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The synthesis of periodic two-dimensional (2D) polymers and characterization of their optoelectronic behaviors are challenges at the forefront of polymer chemistry and materials science. Recently, we showed that layered 2D polymers known as 2D covalent organic frameworks (COFs) can be synthesized as single crystals by preparing COF particles as colloidal suspensions. Here we expand this approach from the condensation of boronic acids and catechols to the dehydrative trimerization of polyboronic acids. The resulting boroxine-linked colloids are the next class of 2D COFs to be obtained as single-crystalline particles, as demonstrated here for four 2D COFs and one 3D COF. Colloidal stabilization enables detailed structural analysis by synchrotron X-ray diffraction and high-resolution transmission electron microscopy. Solution fluorescence spectroscopy revealed that the COF crystallites are highly emissive compared to their respective monomer solutions. Excitation-emission matrix fluorescence spectroscopy indicated that the origin of this enhanced emission can be attributed to through-space communication of chromophores between COF sheets. These observations will motivate the development of colloidal COF systems as a platform to organize functional aromatic systems into precise and predictable assemblies with emergent properties.

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Emissive Single-Crystalline Boroxine-Linked Colloidal Covalent Organic Frameworks

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ABSTRACT: The synthesis of periodic two-dimensional (2D) polymers and characterization of their optoelectronic behaviors are challenges at the forefront of polymer chemistry and materials science. Recently, we showed that layered 2D polymers known as 2D covalent organic frameworks (COFs) can be synthesized as single crystals by preparing COF particles as colloidal suspensions. Here we expand this approach from the condensation of boronic acids and catechols to the dehydrative trimerization of polyboronic acids. The resulting boroxine-linked colloids are the next class of 2D COFs to be obtained as single-crystalline particles, as demonstrated here for four 2D COFs and one 3D COF. Colloidal stabilization enables detailed structural analysis by synchrotron X-ray diffraction and high-resolution transmission electron microscopy. Solution fluorescence spectroscopy revealed that the COF crystallites are highly emissive compared to their respective monomer solutions. Excitation-emission matrix fluorescence spectroscopy indicated that the origin of this enhanced emission can be attributed to through-space communication of chromophores between COF sheets. These observations will motivate the development of colloidal COF systems as a platform to organize functional aromatic systems into precise and predictable assemblies with emergent properties.

Table of Contents Image

INTRODUCTION: The structural and functional diversity of layered, two-dimensional (2D) materials provides them with a collection of technologically useful properties.¹⁻² However, synthetically engineering 2D organic materials through polymerization with a desired combination of chemical functionality, porosity, topology, and electronic structure remains a challenge at the frontier of materials chemistry.³⁻⁵ 2D covalent organic frameworks (COFs) are a class of stable,⁶ layered, permanently porous polymers formed from the simultaneous polymerization and crystallization of directional subunits. 2D COFs are synthetically versatile materials, with several hundred reported structures to date,⁷⁻⁸ which have inspired interest in applications such as gas separations, catalysis, environmental remediation, energy storage, and optoelectronic devices.^{7, 9-14} A limitation of 2D COFs is that they are typically isolated as polycrystalline powders, which complicates their structural, electronic, and optical characterization.¹⁵⁻¹⁸ Recently, we developed a way to overcome this limitation by stabilizing boronate ester-linked COFs as colloidal suspensions by including nitrile-containing cosolvents in the reaction mixture (**Figure 1A**).¹⁹⁻²⁰ We attributed this stabilization to the interaction of nitriles with boron-containing functional groups in the framework.²⁰ This hypothesis led us to postulate that other classes of boron-linked COFs might be stabilized in a similar way.

Figure 1. A) Previous work demonstrating stabilization of 2D boronate-ester COFs as colloidal suspensions. B) Colloidal stabilization is now generalized for 2D and 3D boroxine-linked COFs.

Here we demonstrate that the self-condensation of polyboronic acids in the presence of electron-donating solvents produces colloidal boroxine-linked COFs. These boroxine-linked materials are the second class of 2D COFs to be prepared as stable single-crystalline particles and more than doubles the number of

covalent frameworks synthesized as single crystals (**Figure 1B**). Furthermore, we show that this approach is amenable to the synthesis of a 3D framework, further extending the generality of this controlled polymerization method.

The well-dispersed and isolable nature of these COF particles enabled their structural analysis using low-dose high-resolution transmission electron microscopy (HR-TEM) and synchrotron X-ray diffraction (XRD). By combining these techniques, we were able to gain insight into the interlayer arrangement of 2D polymer sheets, which is challenging to assign in powder COF systems but strongly affects their electronic structure.²¹⁻²² While performing these investigations, we noted that COF samples were highly fluorescent compared to their respective monomers. Therefore, excitation-emission matrix fluorescence spectroscopy (EEMS) was used to probe the intrinsic optical properties of these dispersed crystallites. EEMS revealed that the enhanced emission of the COFs originates from the formation of exciplexes as a consequence of the fluorophores' 2D layered structure. We anticipate that these results will greatly impact approaches to COF synthesis and inform the understanding of through-space electronic communication in 2D polymers and other framework materials.

Results and Discussion: We synthesized **Ph-COF** (previously reported²³ as COF-1) in mixtures of CH₃CN and 4:1 1,4-dioxane:mesitylene. The 1,4-phenylenebis(boronic acid) (PBBA) monomer was first dissolved in the specified solvent mixture at a concentration of 10 mM and then the container was sealed, sonicated, and heated to 90 °C for an additional 3 days (**Figure 2A**). When 0 - 30 vol% CH₃CN was included in the reaction mixture, a white precipitate formed over the course of 3 days. These precipitates were isolated and characterized via Fourier-transform infrared spectroscopy (FT-IR) and XRD, the results of which were consistent with previous reports of **Ph-COF** (**Figure S11**).²³ In contrast, no precipitation was observed when 30 - 80 vol% of CH₃CN was included in the reaction mixture while over the course of 3 days these solutions changed from transparent to opaque-white suspensions (**Figure 2B**) that were stable for at least 6 months. When >80 vol% of CH₃CN was included in the reaction mixture, the heated monomer solution never became transparent, which we attribute to the insufficient solubility of PBBA under these conditions. These observations indicate that boroxine polymerization is not inhibited by the presence of CH₃CN and that a specific range of solvent mixtures is necessary for the successful solubilization of PBBA and stabilization of the **Ph-COF** particles.

