Thiophene-based covalent organic frameworks

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<td>As Published</td>
<td><a href="http://dx.doi.org/10.1073/pnas.1221824110">http://dx.doi.org/10.1073/pnas.1221824110</a></td>
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<tr>
<td>Publisher</td>
<td>National Academy of Sciences (U.S.)</td>
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<tr>
<td>Version</td>
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</tr>
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<td>Accessed</td>
<td>Sun Dec 23 02:09:28 EST 2018</td>
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Thiophene-based covalent organic frameworks

Guillaume H. V. Bertrand, Vladimir K. Michaelis, Ta-Chung Ong, Robert G. Griffin, and Mircea Dincă

We report the synthesis and characterization of covalent organic frameworks (COFs) incorporating thiophene-based building blocks. We show that these are amenable to reticular synthesis, and that bent ditopic monomers, such as 2,5-thiophenediboronic acid, are defect-prone building blocks that are susceptible to synthetic variations during COF synthesis. The synthesis and characterization of an unusual charge transfer complex between thiophene-2,5-diboronic acid and tetracyanoquinodimethane enabled by the unique COF architecture is also presented. Together, these results delineate important synthetic advances toward the implementation of COFs in electronic devices.

electronic materials | polymers | porous materials

Covalent organic frameworks (COFs) have emerged as an important class of polymeric crystalline materials with potential applications that complement those of metal organic frameworks (MOFs) (1–7). In particular, 2D COFs exhibit unique architectures wherein the monomers that make up their 2D layers stack almost perfectly into infinite 1D columns that are ideal for charge and exciton transport (6–12). Such electronic properties are particularly difficult to engineer in microporous MOFs, where high charge mobility and conductivity have only recently been demonstrated (13–15). Despite their layered structures, the typical hexagonal or square lattices of 2D COFs exhibit large 1D channels with well-defined pores that can be subject to reticular chemistry and postsynthetic modification (16, 17), and where complementary donor or acceptor molecules may in principle be inserted. Clearly, the unprecedented combination of high surface area, crystallinity, chemical and pore size tunability, and unique molecular architecture make COFs tantalizing targets for a new generation of electronic devices, including sustainable batteries, field-effect transistors, and photovoltaics. The first steps toward such applications must involve the incorporation of electroactive monomers within the COFs. This has been beautifully exemplified by the insertion of porphyrins (18), phthalocyanines (9), pyrene (8), napthalenetetracarboxydiimide (19), and benzothiadiazole (20) in such materials. Notably, however, one of the most popular monomers in conductive organic polymers, thiophene, has not been incorporated in COFs thus far. Herein, we report the synthesis and characterization of thiophene-based COFs, including materials made from thiophene-, bithiophene-, and thienothiophene-diboronic acids. We also advance a hypothesis regarding the more general synthetic tractability of COFs made from bent ligands. Finally, we show that p-type COFs are amenable to doping with electron acceptors and report an unusual charge-transfer complex with tetracyanoquinodimethane (TCNQ).

Results and Discussion

We prepared thiophene-based COF (T-COFs) under conditions mimicking those used for the synthesis of the prototypical COF-5. Thus, condensation of 2,3,6,7,10,11-hexahydroxypyrrole (HHTTP) with 2,5-thiophenediboronic acid (H2TDB) (21) in dioxane and mesitylene at 120 °C over 72 h afforded (HHTTP)2(TDB)2 (T-COF 1; HOTP = 2,3,6,7,10,11-hexaoxytriphenylene) as an off-white powder. Boronate ester linkages were confirmed by fourier transform infrared spectroscopy (FT-IR) spectroscopy, which revealed stretching frequencies at 1,348, 1,323, and 1,225 cm−1, the vibrational signature of catechol boroxester rings. T-COF 1 is crystalline and shows four main powder X-ray diffraction (PXRD) peaks at 2θ = 3.72°, 6.11°, 9.96°, and 26.38°. Exploration of several possible 2D structures for T-COF 1, including eclipsed, staggered, and slipped-stacked AA and AB sequences of 2D layers (SI Appendix, Fig. S3), confirmed that the best fit for these peaks corresponded to the [100], [110], [210], and [001] reflections of the eclipsed AA structure shown in Fig. 1, with unit cell parameters a = b = 28.51 Å and c = 3.4 Å. Importantly, pure samples of T-COF 1 could be obtained only by using a precise 3:2 H2TDB–HHTTP stoichiometry and rigorous air-free conditions and by minimizing the exposure of the reaction mixture to water. The latter is particularly difficult to achieve with boronate-linked COFs because water is a byproduct of the condensation of boronic acids with catechols. Here, we were able to circumvent this challenge by using vacuum-sealed glass tubes with ample empty volume as the reaction media. The large empty volume left in the sealed tubes, ~20 times greater than that of the solution, is essential because it allows water to vaporize as it is being produced during the boronate-catechol condensation.

