## Single-Crystalline Imine-Linked Two-Dimensional Covalent Organic Frameworks Separate Benzene and Cyclohexane Efficiently

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2D COF (TAPB-DMPDA). The sizes of TAPPy-PDA and TAPB-DMPDA crystals were tuned from 720 nm to 4  $\mu$ m and 450 nm to 20  $\mu$ m in width, respectively. High-resolution transmission electron microscopy revealed that the COF crystals consist of layered, 2D polymers comprising single-crystalline domains. Continuous rotation electron diffraction resolved the unit cell and crystal structure of both COFs, which are single-crystalline in the a-b plane but disordered in the stacking c dimension. Single crystals of both COFs were



incorporated into gas chromatography separation columns and exhibited unusual selective retention of cyclohexane over benzene, with single-crystalline TAPPy-PDA significantly outperforming single-crystalline TAPB-DMPDA. Polycrystalline TAPPy-PDA exhibited no separation, while polycrystalline TAPB-DMPDA exhibited poor separation and the opposite order of elution, retaining benzene more than cyclohexane, indicating the importance of improved material quality for COFs to exhibit properties that derive from their precise, crystalline structures. This work represents the first example of synthesizing imine-linked 2D COF single crystals at ambient pressure and short reaction times and demonstrates the promise of high-quality COFs for molecular separations.

#### INTRODUCTION

The polymerization of monomers into two-dimensional (2D) macromolecular sheets is a longstanding synthetic challenge that will provide organic materials with distinct properties compared to traditional polymer architectures. Direct, solution-based polymerizations provide 2D polymers  $(2DPs)^1$  often known as 2D covalent organic frameworks (COFs),<sup>2-5</sup> which have shown properties of interest for catalysis,<sup>6-9</sup> sensing,<sup>10-13</sup> membranes,<sup>14-17</sup> gas storage and separation,  $^{18-20}$  adsorbents,  $^{21-23}$  energy storage,  $^{24-26}$  and optoelectronic devices.  $^{27-29}$  These applications leverage the precise and tunable structures, permanent nanometer-scale porosity, and layered structures associated with 2D COFs or other 2DPs.1 However, rather than forming the macromolecular sheets with macro- or mesoscale crystalline domains, most COF polymerizations yield insoluble, polycrystalline powders with domain lengths smaller than 100 nm in the plane of the 2D sheet.<sup>30-36</sup> These isolated forms and crystalline domain sizes often limit the full extent of physical properties of the 2D COFs, along with their practical relevance for otherwise promising applications. Therefore, general and operationally

simple methods to obtain 2D COFs with larger crystalline domain sizes and improved processibility remain an important frontier in their development.

To address this need to improve the material quality of polycrystalline COFs, growing COF particles as colloidal suspensions has emerged as a means of preventing uncontrolled aggregation and precipitation,<sup>37</sup> a prerequisite to controlling the nucleation and polymerization processes that provide high 2DP material quality.<sup>38</sup> Subsequently, boronate ester- and boroxine-linked 2D COFs were isolated as singlecrystalline particles by preventing continuous nucleation processes during the polymerization.<sup>39,40</sup> However, 2D COFs formed using Schiff base chemistries,41-48 especially imine linkages,<sup>41</sup> have since emerged as the most common and

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Figure 1. Synthesis of single-crystalline imine-linked (A) TAPPy-PDA and (B) TAPB-DMPDA COFs.

versatile class of 2DPs<sup>1,2</sup> because of the broad scope of available monomers and the good to excellent chemical and thermal stabilities of the resultant 2DPs. Imine-linked COFs may also be transformed to even more stable amide,  $^{43,44}$   $\beta$ ketoenamine,<sup>45,46</sup> or thiazole-linked<sup>47-49</sup> structures, such that achieving improved control of imine-linked 2D COFs might indirectly provide access to many other high-quality 2DPs. Early mechanistic studies of imine-based 2D polymerizations suggested that the rapid formation of a polymer network followed by crystallization by imine exchange reactions occurred under most solvothermal conditions.<sup>50</sup> More recently, imine-linked COF formation was found to be rapid<sup>51,52</sup> and, in some cases, thermally reversible,<sup>53</sup> and two examples of micron-size and larger imine-linked 2D COF single crystals have been reported.54,55 Wei and coworkers reported millimeter-sized crystals of an imine-linked 2D COF, TAPPy-PDA, using supercritical CO<sub>2</sub> as the reaction solvent and reaction times as short as 5 min, although the crystallinity was characterized by transmission electron microscopy (TEM) analysis rather than bulk X-ray diffraction.<sup>55</sup> This 2D polymer had been reported previously as a polycrystalline powder by Bein and coworkers under traditional solvothermal conditions and reaction times of 1-3 days.<sup>56</sup> Zhao and coworkers subsequently reported micron-sized single crystals of the same COF, which were obtained solvothermally using reaction times of 1-3 months.<sup>54</sup> These early examples of high-quality iminelinked 2D COFs inspire our present work, which focuses on conditions that provide 2D COFs of comparable quality, ideally without requiring high pressure reactors or extended reaction times. Furthermore, as examples of higher-quality 2D COFs emerge, we can now explore how their properties differ from their polycrystalline counterparts.