Figure 2. **A)** Synthesis of boroxine-linked **Ph-COF** particles through solvothermal condensation of PBBA (10 mM). **B)** Photograph comparing the transparent monomer solution to typically isolated **Ph-COF** powders²³ and dispersed **Ph-COF** crystallites synthesized in the presence of electron-donating solvents. **C)** Dynamic light scattering (DLS) Z-average size and polydispersity index (PDI) of **Ph-COF** synthesized with variable initial PBBA concentrations.

Inclusion of other nitrile cosolvents (butyronitrile [BuCN], propionitrile [PrCN], and benzonitrile [PhCN]) at 50 vol% of the solvent mixture stabilized **Ph-COF** particles in a similar fashion to CH₃CN, in which transparent solutions became cloudy over the course of heating for 3 days (**Figure 2B**). The inclusion of pyridine in the reaction mixture also resulted in a colloidal suspension of **Ph-COF** particles. However, the transition to a cloudy suspension occurred within approximately 1 minute (**Supplementary Video 1**), which may be due to its stronger interaction with boronic acids and boroxines because of its stronger basicity.²⁴ These results show that the inclusion of Lewis-basic cosolvents in boroxine-linked COF syntheses results in stable colloidal suspensions. These observations are consistent with previous reports that described Lewis-basic cosolvents coordinated to the Lewis-acidic sites of boron-linked COFs.²⁵⁻²⁷ Taken together, stabilization by electron-donating solvents suggests a direct interaction between the cosolvent and COF surface, which we speculate is responsible for the observed colloidal stability, as has been found for other classes of nanoparticles.²⁸

A central advantage of stable nanocrystal suspensions is that their size can be controlled by varying the synthesis and growth conditions.¹⁹ **Ph-COF** particle sizes were controlled by varying the initial PBBA concentration. We found that concentrations lower than 5 mM did not produce colloidal particles, presumably because this is below the critical nucleation concentration for these conditions.²⁹ In contrast, concentrations above 15 mM were not initially soluble and produced a mixture of **Ph-COF** nanoparticles and powder precipitate. However, within the regime where **Ph-COF** nanoparticles were formed exclusively (5–15 mM PBBA), dynamic light scattering (DLS) measurements indicate that initial

monomer concentration is positively correlated with the Z-average size, with particle sizes ranging between 100 and 400 nm, and a polydispersity index (PDI) width between 50 and 200 nm (**Figure 2C**).³⁰ This behavior is consistent with linear condensation polymerizations in which the starting monomer concentration leads to larger average chain length and dispersity.³¹ This observation highlights the potential of using colloidal nanocrystals as a platform to explore mechanisms of COF nucleation and elongation.^{18-19, 29}

Figure 3. A) Monomer structures and optical images of structurally diverse COF nanoparticle suspensions. B) X-ray diffraction (grazing-incidence of dropcast crystallites: **TMPh-COF** or *in solvo* wide-angle X-ray scattering: **Ph-COF**, **BPh-COF**, **DBD-COF**, **Py-COF**) of boroxine-linked COF nanocrystals.

A defining feature of COF chemistry is the modular approach used to synthesize isorecticular crystalline, porous, organic polymers. Interested in understanding the synthetic versatility of boroxine-linked COF colloid stabilization, we self-condensed several polyfunctional boronic acids to form their corresponding boroxine-linked COFs, including 2,7-pyrenebisboronic acid (**Py-COF**), tetraphenylmethylboronic acid (**TMPh-COF**), and two previously unreported COF structures condensed from, 4,4'-biphenylbisboronic acid (**BPh-COF**) and diphenylbutadiynebisboronic acid (**DBD-COF**). All self-condensations were performed in a solvent mixture of CH₃CN:1,4-dioxane:mesitylene 50:40:10 vol% by heating the respective monomers of each COF at 90 °C for 3 days. The solutions became cloudy for all reactions investigated, indicating the formation of solution-stabilized nanoparticles (**Figure 3A**).³²

Synchrotron X-ray diffraction of the colloidal boroxine-linked COF suspensions confirmed their crystallinity and identity (**Figure 3B**). Diffraction features were observed for **Ph-COF** at 0.55 Å⁻¹ and 0.85 Å⁻¹, corresponding to the (100) and (110) Bragg features, respectively. The location of these features is consistent with those reported by Côte *et al.*, which were assigned to an AB offset structure of **Ph-COF** in which adjacent layers are offset by half a unit cell (**Figure S23**).²³ However, the relative intensities of these features were inconsistent with this report. Due to the solvated nature of these crystallites, it was challenging for us to definitively assign their interlayer arrangement based on the few, weak diffraction

