Synthesis and Electrical Properties of Covalent Organic Frameworks with Heavy Chalcogens

Supporting Information

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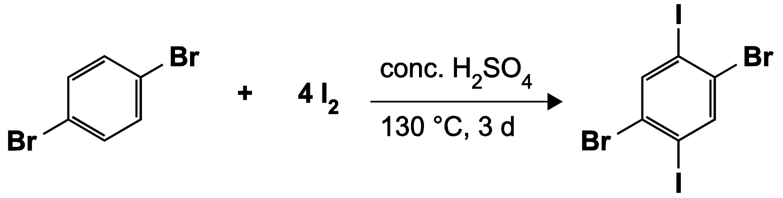
Synthesis

General considerations. All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques. All reagents iodine, 1,4-dibromobenzene, copper iodide, palladium chloride, triphenylphosphine, tert-butyllithium, sulfur, tellurium, boron tribromide, sodium hydroxide, sulfuric acid, hydrochloric acid) were purchased from Sigma-Aldrich or TCI and used without further purification. Trimethylsilylacetylene was purchased from Oakwood Chemical. Selenium powder (99.5+%) was purchased from Acros Organics. Tellurium powder (-325 mesh, 99.998%) was purchased from Alfa Aesar. Synthesis of 1,4-dibromo-2,5-diiodobenzene was based on a previously published report[1] but had to be modified (described below) because the original procedure was not reproducible in our hands. In our hands, syntheses of 2,5-bis(trimethylsilylethynyl)-1,4-dibromobenzene, 2,6-bis(trimethylsilyl)benzo[1,2-b:4,5-b']dithiophene, 2,6-bis(trimethylsilyl)benzo[1,2-b:4,5-b']bis(selenophene), and 2,6-bis(trimethylsilyl)benzo[1,2-b:4,5-b']bis(tellurophene) were based on a previously published report,[2] but each had to be slightly modified (described below) because the reported purification steps did not yield the best results. Benzonitrile, benzene, diisopropylamine, diethyl ether, pentane, hexanes, dichloromethane, toluene, tetrahydrofuran, methanol (MeOH), ethanol (EtOH), isopropanol (iPrOH), mesitylene, and 1,4-dioxane were purchased from Sigma-Aldrich or TCI and dried over molecular sieves. Bis(triphenylphosphine)palladium(II) dichloride was freshly prepared according to previously published report.[3] NMR solvents were obtained from Cambridge Isotope Laboratories and stored over molecular sieves prior to use. ^{1}H NMR spectra were recorded on a Bruker 400 or Varian 300 Mercury NMR spectrometers at room temperature in $CDCl_3$ or DMSO-d_6. Chemical shifts are reported with respect to solvent residual peaks, 7.26 ppm ($CDCl_3$) or 2.50 ppm (DMSO-d_6). Elemental analysis was performed at Complete Analysis Laboratories, Inc. (Parsippany, NJ). UV-Vis spectra, obtained using a solvent reference blank in a cuvette, were recorded on a Varian Carey 5000 spectrophotometer from 230 to 800 nm using matched 1-cm quartz cells. Diffuse reflectance UV-Vis spectra were collected between on the same instrument equipped with a Praying Mantis diffuse reflectance accessory and an environmental chamber (Harrick Scientific Products) and referenced to $BaSO_4$. IR spectra were obtained on a PerkinElmer Spectrum 400 Spectrometer equipped with a Pike Technologies GladiATR accessory with a germanium crystal. PXRD patterns were recorded with a Bruker D8 Advance diffractometer equipped with a $\theta/2\theta$ Bragg–Brentano geometry and nickel-filtered Cu Kα radiation (Kα_1 = 1.5406 Å, Kα_2 = 1.5444 Å, Kα_1/Kα_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. Structure simulation was performed using the method described by Narayan et al.[4] TGA was performed on a TA Instruments Q500 Thermogravimetric Analyzer at a heating rate of 3 °C/min under air or nitrogen at a flow rate of 5 mL/min. Nitrogen adsorption isotherms were measured with a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. Oven-dried sample tubes equipped with TranSeals (Micromeritics) were evacuated and tared. The samples were transferred to the sample tubes, which were then capped with TranSeals. The samples were heated to 200 °C under a vacuum of 2 mtorr for 24 h, at which point the outgas rate was less than 2 mtorr/min. The evacuated sample tubes were weighed again, and the sample mass was determined by subtracting the mass of the empty tubes. Nitrogen isotherms were measured using liquid nitrogen baths (77 K). Ultra high purity grade (99.999% purity) nitrogen and helium, oil-free valves, and gas regulators were used for the free space correction and measurement. Relative pressure (P/P_o) range for BET analysis was taken from 5×10^{-5} to ~0.2. Pellet conductivity was measured with a Keithley Electrometer/High Resistance Meter 6517B using a home-built pellet press as has been described elsewhere.[5] The powder was pressed between two steel rods of 2 mm diameter inside of a glass capillary.

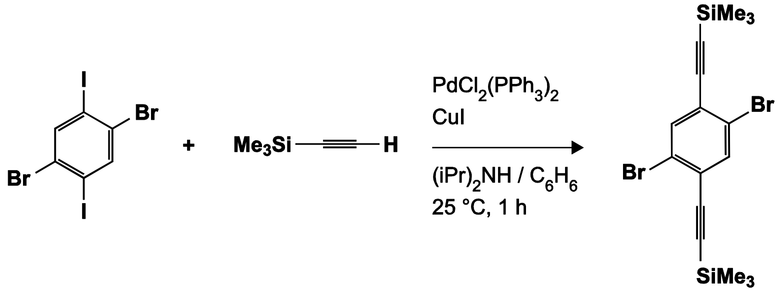
Precursors

Scheme S1. Synthesis of **1,4-dibromo-2,5-diiodobenzene**.



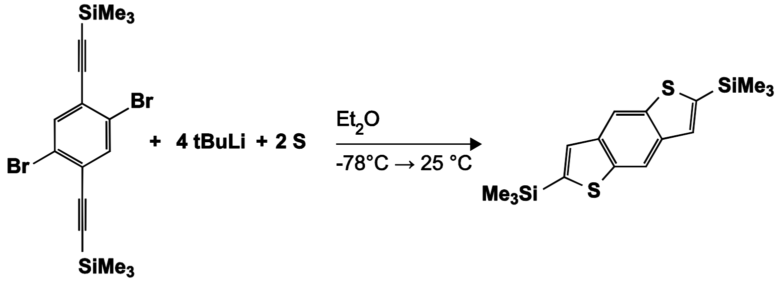
1,4-Dibromo-2,5-diiodobenzene. In a 500-mL round bottom flask, a solution of 1,4-dibromobenzene (5.17 g, 22.00 mmol, 1.0 equiv.) and iodine (22.16 g, 87.00 mmol, 4.0 equiv.) in 100 mL of concentrated H_2SO_4 was vigorously stirred with a magnetic stirrer while the reaction mixture was held at 125-135 ºC for 3 d. *Note: Temperatures above 135 ºC promote further iodination and make separation of products difficult.* The mixture was poured into ice/water and the product was extracted with dichloromethane. Excess iodine, marked by a dark purple color, was removed by washing the dichloromethane layer with aqueous NaOH. The resulting clear solution was dried with $MgSO_4$ and the solvent was removed under vacuum to yield an off-white solid, which was then washed with hexanes and collected onto a filter funnel. Yield: 6.58 g, 62 %. ^1H NMR (300 Hz, $CDCl_3$) δ (ppm): 8.04 (s, 2H, Ar-*H*) and is consistent with the previously published report.

Scheme S2. Synthesis of **2,5-bis(trimethylsilylethynyl)-1,4-dibromobenzene**.



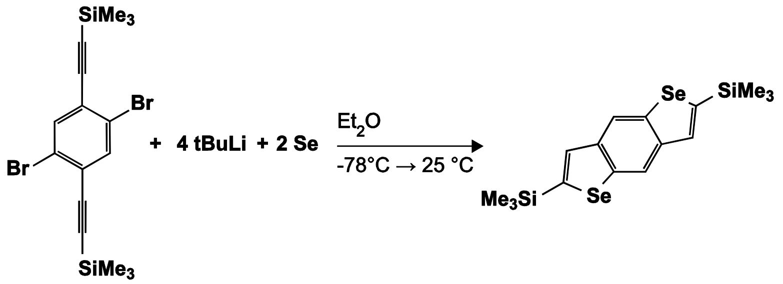
2,5-bis(trimethylsilylethynyl)-1,4-dibromobenzene. In a 100-mL Schlenk flask, CuI (41.0 mg, 0.19 mmol, 0.06 equiv.), $PdCl_2(PPh_3)_2$ (71.3 mg, 0.09 mmol, 0.03 equiv.), and 1,4-dibromo-2,5-diiodobenzene (1.66 g, 3.40 mmol, 1.0 equiv.) were added. The flask was evacuated and refilled with nitrogen, after which 25 mL benzene and 15 mL diisopropylamine were transferred with a syringe. Trimethylsilylacetylene (0.92 mL, 0.65 mmol, 1.9 equiv.) was added to the Schlenk flask and the reaction mixture was stirred at room temperature. After 1 h, the reaction mixture was transferred into a separatory funnel, quenched with water, and the product was extracted with diethyl ether. The organic layer was dried with $MgSO_4$ and diethyl ether was removed under reduced pressure to yield an orange solid, which was then dissolved in pentane and passed through a plug of silica gel. After pentane was removed, the pale yellow crystals were washed with EtOH to remove the color, which yielded white crystals. Yield: 1.46 g, 95 %. ^{1}H NMR (300 Hz, $CDCl_3$) δ (ppm): 7.67 (s, 2H, Ar-*H*), 0.27 (s, 18H, Si-C*H*$_3$) and is consistent with the previously published report.

Scheme S3. Synthesis of **2,6-bis(trimethylsilyl)benzo[1,2-b:4,5-b']dithiophene**.



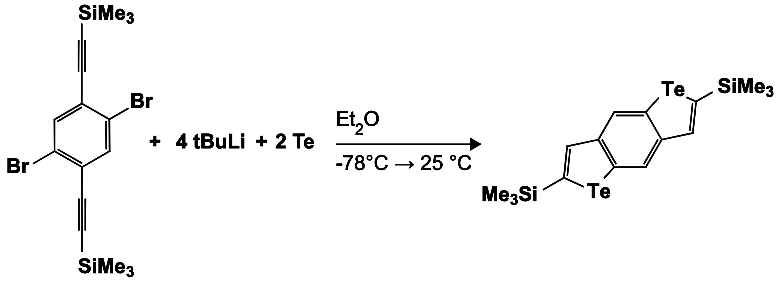
2,6-Bis(trimethylsilyl)benzo[1,2-b:4,5-b']dithiophene. In a three-neck round bottom flask, a stir bar and 2,5-bis(trimethylsilylethynyl)-1,4-dibromobenzene (500.0 mg, 1.20 mmol, 1.0 eq) were added. One side neck was connected to the Schlenk line, while the other was equipped with a solid addition tube containing sulfur powder (84.3 mg, 2.30 mmol, 2.0 eq). The middle neck was capped with a rubber septum. The flask was evacuated and refilled with nitrogen three times, after which dry diethyl ether was added through the rubber septum via a syringe. The solution was cooled to -78 ºC in a dry ice/acetone bath and a pentane solution of tert-butyllithium (2.75 mL of 1.7 M, 4.70 mmol, 4.0 eq) was added to the flask using a syringe. The cold bath was removed and the mixture was allowed to warm up to room temperature. After stirring for 15 min at room temperature, sulfur powder was added and the reaction mixture was allowed to stir for 15 min, after which it was quenched with 30 mL EtOH and allowed to stir for 1 h. The product was extracted with chloroform and washed with water. The organic layer was dried with $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was washed with pentane, dried under reduced pressure, then dissolved in diethyl ether, passed through a plug of silica gel, concentrated, and placed in a freezer to crystallize. Yield: 330.0 mg, 84 %. ^{1}H NMR (300 Hz, $CDCl_3$) δ (ppm): 8.27 (s, 2H), 7.46 (s, 2H), 0.39 (s, 18H, Si-CH_3) and is consistent with the previously published report.

Scheme S4. Synthesis of **2,6-bis(trimethylsilyl)benzo[1,2-b:4,5-b']bis(selenophene)**.



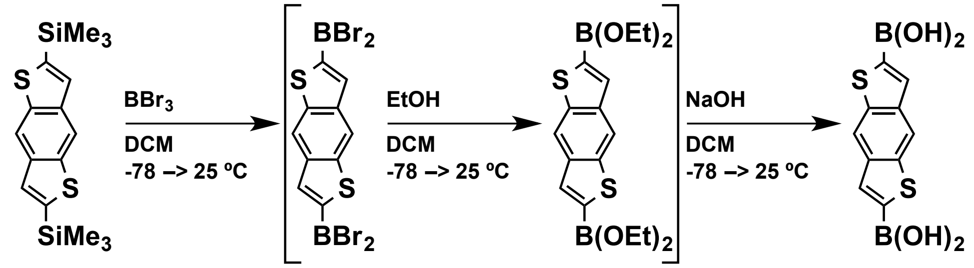
2,6-Bis(trimethylsilyl)benzo[1,2-b:4,5-b']bis(selenophene). In a three-neck round bottom flask, a stir bar and 2,5-bis(trimethylsilylethynyl)-1,4-dibromobenzene (570.0 mg, 1.30 mmol, 1.0 eq) were added. One side neck was connected to a Schlenk line, while the other was equipped with a solid addition tube containing selenium powder (223.0 mg, 2.70 mmol, 2.0 eq). The middle neck was capped with a rubber septum. The flask was evacuated and refilled with nitrogen three times, after which dry diethyl ether was added through the rubber septum via a syringe. The solution was cooled to -78 ºC in a dry ice/acetone bath and a pentane solution of tert-butyllithium (3.2 mL of 1.7 M, 5.30 mmol, 4.0 eq) was added to the flask using a syringe. The cold bath was removed and the mixture was allowed to warm up to room temperature. After stirring for 15 min at room temperature, selenium powder was added and the reaction mixture was allowed to stir for 15 min, after which it was quenched with 30 mL EtOH and allowed to stir for 1 h. The product was extracted with chloroform and washed with water. The organic layer was dried with $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was washed with EtOH, dried under reduced pressure, then dissolved in diethyl ether, passed through a plug of silica gel, concentrated, and placed in a freezer to crystallize. Yield: 371.4 mg, 65 %. ^{1}H NMR (300 Hz, $CDCl_3$) δ (ppm): 8.32 (s, 2H), 7.71 (s, 2H), 0.38 (s, 18H, Si-CH_3) and is consistent with previously published report.

Scheme S5. Synthesis of **2,6-bis(trimethylsilyl)benzo[1,2-b:4,5-b']bis(tellurophene)**.



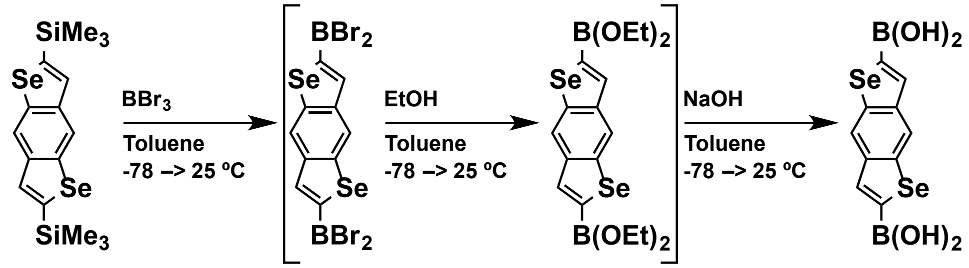
2,6-Bis(trimethylsilyl)benzo[1,2-b:4,5-b']bis(tellurophene). In a three-neck round bottom flask, a stir bar and 2,5-bis(trimethylsilylethynyl)-1,4-dibromobenzene (639.0 mg, 1.50 mmol, 1.0 eq) were added. One side neck was connected to a Schlenk line, while the other was equipped with a solid addition tube containing tellurium powder (382.0 mg, 2.90 mmol, 2.0 eq). The middle neck was capped with a rubber septum. The flask was evacuated and refilled with nitrogen three times, after which dry diethyl ether was added through the rubber septum via a syringe. The solution was cooled to -78 ºC in a dry ice/acetone bath and a pentane solution of tert-butyllithium (3.5 mL of 1.7 M, 6.00 mmol, 4.0 eq) was added to the flask using a syringe. The cold bath was removed and the mixture was allowed to warm up to room temperature. After stirring for 15 min at room temperature, tellurium powder was added and the reaction mixture was allowed to stir for 15 min, after which it was quenched with 30 mL EtOH and allowed to stir for 12 h. The product was extracted with chloroform and washed with water. The organic layer was dried with $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was washed with EtOH, dried under reduced pressure, then dissolved in chloroform, passed through a plug of silica gel, concentrated, and placed in a freezer to crystallize. Yield: 431.0 mg, 62 %. ^{1}H NMR (300 Hz, $CDCl_3$) δ (ppm): 8.33 (s, 2H), 8.12 (s, 2H), 0.33 (s, 18H, Si-CH_3) and is consistent with the previously published report.

Scheme S6. Synthesis of **benzo[1,2-b:4,5-b']dithiophene-2,6-diyldiboronic acid**.



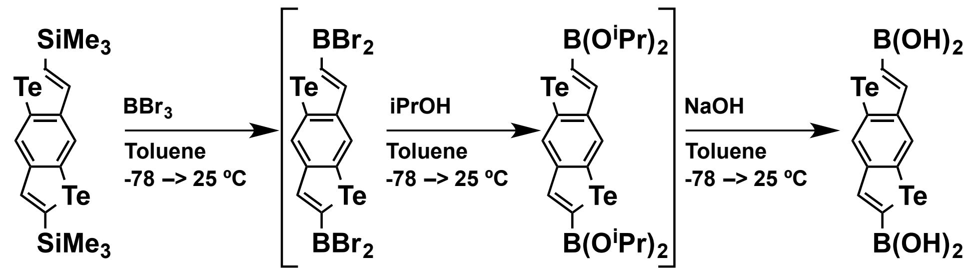
Benzo[1,2-b:4,5-b']dithiophene-2,6-diyldiboronic acid. *This procedure differs from that reported by Medina, et al.,*[6] *who used NaOH to directly hydrolyze the dibromoboranyl intermediate..* Under a nitrogen atmosphere, a dichloromethane solution of 2,6-bis(trimethylsilyl)benzo[1,2-b:4,5-b']dithiophene (431.0 mg, 1.30 mmol, 1.0 eq) in a Schlenk flask was cooled to -78 ºC with a dry ice/acetone bath. Using a syringe, a dichloromethane solution of BBr_3 (4 mL of 1.0 M, 3.90 mmol, 3.0 eq) was slowly added and the resulting green suspension was allowed to stir at -78 ºC for 10 min. The cold bath was removed and the reaction mixture became a bright orange suspension as it warmed up to room temperature. After stirring at 25 ºC for 1 h, the reaction mixture was cooled again to -78 ºC and 15 mL EtOH was added to it slowly. *Note: Use of MeOH instead of EtOH led to protodeboronation as deemed by ^{1}H NMR of the intermediate, which consisted of a mixture of tetramethyl benzo[1,2-b:4,5-b']dithiophene-2,6-diyldiboronate and parent benzo[1,2-b:4,5-b']dithiophene, which was previously synthesized by Takimiya, et al.*[2] The resulting clear yellow solution was warmed to room temperature and stirred for 12 h. Hydrolysis with dilute HCl and vigorous stirring precipitated out an off-white solid, which was extracted with a 1:3 mixture of THF and diethyl ether. The organic layer was concentrated under vacuum, passed through a plug of Celite and collected into a vial filled with pentane, at which point, a pure white solid crashed out. The contents were centrifuged, solvent was decanted, and the solid dried under reduced pressure. Yield: 195.0 mg, 66 %. ^{1}H NMR (300 Hz, DMSO-d$_6$) δ (ppm): 8.54 (s, 4H), 8.50 (s, 2H), 7.99 (s, 2H). Elemental analysis for $C_{10}H_8B_2O_4S_2$ (277.91 g/mol): Calculated C, 43.22; H, 2.90. Found C, 43.23; H, 2.89.