As shown in Table 1, deviations from these rigorous conditions resulted either in phases with poor crystallinity, or in mixed products where a second COF cocrystallizes with T-COF 1. This second product was identified as (HOTP)(TDB)3 (T-COF 2), a material that displays both HOTP and boroxine rings as the three connected nodes. The structure of T-COF 2 and its unit cell of a = b = 20.94 Å and c = 3.4 Å were assigned by matching the relatively broad PXRD pattern, shown in Fig. 2, with the expected AA eclipsed stacking, as in the case of T-COF 1. In T-COF 2, boroxine rings are formed by self-condensation of the boronic acid groups in H2TDB, similar to those formed by the self-condensation of benzene-diboronic acid found in COF-1 (1, 22). As shown in Table 1, T-COF 2 can be accessed in pure form by adding a small amount of water [1% (vol/vol)] to the reaction mixture, by using a Dean–Stark trap instead of a sealed glass tube, or by increasing the H2TDB–HHTTP ratio in the reaction mixture. Although none of the pure samples of T-COF 2 exhibited the same crystallinity observed for T-COF 1, their identity and purity was confirmed by FT-IR spectroscopy, which revealed the 712 cm−1 peak characteristic of boroxine rings, and by satisfactory elemental analysis (see the experimental details and SI Appendix, Fig. S5).

Having identified appropriate conditions for accessing thiophene-based boronate-linked COFs, we turned our attention to extended thiophene boronic acids with lower oxidation potentials that may offer better p-type hosts for electronic applications. Thus, condensation of bithiophene-2,5′-diboronic acid (H2BTDB) with HHTTP under conditions similar to those used for T-COF 1 provided (HOTP)2(BTDB)3 (T-COF 3), which crystallizes in an eclipsed hexagonal 2D lattice with unit cell parameters a = b = 34.55 Å and c = 3.4 Å (Fig. 3). Notably, the formation of boroxine rings is not observed in this case, and no secondary products are observed.
obtained when using acid digestion bombs as the reaction media, although water exposure must once again be minimized (Table 1).

Our last thiophene-based COF target was one containing thieno[3,2-b]thiophene, one of the most promising monomers for organic conducting polymers (23, 24). Reaction of thieno[3,2-β]thiophene-2,5-diboronic acid (H₂TTDB) (25) with HHTTP produced (HOTP)₂(TTDB)₃ (T-COF 4) as an off-white crystalline powder in good yield. T-COF 4 also crystallizes in an eclipsed AA hexagonal 2D lattice with unit cell parameters \( a = b = 31.58 \text{ Å} \) and \( c = 3.41 \text{ Å} \), and is shown in Fig. 4. We found that the synthesis of T-COF 4 is much more tolerant to various reaction conditions, and under all circumstances described in Table 1, T-COF 4 was accessible as a pure material; a sample with the highest crystallinity was obtained by using a Dean–Stark trap.

The relative insensitivity of T-COF 4 formation to reaction conditions may be attributed to the rigidity of the H₂TTDB monomer, which, owing to its fewer degrees of rotational freedom, is less likely to cause defects during crystallization. Additionally, it is empirically evident that the more linear diboronic acids, H₃BTDB and H₂TTDB, where the two boronic acid groups—more precisely, the two B–C bonds—are parallel, are less sensitive to the reaction conditions than H₂TDB. In the latter, the two boronic acid groups are disposed at an angle of 141.5° with respect to each other, which likely causes defects during the crystallization of T-COF 1 and T-COF 2 and lowers the symmetry of these materials compared with other reported 2D COFs. Indeed, of the three conformers stemming from the condensation of one HHTTP with three H₂TDB molecules (Fig. 5), which may serve as nucleation units for both T-COF 1 and T-COF 2, only isomer A has threefold symmetry and is productive toward the formation of crystalline phases in either case. The bent geometry of H₂TDB is therefore most likely responsible for the selective synthesis of these two materials, which respectively crystallize in the very unusual space groups P-62m and P31m. Importantly, these observations suggest that bent linkers may generally be more difficult to incorporate into crystalline extended polymers formed by strong, less reversible bonds such as those in COFs, which allow faster defect propagation during crystallization.