signals observed here. The (100) diffraction feature for both the known **Py-COF** and previously unexplored **BPh-COF** occur at $0.39 \text{ \AA}^{-1}$, consistent with the nearly equivalent lattice dimensions of these two COFs (**Figure S24** and **S26**). This feature, along with higher order diffractions, allowed us to assign these materials as having AA eclipsed structures. The location of the primary diffraction feature ((200) at $0.21 \text{ \AA}^{-1}$) for the newly synthesized **DBD-COF** was consistent with the hexagonal unit cell size expected for a linker of this length. However, its relative intensity pattern was unusual when compared to those of other hexagonally symmetric COFs.³³ Ultimately, we attributed this diffraction pattern to a partially offset structure. We hypothesize that this stacking is governed by the interaction of stacked boroxines given the relatively weak van der Waals forces associated with the COF diphenylbutadiyne moieties.³⁴ Finally, the 3D boroxine-linked COF, **TMPh-COF**, produced diffraction features at 0.59, 0.62, 0.91, and $0.96 \text{ \AA}^{-1}$, which correspond to the (211), (220), (310), and (321) features, respectively. This diffraction pattern is consistent with the previously reported non-interpenetrated diamondoid structure for this material.³⁵ Together, these results show that colloiddally stable particles exhibit the defining structural regularity of COF materials. Additionally, these diffraction results demonstrate that chemically and topologically diverse framework materials are amenable to colloidal stabilization. The limited number and strength of the diffraction features for 2D COFs, including those reported here, impedes definitive assignments of stacking arrangements.¹⁰ Secondary structural characterization of agglomerated polycrystalline COF powders is also challenging and has limited the number of reports aimed at in-depth structural characterization using direct imaging techniques, such as electron microscopy.³⁶ In contrast, dispersed crystallites are an ideal morphology for microscopic structural characterization. With this in mind, we set out to explore COF nanocrystals via high-resolution transmission electron microscopy (HR-TEM).

Figure 4. Orange: **Ph-COF**; Yellow: **BPh-COF**; Green: **DBD-COF**; Blue: **Py-COF**; Red: **TPh-COF**. **A-E)** Low-resolution TEM images of COF particles. **F-J)** High-resolution TEM images of COF particles. Inset; lattice fringes of COF particles. **K-O)** FFTs of COF particles.

By TEM, 2D COFs are visible in micrographs as layered single-crystallites with sizes in agreement with DLS measurements (**Figures 4A-E** and **S17-S21**). When the images of COF crystallites (**Figure 4F-J**) were subjected to a fast Fourier transform (FFT) (**Figure 4K-4O**), we found that all COFs produced a set of symmetric point features rather than ring patterns. This supports the existence of COF crystallites as single-crystalline particles when suspended, as was observed previously for colloidal boronate ester-linked 2D COFs.¹⁹ For **Ph-COF**, discrete particles agglomerated upon drop-casting, but they maintained their hexagonal morphology with clearly visible lattice fringes extending from one end of the particles to the other, confirming the single-crystalline nature of the **Ph-COF** dispersed crystallites (**Figure 4A**). For **Ph-COF**, FFT images exhibited a preeminent lattice spacing of 10 Å (d_{110}). This spacing is consistent with structural models of **Ph-COF** sheets stacked as alternating offset layers.²³ **Py-COF** appeared as agglomerated hexagonally faceted particles with lattice fringes observed at 7.1 Å (d_{200}), consistent with the *in solvo* XRD patterns of these materials. In addition to the d_{200} feature, the FFT pattern of **Py-COF** also exhibited d_{310} features at 4.1 Å. Similarly, the well-dispersed hexagonal **BPh-COF** particles have visible higher-order lattice fringes (d_{400}), consistent with their XRD pattern. For these three materials, a set of spots at 90° to the in-plane diffraction features is observed which is in accordance with the expected interlayer distance of 3–4 Å for van der Waals heterostructures. These d_{001} spacings suggests

the interlayer distance associated with **BPh-COF** is smaller than that associated with **Py-COF**. We attribute this difference to a synchronized offset stacking of alternating phenyl rings that has been reported in other COF systems.³⁷ In contrast, such stacking is not possible in **Py-COF** because of its forced planarity. **DBD-COF** particles were present as predominantly trigonal particles. Furthermore, the observed preeminent lattice spacing of 11 Å is consistent with the model of these crystallites (d_{110}) generated through Pawley refinement of the experimentally collected X-ray diffraction patterns (**Figure S29- S32**). We expect that the prominence of the d_{210} lattice spacing in these crystallites is related to the offset structure assigned from the *in solvo* XRD patterns. The interlayer arrangement of 2D COF sheets seen here adds to a growing body of evidence that interlayer arrangements of polymer sheets are governed by an array of intermolecular forces.³⁷⁻⁴¹ Finally, the 3D **TMPH-COF** crystals were observed to be regularly faceted crystals with a preeminent lattice spacing of 10 Å. This observation is consistent with their previously reported non-interpenetrated diamondoid structure.³⁵ Taken together, TEM imaging demonstrates that a second class of 2D COFs and 3D COFs can be synthesized as single-crystalline particles using a colloidal stabilization approach. Furthermore, these results indicate that emerging TEM technologies, such as direct electron detectors facilitating low-dose imaging, are promising tools in the exploration of interlayer arrangements of 2D polymer sheets and electron beam sensitive materials more generally. This interlayer arrangement remains challenging to observe using other characterization methods but is vastly important for a suite of emergent material properties.

Another limitation of precipitated polycrystalline 2D COF powders is the difficulty associated with characterizing their intrinsic optical or electronic properties because of their propensity to scatter light.⁴² However, because 2D materials are of interest for many electronic applications, it is of paramount importance to explore the optoelectronic nature of these materials. During the course of our investigation, we observed that all of the colloidal 2D COF suspensions were noticeably more fluorescent than their boronic acid monomers at the same fluorophore concentrations (**Figure 5**). Motivated by the results of our previous investigations into enhanced optical characterization of 2D COF colloids,^{19, 43} we set out to explore the origin of enhanced nanocrystal fluorescence using EEMS. While EEMS showed that all 2D COF colloids were more emissive than their respective monomers, we chose to focus our investigation on the highly fluorescent **Py-COF** and **DBD-COF** materials.