Here, we report imine-linked 2D COF solvothermal polymerization conditions that provide **TAPPy-PDA** COF (Figure 1) as micron-sized single crystals in as little as 5 min. These conditions rely on a nitrile-containing solvent, aniline as a monofunctional modulator of the polymerization,<sup>57,38,58,59</sup> benzoic acid as a catalyst for defect correction, and elevated reaction temperature, as key parameters that influence the crystallite size. Similar conditions also provided **TAPB-DMPDA** COF as the first hexagonal imine-linked 2D COF

to be isolated in this single-crystalline form. The COFs exhibit excellent crystallinity and porosity, as determined by powder X-ray diffraction (PXRD) patterns and N<sub>2</sub> adsorption isotherms. High-resolution transmission electron microscopy (HRTEM) analysis confirms that the polymer sheets are single-crystalline domains, and continuous rotation electron diffraction (cRED) reveals that these structures are singlecrystalline in the plane of covalent bonding, yet disordered in the stacking direction, as there are multiple ways that the sheets can be offset with respect to one another. This approach is a readily available and rapid method to prepare high-quality imine-linked COFs that might enable the practical synthesis of other imine-linked 2DPs.

Finally, we demonstrate that the TAPPy-PDA COF single crystals effectively separate benzene and cyclohexane when used as a stationary phase in gas chromatography, whereas polycrystalline samples of the same material show no separation. This separation is an important industrial process that is conventionally difficult by distillation because their boiling points differ by only 0.6 °C, among other similar physical properties.  $^{60-62}$  Chromatographic separations using porous materials as stationary phases have been explored as an energy-efficient alternative.<sup>63,64</sup> In 2015, Yan and coworkers reported the synthesis of nanometer-sized spherical particles of a  $\beta$ -ketoenamine-linked 2D COF for the high-resolution separation of benzene and cyclohexane using a gas chromatography column as a proof of concept.<sup>64</sup> The COFcoated capillary column showed a greater retention of benzene, resulting in the expected elution of cyclohexane before benzene, in accordance with their respective calculated Gibbs free energy changes. In 2021, Macreadie and coworkers reported the efficient separation of benzene and cyclohexane by three metal organic frameworks (MOFs), of which MOF-5 through single-component characterization revealed an unusual, reversed selectivity for cyclohexane adsorption, which was attributed to the pore size and geometry that enabled specific aliphatic/aromatic interactions between the analytes and the stationary phase.<sup>65</sup> More recently, Navarro and coworkers demonstrated the impact of pore flexibility on benzene/cyclohexane adsorption in three-dimensional COFs, where the increased flexibility of COF-300 pores was found to

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Figure 2. (A) Experimental and simulated PXRD patterns (AA stacking), (B)  $N_2$  adsorption and desorption isotherms, and (C) NLDFT pore width distribution of 1  $\mu$ m-sized TAPPy-PDA COF single crystals. (D) Experimental and simulated PXRD patterns (AA stacking), (E)  $N_2$  adsorption and desorption isotherms, and (F) NLDFT pore width distribution of 1  $\mu$ m-sized TAPB-DMPDA COF single crystals.



**Figure 3.** (A) SEM and (B) HRTEM images of 1  $\mu$ m-sized **TAPPy-PDA** COF single crystals with dashed lines drawn around the edges of the crystal as a guide to the eye. (C) Lattice-resolution HRTEM image of the boxed region in panel (B), which shows lattice fringes that extend across the entire crystal, and (D) bandpass-filtered image of panel (C) with enhanced contrast. (E) FFT of the boxed region in panel (B), with spots circled (blue, orange) that correspond to  $d_{100}$  spacings of 23.9 and 24.0 Å, respectively. (F) SEM and (G) HRTEM images of 1  $\mu$ m-sized **TAPB-DMPDA** COF single crystals with dashed lines drawn around the edges of the crystal as a guide to the eye. (H) Lattice-resolution HRTEM images of the boxed region in panel (G), which shows lattice fringes that extend across the entire crystal, and (I) bandpass-filtered image of panel (H) with enhanced contrast. (J) FFT of the boxed region in panel (G), with spots circled (blue, orange, and green) that correspond to  $d_{100}$  spacings of 31.4, 31.1, and 31.5 Å, respectively.

cause greater selective adsorption of benzene over cyclohexane.<sup>66</sup> Here, we show that the **TAPPy-PDA** 2D COF crystals show a fast, high-resolution, and efficient gas chromatographic separation of benzene and cyclohexane in as little as 30 s, also with a reversed preferential retention of cyclohexane. Meanwhile, the polycrystalline samples of the **TAPPy-PDA** COF show no separation as well as shorter retention times for both analytes when tested under the same conditions. Single crystals of the **TAPB-DMPDA** COF show the same reversed preferential retention of cyclohexane, whereas polycrystalline samples of the same COF instead show the normal and expected preferential retention of benzene. We used an inverse gas chromatography (IGC) approach to characterize the physicochemical motivations of separation over **TAPPy-PDA** and **TAPB-DMPDA** COF single crystals as the first COFs to show this reversed selectivity of cyclohexane over benzene. These findings are of great promise for difficult molecular separations and highlight that highquality 2D COF samples exhibit distinct and useful properties relative to polycrystalline samples with the same chemical composition.