Scheme S7. Synthesis of **benzo[1,2-b:4,5-b']bis(selenophene)-2,6-diyldiboronic acid**.



Benzo[1,2-b:4,5-b']bis(selenophene)-2,6-diyldiboronic acid. Under a nitrogen atmosphere, a toluene solution of 2,6-bis(trimethylsilyl)benzo[1,2-b:4,5-b']bis(selenophene) (279.9 mg, 0.65 mmol, 1.0 eq) in a Schlenk flask was cooled to -78 ºC with a dry ice/acetone bath. Using a syringe, a dichloromethane solution of BBr_3 (2 mL of 1.0 M, 1.96 mmol, 3.0 eq) was slowly added and the resulting green suspension was allowed to stir at -78 ºC for 10 min. The cold bath was removed and the reaction mixture became a bright orange suspension (see photo below) as it warmed up to room temperature. After stirring at 25 ºC for 12 h, the reaction mixture was cooled again to -78 ºC and EtOH (5 mL) was added to it slowly. The resulting clear yellow solution was warmed to room temperature and stirred for 1 h. Hydrolysis with NaOH and acidification with dilute HCl precipitated out an off-white solid, which was extracted with a 1:3 mixture of THF and diethyl ether. The organic layer was concentrated under vacuum and pentane was added to crash out a pure white solid. The contents were centrifuged, solvent was decanted, and the solid dried under reduced pressure. Yield: 182.7 mg, 75 %. ^{1}H NMR (300 Hz, DMSO-d_6) δ (ppm): 8.55 (s, 2H), 8.48 (s, 4H), 8.23 (s, 2H). Elemental analysis for $C_{10}H_8B_2O_4Se_2$ (371.77 g/mol): Calculated C, 32.31; H, 2.17. Found: C, 32.33; H, 2.23.

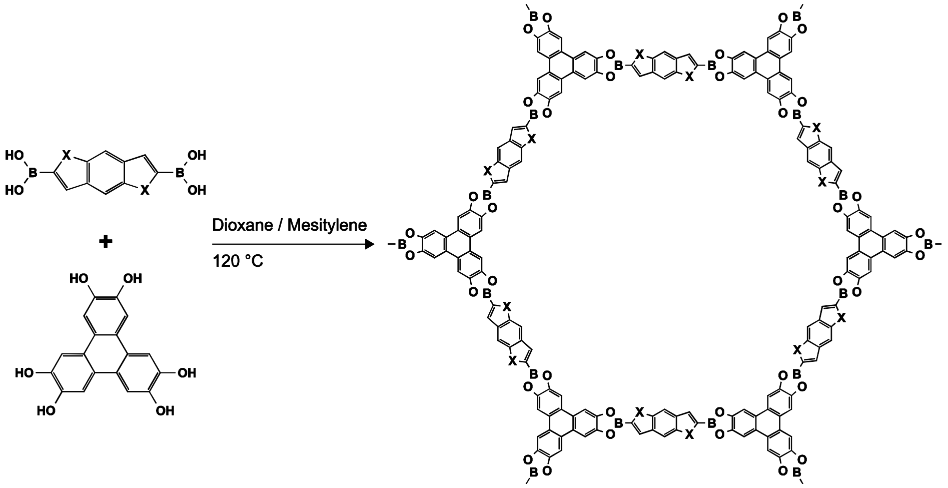
Scheme S8. Synthesis of **benzo[1,2-b:4,5-b']bis(tellurophene)-2,6-diyldiboronic acid**.



Benzo[1,2-b:4,5-b']bis(tellurophene)-2,6-diyldiboronic acid. Under a nitrogen atmosphere, a toluene solution of 2,6-bis(trimethylsilyl)benzo[1,2-b:4,5-b']bis(tellurophene) (314.7 mg, 0.60 mmol, 1.0 eq) in a Schlenk flask was cooled to -78 ºC with a dry ice/acetone bath. A dichloromethane solution of BBr_3 (1.85 mL of 1.0 M, 1.85 mmol, 3.0 eq) was slowly added using a syringe and the resulting grey suspension was allowed to stir at -78 ºC for 10 min. The cold bath was removed and the reaction mixture became a red-purple suspension as it warmed to room temperature. After stirring at 25 ºC for 12 h, the reaction mixture was cooled again to -78 ºC and iPrOH was added to it slowly. The resulting orange suspension was warmed to room temperature and stirred for 12 h. The product was then extracted with NaOH, which was washed with THF. Addition of dilute HCl precipitated out a yellow solid, which was extracted with a 1:3 mixture of THF and diethyl ether. The organic layer was concentrated under vacuum and pentane was added to crash out a bright yellow solid. The contents were centrifuged, solvent was decanted, and the solid dried under reduced pressure. Yield: 202.6 mg, 72 %. ^1H NMR (300 Hz, DMSO-d_6) δ (ppm): 8.67 (s, 2H), 8.56 (s, 2H), 8.32 (s, 4H). Elemental analysis for $C_{10}H_8B_2O_4Te_2$ (468.99 g/mol): Calculated C, 25.61; H, 1.72. Found: C, 25.78; H, 1.90. *Note: The bright yellow product turns bright orange after exposure to light for several days at room temperature. Moreover, use of MeOH and EtOH instead of iPrOH led to protodeboronation as deemed by ^1H NMR of the intermediate, which consisted of a mixture of tetramethylbenzo[1,2-b:4,5-b']bis(tellurophene)-2,6-diyldiboronate or tetraethylbenzo[1,2-b:4,5-b']bis(tellurophene)-2,6-diyldiboronate and parent benzo[1,2-b:4,5-b']bis(tellurophene), which was previously synthesized by Takimiya, et al.*[2]

Covalent organic frameworks

Scheme S9. General synthesis of **1-X** (X = S, Se, Te).



1-S. *This procedure differs from that reported by Medina, et al.,*[6] *who synthesized the material in a Teflon lined stainless steel autoclave at 100 °C*. A 1.4 mL 1,4-dioxane/mesitylene (1:1) suspension of benzo[1,2-b:4,5-b']dithiophene-2,6-diyldiboronic acid (13.3 mg, 0.05 mmol, 1.5 eq) and HHTP (10.7 mg, 0.03 mmol, 1.0 eq) was transferred to a Pyrex glass tube (L = 27 cm, O.D. = 1.1 cm, I.D. = 0.9 cm), which was subjected to three cycles of freezing, evacuation, and thawing before being sealed under vacuum. The reaction mixture was then heated at 120 °C for 24 h, yielding a flocculent grey-green solid, which was washed with 1,4-dioxane and dichloromethane and dried under vacuum for 3 h. Yield: 20.4 mg, 49 %. Elemental analysis for $C_{66}H_{24}B_6O_{12}S_6$ (1266.13 g/mol): Calculated C, 62.61; H, 1.91; S, 15.19. Found: C, 63.69; H, 2.03; S, 14.46.

1-Se. A 1.6 mL 1,4-dioxane/mesitylene (1:1) suspension of benzo[1,2-b:4,5-b']bis(selenophene)-2,6-diyldiboronic acid (11.1 mg, 0.03 mmol, 1.5 eq) and HHTP (6.7 mg, 0.02 mmol, 1.0 eq) was transferred to a Pyrex glass tube (L = 27 cm, O.D. = 1.1 cm, I.D. = 0.9 cm), which was subjected to three cycles of freezing, evacuation, and thawing before being sealed under vacuum. The reaction mixture was then heated at 120 °C for 24 h, yielding a flocculent green solid, which was washed with 1,4-dioxane and dichloromethane and dried under vacuum for 3 h. Yield: 12.4 mg, 39 %. Elemental analysis for $C_{66}H_{24}B_6O_{12}Se_6$ (1547.53 g/mol): Calculated C, 51.23; H, 1.56. Found: C, 52.48; H, 1.63.

1-Te. Heating a 12-mL 1,4-dioxane/mesitylene (1:1) suspension of benzo[1,2-b:4,5-b']bis(tellurophene)-2,6-diyldiboronic acid (89.7 mg, 1.90 mmol, 1.5 eq) and HHTP (43.5 mg, 1.30 mmol, 1.0 eq) at 120 °C for 3 d in a 20-mL scintillation vial yielded a flocculent green solid, which was washed with 1,4-dioxane and dichloromethane and dried under reduced pressure for 3 h. Yield: 109.6 mg, 45 %. Elemental analysis for $C_{66}H_{24}B_6O_{12}Te_6$ (1839.37 g/mol): Calculated C, 43.10; H, 1.32. Found: C, 43.54; H, 1.99.

Characterization

^{1}H NMR spectra

Note: In our hands, the three benzodichalcogenophene diboronic acid precursors are insoluble in all common organic solvents expect ***wet*** *tetrahydrofuran (THF) and dimethylsulfoxide (DMSO). Furthermore, having water (H_2O) as the main peak (2.5 ppm) in the spectra is unavoidable because commercial, fresh DMSO-d_6 that was stored over sieves and kept in a desiccator contains water.*

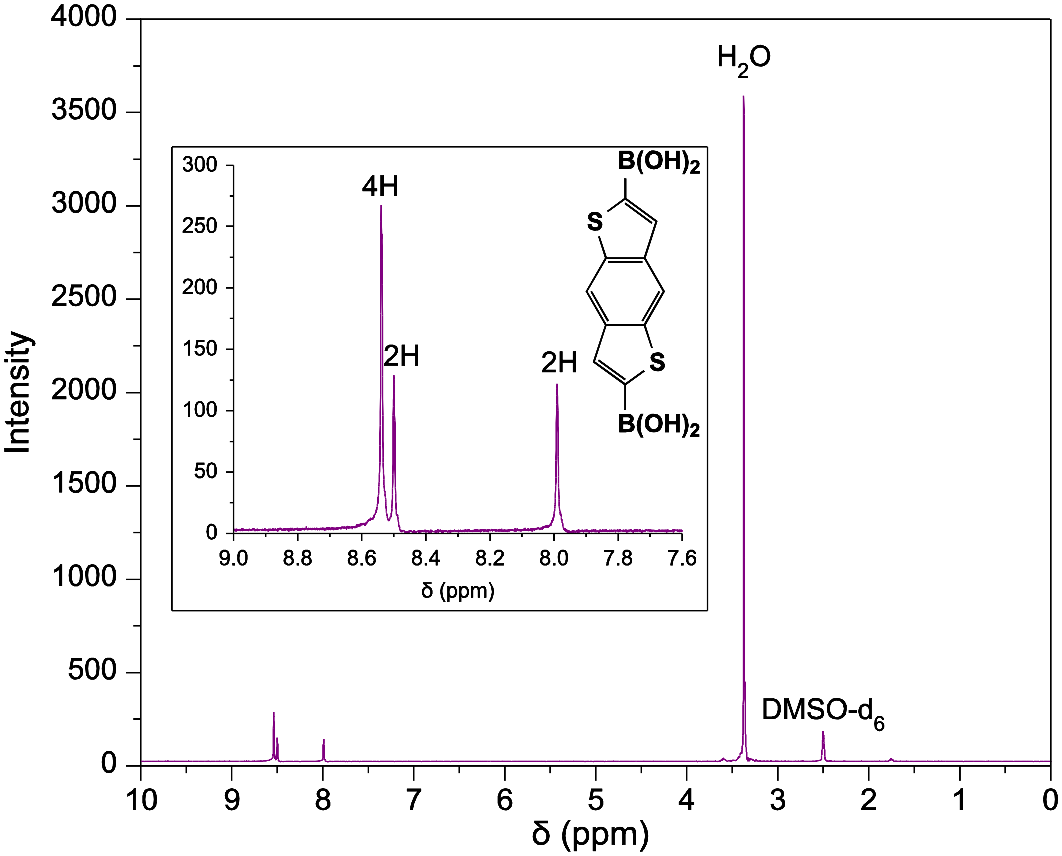


Figure S1. ^{1}H NMR spectrum of **H_2BDS** in DMSO-d_6.

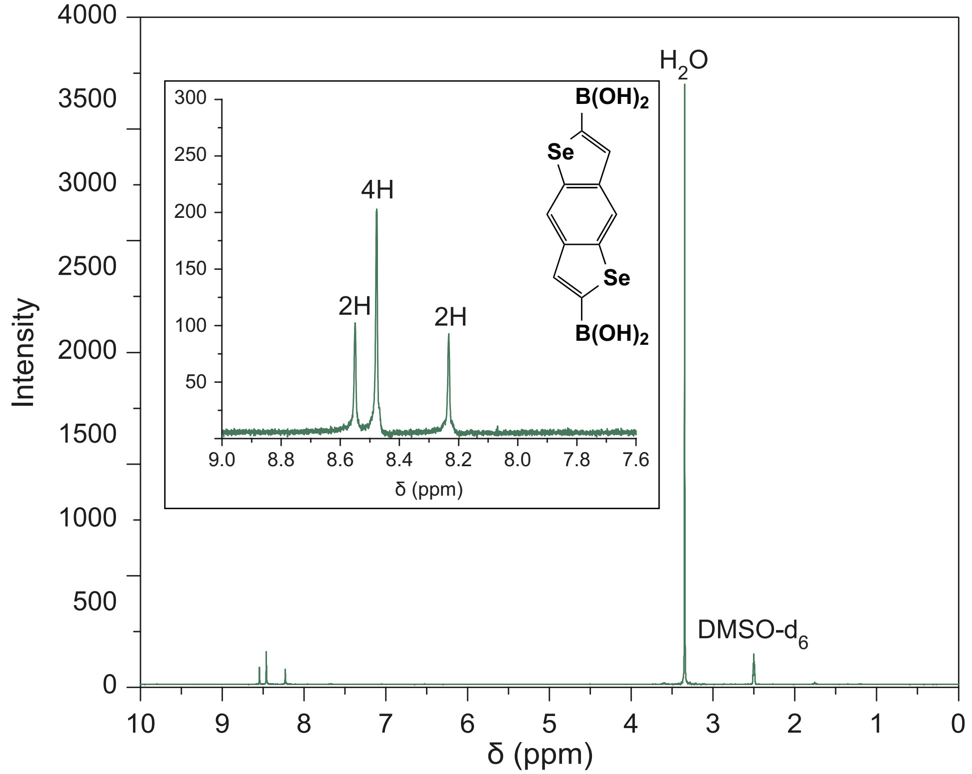


Figure S2. ^{1}H NMR spectrum of **H_2BDSe** in DMSO-d_6.

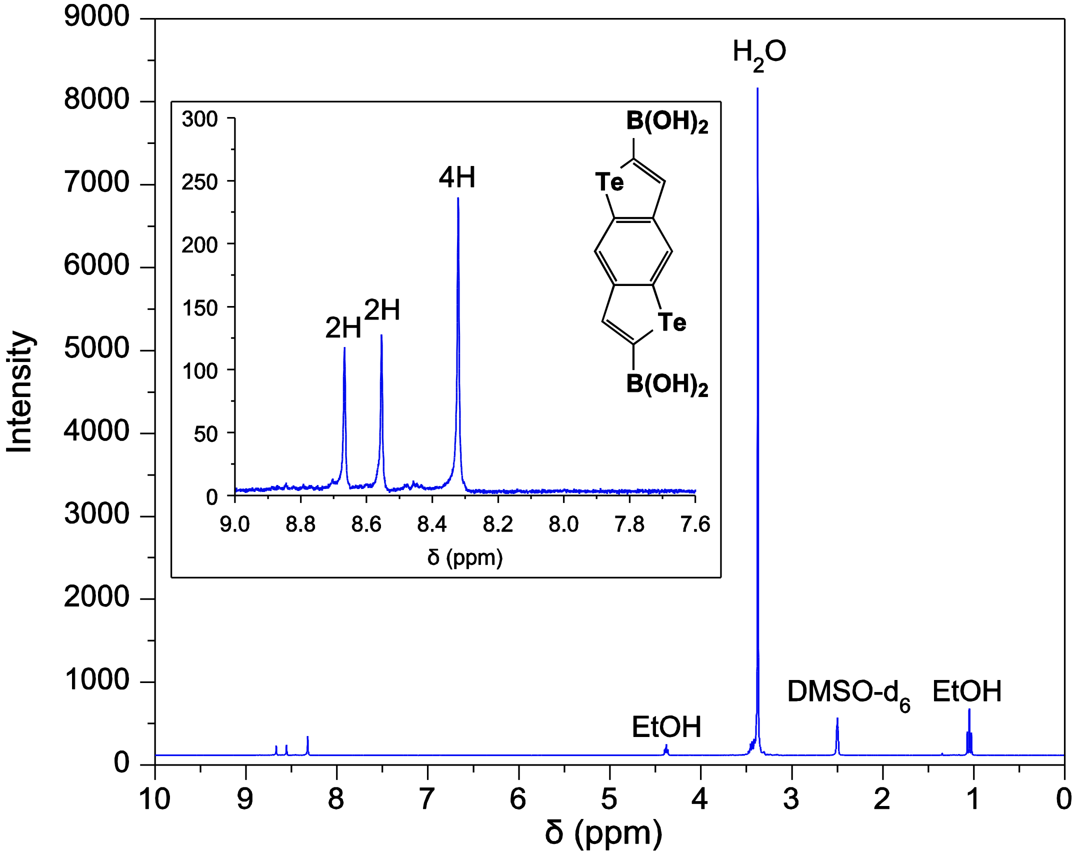


Figure S3. ^{1}H NMR spectrum of $\mathbf{H_2BDTe}$ in DMSO-d_6.

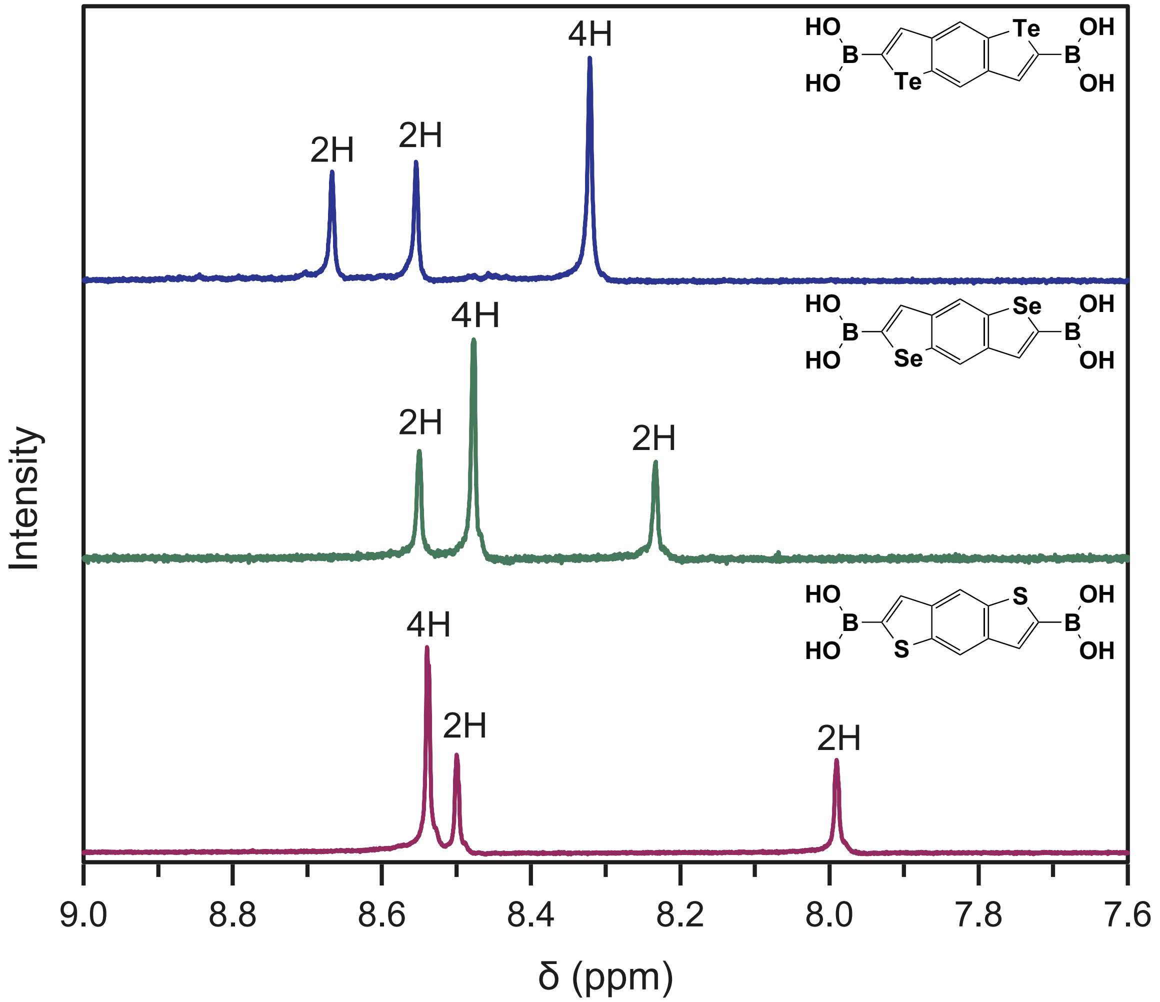


Figure S4. Comparison of ^{1}H NMR spectra of **H_2BDS**, **H_2BDSe**, and **H_2BDTe** in DMSO-d_6.