Figure 5. Orange: **Ph-COF**; Yellow: **BPh-COF**; Green: **DBD-COF**; Blue: **Py-COF**. Photographs of COF monomer solutions and their resultant COF nanocrystals **A)** under natural light and **B)** under UV irradiation.

EEMS shows that both **DBD-COF** (**Figure 6A**) and its respective DPBBA monomer have absorbance maxima at 365 nm (**Figure 6C**). However, the emission of **DBD-COF** at this wavelength is an order of magnitude more fluorescent than the DPBBA monomer (**Figure 6C**). This electronic communication was surprising because boroxines are not conjugated and therefore not thought to allow electronic coupling.⁴⁴ However, the difference in monomer and COF fluorescence seen here indicates there is some electronic coupling between chromophores in the COF structure. This behavior is consistent with the understanding that intersheet diphenylbutadiyne chromophores undergo aggregation-induced fluorescence.⁴⁵⁻⁴⁶ During the polymerization of **DBD-COF**, molecular chromophores are brought into close proximity, similar to their aggregation-induced assembly in previous reports, which restricts their molecular motion and enhances their fluorescence quantum yield.

Py-COF was also noteworthy in our initial observations because its fluorescence under UV irradiation changed color significantly when compared to its monomer, PyBA (**Figure 5B**). Similar to the **DBD-COF**, the local excited-state emission of **Py-COF** broadened (**Figure 6D**), which we attribute to perturbed electronic states of the pyrene chromophores. EEMS of **Py-COF** shows that the emission blue-shifts 50 nm relative to the monomer at an excitation of 325 nm (**Figure 6D**). This behavior is indicative of plane-plane stacking, so **Py-COF** can be assigned as an H-aggregated structure.⁴⁷⁻⁴⁸ Furthermore, **Py-COF** has an additional emission feature at 435 nm, which is consistent with the formation of an exciplex structure and has been observed in previous reports of molecular pyrenes (**Figure 6E**).⁴⁹ This observation is consistent with the assignment of **Py-COF** as an eclipsed structure having inter-sheet pyrenes in physical contact. Taken together, these results show how electronic communication in framework materials can occur in stacked systems even when not conjugated through

covalent bonds. We expect that using nonconjugated COFs to exploit through-space electronic communication will feature prominently in future COF systems.

Figure 6. A) EEMS of **DBD-COF**. Inset; optical image of DPBBA monomer (left) and **DBD-COF** (Right) under UV irradiation B) EEMS of **Py-COF**. Inset; optical image of PyBA monomer (left) and **Py-COF** (Right) under UV irradiation. C) Emission of **DBD-COF** compared to the **DPBBA** monomer at the same concentration. D) Normalized emission intensity of **Py-COF** compared to the PyBA monomer showing a blue shift and broadening of the emission spectra. E) Normalized emission of **Py-COF** under two excitation wavelengths showing the emergence of an excimer emission (430 nm).

Conclusion

2D COFs are promising candidates for many applications, but their investigation and utility has been greatly hampered by the isolation of these materials as weakly polycrystalline aggregates. In the interest of adding 2D COFs to the ever-expanding suite of functional 2D materials, it is imperative to improve their quality and level of characterization, including exploration of their optical properties. The above results demonstrate that colloidal stabilization of boroxine-linked frameworks occurs in the presence of electron-donating solvents. This strategy is amenable to the synthesis of four single-crystalline 2D COF materials, including two newly synthesized systems. Further, we show how this strategy can be topologically expanded to include a 3D COF. Synchrotron XRD and HR-TEM provided insight into the interlayer arrangement of these materials and confirmed their single-crystalline nature. Furthermore, stabilizing COFs as colloidal suspensions allowed us to probe the intrinsic optical properties of these materials with EEMS. The high-quality of the spectroscopy of these materials allowed us to assign the origin of the optical features to the formation of π -exciplexes, which is indicative of through-space electronic communication of chromophores brought into close proximity in the COF structure. We expect that future colloidal COFs will prove to be a versatile platform to investigate emergent optoelectronic

phenomena in 2D polymer systems, such as triplet up-conversion, singlet-singlet annihilation, or photoredox processes.⁵⁰⁻⁵² Understanding these processes, coupled with the high-quality materials this strategy enables, will ultimately facilitate the incorporation of 2D polymers into relevant optoelectronic devices.

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Supporting Information

Emissive Single-Crystalline Boroxine-Linked Colloidal Covalent Organic Frameworks

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Table of Contents

Section	Title and Contents	Pages
I	Materials and Methods	S3 - S5
II	Synthetic Procedures for Covalent Organic Framework Monomers	S6 - S8
	Scheme S1. Synthesis of 2,7-Pyrenebisboronic acid	
	Scheme S2. Synthesis of Synthesis of 4,4'-Diphenylbutadiyne boronic acid	
	Scheme S3. Synthesis of Synthesis of Tetra(4-dihydroxyborylphenyl)methane	
III	Nuclear Magnetic Resonance of Covalent Organic Framework Monomers	S9 - S13
	Figure S1. ¹ H NMR of 2,7-Pyrenebisboronic acid DMSO-d ₆	
	Figure S2. ¹ H NMR of 4,4'-Diphenylbutadiyne pinacoleborane in CDCl ₃	
	Figure S3. ¹ H NMR of 4,4'-Diphenylbutadiyne boronic acid in DMSO-d ₆	
	Figure S4. ¹ H NMR of Tetra(4-bromophenyl)methane in CDCl ₃	
	Figure S5. ¹ H NMR of Tetra(4-dihydroxyborylphenyl)methane in DMSO-d ₆	
IV	Covalent Organic Framework Structures	S14 - S16
	Figure S6. Structure of Ph-COF	
	Figure S7. Structure of BPh-COF	
	Figure S8. Structure of DBD-COF	
	Figure S9. Structure of Py-COF	
	Figure S10. Structure of TPh-COF	
V	Synthesis of Covalent Organic Frameworks	S17 - S19
	Scheme S4. Synthesis of Ph-COF	
	Scheme S5. Synthesis of BPh-COF	
	Scheme S6. Synthesis of DBD-COF	
	Scheme S7. Synthesis of Py-COF	
	Scheme S8. Synthesis of TPh-COF	
VI	Fourier-Transform Infrared Spectroscopy of Covalent Organic Frameworks	S20 - S25
	Figure 11. FT-IR of Ph-COF Powder	
	Figure 12. FT-IR of Ph-COF Colloids	
	Figure 13. FT-IR of BPh-COF Colloids	