#### RESULTS AND DISCUSSION

Synthesis and Characterization of COF Single Crystals. The imine-linked 2D COF derived from 1,3,6,8tetrakis(4-aminophenyl)pyrene (TAPPy) was synthesized at 90 °C by condensing TAPPy and terephthalaldehyde (PDA) in the presence of benzoic acid and aniline in benzonitrile (Figure 1A; see the Supporting Information for detailed procedures). The hexagonal TAPB-DMPDA COF network was synthesized by condensing 1,3,5-tris(4-aminophenyl)benzene (TAPB) and 2,5-dimethoxyterephthalaldehyde (DMPDA) under similar conditions (Figure 1B; see the Supporting Information for detailed procedures). For both polymerizations, brightly colored colloidal suspensions (orange for TAPPy-PDA; red for TAPB-DMPDA) formed within minutes. Scanning electron microscopy (SEM) and HRTEM images of the drop-cast colloidal COF solutions showed 1  $\mu$ mwide square platelets and 1  $\mu$ m-wide hexagonal platelets for the TAPPy-PDA and TAPB-DMPDA COFs, respectively. These faceted particles exhibit the same shapes as the layered square and hexagonal lattices of each COF. The colloids were precipitated from solution by adding saturated aqueous NaCl and methanol, filtered, washed by Soxhlet extraction using methanol, and activated using a supercritical CO<sub>2</sub> dryer. The resulting solids were highly crystalline and porous, as confirmed by PXRD patterns (Figure 2A,D) and N<sub>2</sub> uptake isotherms of the isolated colloids (Figure 2B,E). The PXRD patterns of the TAPPy-PDA and TAPB-DMPDA COFs exhibited sharp 100 Bragg diffraction peaks at  $2\theta = 2.78^{\circ}$  and 3.68°, respectively, as well as the corresponding higher-order Bragg diffraction peaks, consistent with previously reported powder patterns<sup>6,56</sup> and average eclipsed AA models of the COFs, except for broadening of the 001 peaks (Figure 2A,D). Analysis of the N<sub>2</sub> uptake isotherms of both COFs provided Brunauer–Emmett–Teller (BET) surface areas of 2600 m<sup>2</sup> g<sup>-1</sup> for the TAPPy-PDA COF and 2640  $m^2 g^{-1}$  for the TAPB-DMPDA COF (Figure 2B,E), from which non-local density functional theory (NLDFT) analysis provided narrow pore width distributions centered at 22.4 Å and 32.4 Å for the TAPPy-PDA and TAPB-DMPDA COFs, respectively (Figure 2C,F). Additionally, these experimentally measured BET surface areas were within 20% of their Connolly surface areas, indicating that the isolated and activated samples exhibit the permanent porosity as expected for a high-quality COF sample. Collectively, these bulk characterization techniques indicate that the polymerizations of the TAPPy-PDA and TAPB-DMPDA COFs under the conditions reported above provide highly crystalline and porous samples.

The 1  $\mu$ m-sized square **TAPPy-PDA** COF platelets and hexagonal **TAPB-DMPDA** COF platelets showed characteristics attributed to COF single crystals, as determined by lowdose HRTEM (Figure 3B–E,G–J). TEM imaging at low magnification confirmed that the **TAPPy-PDA** COF platelets had a uniform four-fold symmetry and were faceted squares, consistent with their visualization by SEM (Figure 3A) and atomic force microscopy (AFM) (Figure S1), while the hexagonally faceted platelets of the **TAPB-DMPDA** COF exhibited a uniform six-fold symmetry, which was also consistent with these imaging techniques (Figure 3F and Figure S2). The COF crystals were preferentially oriented with their intersheet stacking dimension normal to the TEM substrate, which is likely due to their z dimension (particle thickness) being smaller than their lateral dimensions (Figure 3B,G). Furthermore, lattice-resolution TEM images of individual COF particles suggested that they are singlecrystalline with consistent and continuous lattice fringes that extended throughout the particles (Figure 3B–E,G–J). For the TAPPy-PDA COF particle shown in Figure 3B, the lattice spacings were 23.9 and 24.0 Å, as measured by fast Fourier transform (FFT; Figure 3E), which match the expected  $d_{100}$ spacing. For the **TAPB-DMPDA** COF (Figure 3H), the  $d_{100}$ spacings were 31.1, 31.4, and 31.5 Å, as measured by FFT (Figure 3J). Additional images and FFT patterns of other regions of these COF particles (Figures S3 and S4) also exhibited identical  $d_{100}$  features at 24.0 Å (for TAPPy-PDA) and 31.5 Å (for TAPB-DMPDA). Taken together, the HRTEM images and the FFT patterns of the TAPPy-PDA and TAPB-DMPDA COF crystals are consistent with the formation of layered 2D polymers in which each sheet comprises a single-crystalline domain.