Infrared (IR) spectra

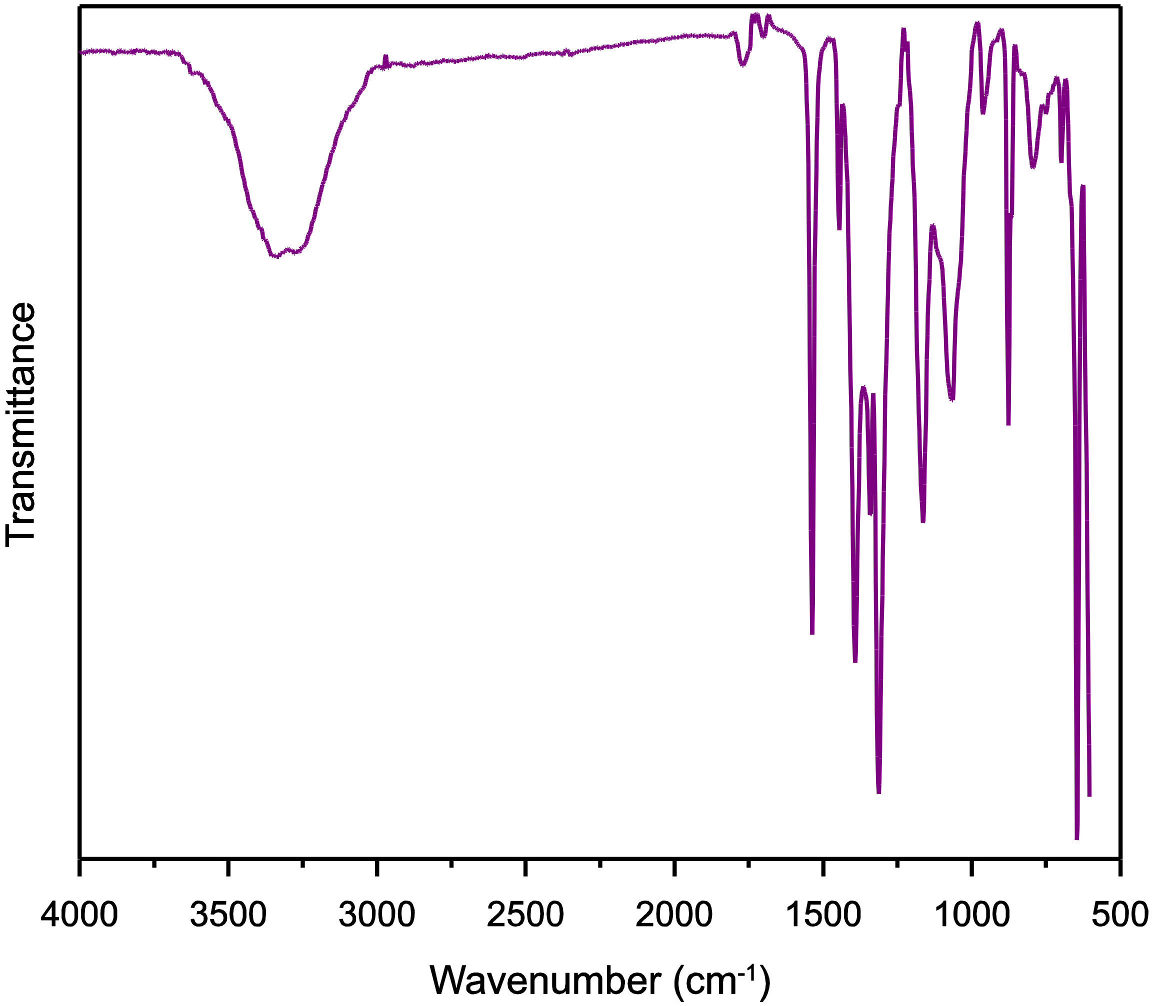


Figure S5. IR spectrum of **H_2BDS.**

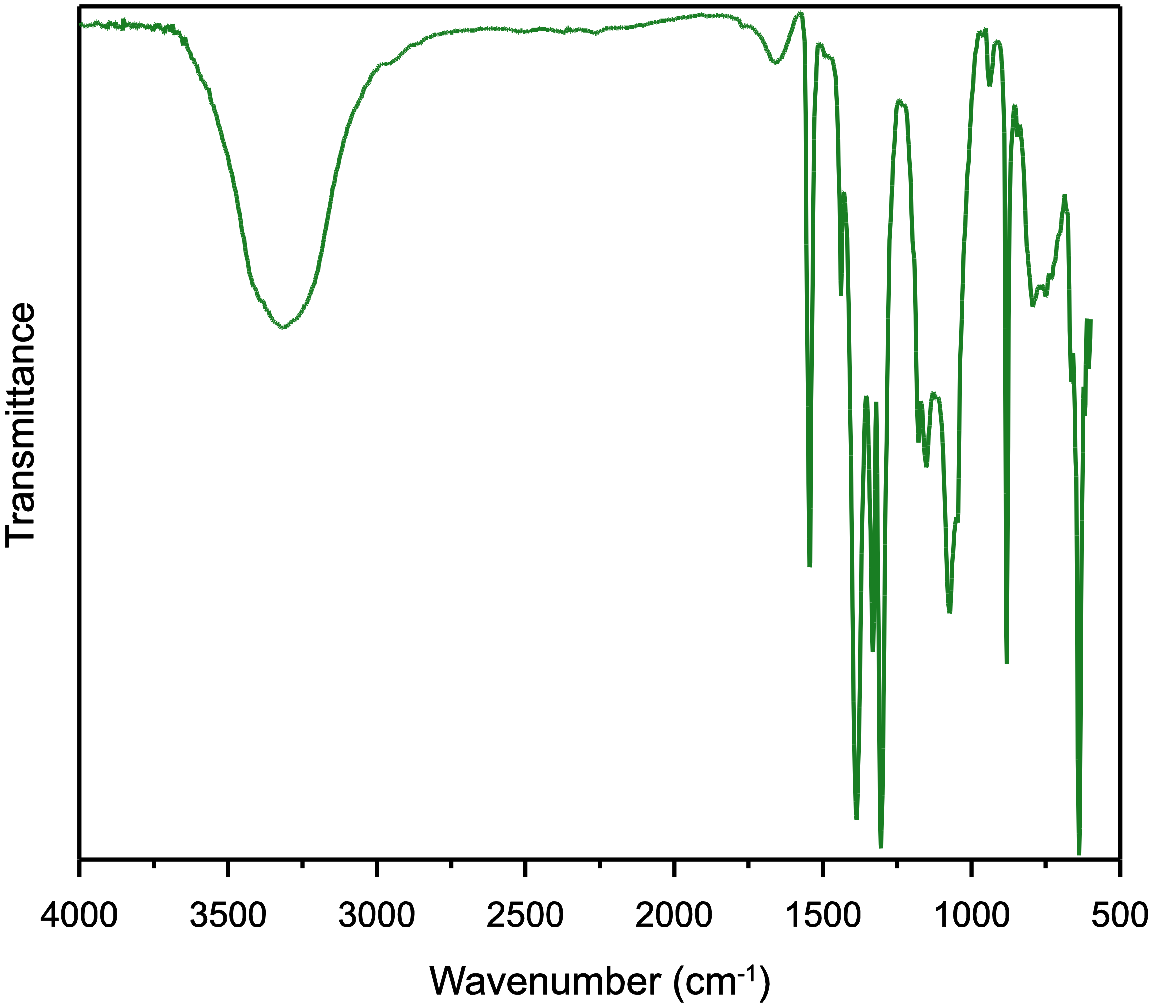


Figure S6. IR spectrum of $\mathbf{H_2BDSe}$.

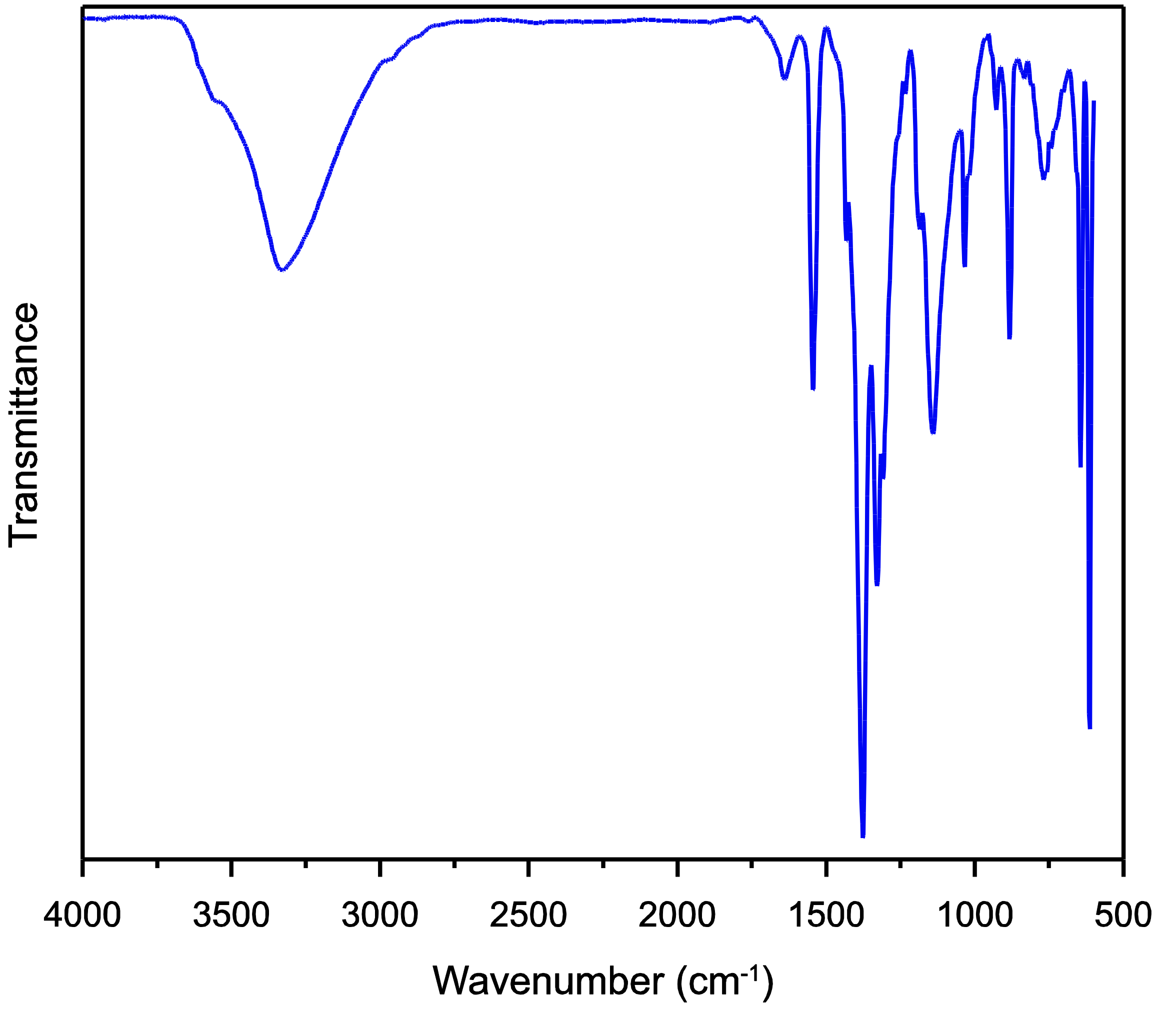


Figure S7. IR spectrum of **H_2BDTe**.

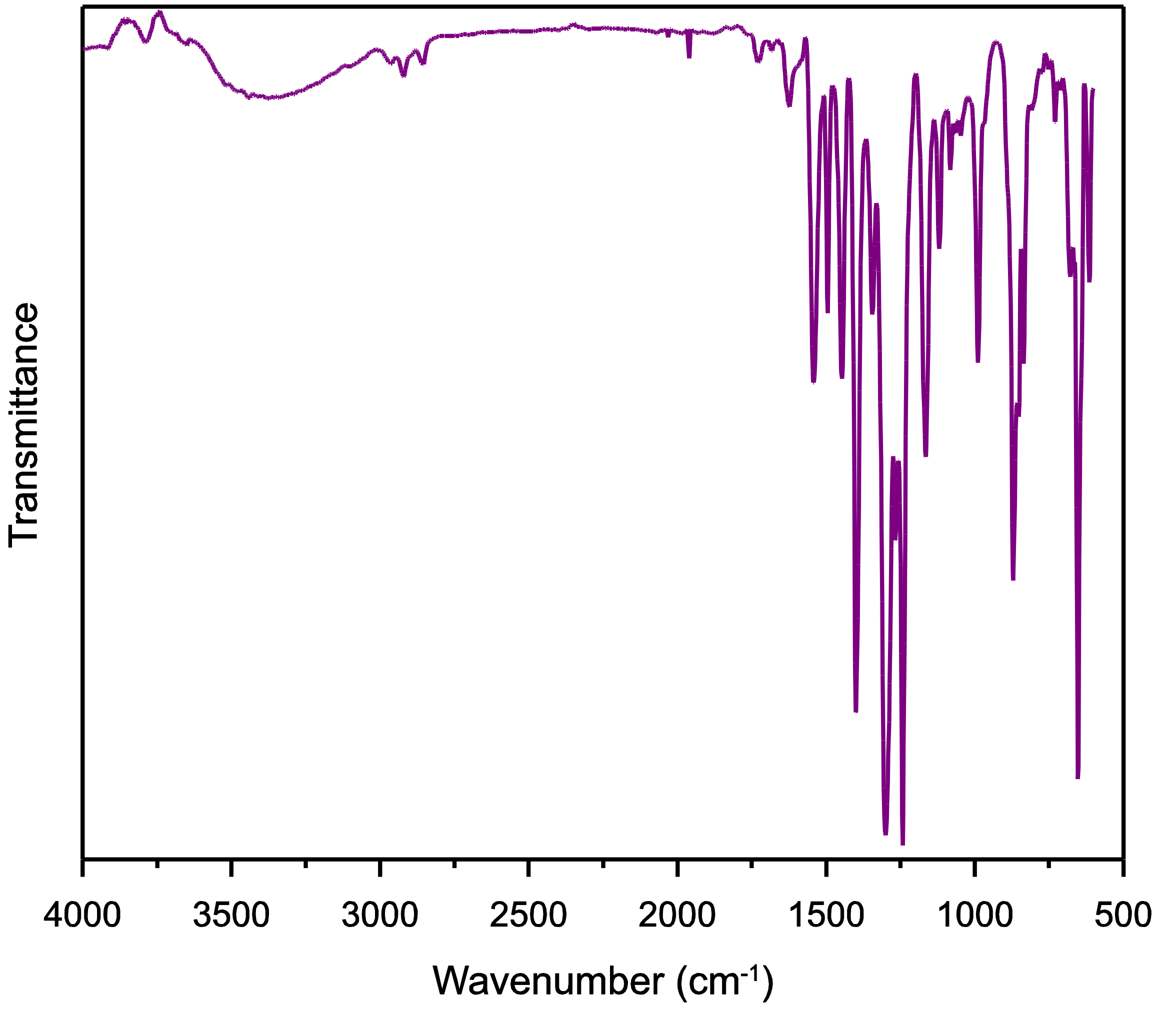


Figure S8. IR spectrum of **1-S**.

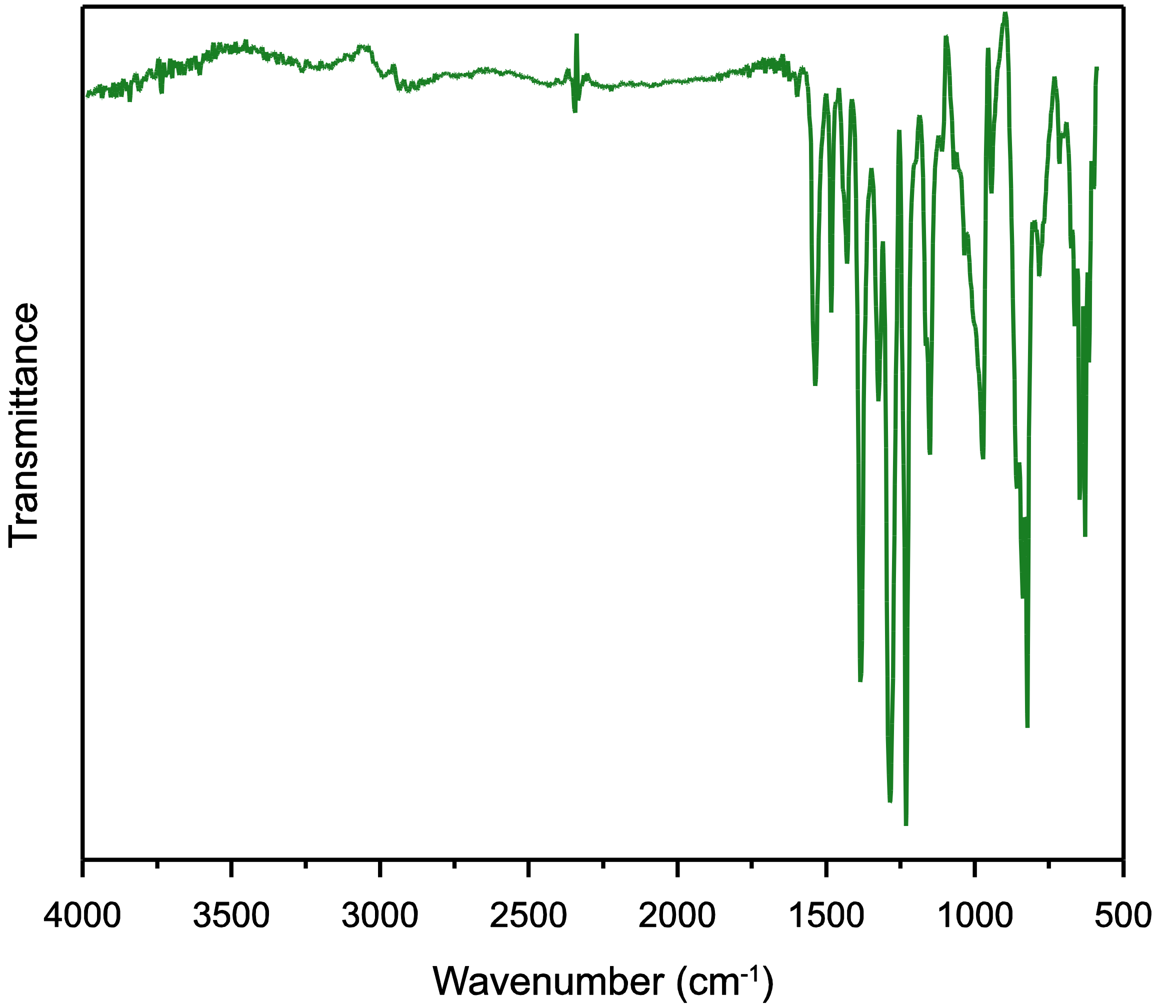


Figure S9. IR spectrum of **1-Se**.