To investigate the porosity of the thiophene boronate materials, thermogravimetric analyses (TGAs) were conducted on pristine samples of T-COF 1–4. As shown in SI Appendix, Figs. S2, S6, S9, and S13, all of the samples lose guest solvent molecules upon heating to below 180–200 °C. Accordingly, all of the T-COFs were desolvated by heating under vacuum at 200 °C, and their integrity was confirmed by PXRD analysis. \( \text{N}_2 \) adsorption isotherms performed on the desolvated materials revealed that all four are porous and adsorb 466, 172, 295, and 431 cm³/g at \( \sim 760 \text{ torr and 77 K} \) for T-COF 1 through T-COF 4, respectively (Fig. 6). Brunauer–Emmett–Teller (BET) analysis fits to the microporous region of the \( \text{N}_2 \) adsorption isotherms (i.e., \( \text{P/P}_0 < \sim 0.2 \)) revealed apparent surface areas of 927 (8), 562 (2), 344 (8), and 904 (2) m²/g for T-COF 1, 2, 3, and 4, respectively, for the 

### Table 1. Methodology for T-COF synthesis

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<tr>
<th>Thiophene monomers</th>
<th>Sealed tube</th>
<th>Dean–Stark</th>
<th>Sealed tube + 1% water</th>
<th>Microwave*</th>
<th>( \text{N}_2 ) sealed bomb</th>
<th>Air sealed bomb</th>
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<tr>
<td>( \text{HO} )</td>
<td>T-COF 1</td>
<td>T-COF 2</td>
<td>T-COF 1 + T-COF 2</td>
<td>T-COF 2</td>
<td>T-COF 1 + T-COF 2</td>
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<tr>
<td>( \text{HO} )</td>
<td>T-COF 3'</td>
<td>NR'</td>
<td>NR'</td>
<td>NR</td>
<td>T-COF 3'</td>
<td>T-COF 3'</td>
</tr>
<tr>
<td>( \text{HO} )</td>
<td>T-COF 4</td>
<td>T-COF 4</td>
<td>T-COF 4</td>
<td>T-COF 4</td>
<td>T-COF 4</td>
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NR, no reaction.

*Microwave power = 150 W, 30 min.

†120 °C, 8 d.

In their native form, all of the T-COFs are off-white powders, which is indicative of wide bandgap materials and insulators. To take advantage of the electron donating ability of the thiophene units, we pursued doping experiments hoping either to form charge-transfer complexes, an important step toward promoting electron transfer for functional devices, or to provide a sufficient concentration of charge carriers to induce electric conductivity. Thus, immersing samples of T-COF 1 through T-COF 4 in solutions of strong oxidizers such as 2,3-dichloro-5,6-dicyano-1,4-benzquinone (DDQ) and chloranil produced dark materials, possibly indicative of charge transfer (CT) or even...
electron transport, but also induced amorphization of all of the T-COFs. We surmised that DDQ and chloranil may oxidize the HHTP core itself or attack the oxidatively-prone B–C bond (29), both of which would explain the observed decomposition. Accordingly, we turned our attention to less potent oxidizers such as I₂ and TCNQ, the latter being a widely used electron acceptor. N stretch, which is not

unit cell


defined by


SIMULATED (RED) AND EXPERIMENTAL (BLACK) PXRD PATTERNS OF T-COF 2.

Inset shows its building blocks and the partial structure viewed normal and parallel to the ab plane. Yellow, red, gray, and pink spheres represent S, O, C, and B atoms, respectively. Extensive attempts to improve the crystallinity of this compound were unsuccessful; we assign it to the bent nature of H₂TDB (vide infra and Fig. 5).

Fig. 2. Simulated (red) and experimental (black) PXRD patterns of T-COF 2. Inset shows its building blocks and the partial structure viewed normal and parallel to the ab plane. Yellow, red, gray, and pink spheres represent S, O, C, and B atoms, respectively. Extensive attempts to improve the crystallinity of this compound were unsuccessful; we assign it to the bent nature of H₂TDB (vide infra and Fig. 5).