Larger crystals of each COF were prepared by varying their crystallization conditions to provide 4  $\mu$ m-wide squares of TAPPy-PDA and 20 µm-sized hexagons of the TAPB-DMPDA COF by optimizing the monomer concentration, aniline amounts, and reaction temperature (Figures S15-S19; see the Supporting Information for detailed procedures). Varying the monomer concentration between 8 and 16 mM and varying the aniline loadings between 1.0 and 1.6 equiv at the initial reaction temperature of 90 °C resulted in a broad range of final TAPPy-PDA COF crystal sizes, from 720 nm to 4  $\mu$ m in diameter and up to 1  $\mu$ m in thickness (Figure S15). TAPB-DMPDA COF crystal sizes varied from 0.45 to 7.0  $\mu$ m in diameter and 0.10 to 1.4  $\mu$ m in thickness when the monomer concentration was increased from 8 to 16 mM and aniline loadings were increased from 0.4 to 0.8 equiv (Figure S17). Based on SEM images of drop-cast aliquots of the TAPB-DMPDA COF polymerizations isolated at different reaction times, the crystals reached their final sizes within 6 min (Figure S19A). We hypothesized that increasing the reaction temperature would slow nucleation based on our recent study of COF recrystallization<sup>53</sup> and the temperaturedependence of the imine/aldehyde equilibrium. Indeed, a polymerization temperature of 150 °C produced TAPB-DMPDA COF crystals of up to 20  $\mu$ m in size. Notably, despite the higher reaction temperature, these conditions required reaction times of 48 h to reach their final sizes. This observation is consistent with the increased crystal size deriving from imine formation being less favorable at elevated temperatures. Similarly, polymerization at 120 °C provided slightly larger TAPPy-PDA COF crystals with 4  $\mu$ m lateral dimensions after 48 h. However, further temperature increases did not provide larger TAPPy-PDA COF crystals, presumably because the nucleation of COF particles was not significantly attenuated over this temperature range. In general, the largest crystals of both COFs exhibit a greater degree of crystal twinning, as seen from the rougher surface texture (Figures S16 and S18) in the SEM images. Overall, the combination of larger crystals and longer reaction times at elevated temperatures suggests that the reduced driving force for imine formation influences the COF nucleation and growth processes. These results demonstrate that reaction parameters such as monomer concentration, aniline concentration, and temperature impact the nucleation and growth processes of



**Figure 4.** 3D reciprocal lattices of (A,B) the **TAPPy-PDA** COF at 4.4 Å resolution and(D,E) **TAPB-DMPDA** COF at 4 Å resolution, as determined by low-dose cRED. (C,F) Rietveld refinements for **TAPPy-PDA** and **TAPB-DMPDA** COFs, respectively, with the **TAPPy-PDA** COF having refinement parameters  $R_p = 5.50\%$  and  $R_{wp} = 8.37\%$ , and **TAPB-DMPDA** COF having refinement parameters  $R_p = 4.77\%$  and  $R_{wp} = 6.71\%$ .

imine-linked 2D COFs and suggest further opportunities for monomer design or other additives that might be explored to further control these 2D polymerizations.

**Structure Determination by Continuous Rotation Electron Diffraction.** Continuous rotation electron diffraction (cRED) was used to elucidate the unit cells of **TAPPy-PDA** and **TAPB-DMPDA** COF single crystals (Figure 4A– D). The cRED data was collected at a low dose mode at 99 K on a JEOL 2100-plus TEM and equipped with a MerlinEM direct electron detector under 200 kV. For the **TAPPy-PDA** COF, 178 electron diffraction (ED) patterns were collected with the tilting angle ranging from -55.07° to 44.52°. Data collection for the **TAPB-DMPDA** COF was conducted similarly, except that 156 ED patterns were collected with the tilting angle ranging from -39.86° to 48.04°. Each frame was collected with an exposure time of 0.750 s, resulting in a 0.56° wedge per frame. The three-dimensional (3D) reciprocal space was reconstructed using the program REDp.

Figure 4B,E shows a series of streaks along the  $c^*$  axis, which indicates that the crystals of both COFs are ordered in the a-bplane but disordered in the stacking dimension. The unit cell of the **TAPPy-PDA** COF was determined as a monoclinic *C*lattice with a = 32.52 Å, b = 34.36 Å, and  $\beta = 85.77^{\circ}$ . For the **TAPB-DMPDA** COF, the diffraction data could be indexed by a hexagonal *P* lattice with a = 35.47 Å and b = 35.48 Å. Based on the unit cells determined by REDp, initial structure models were built using the Materials Studio software package, and their simulated PXRD patterns were consistent with the experimental patterns. The results of Pawley refinements showed low residuals of  $R_p$  and  $R_{wp}$  as well as excellent agreement with the experimental PXRD patterns in the peak positions and relative intensities (Figure S20). Finally, more accurate structure models were obtained by the Rietveld refinement (space group: C2/*m* for **TAPPy-PDA** COF with *a* = 32.545(2) Å, *b* = 34.286(8) Å, *c* = 3.846(2) Å,  $\alpha = \gamma = 90^{\circ}$ , and  $\beta = 85.371(6)^{\circ}$ ; space group: P6 for **TAPB-DMPDA** COF with *a* = *b* = 36.358(9) Å, *c* = 3.5127(8) Å,  $\alpha = \beta = 90^{\circ}$ , and  $\gamma$ = 120°; the Rietveld refinements for both COFs show low  $R_{wp}$ and  $R_p$  values, 8.37% and 5.50%, and 6.71% and 4.77%, for **TAPPy-PDA** and **TAPB-DMPDA** COFs, respectively, which helps us rationalize the interlayer structures (Figure 4C,F).