	Figure 14. FT-IR of DBD-COF Colloids	
	Figure 15. FT-IR of Py-COF Colloids	
	Figure 16. FT-IR of TMPh-COF Colloids	
VII	Dynamic Light Scattering of Covalent Organic Frameworks	S26 - S31
	Figure 17. Dynamic light scattering number distribution of Ph-COF	
	Figure 18. Dynamic light scattering number distribution of BPh-COF	
	Figure 19. Dynamic light scattering number distribution of DBD-COF	
	Figure 20. Dynamic light scattering number distribution of Py-COF	
	Figure 21. Dynamic light scattering number distribution of TMPh-COF	
VIII	X-ray Diffraction of Collected COF Powders	S32
	Figure 22. X-ray diffraction of wet Ph-COF	
IX	COF Structural Models	S33 - S34
	Figure 23. Structure of Ph-COF	
	Figure 24. Structure of BPh-COF	
	Figure 25. Structure of DBD-COF	
	Figure 26. Structure of Py-COF	
	Figure 27. Structure of TMPh-COF	
	Figure 28. Structure of TMPh-COF – Zoomed in	
X	COF Modeled Diffraction Patterns	S35 - S37
	Figure S29. BPh-COF Diffraction Patterns	
	Figure S30. DBD-COF Diffraction Patterns	
	Figure S31. TMPh-COF Diffraction Patterns	
	Figure S32. Py-COF Diffraction Patterns	
XI	Additional COF Fluorescence	S38
	Figure S33. Excitation-Emission Matrix Spectroscopy of Ph-COF	
	Figure S34. Excitation-Emission Matrix Spectroscopy of BPh-COF	
XII	Additional Transmission Electron Microscopy Images	S39 - S40
	Figure S35. Additional TEM images	
	Figure S36. Additional High Resolution TEM images	
XIII	Fluorescence of COF Colloids versus Powders	S41 - S42
	Figure S37. Fluorescence Spectroscopy of Py-COF	
	Figure S38. Fluorescence Spectroscopy of DBD-COF	
XIV	References	S43

I. Materials and Methods

Materials. All monomers, solvents, and catalysts were either purchased from commercial sources or prepared following literature reported protocols. All materials were used as received without further purification. Anhydrous THF was obtained from a solvent purification system (JC Myer System).

Solution Nuclear Magnetic Resonance. ^1H NMR spectra were acquired on a 400 MHz Agilent DD MR-400 system or Bruker Avance III 500 MHz spectrometer and recorded at 25 °C. All chemical shifts were calibrated using residual solvent as internal reference (CDCl_3 : 7.26 ppm for ^1H NMR. DMSO: 2.5 ppm for ^1H NMR).

Dynamic Light Scattering. Dynamic light scattering (DLS) data were collected using a Malvern Zetasizer equipped with a 633nm He-Ne 5mW laser in a quartz cuvette with a 10mm pathlength at room temperature. Data was analyzed using the proprietary Zetasizer software.

Fourier-Transform Infrared Spectroscopy. Infrared spectra were collected on a Nicolet iS10 FT-IR spectrometer equipped with a ZnSe crystal in attenuated total reflection mode. Spectra were background subtracted to remove contribution from atmospheric species. Spectra as shown were not corrected or calibrated to any IR feature.

In solvo X-ray Diffraction. Small- and wide-angle X-ray scattering (SAXS/WAXS) patterns were collected at Argonne National Lab's (ANL) Advanced Photon Source (APS) at both sectors 5-ID-D (DND-CAT) and 12-ID-D with a capillary transmission geometry. Experiments conducted at 12-ID-D were collected at a beam energy of 12 keV and experiments conducted at 5-ID-D were collected at a beam energy of 13.3 keV. Individual frames were collected on a set of Pilatus detectors, which were then summed and radially integrated to produce a linear XRD pattern using proprietary software available at the APS. Scattering intensity is reported as a function of the modulus of the scattering vector q , related to the scattering angle 2θ by the equation $q = (4\pi/\lambda) \sin \theta$, where λ is the X-ray wavelength. The sample-to-detector distance was adjusted to measure across relevant detection ranges. Capillary experiments were conducted using 2.0 mm OD borosilicate capillaries with 0.2 mm wall thicknesses purchased from Hilgenberg GmbH.

Grazing-Incidence X-ray Diffraction. As noted in the text, several reported X-ray scattering patterns were collected by drop casting undiluted samples of COF nanocrystals onto silicon wafers and allowing the solvent to evaporate. GIWAXS measurements were then performed at Advanced Photon Source at Argonne National Laboratory using the 8-ID-E Beamline under vacuum. The crystallites were irradiated until the detector was 80 % of saturated an incidence angle of 0.14° in vacuum using 10.92 keV ($1.135 \text{ \AA}$) X-rays. The scattering was recorded on a Pilatus 1 M detector located 228 mm from the sample. In all cases, significant silicon substrate scatter was observed. The raw images were merged, pixel coordinates were transformed to q -space, line cuts generated using GIXSGUI for Matlab.¹