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Ultraviolet-visible-near infrared (UV-Vis-NIR) diffuse reflectance spectroscopy suggested that the new material owes its dark color to a wide CT absorption band centered at 850 nm, shown in an inset of Fig. 7, rather than to delocalized electrons. Although planned charge mobility measurements are necessary to completely rule out electron transfer within TCNQ-T-COF 4, we note that control experiments aimed at preparing donor–acceptor dyads or CT complexes by mixing TCNQ with free HHTP, H₂TDB, or with thieno[3,2-b]thiophene in the same ratios and concentrations as those used for the formation of TCNQ-T-COF 4 did not result in the formation of dark materials and no stable CT complexes could be isolated. This suggested that TCNQ-T-COF 4 contains weakly associated donor–acceptor pairs that are only stabilized in the rigid COF matrix and are not isolable from solution. Indeed, attempts to evacuate the solvent molecules from TCNQ-T-COF 4 in preparation for gas sorption measurements to assess its porosity resulted in sublimation of TCNQ from the black material and recovery of clean T-COF 4. Further evidence for the weak association between TCNQ and T-COF 4 came from a competitive experiment in which TCNQ-T-COF 4 was immersed in mesitylene, which caused rapid bleaching of the black material, recovery of T-COF 4, and isolation of a red solution of the known mesitylene–TCNQ CT adduct (30, 31), which is therefore thermodynamically favored over the TCNQ-T-COF 4 complex. Finally, an EPR experiment of TCNQ-T-COF 4 did not reveal a radical species, suggesting once again that the interaction of TCNQ with T-COF 4, does not involve the complete transfer of an electron from the valence band of T-COF 4 to TCNQ and that TCNQ most likely remains neutral.

To probe the nature of the interaction of TCNQ with T-COF 4, we analyzed the black material by FT-IR spectroscopy. Shifts in the C=CN (ν(CN)) and C = C (ν(CC)) stretches, and the out-of-plane C–H bend (δ(CH)), which occur respectively at 2,226, 1,545, and 860 cm⁻¹ in neat TCNQ, are typically used to discern the degree of CT in TCNQ CT complexes (32). Albeit small, shifts of ν(CC) and δ(CH) to lower energy (1,537 and 798 cm⁻¹, respectively) are in line with partial negative charge being transferred from T-COF 4 to TCNQ. However, accumulation of negative charge should also partially populate the π* orbital of the nitrile groups and shift ν(CN) to lower frequency. Instead, we observe an unusual shift of ν(CN) to higher energy, from 2,226 to 2,233 cm⁻¹ (Fig. 7, Inset). Although hypsochromic shifts of ν(CN) are not unprecedented for TCNQ and other nitriles, they are usually associated with sigma-only N-coordination of TCNQ to heavier metals (33, 34). However, 1H magic angle spinning (MAS) NMR spectroscopy of TCNQ-T-COF 4 attested that the boron atoms, the only likely candidates for TCNQ binding, remain trigonal (δ(B) = 12–40 ppm) and are not pyramidalized (δ(B) = 5–10 ppm), as expected if they acted as Lewis acids toward TCNQ (SI Appendix, Fig. S18). Additionally, coordination of one of the nitrile groups typically splits the B1u and B2u normal modes of the C = N stretch, which is not observed in our case, and confirms the coordinatively innocent nature of the TCNQ molecule. As such, we tentatively assign the unusual shift of ν(CN) to a symmetric intercalation of TCNQ guests between the 2D layers of T-COF 4, which may cause a rigidification of TCNQ to the extent that it affects the CN bonds by stiffening them. This qualitative hypothesis agrees with the observed elongation of the c axis in TCNQ-T-COF 4 relative to T-COF 4 itself, and clearly merits further investigation, as planned in our laboratory.

Fig. 3. Simulated (red) and experimental (black) PXRD patterns of T-COF 3. Inset shows its building blocks and the partial structure viewed normal and parallel to the ab plane. Yellow, red, gray, and pink spheres represent S, O, C, and B atoms, respectively.
In conclusion, we reported the synthesis of COFs containing thiophene-based monomers. We have shown that these are amenable to reticular synthesis principles, but that bent diboronic acids are defect-prone building blocks that are more susceptible to synthetic variations during COF synthesis. These, combined with the characterization of the first CT complex isolated postsynthetically inside a COF, are important steps toward the implementation of such materials in electronic devices. The search for adequate redox partners that will not disrupt the crystalline structure and will promote full electron transfer, thereby providing a sufficient concentration of charge carriers, will be an important challenge for eventually achieving electric conductivity in these extraordinary materials.