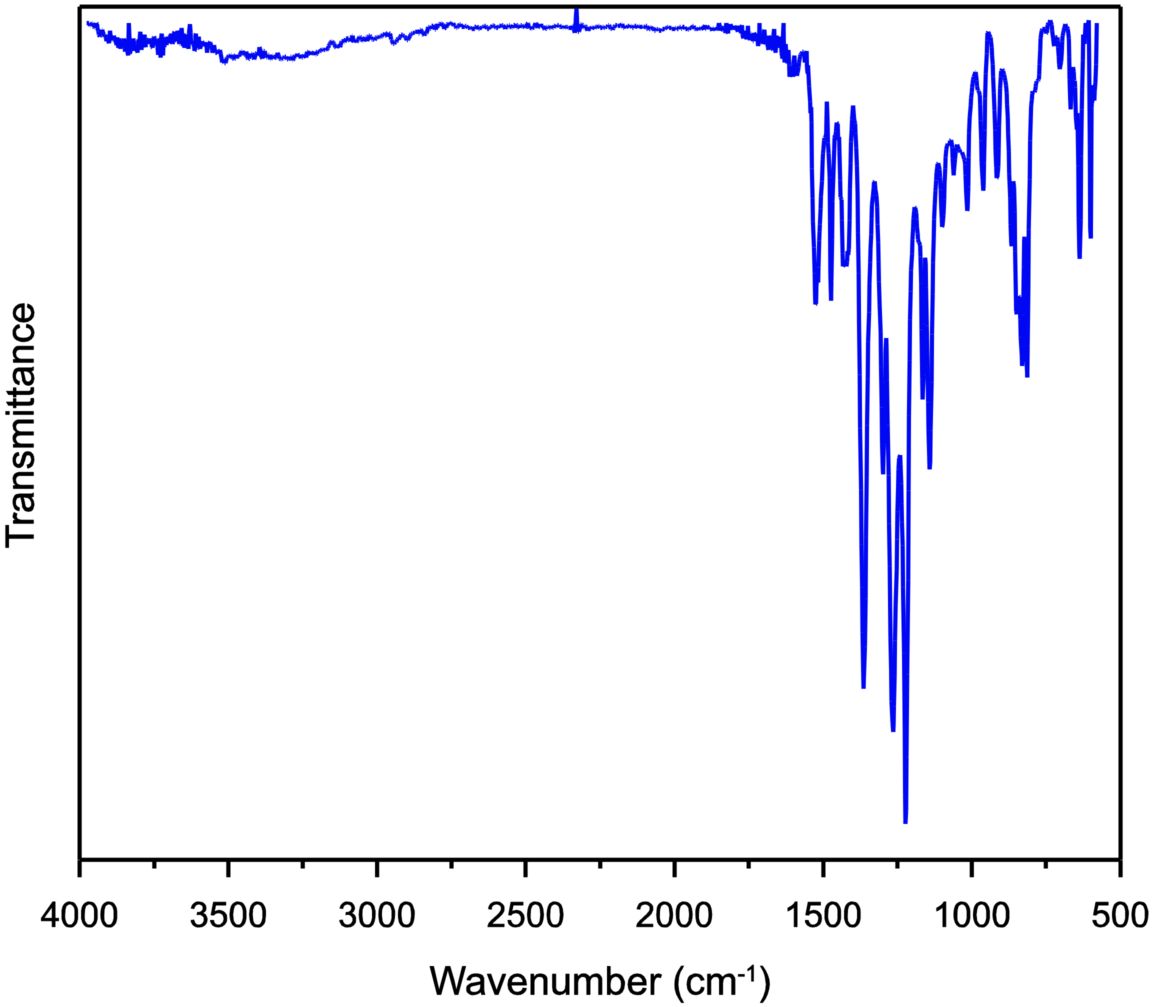


Figure S10. IR spectrum of **1-Te**.

Powder X-ray diffraction (PXRD) patterns

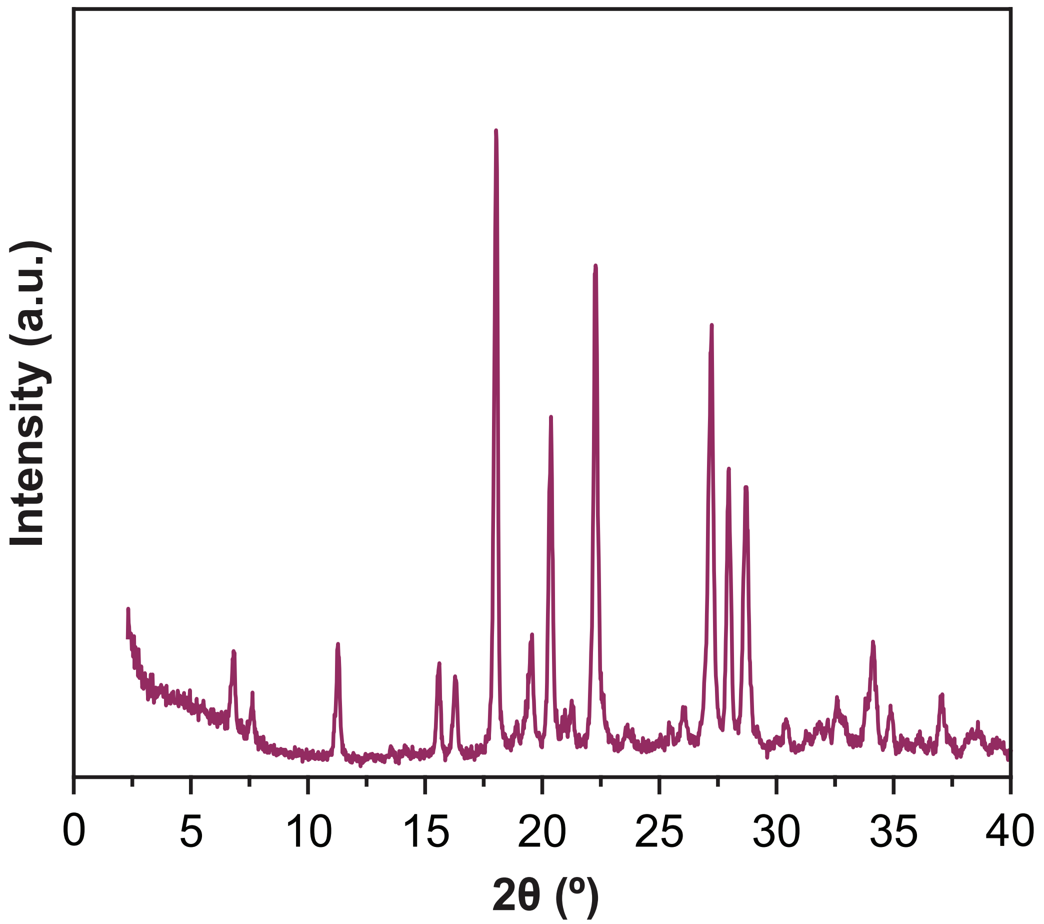


Figure S11. PXRD pattern of **H_2BDS**.

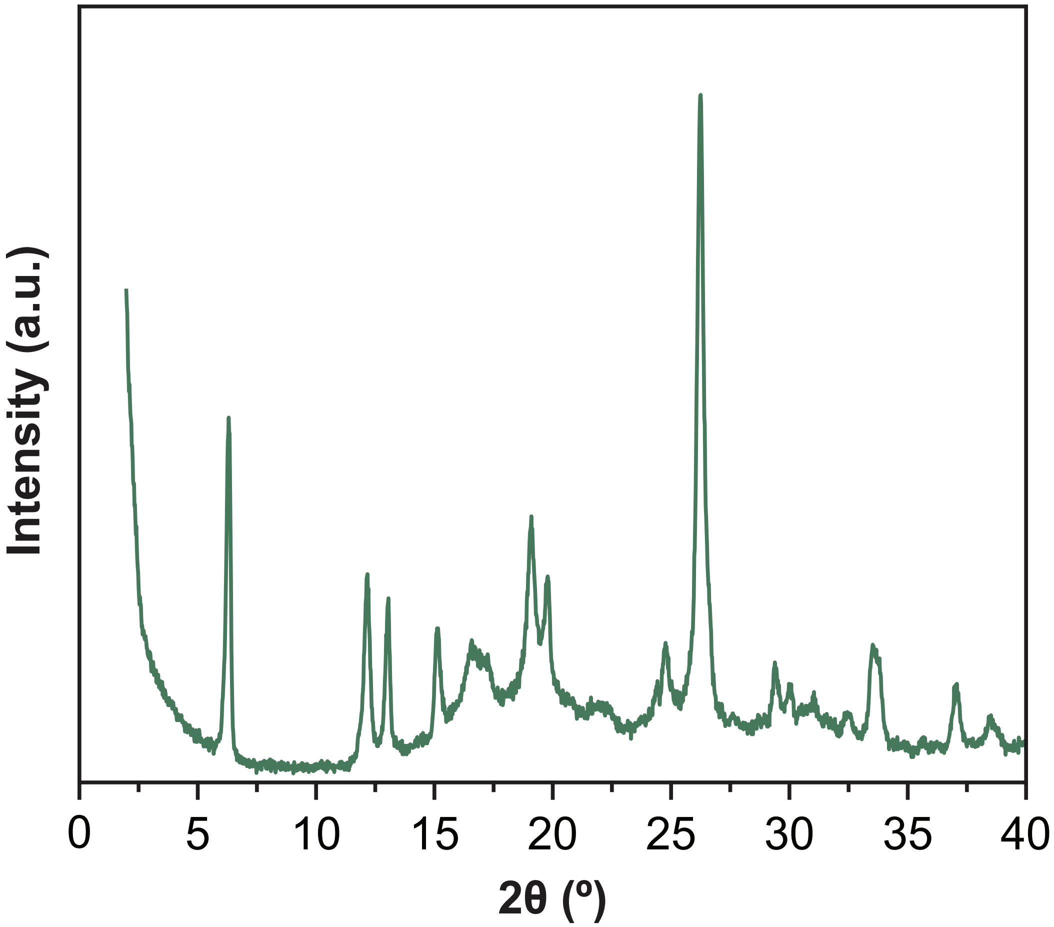


Figure S12. PXRD pattern of **H_2BDSe**.

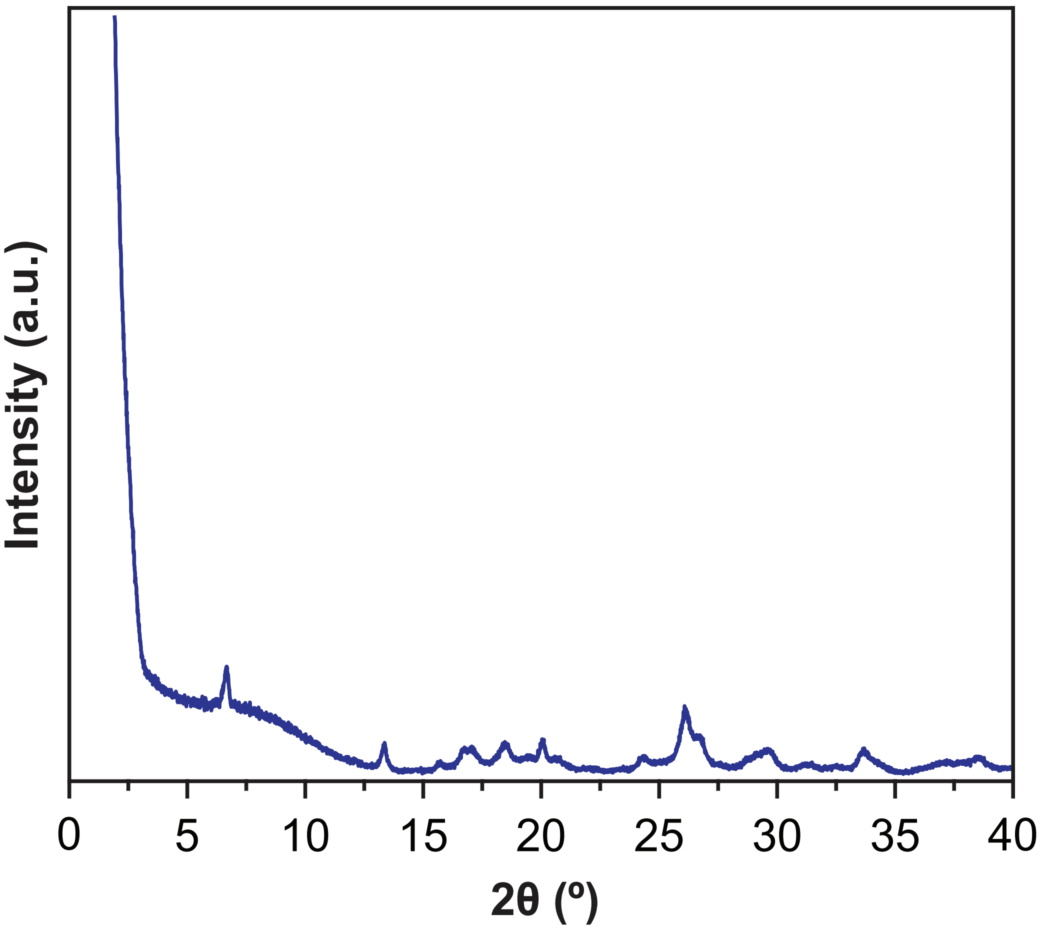


Figure S13. PXRD pattern of **H_2BDTe**.

Simulated structures

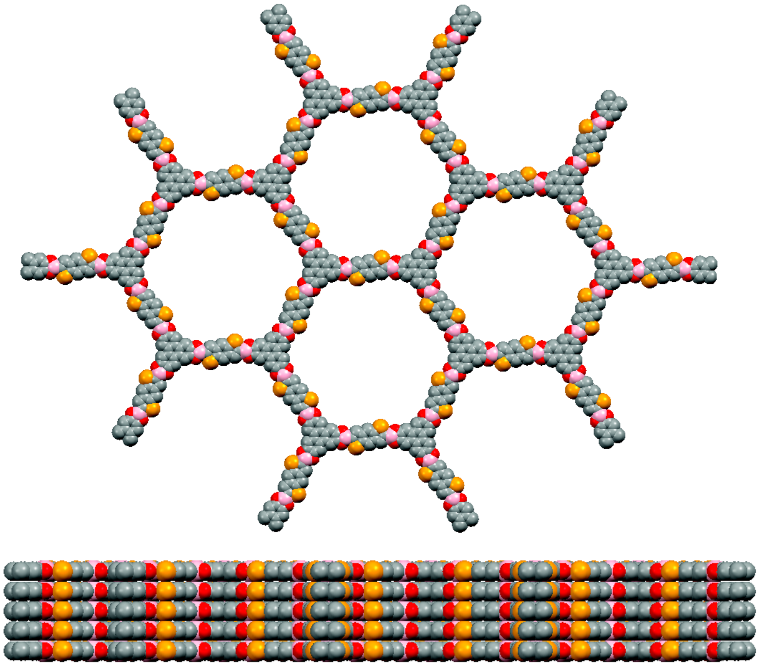


Figure S14. Simulated structure of **1-Se**.

Table S1. Unit cell parameters of **1-Se**.

Space Group	**a** (Å)	**b** (Å)	**c** (Å)	**α** (°)	**β** (°)	**γ** (°)	**V** (Å^3)
P6/m	36.5	36.5	3.45	90	90	120	4200

Table S2. Fractional coordinates of **1-Se**.

Label	Atom	Fractional Coordinates		
		x	y	z
B1	B	0.843067	0.427448	0.500000
C1	C	0.702067	0.371448	0.500000
C2	C	0.704067	0.333448	0.500000
C3	C	0.743067	0.335448	0.500000
C4	C	0.779067	0.374448	0.500000
C5	C	0.777067	0.410448	0.500000
C6	C	0.740067	0.409448	0.500000
C7	C	0.891730	0.453807	0.500000
C8	C	0.958478	0.465365	0.500000
C9	C	0.917068	0.434551	0.500000
C10	C	0.963838	0.505622	0.500000
C11	C	1.004674	0.540604	0.500000
O1	O	0.817067	0.446448	0.500000
O2	O	0.820067	0.381448	0.500000
Se1	Se	0.917552	0.515780	0.500000

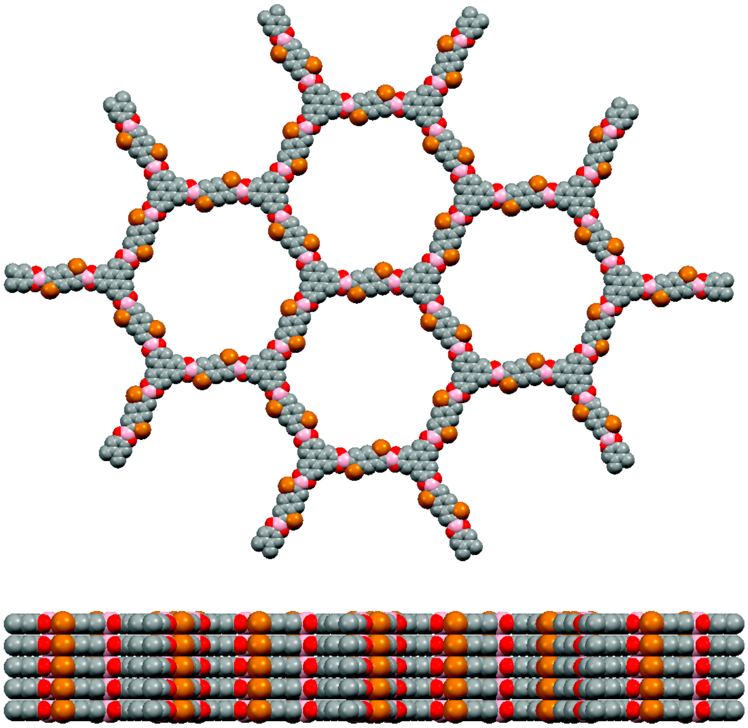


Figure S15. Simulated structure of **1-Te**.

Table S3. Unit cell parameters of **1-Te**.

Space Group	**a** (Å)	**b** (Å)	**c** (Å)	**α** (°)	**β** (°)	**γ** (°)	**V** ($Å^3$)
P6/m	36.50	36.50	3.45	90	90	120	4400

Table S4. Fractional coordinates of **1-Te**.

