Significant research has been devoted to capturing the Sun’s energy with both inorganic and organic materials. Although the challenges are myriad, transformative discoveries in the latter class fall squarely in the realm of synthetic chemistry. Despite being lightweight, mechanically flexible, as well as easily and affordably processed, organic photovoltaics suffer from lower efficiencies and lifetimes than commercial inorganic solar cells. Such limitations stem both from morphological defects and from weak electronic coupling coupled to strong electron–phonon interactions. These work together to affect exciton formation, migration, and dissociation, as well as charge transfer and separation at the electrodes.1−5 Controlling the way donor and acceptor moieties are assembled is thus key to improving the performance of photovoltaics and other organic electronic devices.6

One class of materials that can address this challenge are covalent organic frameworks (COFs),7−28 whose periodicity, dimensionality, and rigidity allow for optimization of molecular architecture and of intra- and intermolecular interactions. Although the majority of COFs lack significant bulk electrical conductivity, their potential to harvest light and conduct electricity is beginning to be tapped.29−37 Most relevantly, Jin et al. explored charge dynamics in donor–acceptor COFs and showed that the inherent bicontinuous heterojunction allows direct coupling of light absorption, exciton generation, and charge separation.38 In 2013, chalcogenophene-based COFs were reported with the use of thiophene, dithiophene, and thieno[2,3-b]thiophene diboronic acids. These materials engage in direct electron transfer interactions within the framework.33 A first requirement for developing charge and exciton-diffusion materials, and can be used as active materials for organic photovoltaic devices.34 Even more recently, reports on COFs based on benzothiophene35 and tetrathiafulvalene36−38 were published.

Here, we report our efforts to leverage the structural features of COFs and introduce the first heavier chalcogen-based materials in the form of fused benzodiselenophenes and benzoditellurophenes. The motivation behind the design of chalcogenophene-containing fused-organic COFs stems from the leading role of fused chalcogenophenes in synthetic organic conductors, narrow band gap polymers, and field-effect transistors.39−45 Use of heavy chalcogen atoms has been shown to increase charge mobility in organic photovoltaic materials, presumably through the enhanced orbital overlap afforded by the 3p and 4p orbitals of selenium and tellurium atoms, respectively, or through enhanced spin–orbit coupling effects.44−46 Indeed, whereas thiophene-based polymers have larger optical band gaps (1.9 eV in polythiophene vs. 1.5 eV in CdTe47) and much smaller charge mobility values than inorganic semiconductors (0.1 cm2 V−1 s in polythiophene vs. 100−1000 cm2 V−1 s in indium zinc oxide48), replacing sulfur with selenium reduces the optical band gap to 1.6 eV.49−51 The close stacking of selenium and tellurium is also expected to reduce the impact of disorder in the self-assembly process required for COF synthesis and generate more disperse bands to enhance interchain packing of the framework. This should lead to increased conductivity for the heavier chalcogen materials without significantly changing the structure or the unit cell size of the resulting extended networks.52 Herein, we report the synthesis and characterization of the first COFs that incorporate selenium and tellurium atoms into the backbone and show that the presence of the heavier chalcogens indeed leads to superior electrical properties relative to the thiophene analogue.

Treatment of trimethylsilyl-protected benzo[1,2-b:4,5-b′]-diselenophene and benzo[1,2-b:4,5-b′]ditellurophene53 with BBr3 followed by basic hydrolysis and subsequent acidification afforded the new diboronic acids benzo[1,2-b:4,5-b′]-diselenophene (H2BDSe) and benzo[1,2-b:4,5-b′]-ditellurophene (H2BTDte) in good yields (Scheme 1). For comparison purposes, we also synthesized the reported benzothiophene analogue (H3BDS).55 All three benzodichalcogenophene diboronic acids were fully characterized using standard methods.

Condensation of the diboronic acids with 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) in a 1:1 mixture of mesitylene and 1,4-dioxane led to the isolation of crystalline powders after heating at 120 °C for 24−72 h (Scheme 2). After washing with fresh 1,4-dioxane and dichloromethane, then drying under reduced pressure for 12 h, these powders were formulated as (HOTP)2(BDT)3 (1-S-
HOTP = 2,3,6,7,10,11-hexaoxytriphenylene, BDT = benzodi-thiophene diboronate, (HOTP)\(_2\)(BDSe)\(_3\) (1-Se; BDSe = benzodiselenophene diboronate), and (HOTP)\(_2\)(BDTe)\(_3\) (1-Te; BDTe = benzoditellurophene diboronate) and verified by C, H, and N elemental analyses.

