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Bulk Synthesis of Exfoliated Two-Dimensional Polymers Using Hydrazone-Linked Covalent Organic Frameworks

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S *Supporting Information*

ABSTRACT: Two-dimensional (2D) polymers assemble organic subunits into covalently linked, high-aspect-ratio networks with long-range order. Despite recent advances in 2D polymerization, scalable and general methods to access few- and single-layer materials are limited. Here we exfoliate a hydrazone-linked covalent organic framework (COF) to yield bulk quantities of few-layer two-dimensional (2D) polymers. Immersing the COF powder in several laboratory solvents exfoliates and disperses thin COF-43 samples, which maintain their characteristic periodic hexagonal structure. This phenomenon was characterized using infrared spectroscopy, dynamic light scattering, atomic force microscopy, transmission electron microscopy, and selected area electron diffraction. 2D COFs with reduced interlayer interaction energies offer a new means to access high-aspect-ratio 2D polymers whose structure may be designed using established principles of COF synthesis.

Two-dimensional (2D) polymers exhibit periodic covalent bonding in two orthogonal directions such that they precisely organize chemical functionality over large areas. High-aspect-ratio 2D polymers might someday serve as lithographic templates, nanoporous membranes, photocurrent generators, or drug release platforms, but these applications remain speculative because reliable polymerization methods are only now emerging.[1] These polymerizations employ polyfunctional monomers that fuse into covalently bonded sheets whose formation is usually templated by a surface or a molecular interface. Covalent organic framework (COF) synthesis, in which monomers condense into crystalline networks under reversible bond-forming conditions, is the most general 2D polymerization approach and typically provides multilayer polycrystalline powders.[2] Scalable methods to access single- or few-layer structures remain limited. 2D polymerizations on surfaces yield single-layer polymers amenable to atomically precise characterization, albeit in minute quantities.[2f,3] Sakamoto and co-workers elegantly demonstrated the first scalable synthesis of single- and few-layer structures, which employed a 2D topochemical polymerization within a layered crystal, followed by solvent-mediated exfoliation.[4] However, the generality of this method is unproven, as designing new monomers that form layered crystals capable of such topochemical reactions is not trivial.[5]

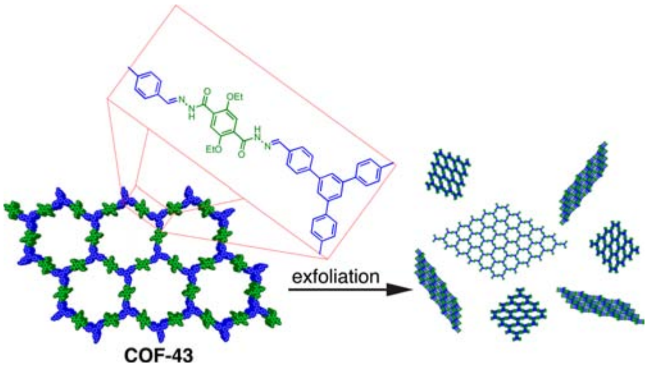

Figure 1. Exfoliation of COF-43 yields a suspension of few-layer 2D polymers.

Exfoliating 2D COFs might provide access to various few-layer 2D polymers,[6] but this phenomenon is underexplored because 2D COFs feature high-surface-area interlayer van der Waals interactions[7] that template their formation. Only a single example of the sonichemical exfoliation of a boronate ester-linked COF into few-layer structures has been reported.[8] Furthermore, boronate ester-linked COFs exhibit poor hydrolytic and oxidative stability[9] and have appreciable interlayer stacking energies[10] that are likely to complicate downstream applications of their few-layer forms. In contrast, acyl hydrazones, recently introduced as linkages in 2D COFs,[11] offer improved hydrolytic and oxidative stability and lack the interlayer B−O Lewis acid−base interactions present in boronate ester-linked COFs, both of which facilitate their exfoliation. Here we exfoliate the 2D hydrazone-linked COF-43 under mild conditions and confirm that long-range order is maintained in the resulting few-layer materials (Figure 1). We anticipate that these findings will prove general for 2D COFs with moderate interlayer stacking energies, providing a straightforward means to rationally design few-layer or even single-layer 2D polymers.