Label	Atom	Fractional Coordinates		
		x	y	z
B1	B	0.843067	0.427448	0.500000
C1	C	0.702067	0.371448	0.500000
C2	C	0.704067	0.333448	0.500000
C3	C	0.743067	0.335448	0.500000
C4	C	0.779067	0.374448	0.500000
C5	C	0.777067	0.410448	0.500000
C6	C	0.740067	0.409448	0.500000
C7	C	0.891730	0.453807	0.500000
C8	C	0.958478	0.465365	0.500000
C9	C	0.917068	0.434551	0.500000
C10	C	0.963838	0.505622	0.500000
C11	C	0.004674	0.540604	0.500000
O1	O	0.817067	0.446448	0.500000
O2	O	0.820067	0.381448	0.500000
Te1	Te	0.913694	0.518739	0.500000

Ultraviolet-visible (UV-Vis) spectra

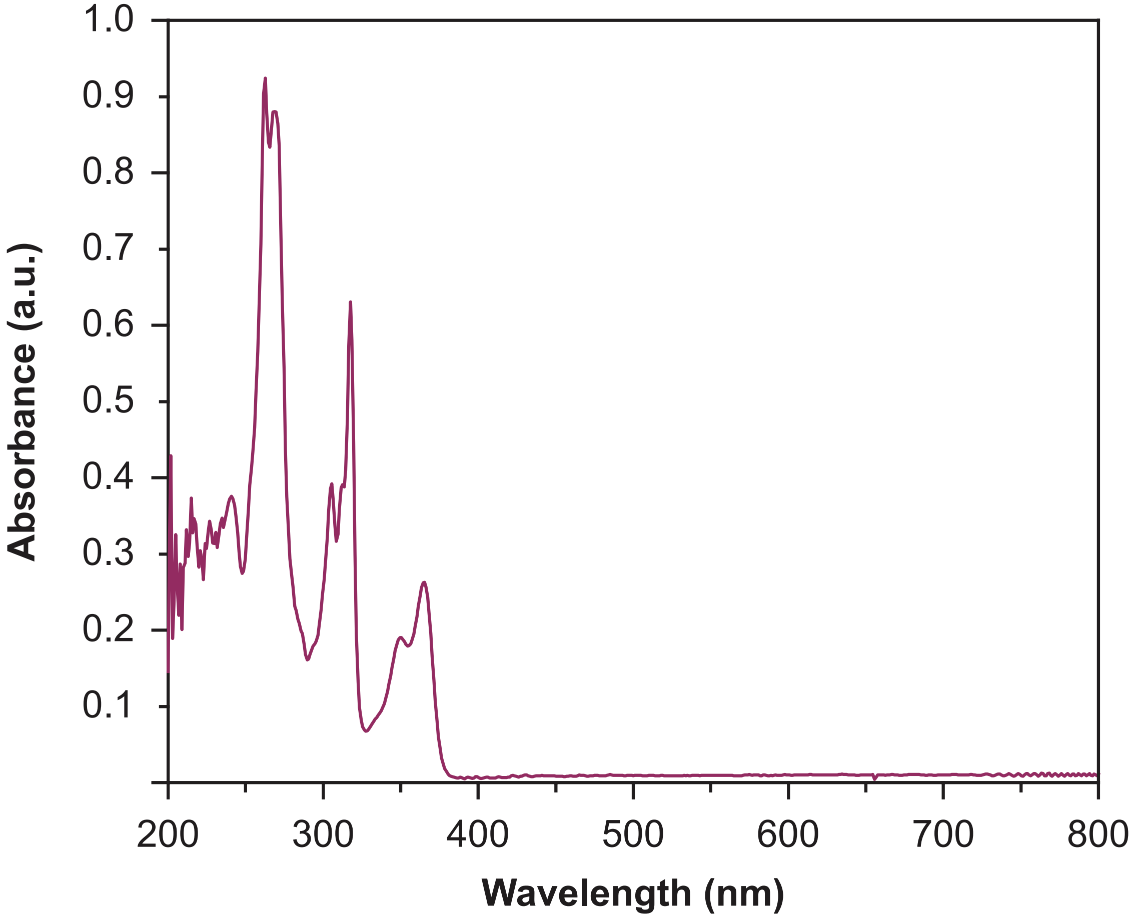


Figure S16. UV-Vis spectrum of **H_2BDS** (0.01 mM in THF).

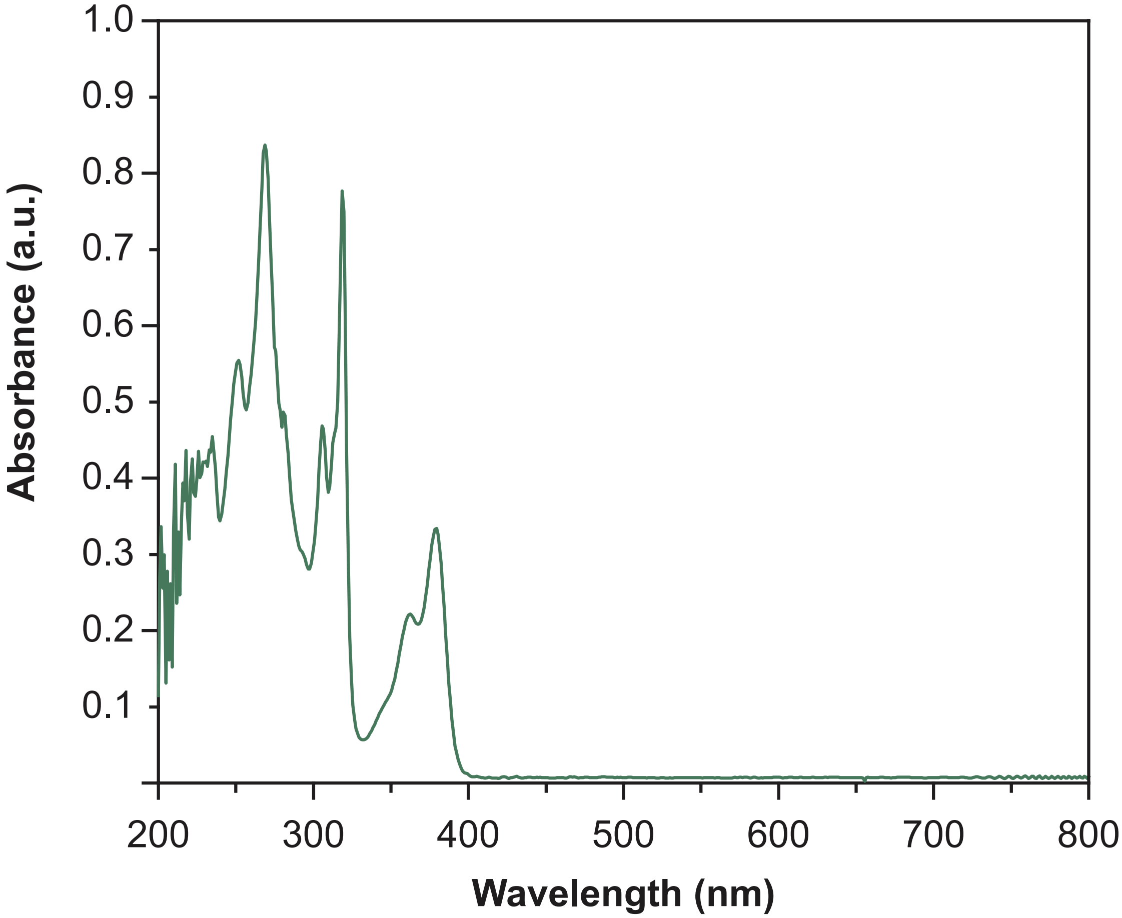


Figure S17. UV-Vis spectrum of **H_2BDSe** (0.03 mM in THF).

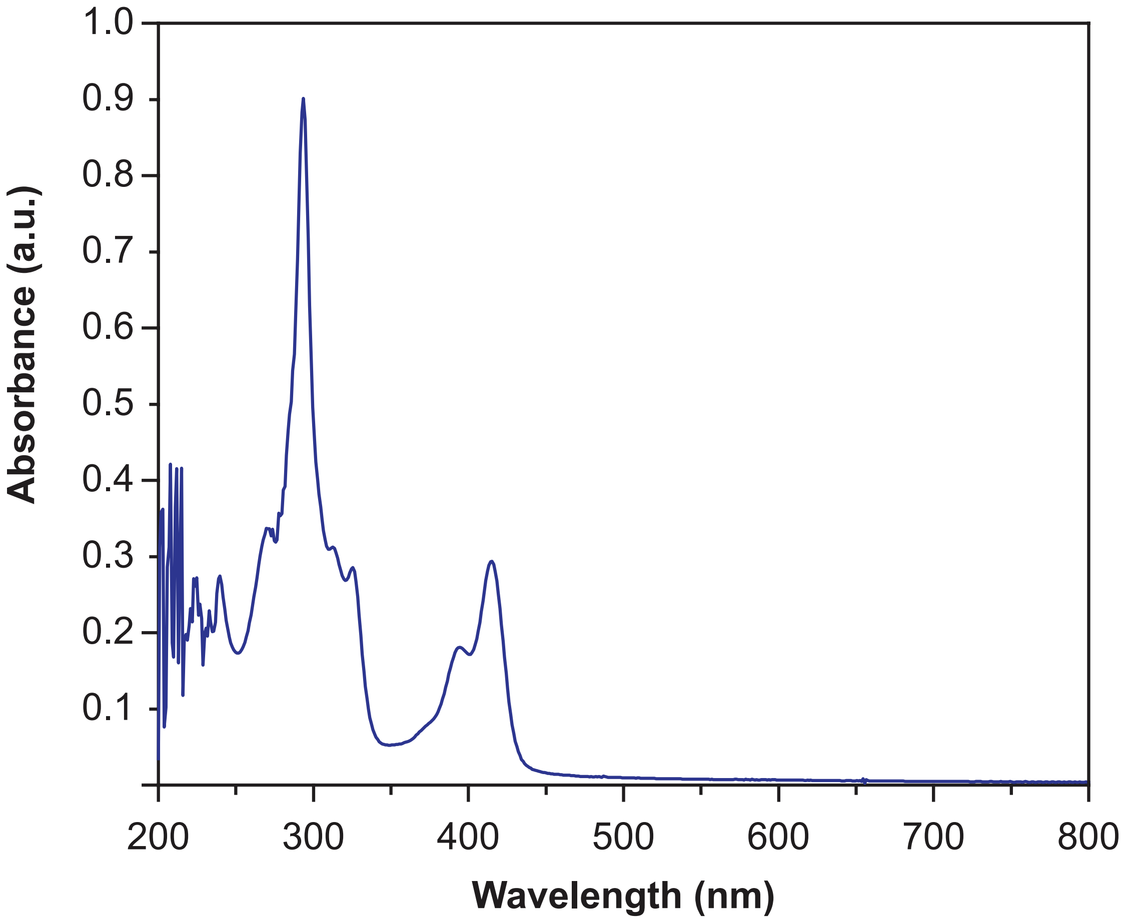


Figure S18. UV-Vis spectrum of $\mathbf{H_2BDTe}$ (0.01 mM in THF).

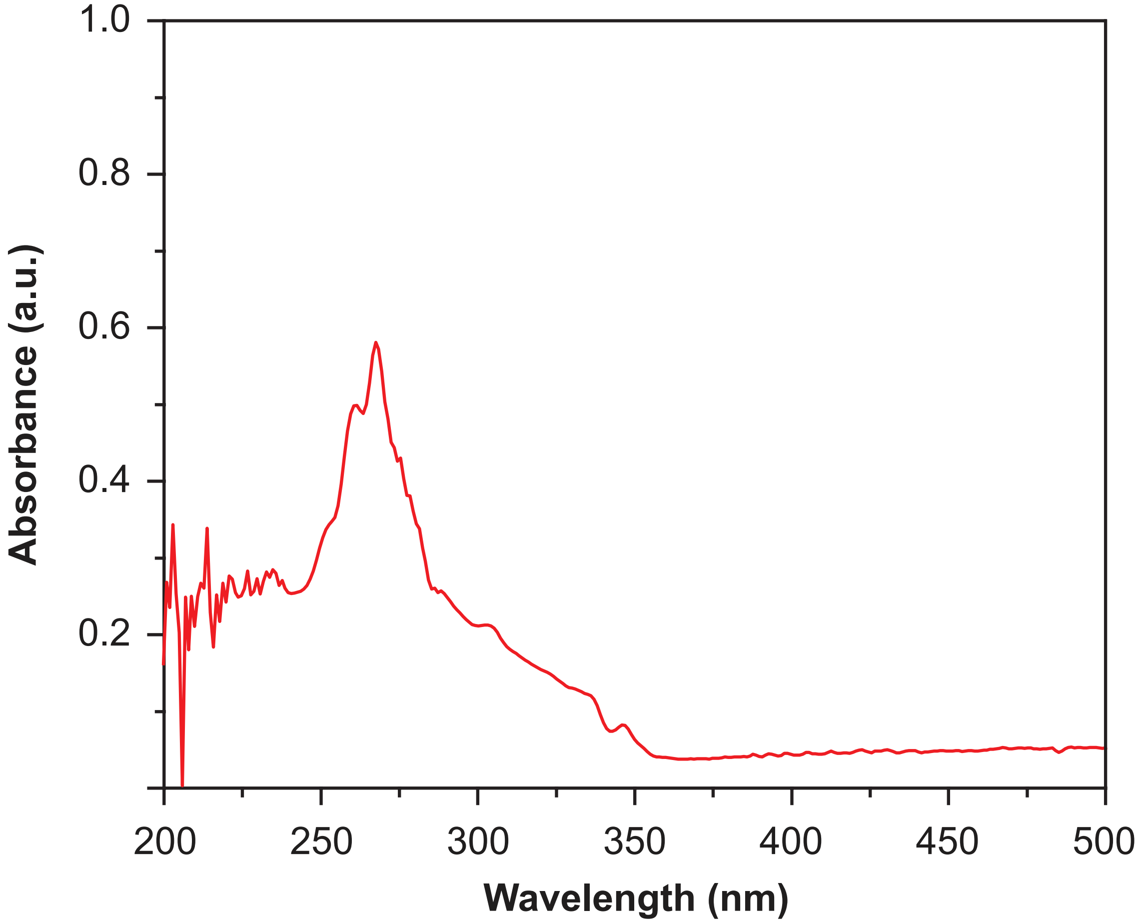


Figure S19. UV-Vis spectrum of **HHTP** (0.01 mM in THF).

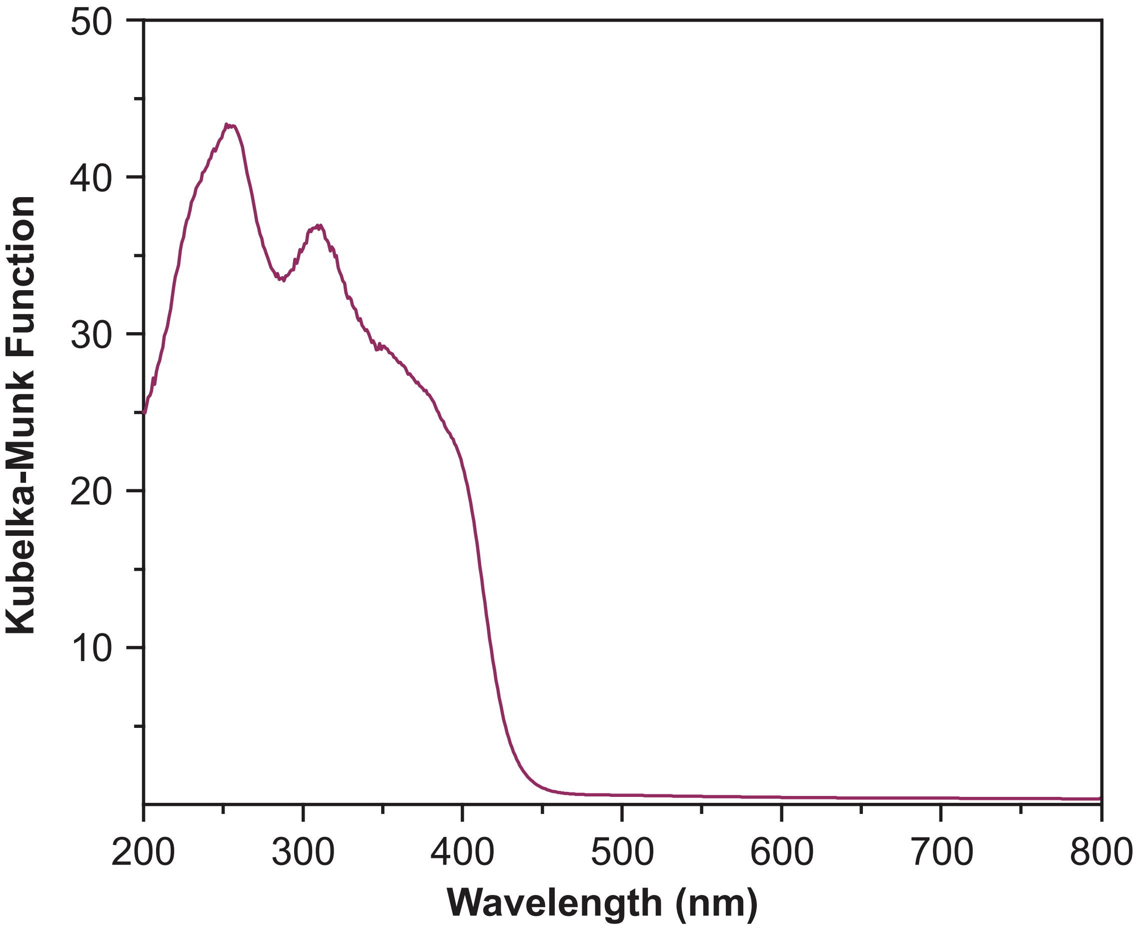


Figure S20. UV-Vis diffuse reflectance spectrum of **1-S**.

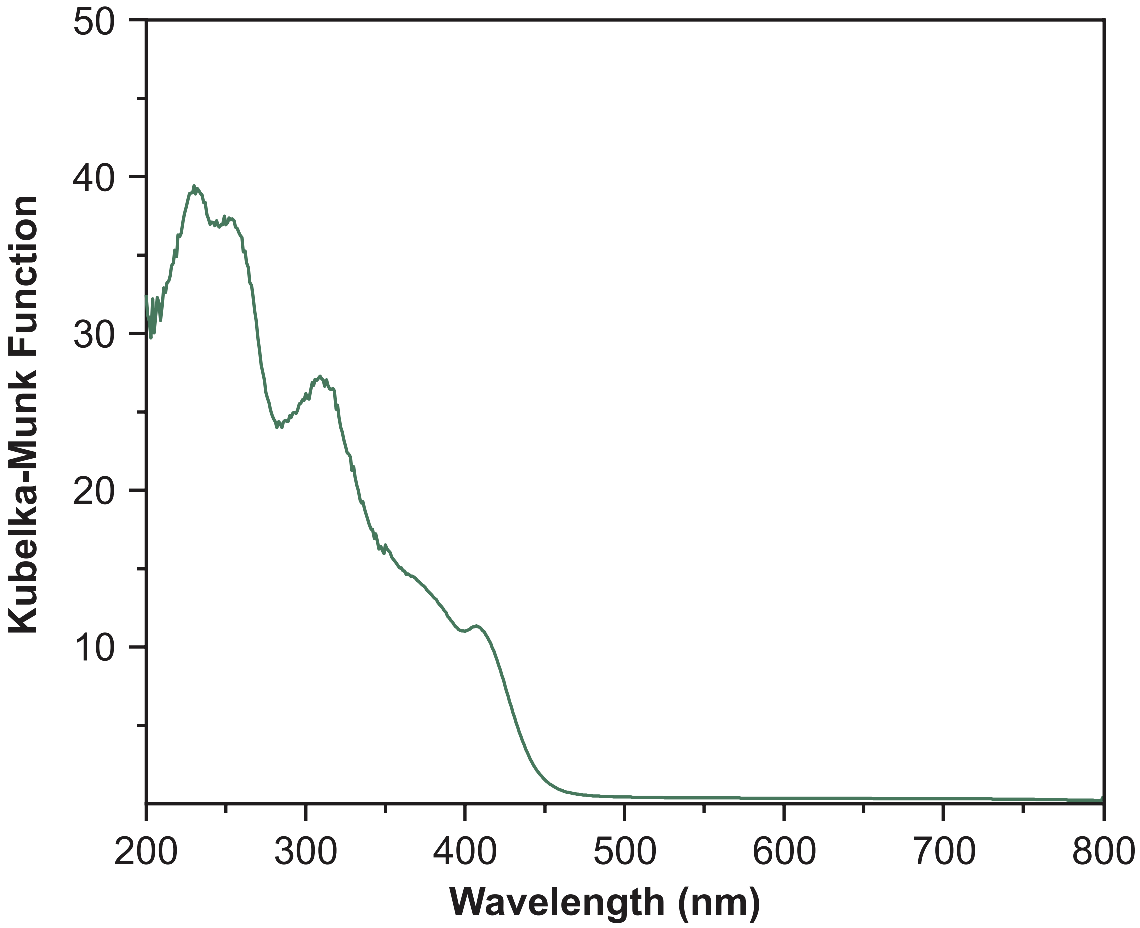


Figure S21. UV-Vis diffuse reflectance spectrum of **1-Se**.