COF Modeling and Structural Refinement. Crystal modeling of the COF structures was carried out using the Materials Studio (ver.5.0) suite of programs by Accelrys.² The initial structures were

constructed piecewise starting with a primitive hexagonal unit cell of a P6 space group. The cell parameter was estimated according to the distance between the center of the vertices for each COF, and c parameter was chosen as 3.35 Å, which has been observed for similar materials.³ Initially, these structures were estimated to be eclipsed. The structures were optimized using a Geometry Optimization routine including energy minimization with cell parameters optimization, using the parameters from the Universal Force Field. Calculation of the simulated powder diffraction patterns and Pawley refinements were performed in the Materials Studio Reflex Plus Module using a Bragg-Brentano geometry. When the first ~2 features were seen to align but relative intensities were seen to be inconsistent, we assigned this to a noneclipsed structure. If this was the case, supercells of the crystallites were generated and different stackings (AB, ABC, partial AB, etc. were attempted). The intensity profile which matched most closely was used to refine. The observed diffraction patterns were subjected to a polynomial background subtraction and then to Pawley refinement wherein peak profile were refined using the Pseudo-Voigt peak shape function and asymmetry was corrected using the Berar-Baldinozzi function. Crystallite size was then estimated by the LeBail method which was Pawley refined to the experimental data.

Transmission Electron Microscopy Sample Preparation for Ph-COF and TPh-COF. All COF samples (Ph-COF and TPh-COF) were prepared by drop-casting ~3-4 µL (using a micropipette) of the COF sample solution (CH₃CN:1,4-dioxane:mesitylene, 50:40:10 by volume) after synthesis was complete onto lacey-carbon substrate (Cu mesh) TEM grids (Electron Microscopy Sciences, Hatfield, PA). The droplets of COF sample were allowed to sit on the grids in ambient conditions for ~20-30s and were then wicked dry with filter paper. The prepared TEM grids were then stored in a desiccator until they were used for TEM characterization.

Transmission Electron Microscopy for Ph-COF and TPh-COF. TEM was performed using a FEI (FEI Company, Hillsboro, OR) Polara cryoTEM operating at 200 keV equipped with a Gatan (Roper Technologies, Sarasota, FL) K2 “direct electron” detector (FEG extraction: 4350 V, FEG emission: 108 µA, spot size 5, 70 µm OL aperture, 70 µm CL aperture). The Polara cryoTEM is a cartridge-loaded microscope, where the column is continually maintained at L-N₂ temperature (<-180° C). The grids that were prepared previously and dried, were loaded into the microscope’s cartridge after being submerged in L-N₂, and the cartridge with grids was inserted into the microscope (maintained at L-N₂ temperature). The Polara was aligned for low-dose imaging, measuring the dose rate on the K2 detector through vacuum (no grid inserted). The dose rate used was 5.12 e- Å⁻² s for high-magnification (115 kx) images (1.78 Å pixel size, 3708 x 3838 pixels), with an image exposure of time of 5 s (~25.6 e- Å⁻² cumulative dose per image). The dose rate was not directly measured for the low magnification images, but the dose rate was orders magnitude lower for those images than for the high magnification images (low magnification images: 1 s exposure time, 10.1034 nm pixel size, 1852 x 1918 pixels, binning 2). All image acquisition was performed using SerialEM software which applies auto focusing on adjacent regions of the grid to minimize dose on the sample.⁴

Transmission Electron Microscopy Sample Preparation for BPh-COF, DBD-COF, and Py-COF. All COF samples were prepared by drop-casting ~4 µL (using a micropipette) of the COF sample solution (CH₃CN:1,4-dioxane:mesitylene, 50:40:10 by volume) onto lacey-carbon

substrate (Cu, 400 mesh) TEM grids (Ted Pella, Redding, CA). The droplets of COF sample were allowed to sit on the grids in ambient conditions for ~10 s and were then wicked dry with filter paper.

Transmission Electron Microscopy for BPh-COF, DBD-COF, and Py-COF. Low magnification TEM was performed using a JEOL (JEOL USA, Inc., Peabody, MA) ARM300 GrandARM TEM operating at 300 keV equipped with a Gatan (Gatan, Inc., Pleasanton, CA) OneView-IS camera (FEG Emission: 15 μ A, spot size 4, 100 μ m CL aperture, 40 μ m objective aperture). All image acquisition was done using the Gatan Microscopy Suite (GMS), Digital Micrograph (Gatan, Inc., Pleasanton, CA).

High resolution TEM was performed using a JEOL (JEOL USA, Inc., Peabody, MA) 3200FS TEM operating at 300 keV equipped with a Gatan (Gatan, Inc., Pleasanton, CA) K2 summit direct electron detector ($\sim 5 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$ dose per image) using Leginon where all alignment was done at 4k or lower.⁵

Fluorescence Spectroscopy Sample Preparation. Monomer solutions were prepared at a concentration of 15 mM in a 4 mL mixture of CH₃CN:1,4-dioxane:mesitylene (50:40:10 v/v/v). This monomer solution was then sonicated for five minutes and briefly heated to aid in solvation of the monomers. This 4 mL sample was split into two fractions of 2 mL apiece and each sealed. One of these solutions was heated at 70 °C for 72 hours while the other was left at room temperature. Emission-Excitation Matrix Fluorescence Spectroscopy (EEMS) was performed on all samples.

Emission-Excitation Matrix Spectroscopy. Emission and excitation spectra were recorded on a Horiba Jobin Yvon Fluorolog-3 fluorescence spectrophotometer equipped with a 450 W Xe lamp, double excitation and double emission monochromators, a digital photon-counting photomultiplier and a secondary InGaAs detector for the NIR range. Correction for variations in lamp intensity over time and wavelength was achieved with a solid-state silicon photodiode as the reference. The spectra were further corrected for variations in photomultiplier response over wavelength and for the path difference between the sample and the reference by multiplication with emission correction curves generated on the instrument. Emission-Excitation Matrix Spectroscopy was conducted on these samples by scanning the emission profile of different excitation wavelengths.