Due to the high surface areas and large interfacial energies of both the TAPPy-PDA and TAPB-DMPDA COFs, it is possible that the layers may be slip-stacked with respect to each other to minimize the free energy.<sup>67</sup> Most 2D COFs contain varying degrees of stacking disorder, and only rarely do they exist as single crystals with perfectly eclipsed AA stacking. Deng and coworkers also proposed an offset mode through scanning transmission electron microscopy (STEM) and the ratio of intensities of the 130 and 040 reflections in the PXRD patterns.<sup>68</sup> In the recent report of the TAPPy-PDA COF single crystals synthesized by Zhao and coworkers, only about 10% of the crystals adopt a fully eclipsed structure, whereas almost 90% of the crystals adopt a structure containing 6 different stacking layers within the unit cell.<sup>54</sup> In general, the disordered stacking in 2D COFs is the primary reason their crystal structures cannot be solved directly even when their individual 2D polymer sheets are single crystals with micron-

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Figure 5. Layer offset directions of (A) TAPPy-PDA and (D) TAPB-DMPDA COFs, respectively. DIFFaX-simulated PXRD patterns from average eclipsed AA stacking (bottom-most trace) to random stacking (trace under experimental PXRD pattern) for (B,C) the TAPPy-PDA COF and (E,F) TAPB-DMPDA COF. Boxed regions in panels (C) and (F) show 001 reflections.

scale lateral dimensions. To further understand the nature of the stacking disorder in our TAPPy-PDA and TAPB-DMPDA COF crystals, DIFFaX modeling was performed to simulate the PXRD patterns of different stacking scenarios. For both the TAPPy-PDA and TAPB-DMPDA COFs, we used three different offset directions and distances (Figure 5A,D). Zhao and coworkers recently solved the accurate structure of the **TAPPy-PDA** COF single crystal,<sup>54</sup> from which we obtained an offset distance of 0.36 Å. However, the structure of the TAPB-DMPDA COF has not yet been solved. Lotsch and coworkers have proposed an optimum stacking offset of 1.6 Å for this COF from density functional theory (DFT) calculations.<sup>67</sup> We calculated a projected distance between the centers of pyrene rings in two adjacent layers of 0.36 Å. We defined 6 different layers in DIFFaX, wherein the offset between adjacent layers was used to slide layers along the hole wall direction. We then obtained the offset vector coordinates and defined the probability of biasing toward a single direction. As the probability gradually decreased, the stacking faults between adjacent layers became more and more irregular. The stacking became random when the probability of offset in all directions was the same. Finally, we built a supercell containing 18 layers, which comprised layers stacked in fully eclipsed AA stacking as well as offset stacking in different directions. Using these insights, we simulated the stacking of both the TAPPy-PDA and TAPB-DMPDA COFs, going gradually from fully eclipsed AA to random stacking (Figure 5B,E). The experimental PXRD patterns of the TAPPy-PDA and TAPB-DMPDA COFs (top traces, Figure 5B,E) are similar to those of the AA stacking (bottom traces, Figure 5B,E) on hk0 reflections. However, when compared to the AA stacking trace, the 00l)

stacking reflections in the experimental PXRD patterns are weaker and more widened significantly, which suggests that the real COF structure likely does not adopt AA stacking. The experimental 001 stacking reflections (boxed region in Figure 5C,F) fit best when the stacking becomes close to a random model. In addition, we simulated 18 randomly stacked layers and calculated the diameters of the biggest spheres that can traverse the pores created by this arrangement (Figure S21, Table S1)<sup>69</sup> to obtain average pore sizes of 23.27 Å and 34.26 Å for the TAPPy-PDA and TAPB-DMPDA COFs, respectively. These values are in good agreement with the pore sizes obtained from NLDFT analysis of the BET isotherms of the two COFs (Figure 2C,F and Table S1). Taken together, these electron diffraction results provide critical insight into the structures of the TAPB-DMPDA and TAPPy-PDA COFs, suggesting that the materials are singlecrystalline in the a-b planar dimensions but disordered in the stacking c dimension. We speculate that this behavior is common among most 2D COFs and establishes the design of specific and directional interlayer interactions as an important frontier when materials with precise structures in all three dimensions are desired.<sup>70</sup> This behavior, however, is otherwise likely to impact most or all 2D COFs that are not engineered specifically to be ordered along the stacking direction.

Gas Chromatography Separation of Benzene and Cyclohexane. Having isolated high-quality samples of TAPPy-PDA and TAPB-DMBPDA COFs, we explored their properties as stationary phases for the gas chromatographic separation of benzene and cyclohexane. A capillary column (20 m long, 0.25 mm internal diameter) was coated with solutions of either single crystals or polycrystalline colloids of either



**Figure 6.** Gas chromatography separation performance of capillary columns (20 m length, 0.25 mm i.d.) coated with the **TAPPy-PDA** COF (single and polycrystalline) and commercial standard **TR-SMS** column of the same dimensions. Data recorded at 423 K and 0.2 MPa.