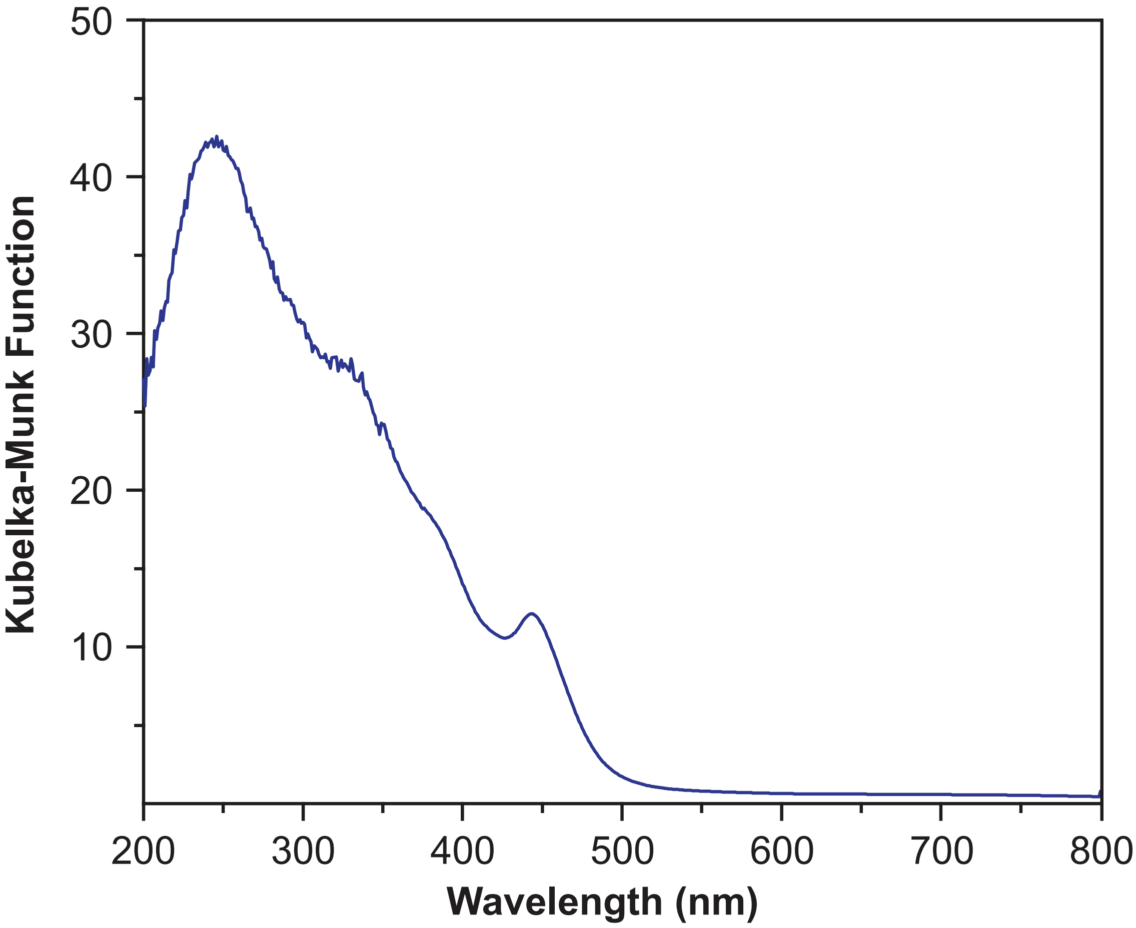


Figure S22. UV-Vis diffuse reflectance spectrum of **1-Te**.

Thermogravimetric analysis (TGA)

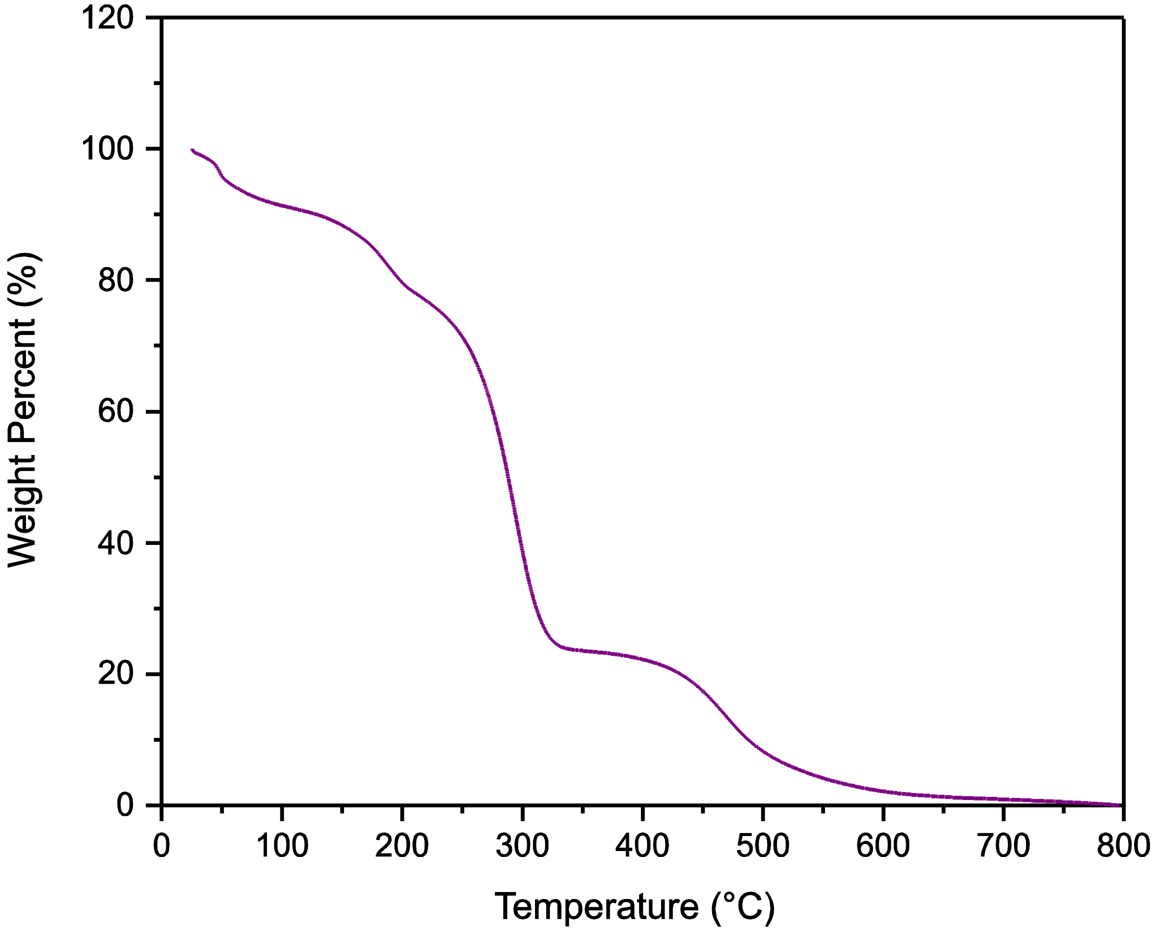


Figure S23. TGA curve of **H_2BDS** under the flow of air.

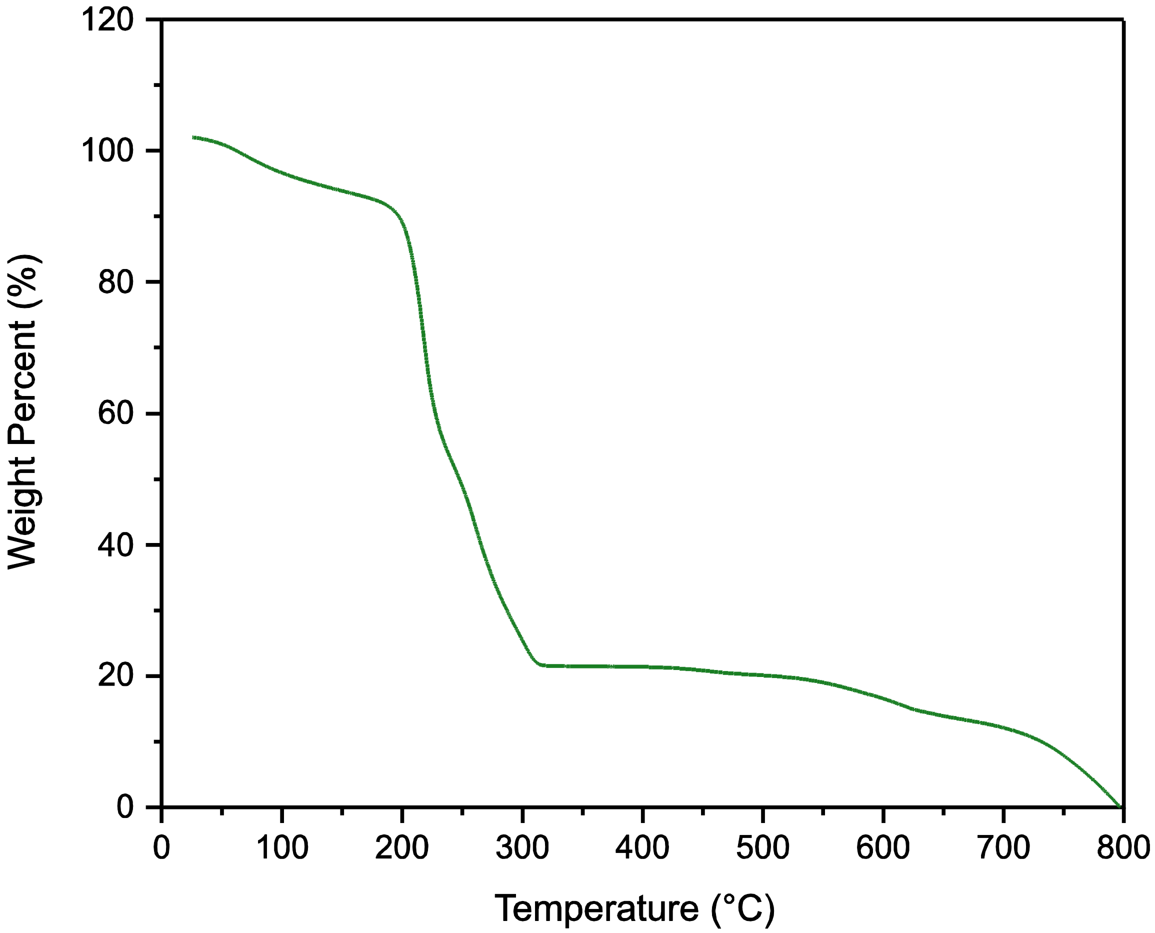


Figure S24. TGA curve of **H_2BDSe** under the flow of air.

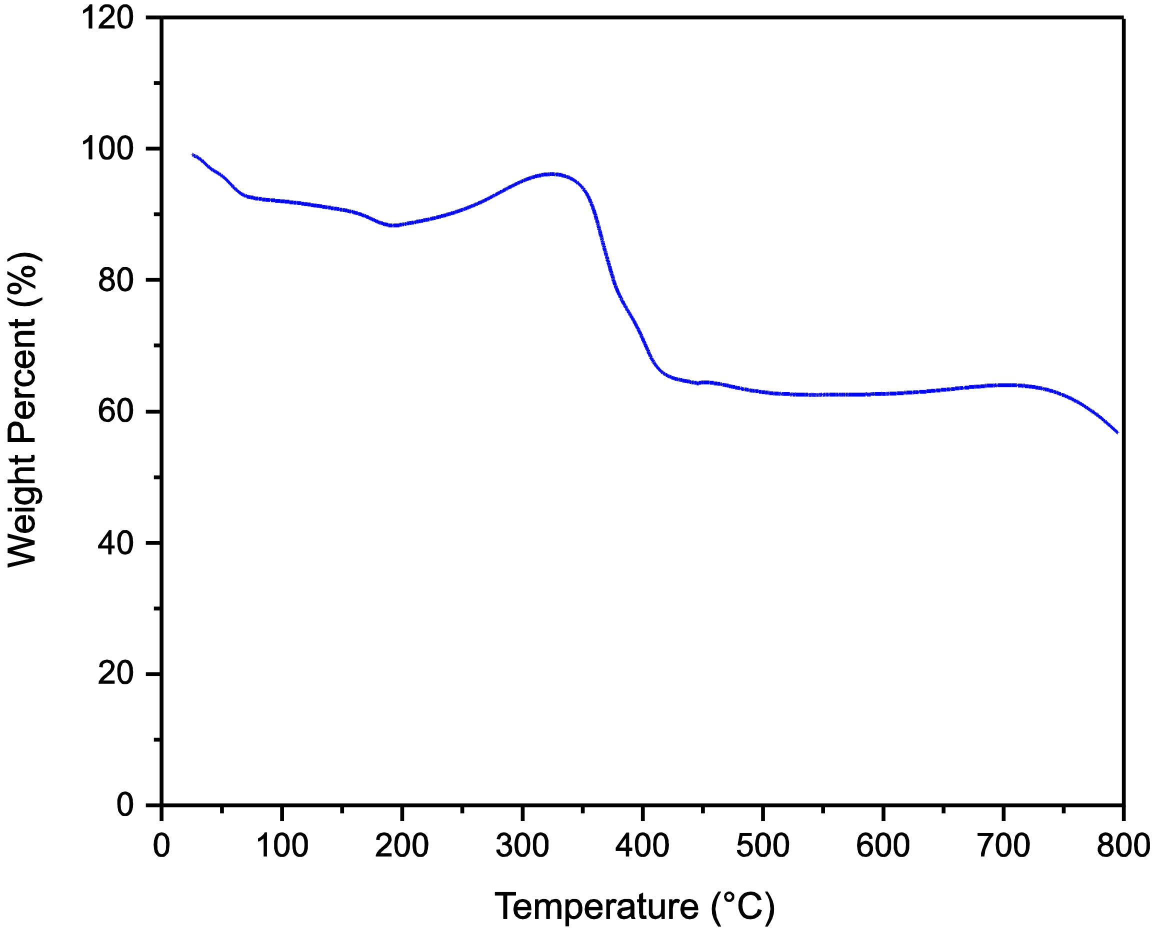


Figure S25. TGA curve of **H_2BDTe** under the flow of air.

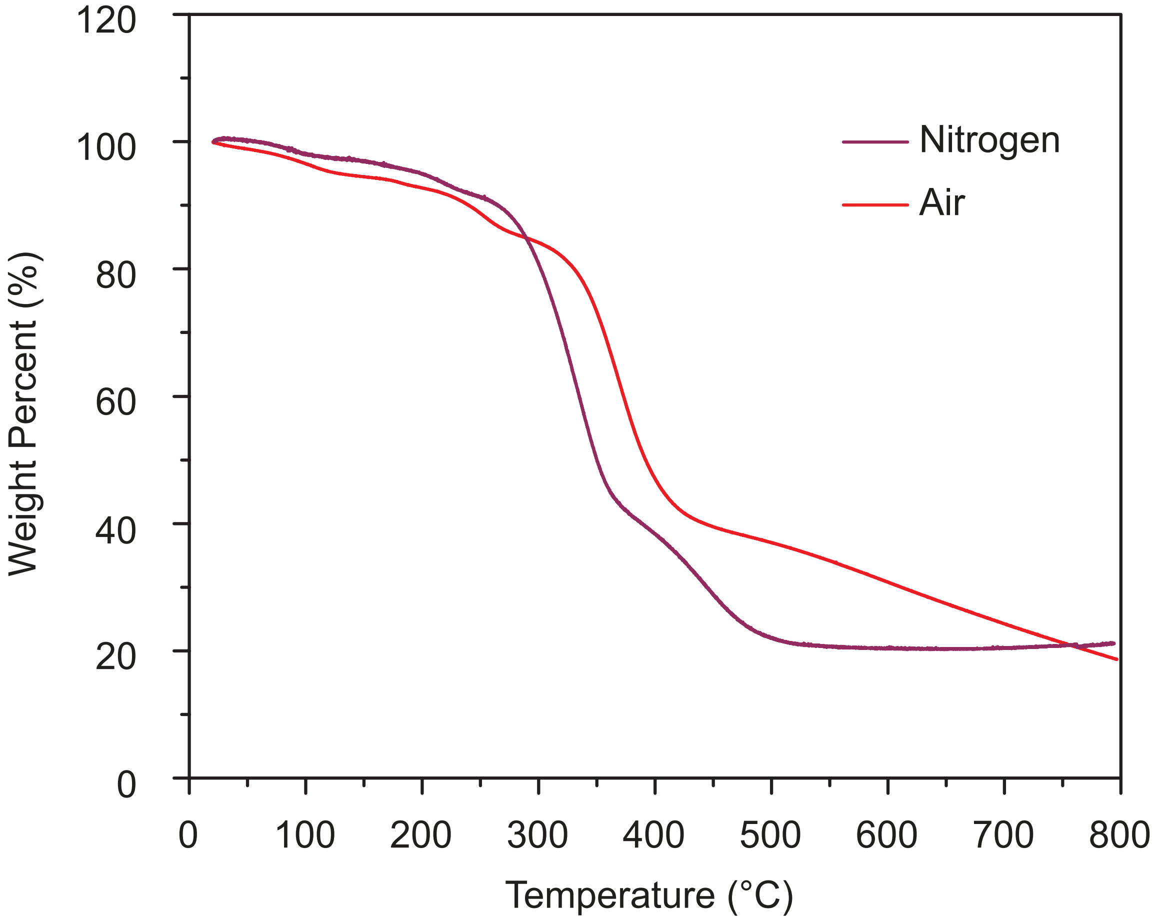


Figure S26. TGA curve of **1-S** under the flow of air (red) and nitrogen (purple).

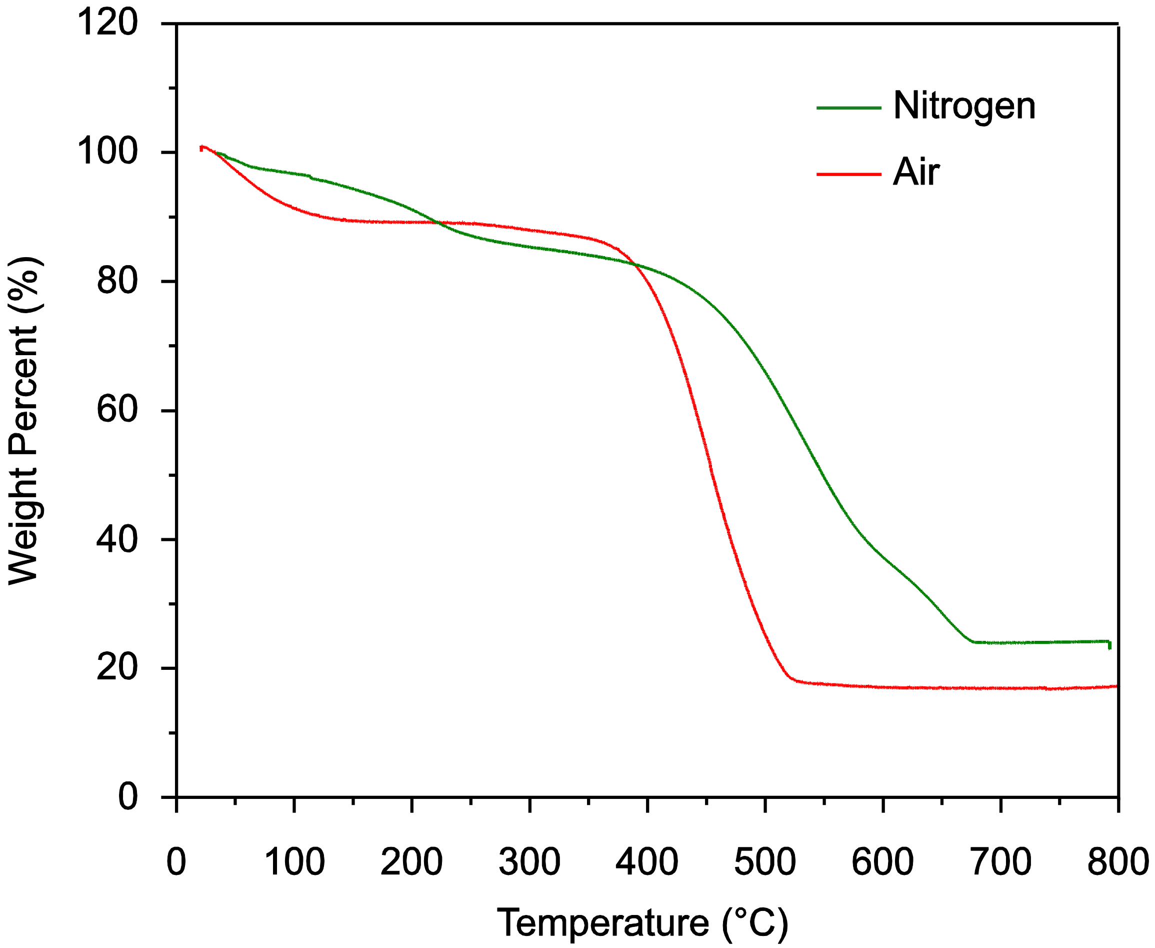


Figure S27. TGA curve of **1-Se** under the flow of air (red) and nitrogen (green).