COF-43 was crystallized under solvothermal conditions modified from those reported by Yaghi and co-workers,[11] and the resulting microcrystalline powder was washed with THF to remove residual byproducts and solvents. Powder X-ray diffraction (PXRD) of this material exhibited peaks characteristic of the COF-43 hexagonal network (Figure 2, black). The (100), (200), (010), and (300) reflections are observed at 2.46, 4.14, 4.86, and 6.42°, respectively. Given the expected stability of hydrazone linkages, we were surprised to observe a complete loss in crystallinity when COF-43 was immersed in dioxane

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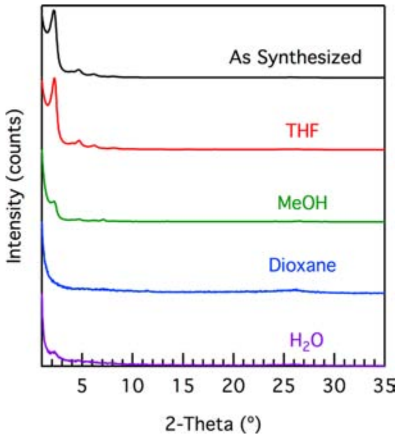

Figure 2. PXRD patterns of COF-43 immersed in various solvents for 2 h show a loss in bulk crystallinity for dioxane and H_2O. Results for soaking COF-43 in several additional solvents are shown in Figure S1.

under ambient laboratory conditions (Figure 2, blue). We evaluated the generality of this phenomenon by re-exposing as-synthesized COF-43 to THF, as well as several common laboratory solvents. Samples exposed to THF, $CHCl_3$, PhMe, and MeOH retained their original diffraction patterns, while those exposed to dioxane, H_2O, and DMF appeared amorphous (Figure S1). Although crystallinity loss might arise from framework hydrolysis, hydrazones are typically stable under each of the above conditions.[12] We speculated that the apparent crystallinity loss might instead arise from exfoliation of the COF-43 multilayers without disrupting its covalent linkages.

We first ruled out the possibility of hydrolysis of the acyl hydrazone linkages within COF-43 using Fourier transform infrared spectroscopy (FTIR). These moieties exhibit characteristic absorbances that correspond to C═O and C═N stretches at 1656 and 1597 cm^{-1}, respectively. These signals remained unchanged in the reactivated powders that were exposed to each of the solvents listed above (Figures 3 and S2). Furthermore, no additional peaks appear and the spectra are devoid of absorbances corresponding to free aldehyde and hydrazide hydrolysis products (Figure S3). We also monitored solutions containing solid COF-43 for the appearance of soluble aldehydes and hydrazides using in situ IR spectroscopy. No new chemical species were detected while soaking COF-43 in THF, in which crystallinity is retained (Figure S5), or dioxane, in which crystallinity is lost (Figure S4). These solid and solution-state IR experiments demonstrate that hydrazone COFs are chemically stable in each solvent, such that their loss of crystallinity in dioxane, water, and DMF cannot be attributed to hydrolysis processes.

Soaking COF-43 in solvent provided suspended or dispersed polymers whose size depended on whether the solvent induced apparent crystallinity loss. Atomic force microscopy (AFM) of suspensions sonicated in dioxane indicated intact, high aspect ratio platelets with lateral widths of 200 nm and average heights of 1.32 ± 0.37 nm (Figures 4b and S14), corresponding to 3−5 layers. Structures as thin as 3.3 Å were obtained after deposition from H_2O (Figures S19 and S20), suggesting the formation of bi- or even single-layer structures. Polymers deposited from non-exfoliating solvents, such as THF, also yielded relatively high aspect ratio structures, but they were much thicker (Figure 4a) and were reminiscent of the discotic morphology seen in the scanning electron micrographs (SEMs) of the bulk powder (Figure S8). Micrographs of COF-43 dispersions in MeOH indicated few dispersed structures (Figure S16), and instead revealed thicker aggregates consistent with limited exfoliation. In all cases, the isolated structures showed lateral dimensions larger than the crystallite sizes measured by PXRD (17 ± 4 nm), indicating that these sheets of COF-43 are polycrystalline. Grain boundaries might serve as weak points in COF-43 assemblies, where sheet fracture is likely to occur during exfoliation. AFM analysis of suspensions stored on the bench for 50 d provided structures of similar size, indicating their long-term stability. Exfoliated COF-43 could also be interfaced with highly ordered pyrolytic graphite (HOPG), a conductive substrate, using the same exfoliation and drop-casting procedure (Figure S21). This method offers a future means to study the electronic properties of these 2D polymers without requiring UHV deposition methods. The size of the dispersed 2D polymers in solution was also characterized using dynamic light scattering (DLS). Significant size differences of these dispersed species were observed, depending on whether an exfoliating (H_2O, 447 ± 46 nm) or non-exfoliating (THF, 72.2 ± 3.6 nm) solvent was employed (Figures 5 and S6). Taken together, these observations indicate that exfoliating solvents disperse high aspect ratio COF-43 platelets, whereas non-exfoliating solvents provide poorly defined COF-43 multilayers.