Centrifugation. Centrifugation was conducted using an Eppendorf Centrifuge 5430 V 4.4. Samples were collected in falcon tubes, balanced, and spun for 5 minutes at 7830 rpm. This was repeated twice to attempt to remove any small species not firmly collected.

II. Synthetic Procedures for Covalent Organic Framework Monomers

Scheme S1. Synthesis of 2,7-Pyrenebisboronic acid

2,7-Pyrenebisboronic acid. This compound was synthesized according to published procedure⁶ but with minor modification. In a 250 mL round bottom flask, bis(pinacolato)diboronic ester (1.00 g, 2.20 mmol, 1.00 equiv) and sodium periodate (2.84 g, 13.4 mmol, 6.00 equiv) were dissolved in a THF:H₂O mixture (4:1 v/v, 60 mL). This mixture was stirred at room temperature with nitrogen actively bubbling through it for 30 minutes. (NOTE: HCl was **not** added to this reaction mixture as was done in previous reports[REF] thereby reducing orange/brown impurities in the final compound.) The reaction vessel was subsequently sealed and allowed to stir for an additional 24 hours. At this point, 60 mL of H₂O was added to the reaction mixture, which was then filtered through a Büchner funnel, and the product was washed with an additional 100 mL of H₂O. This product was then flushed with 100 mL of diethyl ether. This powder was dried under vacuum for 2 hours to afford a fine white powder (520 mg, 82%). NMR analysis of this product was consistent with a previous report.⁶

Scheme S2. Synthesis of Synthesis of 4,4'-Diphenylbutadiyne boronic acid

4,4'-Diphenylbutadiyne pinacole borane. The synthesis of this product was adapted from a previous report.⁷ A 100 mL round bottom flask was charged with CuI (0.752 g, 3.94 mmol), NiCl₂• 6H₂O (0.936 g, 3.94 mmol), and tetramethylethylenediamine (TMEDA) (1.836 g, 15.784 mmol). Acetone (50 mL) was added, and as the solids dissolved the mixture became dark green. 4-ethynylbenzeneboronic acid pinacole ester (18 g, 78.8 mmol) was added to this mixture, which was then stirred for 16 hours. The solvent was removed by rotary evaporation to yield a green residue that was washed with H₂O (300 mL). The resultant solid was isolated, subsequently recrystallized from CH₃CN as a white solid, collected via filtration, and

dried under vacuum (5.25 g, 30 %). NMR analysis of this product was consistent with a previous report.⁷

4,4'-Diphenylbutadiyne boronic acid. The synthesis of this compound was adapted from a previous report.⁸ In a 20 mL scintillation vial, 4,4'-diphenylbutadiyne pinacole borane (1.00 g, 2.20 mmol, 1.00 equiv) and sodium periodate (1.0 g, 5.00 mmol, 2.27 equiv) were dissolved in THF:H₂O (4:1 v/v, 12 mL). This mixture was stirred at room temperature with nitrogen actively bubbling through it for 30 minutes, after which 1M HCl (5 mL) was added via syringe. The reaction vessel was subsequently sealed and allowed to stir for an additional 24 hours. At this point, the reaction mixture was poured into 50 mL of H₂O, filtered through a Büchner funnel, and washed with an additional 100 mL of H₂O. This product was then flushed with 100 mL of diethyl ether. This powder was dried under vacuum for 10 minutes to afford a fine white powder (444 mg, 69%). NMR analysis of this product was consistent with a previous report.⁷

Scheme S3. Synthesis of Tetra(4-dihydroxyborylphenyl)methane

Tetra(4-bromophenyl)methane. The synthesis of this compound was adapted from a previous report.⁹ A 100 mL three-necked flask was equipped with a magnetic stir bar and charged with tetraphenylmethane (9 g, 25 mmol). Two of the flask necks were covered with septa and a condenser with a hose at the top was inserted into the third neck, which was attached to a concentrated $\text{Na}_2\text{S}_2\text{O}_3$ solution. (Note: This was included so as to neutralize any escaped Br_2 gas in the following step.) Neat Br_2 (10 mL, 0.175 mmol) was added slowly via syringe to the stirring mixture through one of the septa, yielding a dark orange slurry that was stirred for an additional 20 minutes. This mixture was poured into cold ethanol (200 mL, -78°C). The precipitated solid from this reaction was combined with saturated aqueous NaHSO_3 (80 mL) and filtered and washed with an additional 80 mL of NaHSO_3 two times. At this point, the filtered liquid was transparent. The crude solid was recrystallized from a 1:1 chloroform/ethanol mixture and isolates as a pale yellow solid (5.85 g, 37 %). NMR analysis of this product was consistent with a previous report.⁹

Tetra(4-dihydroxyborylphenyl)methane. The synthesis of this compound was adapted from a previous report.¹⁰ A solution of tetra(4-bromophenyl)methane (1.27 g, 2.00 mmol) in anhydrous THF (125 mL) was stirred at -78°C under a N_2 atmosphere. To this, n -butyllithium (6.4 mL, 2.5 M THF, 16 mmol) was added dropwise via cannula through a pre-marked secondary container, after which the solution became cloudy. The resulting mixture continued to stir for 30 minutes at 78°C , whereupon $\text{B}(\text{O}^i\text{Pr})_3$ (5.5 mL, 23.8 mmol) was added dropwise via cannula through a pre-marked secondary container. The mixture was stirred at -78°C for an additional 20 minutes and then slowly warmed to room temperature, where it was stirred for an additional 12 hours. After acidification with 1 M HCl (25 mL), the mixture was concentrated by partial evaporation of volatiles under reduced pressure, which yielded a white solid. This concentrate was treated

with 1M NaOH (25mL) and then filtered. The filtrate was acidified with 1M HCl until a white precipitate was observed. The precipitate was collected by filtration, washed with Et₂O, and dried under vacuum to afford tetra(4-dihydroxyborylphenyl)methane as a white solid (0.301 g, 30.4%). NMR Analysis of this product was consistent with a previous report.¹⁰