Materials and Methods

Starting materials were purchased from Sigma-Aldrich or TCI and used without further purification. Mesitylene and 1,4-dioxane were purchased from TCI. N,N-Dimethylformamide (DMF), hexane, ethyl acetate, and silica-gel were purchased from VWR. THF was taken from an alumina column solvent purification system. NMR spectra were recorded on a Varian 300 Mercury NMR spectrometer and a Bruker Avance-400 NMR spectrometer. \(^1\)H and \(^13\)C chemical shifts are reported in ppm from TMS with the residual solvent resonances as internal standards. Peaks in infrared spectra are assigned as weak (w), medium (m), or strong (s). Elemental analyses were performed by Midwest Microlab.

PXRD patterns were recorded with a Bruker D8 Advance diffractometer equipped with a 0/20 Bragg–Brentano geometry and nickel-filtered Cu Kα radiation (\(K_{\alpha 1} = 1.5406 \text{ Å}, K_{\alpha 2} = 1.5444 \text{ Å}, K_{\alpha 1}/K_{\alpha 2} = 0.5\)). The tube voltage and current were 40 kV and 40 mA, respectively. Samples for PXRD were prepared by placing a thin layer of the designated materials on a zero-background silicon (510) crystal plate.

A Micromeritics ASAP 2020 Surface Area and Porosity Analyzer was used to measure the nitrogen adsorption isotherms. Oven-dried sample tubes equipped with TranSeals (Micromeritics) were evacuated and tared. The samples were transferred to the sample tubes, which were then capped by TranSeals. The samples were heated to 200 °C under a vacuum of 2 mtorr for 12 h, at which point the outgas rate was less than 2 mtorr/min. The evacuated sample tubes were weighed again, and the samples’ mass were determined by subtracting the mass of the previously tared tubes. \(N_2\) isotherms were measured using liquid nitrogen baths (77 K). Ultra high purity grade (99.999% purity) \(N_2\) and He, oil-free valves, and gas regulators were used for the free space correction and measurement. Relative pressure (P/P\(_0\)) range for BET analysis was taken from 5×10\(^{-3}\) to ~0.2. Pore sizes were determined using the DFT N\(_2\) model for the cylindrical pores geometry, with relative pressure (P/P\(_0\)) range from 0.003 to 0.1.

Infrared spectra were obtained on a PerkinElmer Spectrum 400 Spectrometer equipped with a Pike Technologies GladiATR accessory with a germanium crystal. Diffuse reflectance UV-Vis spectra were collected on a Varian Cary 5000 UV-Vis-NIR spectrometer equipped with a Praying Mantis diffuse reflectance accessory and an environmental chamber (Harrick Scientific Products) and were referenced to BaSO\(_4\).

\(2,2'\)-Bithiophene-5,5'-Diboronic Acid (H\(_2\)BTD)

In a 250 mL round-bottom flask, 3.00 g (7.18 mmol) of 5,5'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithiophene were dissolved in 20 mL of THF and 5 mL of water. The mixture was stirred for 2 h at room temperature, followed by the addition of 5 mL of a 6 M aqueous solution of HCl. The resulting mixture was stirred for 12 h. Water (150 mL) was then added to precipitate the desired product, which was recovered by filtration as a fine white powder. After air drying and drying under high vacuum (10\(^{-3}\) torr), we obtained 1.91 g (7.11 mmol, 99.25%). Low-carbon analysis is typical for boron-containing compounds (37.84%), H (3.18%), and S (25.26%). Found, C (35.21%), H (3.14%), and S (25.25%). Low-carbon analysis is typical for boron-containing compounds due to the formation of refractory boron carbide (BC) during the analysis.

\(2,5\)-Dibromothiophene[3,2-b]Thiophene

In a 250 mL round-bottom flask wrapped with aluminum foil, 5.00 g (1.00 equivalent (eq), 35.7 mmol) of thiophene[3,2-b]thiophene and 19.06 g of N-bromosuccinimide (3.00 eq, 107 mmol) were dissolved in 100 mL of DMF. The colorless reaction mixture was stirred in the dark for 12 h. The resulting deep orange solution was poured in 500 mL of water. A pale pink solid precipitated and was isolated by air drying and drying under high vacuum (10\(^{-3}\) torr), we obtained 2.22 g (7.18 mmol, 85%) of 2,5-dibromothiophene[3,2-b]thiophene as a white powder. \(^1\)H NMR (400 MHz, DMSO-d\(_6\)), \(\delta\) 7.61 (s, 2 H), \(^13\)C NMR (101 MHz, DMSO-d\(_6\)), \(\delta\) 134.1 (2 C, quaternary),
In a 20-cm-long Pyrex glass tube (i.d. = 1.1 cm), 38 mg (3.0 eq, 0.15 mmol) of H<TDBD and 33 mg (2.0 eq, 0.10 mmol) of HHTP were dissolved in 1 mL of dry dioxane and 1 mL of dry mesitylene. The tube was connected to a vacuum line, and the reaction mixture was subjected to four cycles of freezing (with liquid N<sub>2</sub>) and thawing, and was then sealed under vacuum. The tube was heated at 120 °C for 8 d in a pre-heated oven, and then cooled to room temperature overnight. The yellow flocculent solid was washed with dry dioxane (5 mL) and dry CH<sub>2</sub>Cl<sub>2</sub> (15 mL) and recovered by centrifugation or filtration. The remaining powder was dried under vacuum (10<sup>−3</sup> torr) for 2 h. The material was desolvated at 200 °C under high vacuum (10<sup>−6</sup> torr) overnight to obtain 40.0 mg of T-COF 3 (15.20%). Found, C (50.66%), H (1.85%), and S (14.17%). Low-carbon analysis is typical for boron-containing compounds due to the formation of refractory BC during the analysis. TGA analysis was performed before any evacuation/activation.

