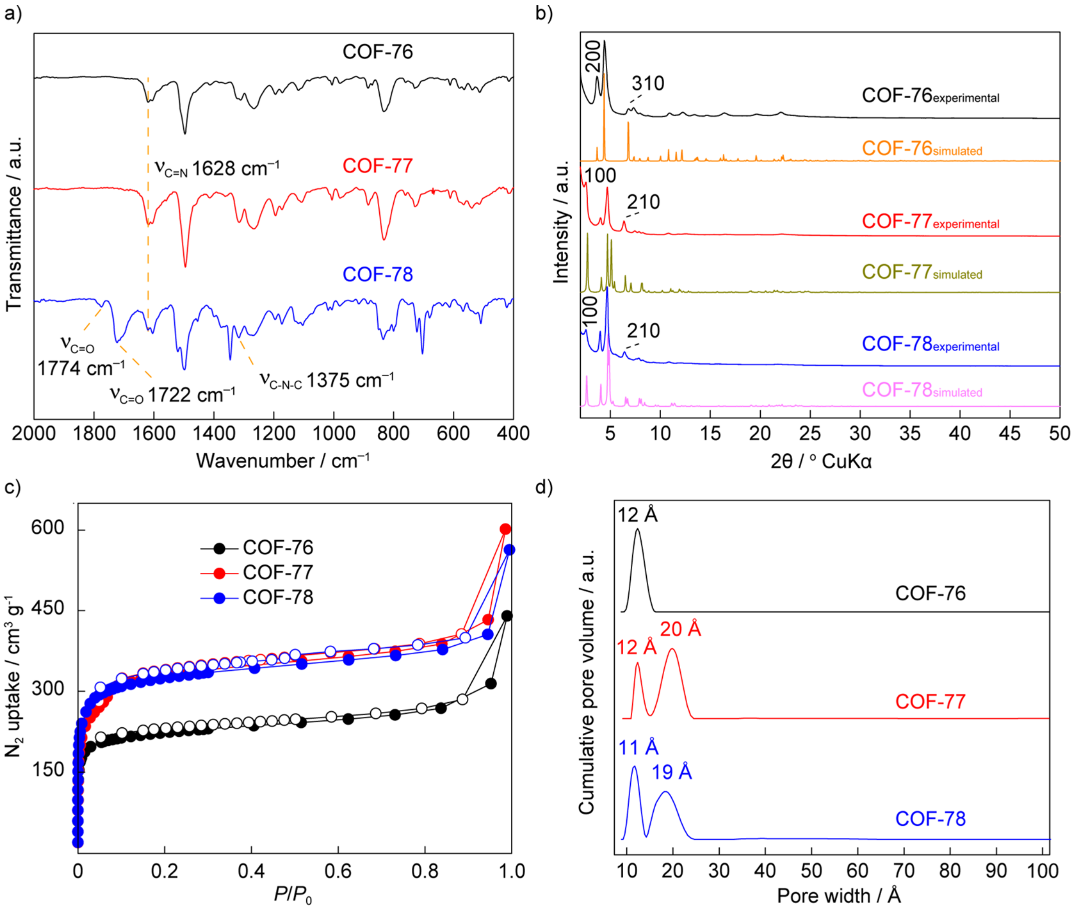

Figure 3. Overlay of FT-IR spectra of COF-76, COF-77, and COF-78 with vibrational bands of characteristic functional groups (a). Experimental and simulated PXRD traces of COF-76, COF-77, and COF-78 (b). N_2 isotherms of COF-76 (black), COF-77 (red), and COF-78 (blue) at 77 K. Pore size distributions of COF-76, COF-77, and COF-78 (d).

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agreement with the calculated value obtained from PLATON[29] using the Void Calculation function (0.44 $cm^3 g^{-1}$).

To afford the extended 2D COF, we linked COF-76 through the unreacted amine groups on the backbone. Two types of linkages were targeted, namely an imine-based and an imide-based linkage, leading to COF-77 and COF-78, respectively (Figure 1).

The imine-based linking relies on the condensation of the free amine groups of the 1D COF-76 with BDA, whereas the imide-based linking involves reaction of the free amine groups of COF-76 with PMDA to form the extended 2D COF-78 (Figure 1). Two synthetic strategies are reported for COF-77 and -78. The first one follows the stepwise synthesis of the 1D ribbon from the TFPPy and TAA. After isolation and characterization, the 1D ribbon is subjected to linking conditions to obtain the extended 2D structure (either imine or imide conditions). The second strategy follows an *in situ* method, where the 1D ribbon and the 2D COF are formed in one step. Both strategies lead to the same 2D framework products, COF-77 and COF-78, possessing a **bex** topology (see SI, Section S5).[24]

Following the stepwise approach, COF-76 and BDA (1 equiv) were immersed in 2 mL of nitrobenzene/mesitylene (3:1) with 2 v% of TFA. COF-77 was obtained as a crystalline solid after 5 d at 85 °C. A comparable crystallinity was obtained by *in situ* formation of COF-77. The three small molecular linkers—TFPPy, TAA, and BDA—were dissolved in a 1:2:1 stoichiometric ratio in nitrobenzene/mesitylene (3:1); *p*-toluidine (20 equiv) was added as a modulator, and the solution was heated for 5 d at 85 °C.