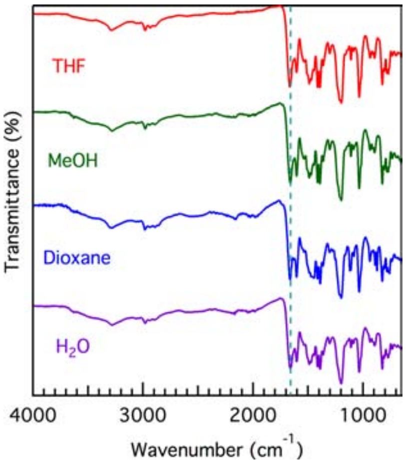

Figure 3. FTIR spectra of COF-43 after solvent exposure indicate no attenuation of the hydrazone C═O stretch (dashed line). New signals corresponding to aldehyde or hydrazide hydrolysis products are not observed. Similar spectra were obtained when COF-43 was soaked in other solvents (Figure S2).

We next employed transmission electron microscopy (TEM) to confirm the presence of layered structures and probe the

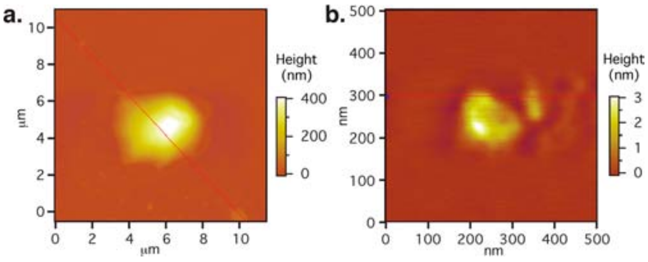

Figure 4. Atomic force micrographs of COF-43 deposited onto freshly cleaved mica from (a) THF indicate particle sizes corresponding to hundreds of layers, whereas micrographs from (b) dioxane show platelets corresponding to few-layer structures.

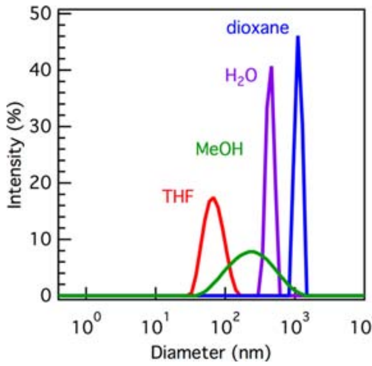

Figure 5. Average size of COF-43 dispersions derived from DLS of solutions that were briefly sonicated in the presence of COF-43 powder and then passed through a 5 μm filter. Larger dispersed macromolecules are observed in exfoliating solvents (H_2O, dioxane) as compared to non-exfoliating solvents (THF, MeOH).

local ordering of the 2D polymers. Carbon-coated TEM grids were dip-coated in unsonicated dispersions of COF-43 and imaged with a low accelerating voltage (80 kV) to minimize sample degradation in the electron beam. Micrographs of samples prepared from the non-exfoliating solvent THF revealed large structures reminiscent of COF-43 crystallites (Figure 6a). The presence of moiré fringes suggests that the layered crystallites adopt slight interlayer offsets typical of stacked aromatic systems that have been identified computationally for 2D COFs.[10] Similar interference patterns have been observed with other layered 2D polymers, including bi- and trilayer graphene.[13] Selected area electron diffraction (SAED) of these multilayers was consistent with their polycrystalline, hexagonally ordered structure (Figure 6a, inset). In contrast, dioxane solutions, which exfoliate COF-43, revealed smaller structures (Figure 6b) with moiré fringes (Figure S22), suggesting the retention of some vertical stacking. While a thickness is not available from these measurements, assemblies of similar lateral dimensions and 40−50 nm high were observed by AFM from unsonicated dispersions of COF-43 in dioxane.