T-COF 4. Both Dean–Stark and sealed tube setups gave high yield and crystallinity. In a 100 mL round bottom flask, 171 mg (3.00 eq, 0.75 mmol) of H4<TDBD and 165 mg (2 eq, 0.50 mmol) of HHTP were dissolved in 15 mL of dry dioxane and 15 mL of dry mesitylene. A Dean–Stark apparatus was placed on top of the flask and filled with mesitylene. The setup was purged three times with N<sub>2</sub> and heated at 120 °C for 2 d under N<sub>2</sub>. The gray flocculent solid was washed with filtration or centrifuge with dry dioxane (20 mL) and dry CH<sub>2</sub>Cl<sub>2</sub>. The remaining powder was dried under vacuum (10<sup>−3</sup> torr) for 2 h. Total desolvation can be performed at 200 °C under high vacuum (10<sup>−6</sup> torr) overnight to obtain 132 mg of T-COF 4 (0.21 mmol, 82%). IR (Ge ATR), 662 (m), 867 (m), 1127 (s), 1127 (s), 1183 (w), 1315 (s), 1491 (w), 1540 (m), and 1585 (m) cm<sup>−1</sup>. Elemental analysis calculated for C<sub>31</sub>H<sub>24</sub>B<sub>6</sub>O<sub>9</sub>S<sub>2</sub> (35.65%), H (2.33%), and S (16.11%). Found, C (55.86%), H (2.40%), and S (15.98%). Low-carbon analysis is typical for boron-containing compounds due to the formation of refractory BC during the analysis. TGA analysis was performed before any evacuation/activation.

**Fig. 7.** Simulated (green) and experimental PXRD patterns for T-COF 4 (red), and TCNO<sub>T</sub>-COF 4 (black). Insets show, in clockwise order from the Upper Left, FTIR spectra, diffuse reflectance UV/Vis-NIR spectra, and a zoom-in of the [001] reflection in the PXRD patterns. Arrows indicate peak shifts.
overnight to obtain 254 mg of T-COF 4 (0.23 mmol, 91%). IR (Ge ATR), 650 (w), 798 (s), 1,017 (s), 1,091 (s), 1,162 (m), 1,239 (m), 1,260 (s), 1,357 (s), 1,442 (s), 1,486 (s), and 2,962 (s). Elemental analysis calculated for C_{28}H_{18}B_8O_5N_8S_4: C (58.12%), H (1.63%), and S (17.24%). Found, C (54.55%), H (1.74%), and S (17.14%). Low-carbon analysis is typical for boron-containing compounds due to the formation of refractory BC during the analysis. TGA analysis was performed before any evacuation/activation.

A control experiment was performed by mixing TCNQ (20.4 mg, 0.1 mmol) with H_{2}TTDB (23.4 mg, 0.1 mmol) or thieno[3,2-b]thiophene (14.4 mg, 0.1 mmol) in CH_{2}Cl_{2} (10 mL) in the dark for 48 h. In each case, the powders isolated after filtration did not show a nitrile stretch in the IR spectra, which matched the IR spectra of the neat thiophene monomers.

**ACKNOWLEDGMENTS.** This work was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences under Award DE-SC0000937 (all work except NMR studies). G.H.V.B. was supported by a Fondation Monahan postdoctoral fellowship. NMR studies were supported by the National Institute of Health through Grants EB001960 and EB002026 (to R.G.G.). V.K.M. was supported by a Natural Sciences and Engineering Research Council of Canada postdoctoral fellowship.