These two strategies were also applied for the imide-based COF-78. We initially followed the stepwise approach, where COF-76 and PMDA (1 equiv) were immersed in mesitylene/*N*-methyl-pyrrolidone/isoquinoline in a 1:0.2:0.02 volumetric ratio (1.22 mL). The crystalline COF-78 was obtained after 5 d at 160 °C. This method was then compared to the product of the *in situ* approach, where TFPPy and TAA (1:2 stoichiometric ratio) were dissolved in nitrobenzene/mesitylene (3:1) with 2 v % of TFA and *p*-toluidine (20 equiv). After 1 d at 85 °C, PMDA in mesitylene/*N*-methyl-pyrrolidone/isoquinoline (1:0.2:0.02 volumetric ratio) was added and the suspension was heated for 5 d at 160 °C. Both procedures yielded comparably high crystallinity, as indicated by similar elemental analysis results, PXRD, and surface area (see SI, Sections S2, S5, and S6). When TFPPy, TAA, and PMDA were dissolved under the same reaction conditions and heated to 85 °C, only the formation of COF-76 was observed. This further substantiated the formation of the 1D ribbon prior to reticulation.

COF-77 and COF-78 were solvent-exchanged with chloroform for 12 h and subsequently activated under vacuum at 90 °C for 3 h to ensure complete removal of residual solvent in the pores.

The successful linking of COF-76 to afford COF-77 and -78 was followed by FT-IR spectroscopy analysis. The disappearance of the free amine band at ν_{N-H} = 3352 cm^{-1} present in COF-76 was indicative of the successful formation of the imine linkage in COF-77. For COF-78, the FT-IR traces showed the formation of new bands, corresponding to the characteristic imide stretches at $\nu_{C=O}$ = 1774 cm^{-1} and $\nu_{C=O}$ = 1722 cm^{-1}. The FT-IR stretch at ν_{C-N-C} = 1375 cm^{-1} is consistent with the formation of the C−N−C functionality present in the imide linkage (Figure 3a).[30] The ^{13}C CP-MAS NMR spectroscopic resonances at 162.9 and 163.6 ppm, stemming from the imine-carbon, are present in COF-77 and -78, respectively. Additionally, the solid state spectroscopic traces of COF-78 showed a signal at 164.6 ppm corresponding to the carbonyl-functionality of the imide linkage (see SI, Section S4).[30] No residual signals of unreacted amine functionalities (α-carbon of the amino phenyl group) were observed; instead, the resonance assigned to the α-carbon of the imide shifted from 146.0 ppm for the free amine to the broadened resonance at 156.7 ppm for COF-77 and 155.6 ppm for COF-78 (see SI, Section S4).

COF-77 and COF-78 were structurally characterized by PXRD, followed by analysis and comparison of the PXRD traces with COF-76 (Figure 3b). Two new low-angle intense diffraction peaks evidenced the formation of an increased unit cell for COF-77 and -78 (2θ/CuKα = 2.4° and 6.3°; 2.6° and 6.6° respectively; Figure 3b). The structures were assigned to the **bex** topology, which is a binodal net constructed from 3-c and 4-c secondary building units (see SI, Figure S11). This results in two kinds of pores, the smaller one originating from the 1D ribbon (12 Å) and the larger one from linking the ribbon into the 2D extended structure (19−20 Å, Figure 1). The structural models for COF-77 and COF-78 are detailed in the SI, Section S5.

The N_2 sorption isotherm at 77 K confirmed permanent porosities of COF-77 and -78. Both frameworks display a Type I isotherm with a BET surface area of 1288 $m^2 g^{-1}$ and 1265 $m^2 g^{-1}$, respectively (see SI, Section S6). This accounts for a substantial increase in the BET surface area compared to COF-76 (860 $m^2 g^{-1}$; Figure 3c). The BET surface area of COF-78 as synthesized by the stepwise approach is slightly smaller than the one measured after the *in situ* synthesis (1080 $m^2 g^{-1}$; see SI, Section S6). The pore size distribution for COF-77 and COF-78 was calculated from their N_2 sorption isotherms based on the same model used for COF-76. The values obtained from this model are in good agreement with the structural model of COF-77 and COF-78 (12 and 11 Å, respectively, for the smaller pores; 20 and 19 Å for the larger pores; Figure 3d).

We have reported a new concept of assembling discrete organic molecules into 1D ribbons, followed by their linking into 2D frameworks. Our approach relies on a protecting-group-free strategy to produce 1D ribbons bearing reactive functional amine groups on the backbone. The functional groups are then employed to reticulate the 1D ribbons by imine and imide chemistry to obtain the crystalline 2D frameworks COF-77 and 78 in a **bex** topology.

This work showcases the use of infinite molecular building blocks for the synthesis of crystalline frameworks. We highlight this concept through imine and imide chemistry and emphasize the generalizability and applicability of this strategy to other linkages.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.9b13971.

Synthesis and full characterization details of COF-76, COF-77, and COF-78 including elemental analysis, Fourier-transform infrared spectroscopy, solid-state nuclear magnetic resonance spectra, powder X-ray diffraction analysis data, computational modeling, gas uptake measurements, and thermogravimetric analysis (PDF)

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Notes

The authors declare no competing financial interest.

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