Notably, SAED of these materials exhibited a hexagonal diffraction pattern (Figure 6b, inset), indicative of ordering on the hundred-nanometer scale. This observation indicates that exfoliated COF-43 retains its long-range order within the covalently linked sheets. As is common for organic materials characterized by TEM, these materials visibly degraded during imaging, especially during electron diffraction, and the intensity of the diffraction pattern faded over time. Still, these observations implicate SAED as a means of characterizing the local crystallinity of multilayer COF samples. For COF-43 soaked in dioxane, these measurements confirm their long-range hexagonal ordering and indicate that periodicity is retained within the sheets after exfoliation.

We have demonstrated that 2D hydrazone-linked COFs have relatively weak interlayer interactions, such that they are exfoliated into few-layer 2D polymers under mild conditions. Immersion in several common laboratory solvents revealed an apparent loss of COF-43 crystallinity by PXRD, despite no apparent changes in its covalent linkages by solid-state and in situ FTIR. The exfoliated COF-43 polymers displayed high aspect ratios characterized by AFM, and SAED confirmed the hexagonal periodicity of few-layer samples. As such, exfoliating 2D COF multilayers provides a means to obtain bulk quantities of dispersed 2D polymers. These findings are also important in the context of synthesizing new 2D COFs, because they demonstrate that exposure to an exfoliating solvent can obfuscate a sample's crystallinity, as measured by PXRD. COF synthesis is more modular than other 2D polymerization techniques, such that we anticipate that these findings will expand the scope of bulk-scale 2D polymers amenable to further study and facilitate the development of these emerging macromolecular architectures.

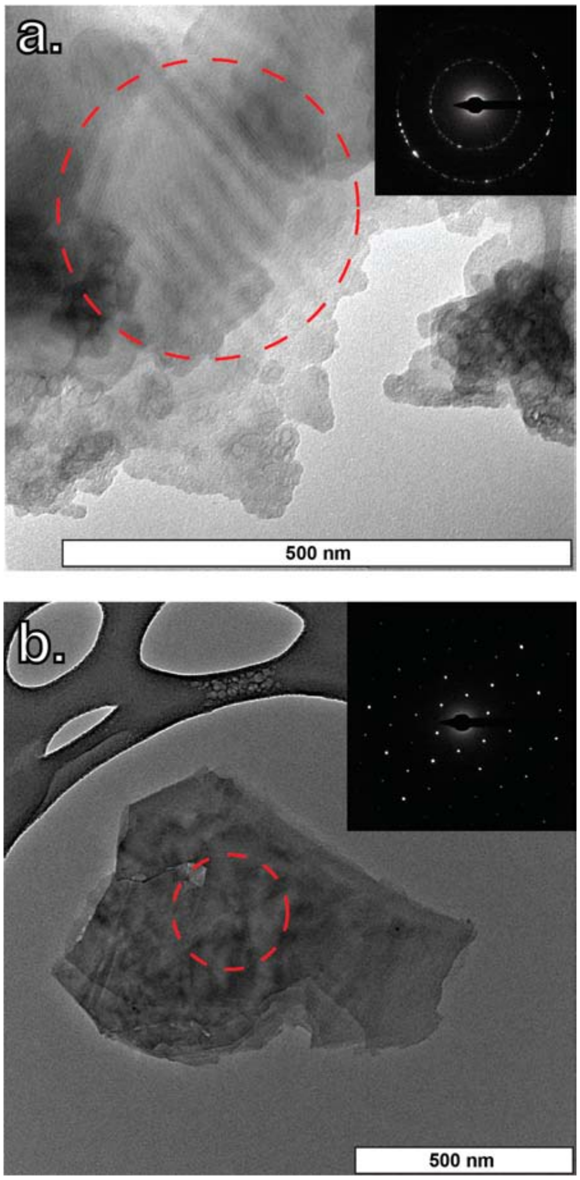

Figure 6. Transmission electron micrographs of COF-43 suspensions in (a) THF and (b) dioxane. SAED (red circle) shows hexagonal order within the sheet (inset).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Extensive discussion of DLS measurements, AFM data, and additional characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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