TAPPy-PDA or TAPB-DMPDA COFs. A binary (50:50) mixture of benzene and cyclohexane was separated over the TAPPy-PDA COF under 0.2 MPa pressure and at a temperature range of 393-423 K. In contrast, the same mixture showed the best separation by TAPB-DMPDA COF single crystals at 0.05 MPa pressure and a temperature range of 363-393 K. The column containing single crystals of the TAPPy-PDA COF exhibited excellent separation of the benzene/cyclohexane mixture with an unusual preferential adsorption of cyclohexane over benzene, as characterized by their respective retention times (Figure 6). In contrast, no separation of the benzene/cyclohexane mixture was observed under the same conditions on an identical column coated with the polycrystalline TAPPy-PDA COF (Figure 6). Further optimization of the GC parameters did not identify other conditions where the polycrystalline TAPPy-PDA COF separated the two analytes (Table S8). The column containing single crystals of the TAPB-DMPDA COF also exhibited preferential adsorption of cyclohexane over benzene. However, only partial separation of the binary mixture was observed (Figure 7), with an average separation factor of 1.07 and average resolution of 0.8 corresponding to a 6.6% overlap.<sup>7</sup> Likewise, a commercially available capillary column of similar dimensions, TR-5MS (made of 5% phenyl polysiloxane), did not show any separation of the adsorbates under either of the above chromatography conditions (Figures 6 and 7). Unlike the column containing polycrystalline TAPPy-PDA, the column coated with the polycrystalline TAPB-DMPDA COF was able to partially separate the benzene/cyclohexane mixture, but it showed the opposite preferential adsorption (benzene was retained preferentially) compared to its singlecrystalline counterpart (cyclohexane was retained preferentially, Figure 7), from which the average separation factor was calculated to be 0.83 and the average resolution was calculated to be 0.22, corresponding to a 31% overlap.<sup>7</sup> The fundamentally different separation behaviors of the singlecrystal COFs compared to their polycrystalline counterparts suggest that the analytes interact with the different material forms through distinct mechanisms. We speculate that the polycrystalline COF pores are not as accessible to the adsorbates under the chromatography conditions compared to the pores of the single crystals. We speculate that most of



**Figure 7.** Gas chromatography separation performance of capillary columns (20 m length, 0.25 mm i.d.) coated with the **TAPB-DMPDA** COF (single and polycrystalline) and commercial standard **TR-SMS** column of the same dimensions. Data recorded at 393 K and 0.05 MPa. Each probe was injected separately to illustrate the degree of overlap and calculate the average resolution and separation factor.

the interactions between the adsorbates and the polycrystalline COFs occurr on the outer surface of the 2D structure and not within the pores, where cyclohexane may exhibit preferential non-covalent interactions with groups on the pore walls. Taken together, these observations indicate that these analytes interact differently with polycrystalline and single-crystalline COF samples, underscoring the importance of testing high-quality COF samples before structure—property relationships for these separations are established.

The reversed adsorption selectivity for cyclohexane over benzene observed for both single-crystalline COFs (Figures 6 and 7) is unusual and motivated further investigation. Adsorbents with pore widths in the range of 7-10 Å have exhibited this reversed selectivity,<sup>72</sup> but the 2.24 nm and 3.24 nm-sized pores (Figure  $2C_{1}F$ ) of the TAPPy-PDA and TAPB-DMPDA COFs, respectively, are too large to operate by a size sieving mechanism for these analytes. The adsorption enthalpy  $(\Delta H_A)$  and adsorption entropy  $(\Delta S_A)$  were calculated using an IGC study performed at varying temperatures and constant pressure. The linear relations in the van't Hoff plots (Figures S25-S27) indicated that there was no change in the mechanism of interaction over the measured temperature ranges for both COFs (393-423 K and 363-393 K for TAPPy-PDA and TAPB-DMPDA COFs, respectively). Furthermore, the negative values of the Gibbs free energies of adsorption ( $\Delta G_A$ ) suggested spontaneous transfer of the adsorbates from the stationary to the mobile phase (Table 1 and Figures S8 and S9). The  $\Delta G_A$  values of cyclohexane molecules  $(-23.4 \pm 0.02 \text{ kJ mol}^{-1}; \text{ Table 1})$  in the column coated with TAPPy-PDA COF single crystals were more negative than those of the benzene molecules  $(-22.6 \pm 0.02 \text{ kJ})$ mol<sup>-1</sup>; Table 1), and this difference was determined to be significant by a statistical *t*-test at a 95% confidence interval. The  $\Delta G_A$  values of both adsorbates were more negative in the column coated with TAPPy-PDA COF single crystals (-23.4  $\pm$  0.02 kJ mol<sup>-1</sup> and  $-22.6 \pm 0.02$  kJ mol<sup>-1</sup> for cyclohexane and benzene, respectively) than its polycrystalline COF-coated counterpart (-22.4  $\pm$  0.04 kJ mol<sup>-1</sup> and -22.6  $\pm$  0.04 kJ mol<sup>-1</sup> for cyclohexane and benzene, respectively; Table 1), and this difference was also statistically significant at the 95%

Table 1. Enthalpy  $(\Delta H_A)$ , Entropy  $(\Delta S_A)$ , and Gibbs Free Energy  $(\Delta G_A)$  of Adsorption of Benzene and Cyclohexane on Single-Crystalline and Polycrystalline TAPPy-PDA COF-Coated Columns at a Pressure of 0.2 MPa and on Single-Crystalline and Polycrystalline TAPB-DMPDA COF-Coated Columns at a Pressure of 0.05 MPa<sup>b</sup>

		$-\Delta H_{\rm A} \ (\rm kJ \ mol^{-1})^{a}$		$-\Delta S_{\rm A}~({\rm kJ~mol^{-1}})$		$-\Delta G_{\rm A} \; ({\rm kJ} \; {\rm mol}^{-1})$	
COF	probe	single-crystalline	polycrystalline	single-crystalline	polycrystalline	single-crystalline	polycrystalline
TAPPy-PDA	benzene	$47.1 \pm 0.34$	$58.9 \pm 0.76$	$62.2 \pm 1.41$	$92.4 \pm 2.03$	$22.6 \pm 0.02$	$22.6 \pm 0.04$
	cyclohexane	$47.5 \pm 0.69$	$58.9 \pm 0.76$	60.6 ± 1.25	$92.7 \pm 2.03$	$23.4 \pm 0.02$	$22.4 \pm 0.04$
TAPB-DMPDA	benzene	$45.8 \pm 0.25$	$66.5 \pm 1.79$	$68.7 \pm 0.67$	$115.3 \pm 5.1$	$18.9 \pm 0.02$	$21.2 \pm 0.22$
	cyclohexane	$45.1 \pm 0.41$	$61.7 \pm 2.56$	$66.3 \pm 1.12$	$104.4 \pm 6.7$	$19.0 \pm 0.01$	$20.6\pm0.07$
<sup>a</sup> The enthalpy of ad	sorption $(\Delta H_A)$	was recorded at a	temperature rang	ge of 423–393 K fo	or TAPPy-PDA a	nd 393–363 K for	TAPB-DMPDA