Powder X-ray diffraction (PXRD) patterns of each of these materials (Figure 1) exhibited peaks indicative of the formation of hexagonal 2D layers stacked in an eclipsed manner, with unit cell lengths, \(a = b = 36.5\) and \(36.7\) Å, and interlayer distance, \(c = 3.40\) and \(3.45\) Å for 1-Se and 1-Te, respectively.

Strong bands observed at 1398, 1395, and 1383 cm\(^{-1}\) (Figure 2) in the infrared (IR) spectra of 1-S, 1-Se, and 1-Te, respectively, attributed to the asymmetric B–O stretches, confirmed the formation of boronate ester links.\(^{54}\) Furthermore, for all three COFs, characteristic bands corresponding to C–B stretches in the chalcogenophene and C–O stretches in the catechol moieties were observed at approximately 1062 and 1241 cm\(^{-1}\), respectively. Thermogravimetric analyses (TGA) (Figures S26–S28) revealed the most drastic weight loss to be at \(\sim 380^\circ\)C for 1-S and 440–500 \(^\circ\)C for 1-Se and 1-Te. The weight loss at lower temperatures is attributed to evaporation of dioxane (b.p. 101 \(^\circ\)C) and mesitylene (b.p. 160 \(^\circ\)C) guest molecules.

After degassing at 200 \(^\circ\)C for 24 h at 2 mTorr, samples of 1-S and 1-Se adsorbed 701 and 672 cm\(^3\) of N\(_2\) gas per gram, respectively, at 77 K and 760 Torr (Figure 3). Fitting the \(P/P_0\) ≤ 0.2 region of the N\(_2\) adsorption isotherms to the BET model revealed surface areas of 1125 m\(^2\)/g (1424 m\(^2\)/mmol) and 1056 m\(^2\)/g (1634 m\(^2\)/mmol), for 1-S and 1-Se, respectively. Measurements of two different sample batches of 1-Te, activated under similar conditions, led to uptakes of only 148–164 m\(^2\)/g per gram, which corresponds to a BET surface area of 302–352 m\(^2\)/g (555–647 m\(^2\)/mmol). Unlike 1-S and 1-Se, 1-Te becomes less crystalline upon activation (Figure S27). Activation at 150 \(^\circ\)C showed no improvement in surface area measurements. Although it is unclear what causes the difference in N\(_2\) uptake between these compounds, possible explanations include the somewhat lower crystallinity of 1-Te and potential surface pore blocking effects.\(^{55}\)

Despite its lower crystallinity, which likely leads to an increase in overall resistance because of grain boundaries, 1-Te exhibits the highest bulk conductivity of the three COFs. Indeed, two-point probe electrical conductivity measurements of compressed pellets of these materials revealed values of
3.7(±0.4) × 10⁻¹⁰ S/cm for 1-S, 8.4(±3.8) × 10⁻⁹ S/cm for 1-Se, and 1.3(±0.1) × 10⁻⁷ S/cm for 1-Te (Figure 4). Notably, all three COFs show conductivities that are higher than those of the diboronic acid precursors ($σ = 8.0(±1.7) × 10⁻¹³ S/cm$ for H₂BDS; $σ = 1.2(±0.2) × 10⁻¹⁰ S/cm$ for H₂BDSe; $σ = 6.2(±2.6) × 10⁻⁹ S/cm$ for H₂BDTe). However, the conductivity of the HHTTP precursor itself was 2.5(±0.1) × 10⁻⁸ S/cm.

Although the increase in going from the diboronic acid precursors to the COFs may be due to the addition of HHTTP, especially in an ordered 2D fashion, this suggests that the conductivity increase in the order $S < Se < Te$ in both the precursors and COFs is indeed due to the presence of increasingly larger chalcogens. The foregoing results highlight the utility of the heavier chalcogens for improving the charge transport properties of COFs. The first examples of COFs based on selenium and tellurium should provide a blueprint for similar studies in this burgeoning area. Our efforts are now focused on engineering thin films of these materials for use in solar cell and field-effect transistors.

**REFERENCES**


(22) Feng, X.; Liu, L.; Honsho, Y.; Saeki, A.; Seki, S.; Irie, S.; Dong, Y.; Nagai, A.; Jiang, D. High-Rate Charge-Carrier Transport in...