III. Nuclear Magnetic Resonance of Covalent Organic Framework Monomers

Figure S1. ^1H NMR of 2,7-Pyrenebisboronic acid DMSO-d_6

Figure S2. ¹H NMR of 4,4'-Diphenylbutadiyne pinacoleborane in CDCl₃

Figure S3. ^1H NMR of 4,4'-Diphenylbutadiyne boronic acid in DMSO-d_6

Figure S4. ^1H NMR of Tetra(4-bromophenyl)methane in CDCl_3

Figure S5. ¹H NMR of Tetra(4-dihydroxyborylphenyl)methane in DMSO-d₆

IV. Covalent Organic Framework Structures

Figure S6. Structure of **Ph-COF**

Figure S7. Structure of **BPh-COF**

Figure S8. Structure of **DBD-COF**

Figure S9. Structure of **Py-COF**

Figure S10. Structure of TMPh-COF

V. Synthesis of Covalent Organic Frameworks

Scheme S4. Synthesis of **Ph-COF**

Ph-COF. Phenylenebisboronic acid (PBBA) (10 mM, 33.2 mg)* was dissolved in either a mixture of 4:1 1,4-dioxane:mesitylene (20 mL) when attempting powder synthesis of **Ph-COF** or a mixture of CH₃CN**:1,4-dioxane:mesitylene (20 mL) (50:40:10, v/v/v) *** when attempting colloidal syntheses. The PBBA solution was then heated to 70 °C for 72 hours. During this time, the clear solutions became white and opaque.

*For experiments where PBBA concentrations were varied, all other factors were kept the same.

**For experiments where other cosolvents were tested, those solvents were substituted for the acetonitrile.

***For experiments where the total ratio of solvents were varied, the mixtures varied between 90-0 CH₃CN vol % with the rest of the solvent being constructed from 1:4 mesitylene:1,4-dioxane.

Scheme S5. Synthesis of **BPh-COF**

BPh-COF. Biphenylenebisboronic acid (BBBA) (10 mM, 12 mg) was dissolved in a mixture of CH₃CN:1,4-dioxane:mesitylene (5 mL) (50:40:10, v/v/v) when attempting colloidal syntheses. The BBBA solution was then heated to 70 °C for 72 hours. During this time, the clear solutions became white and opaque.

Scheme S6. Synthesis of DBD-COF

DBD-COF. Diphenylbutadiynbisboronic acid (DBD-BA) (10 mM, 14.5 mg) was dissolved in a mixture of CH₃CN:1,4-dioxane:mesitylene (5 mL) (50:40:10, v/v/v) when attempting colloidal syntheses. The DBD-BA solution was then heated to 70 °C for 72 hours. During this time, the clear solutions became white and opaque.

Scheme S7. Synthesis of Py-COF

Py-COF. Pyrenebisboronic acid (PyBA) (10 mM, 14.5 mg) was dissolved in a mixture of CH₃CN:1,4-dioxane:mesitylene (5 mL) (50:40:10, v/v/v) when attempting colloidal syntheses. The Py-BA solution was then heated to 70 °C for 72 hours. During this time, the clear solutions became white and opaque.

Scheme S8. Synthesis of **TMPh-COF**

TMPh-COF. Tetrakis(phenylboronic acid)methane (TMPh-BA) (10 mM, 24.5 mg) was dissolved in a mixture of CH₃CN:1,4-dioxane:mesitylene (5 mL) (50:40:10, v/v/v) when attempting colloidal syntheses. The TMPh-BA solution was then heated to 70 °C for 72 hours. During this time, the clear solutions became white and opaque.

VI. Fourier-Transform Infrared Spectroscopy of Covalent Organic Frameworks

Figure 11. FT-IR of Ph-COF Powder

Figure 12. FT-IR of Ph-COF Colloids

Figure 13. FT-IR of BPh-COF Colloids

Figure 14. FT-IR of DBD-COF Colloids

Figure 15. FT-IR of Py-COF Colloids

Figure 16. FT-IR of TMPH-COF Colloids

VII. Dynamic Light Scattering of Covalent Organic Frameworks

Figure 17. Dynamic light scattering number distribution of Ph-COF

Figure 18. Dynamic light scattering number distribution of BPh-COF

Figure 19. Dynamic light scattering number distribution of DBD-COF

Figure 20. Dynamic light scattering number distribution of Py-COF

Figure 21. Dynamic light scattering number distribution of TPh-COF

VIII. X-ray Diffraction of Collected COF Powders

Figure 22. X-ray diffraction of wet Ph-COF

IX. COF Structural Models

Figure 23. Structure of Ph-COF

Figure 24. Structure of BPh-COF

Figure 25. Structure of **DBD-COF**

Figure 26. Structure of **Py-COF**

Figure 27. Structure of TMPH-COF

Figure 28. Structure of TMPH-COF – Zoomed in

X. COF Modeled Diffraction Patterns

Figure S29. BPh-COF Diffraction Patterns

Figure S30. DBD-COF Diffraction Patterns

Figure S31. TMPH-COF Diffraction Patterns

Figure S32. Py-COF Diffraction Patterns

XI. Additional COF Fluorescence

Figure S33. Excitation-Emission Matrix Spectroscopy of **Ph-COF**

Figure S34. Excitation-Emission Matrix Spectroscopy of **BPh-COF**

XII. Additional Transmission Electron Microscopy Images

Figure S35. Additional TEM images

Figure S36. Additional High Resolution TEM images

XIII. Fluorescence of COF Colloids versus Powders

Figure S38. Fluorescence Spectroscopy of **DBD-COF**

XIV. References

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