COFs, respectively. <sup>b</sup>Data recorded at 393 K.

confidence interval. The  $\Delta G_A$  value of cyclohexane molecules  $(-19.0 \pm 0.01 \text{ kJ mol}^{-1}; \text{ Table 1})$  in the column coated with TAPB-DMPDA COF single crystals was more negative than that of the benzene molecules ( $-18.9 \pm 0.02 \text{ kJ mol}^{-1}$ ; Table 1), whereas the  $\Delta G_A$  value of benzene molecules (-21.2  $\pm$ 0.22 kJ mol<sup>-1</sup>; Table 1) in the column coated with the polycrystalline TAPB-DMPDA COF was more negative than that of the cyclohexane molecules  $(-20.6 \pm 0.07 \text{ kJ mol}^{-1})$ ; Table 1), corresponding to the elution order of benzene and cyclohexane adsorbates on both materials (the higher the  $\Delta G_{A}$ the greater the retention of the adsorbed probe). This difference in  $\Delta G_A$  values was determined to be significant by a statistical t-test at a 95% confidence interval. In contrast, the difference between the  $\Delta G_A$  values for benzene (-22.6  $\pm$  0.04 kJ mol<sup>-1</sup>; Table 1) and cyclohexane  $(-22.4 \pm 0.04 \text{ kJ mol}^{-1};$ Table 1) in the polycrystalline TAPPy-PDA-COF-coated column was not statistically significant, consistent with their lack of separation. Unlike the TAPPy-PDA COF, the  $\Delta G_A$ values of both adsorbates were less negative in the column coated with TAPB-DMPDA COF single crystals (-19.0  $\pm$ 0.01 kJ mol<sup>-1</sup> and  $-18.9 \pm 0.02$  kJ mol<sup>-1</sup> for cyclohexane and benzene, respectively; Table 1) than in the polycrystalline **TAPB-DMPDA-**COF-coated counterpart  $(-20.6 \pm 0.07 \text{ kJ})$  $mol^{-1}$  and  $-21.2 \pm 0.22$  kJ  $mol^{-1}$  for cyclohexane and benzene, respectively; Table 1), and this difference was also statistically significant at the 95% confidence interval. These observations suggest that surface functionality and grain boundaries dominate the retention behavior of the polycrystalline TAPB-DMPDA COF, and these iterations are stronger than those responsible for the opposite adsorption selectivity in the single-crystalline samples.  $\Delta G_{\rm A}$  values were more negative in the TAPPy-PDA COF single crystals than in the polycrystalline TAPPy-PDA COF. Considering the Gibbs free energy of adsorption ( $\Delta G_A$ ) as a function of the adsorption density, we attribute these observations to the benzene and cyclohexane interacting with the outer surfaces with polycrystalline samples of both TAPPy-PDA and TAPB-DMPDA COFs.

Additionally, adsorption enthalpies ( $\Delta H_A$ ) were determined from the slope of ln  $V_g$  plotted as a function of  $T^{-1}$  (Figures S28–30), where the linear dependence implied a constant value of  $\Delta H_A$  in the range of measured temperatures (393– 423 K and 363–393 K for TAPPy-PDA and TAPB-DMPDA COFs, respectively). For both the single-crystalline and polycrystalline TAPPy-PDA and TAPB-DMPDA COFs, the enthalpies of adsorption of benzene and cyclohexane were more negative than the enthalpy of liquefication ( $\Delta H_{liqi}$  Table S12), indicating that the adsorbate–adsorbate interactions. The small difference between the enthalpies of adsorption and liquefication for benzene and cyclohexane also suggested that the predominant interactions across the interface stemmed from the secondary weak intermolecular forces or Liftshitz– van der Waals forces. Thus, the surfaces of both singlecrystalline and polycrystalline **TAPPy-PDA** and **TAPB-DMPDA** COFs seemed to be energetically homogeneous toward the adsorption of benzene and cyclohexane.