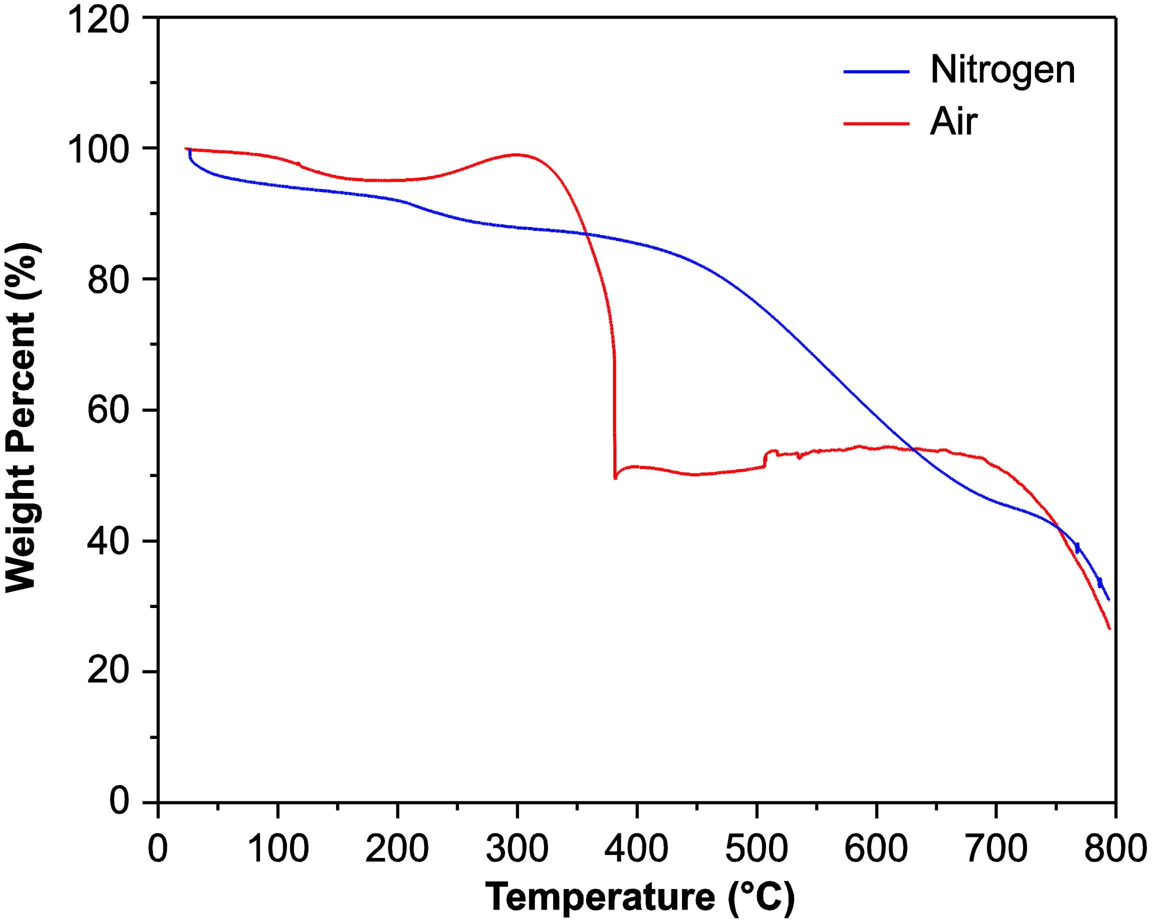


Figure S28. TGA curve of **1-Te** under the flow of air (red) and nitrogen (blue).

Adsorption isotherms

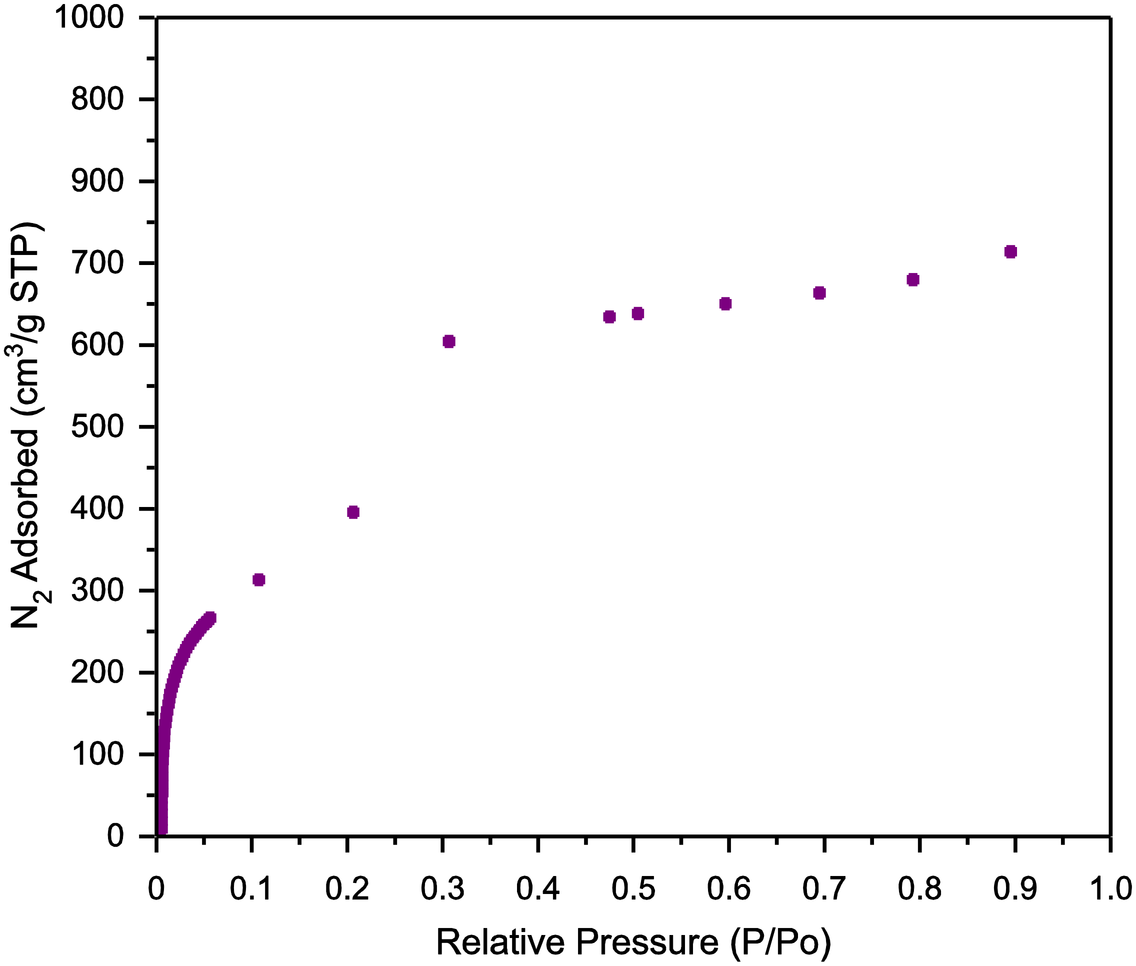


Figure S29. Nitrogen adsorption isotherm of **1-S**.

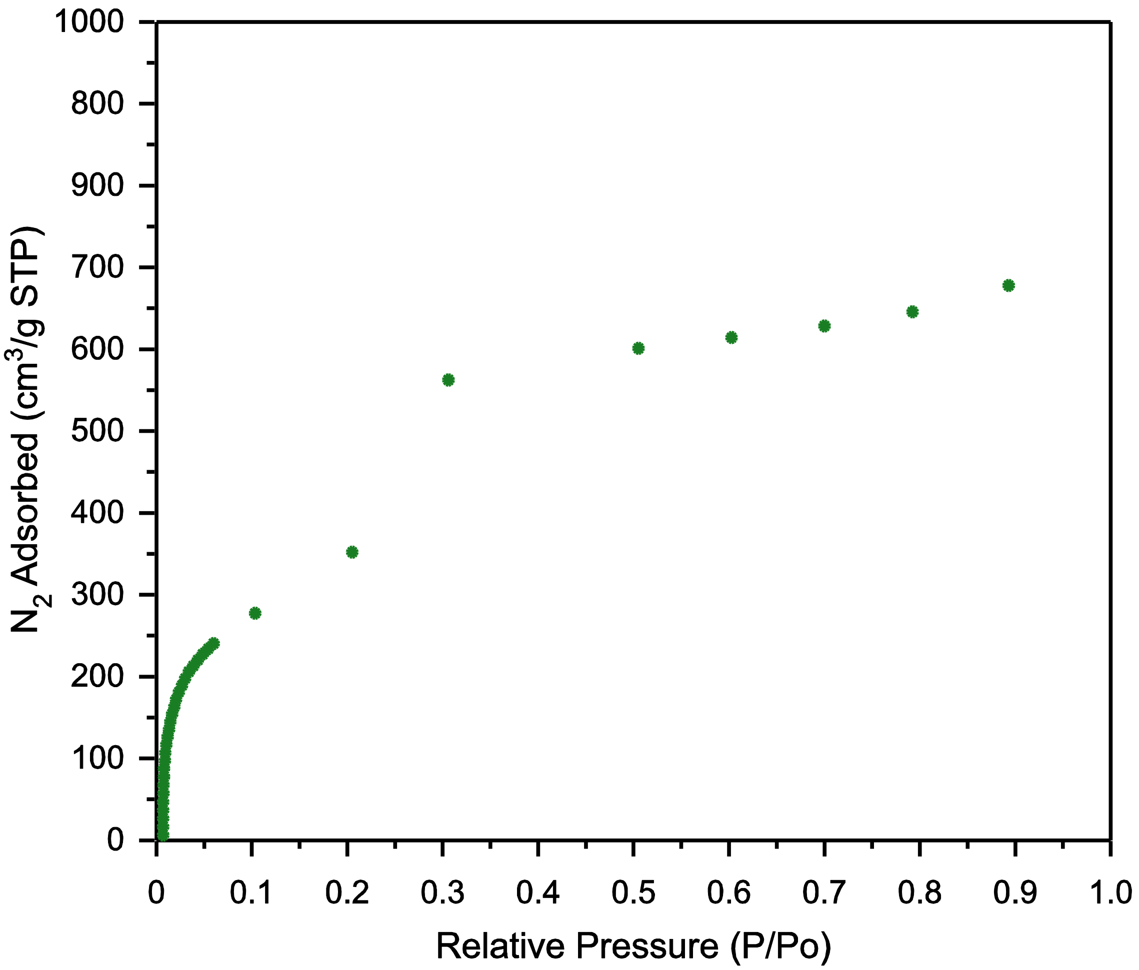


Figure S30. Nitrogen adsorption isotherm of **1-Se**.

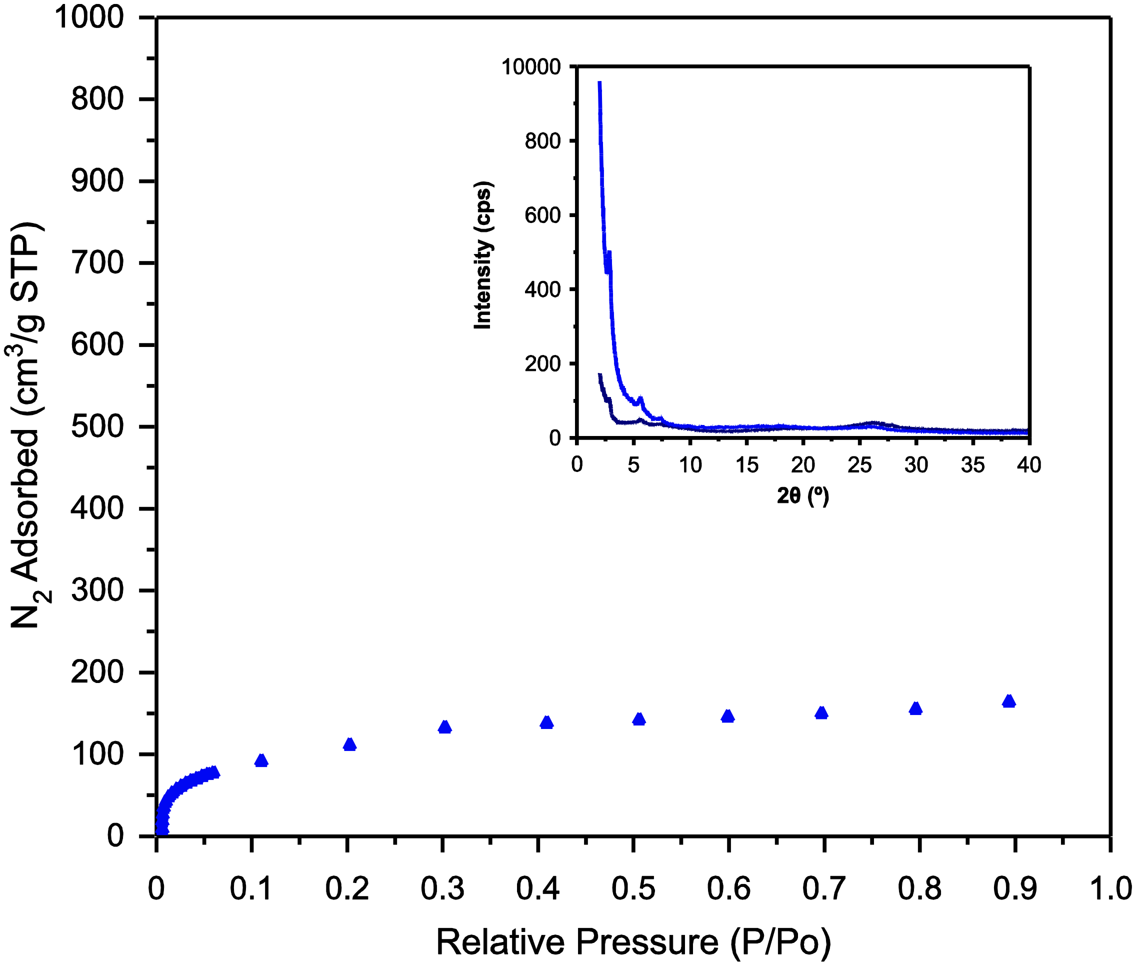


Figure S31. Nitrogen adsorption isotherm of **1-Te**. Inset shows loss of crystallinity after measurement.

Pellet Conductivity: Current-Voltage (I-V) curves

Note: Values of L (in cm) represent the thickness of each pellet.

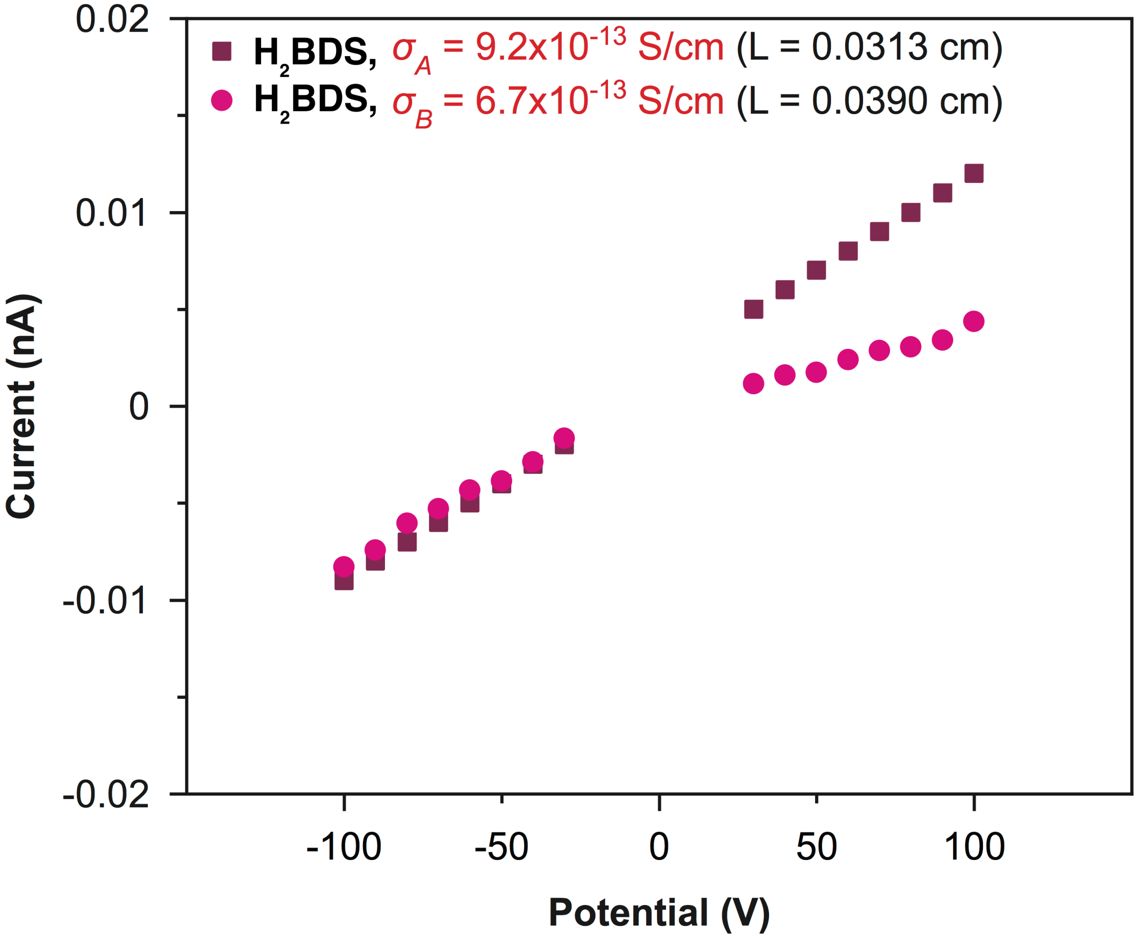


Figure S32. I-V curve of **H_2BDS** pellet with a 2 mm diameter.