Despite the preferential adsorption of cyclohexane on the single-crystalline TAPPy-PDA COF coated column, the more negative value of the  $\Delta H_A$  of cyclohexane was not statistically significant relative to that of benzene, indicating no enthalpic preference between the adsorbates. The calculated values of  $\Delta H_{\rm A}$  of benzene and cyclohexane in the column coated with **TAPPy-PDA** COF single crystals were  $-47.1 \pm 0.34$  kJ mol<sup>-1</sup> and  $-47.5 \pm 0.69 \text{ kJ mol}^{-1}$ , respectively, at a 95% confidence level (Table 1). However, despite the TAPB DMPDA COF coated column exhibiting the same preferential adsorption of cyclohexane over benzene, the  $\Delta H_A$  values of benzene (-45.8  $\pm$  0.25 kJ mol<sup>-1</sup> and -66.5  $\pm$  1.79 kJ mol<sup>-1</sup>, in singlecrystalline and polycrystalline TAPB-DMPDA COF-coated columns, respectively; Table 1) were significantly higher than those of cyclohexane on both single-crystalline and polycrystalline TAPB-DMPDA COFs ( $-45.1 \pm 0.41$  kJ mol<sup>-1</sup> and  $-61.7 \pm 2.56$  kJ mol<sup>-1</sup>, in single-crystalline and polycrystalline TAPB-DMPDA COF-coated columns, respectively; Table 1) at a 95% confidence level. The entropy of adsorption ( $\Delta S_A$ ) of benzene on the column coated with TAPPy-PDA COF single crystals at 393 K ( $-62.2 \pm 1.41$  J mol<sup>-1</sup> K<sup>-1</sup>) was significantly more negative than that of cyclohexane  $(-60.6 \pm 1.25 \text{ J mol}^{-1}$  $K^{-1}$ ; Table 1) as determined by a statistical *t*-test at a 95% confidence level, indicating that cyclohexane molecules maintained more conformational freedom than benzene molecules in the pores of the single crystals. Likewise, the entropy of adsorption ( $\Delta S_A$ ) of benzene on the column coated with single-crystalline and polycrystalline TAPB-DMPDA COFs at 393 K (-68.7  $\pm$  0.67 J mol<sup>-1</sup> K<sup>-1</sup> and -115.3  $\pm$ 5.1 J mol<sup>-1</sup> K<sup>-1</sup>, respectively; Table 1) was significantly more negative than that of cyclohexane  $(-66.3 \pm 1.12 \text{ J mol}^{-1} \text{ K}^{-1})$ and 104.4  $\pm$  6.7 J mol<sup>-1</sup> K<sup>-1</sup>; Table 1) as determined by a statistical t-test at a 95% confidence level. The higher values of  $\Delta H_A$  and  $\Delta S_A$  of adsorption of benzene on the polycrystalline TAPB-DMPDA COF-coated column and the elution order and preferential adsorption of benzene over cyclohexane indicated an enthalpic-entropic-driven separation. On the other hand, despite the preferential adsorption of cyclohexane over benzene on the single-crystalline TAPB-DMPDA COFcoated column, the values of  $\Delta H_{\rm A}$  and  $\Delta S_{\rm A}$  of benzene adsorption were more negative than those of cyclohexane adsorption (Table 1), also indicating that cyclohexane molecules maintained more conformational freedom than

benzene molecules in the pores of the TAPB-DMPDA COF single crystals. Additionally, the absolute values of the  $\Delta H_A$ and  $\Delta S_A$  of both benzene and cyclohexane molecules on the column coated with polycrystalline TAPPy-PDA and TAPB-DMPDA COFs were greater than their counterparts on the column coated with TAPPy-PDA and TAPB-DMPDA COF single crystals, despite the polycrystalline COFs having significantly lower BET surface areas (Figures S9B and S10B). Although the equilibrium constants (Henry's constants; Table S4) for the polycrystalline TAPPy-PDA COF were lower than those for its single-crystalline counterpart and the equilibrium constants (Henry's constants; Table S5) for the polycrystalline TAPB-DMPDA COF were higher than those for its single-crystalline counterpart, the adsorption preference was related only to the energetics of the adsorption sites. Thus, cyclohexane molecules seemed to have an entropic advantage over benzene molecules in being adsorbed into the COF pores.

#### CONCLUSIONS

We prepared single-crystalline 2D imine-linked COF crystals of two topologies: a square TAPPy-PDA COF and a hexagonal TAPB-DMPDA COF. Varying the polymerization conditions identified the monomer concentration, modulator loadings, and reaction temperature as important factors to increase the sizes of TAPPy-PDA and TAPB-DMPDA COFs from 720 nm to 4  $\mu$ m and 450 nm to 20  $\mu$ m lateral dimensions, respectively. All the COF crystals exhibit excellent crystallinity and porosity, as determined by PXRD and N2 adsorption isotherms, are faceted, as characterized by SEM and HRTEM imaging, and are single-crystalline in two dimensions, as corroborated by cRED characterization. 2D polymers have yet to be explored systematically for separation applications, although they offer many potentially desirable attributes for these applications. The TAPPy-PDA COF single crystals showed efficient and complete gas chromatography separation of benzene and cyclohexane, two industrially important organic molecules that are challenging and energetically expensive to separate by conventional distillation. Meanwhile, the TAPB-DMPDA COF single crystals showed partial gas chromatography separation of the same binary benzene/cyclohexane mixture. Furthermore, single crystals of both COF networks showed an unusual preferential adsorption of cyclohexane over benzene, indicating that the degree of crystallinity impacts the order of elution of analytes. Taken together, these results demonstrate a novel synthetic strategy in which large, single-crystalline 2D imine-linked COFs were prepared in a highly facile and versatile manner and used toward a targeted separation application. Ultimately, this work will enable the synthesis of a much broader class of 2D polymer structures and exploration of their properties.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c07166.

Materials and instrumentation, experimental procedures, additional COF characterization, BET plots, crystal size control studies, cRED studies, and GC studies (PDF)

# Pubs.acs.org/JACS AUTHOR INFORMATION

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#### Notes

The authors declare no competing financial interest.

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