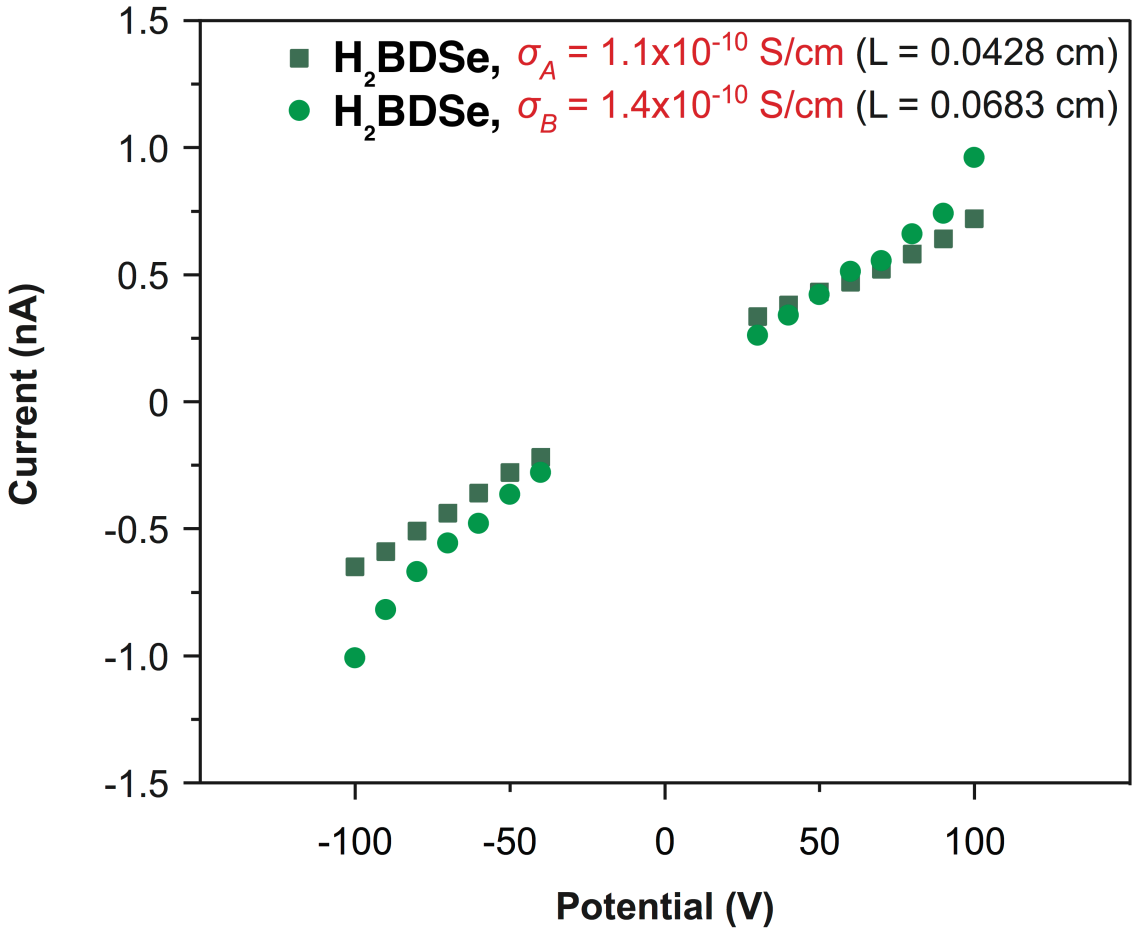


Figure S33. I-V curve of **H_2BDSe** pellet with a 2 mm diameter.

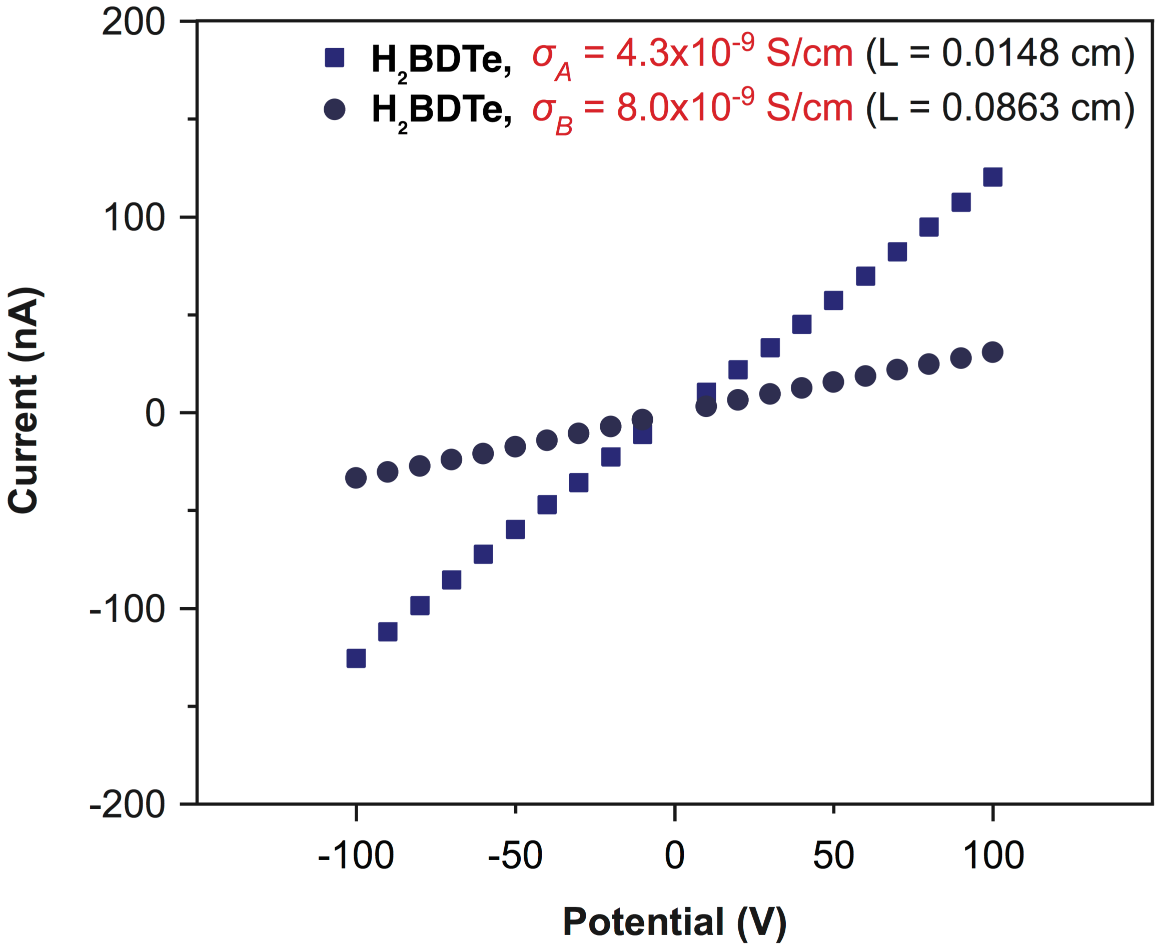


Figure S34. I-V curve of **H_2BDTe** pellet with a 2 mm diameter.

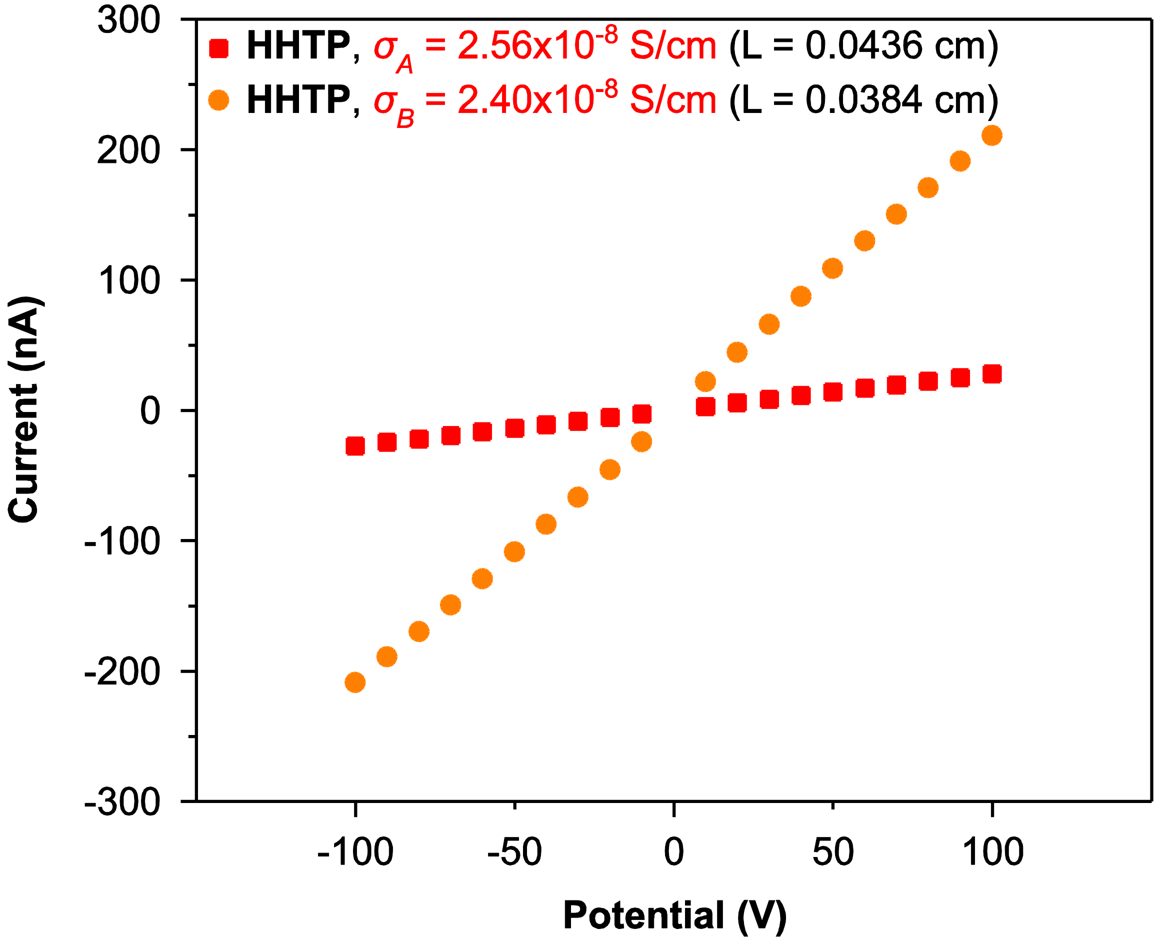


Figure S35. I-V curve of **HHTP** pellet with a 2 mm diameter.

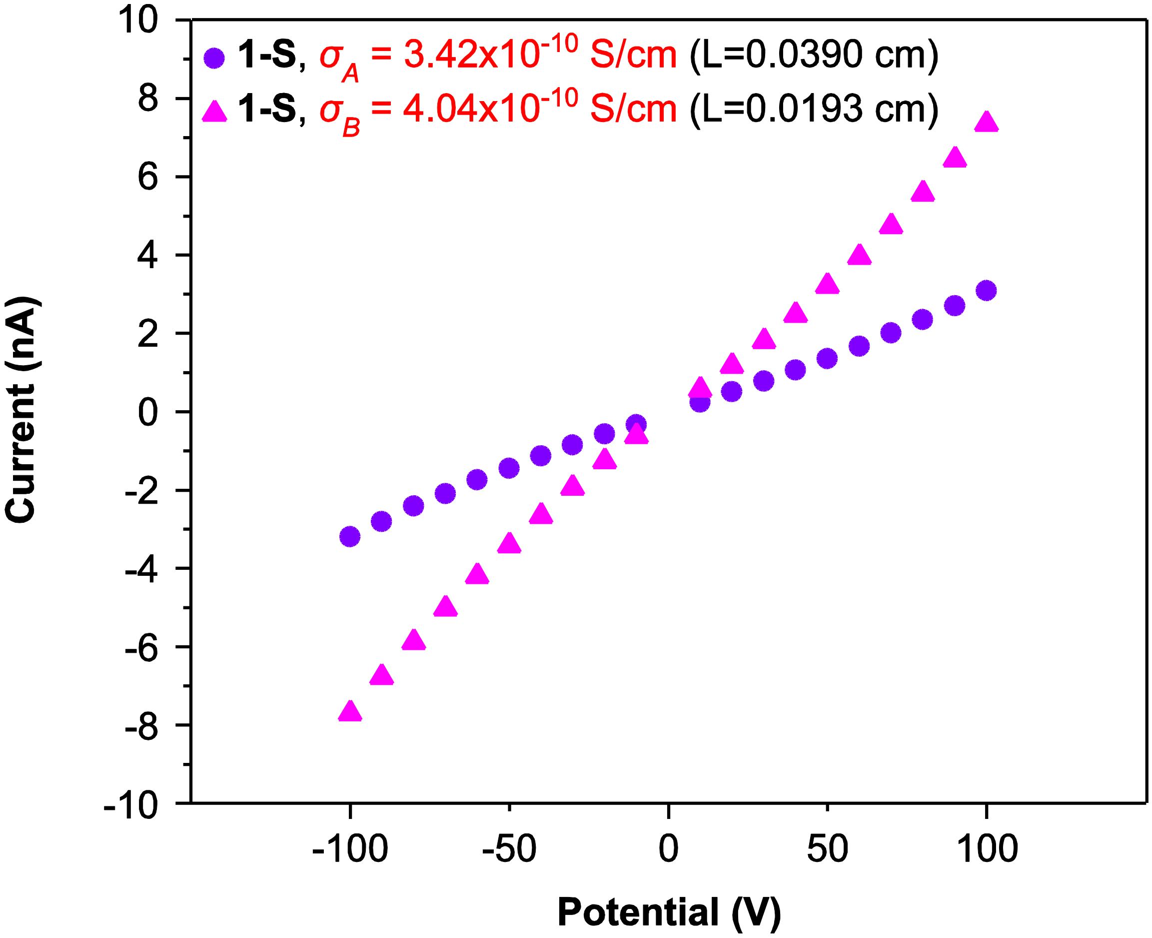


Figure S36. I-V curve of **1-S** pellet with a 2 mm diameter.

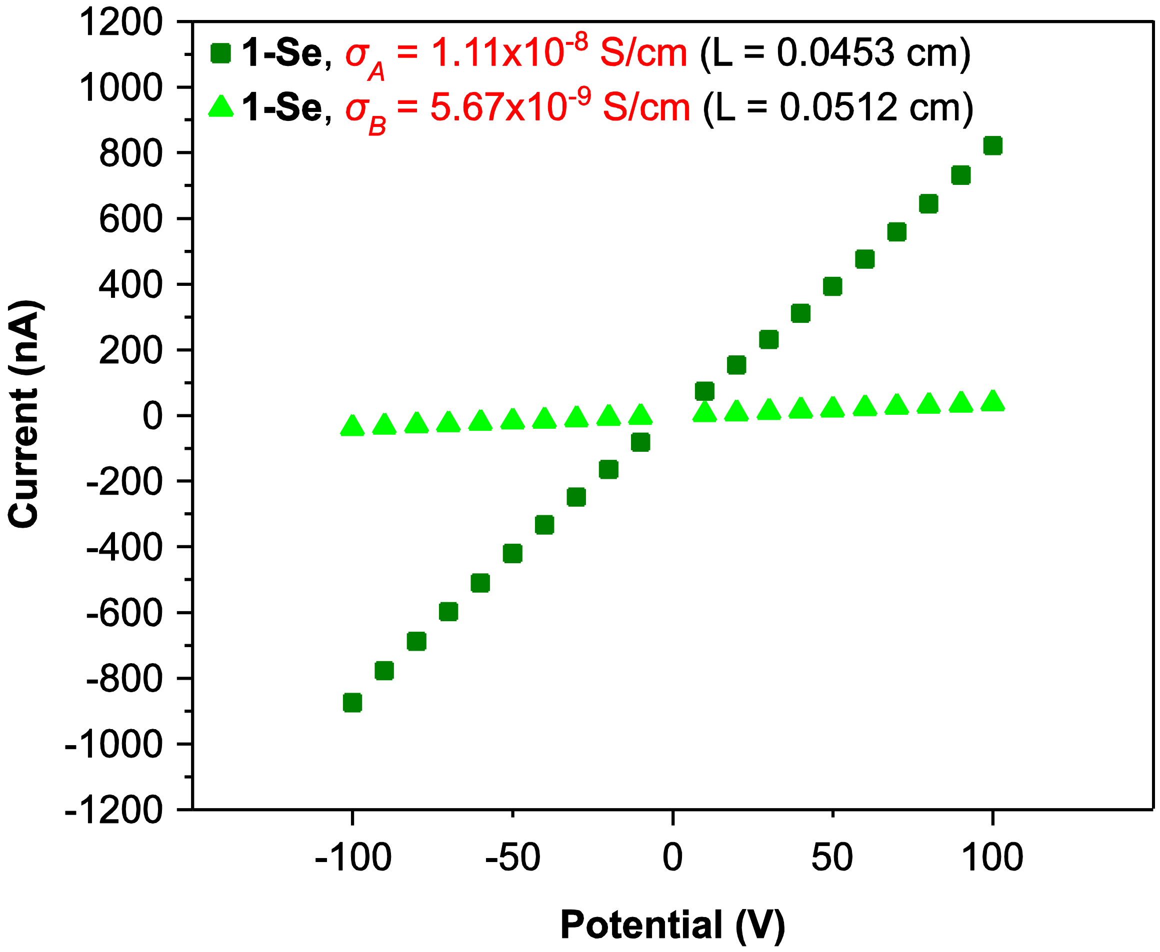


Figure S37. I-V curve of **1-Se** pellet with a 2 mm diameter.

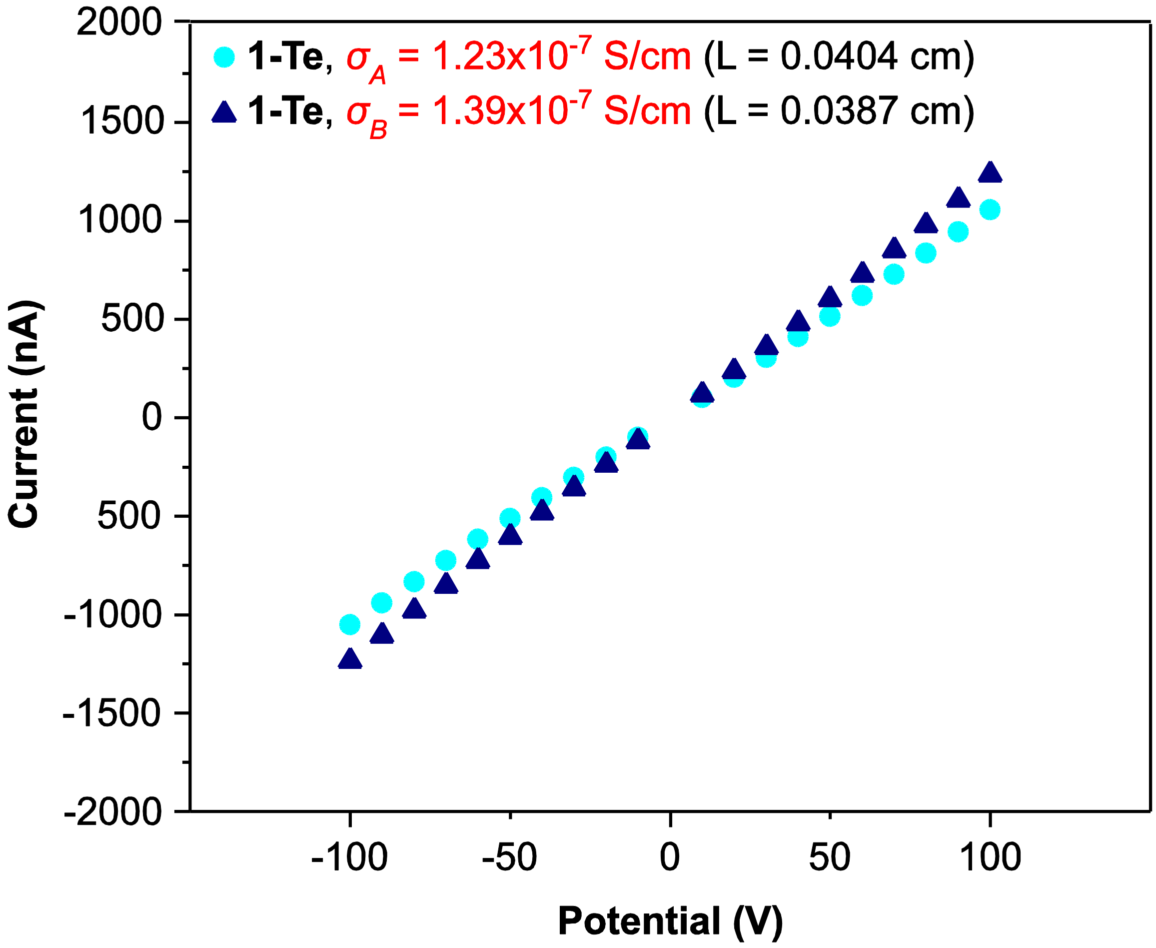


Figure S38. I-V curve of **1-Te** pellet with a 2 mm diameter.

References

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(3) N. Miyaura and A. Suzuki. Palladium-catalyzed reaction of 1-alkenylboronates with vinylic halides. *Org. Synth.* **1990**, *68*, 130.

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