

## Electronic Supplementary Information

### Facile synthesis, precise species control and chemical transformation of highly conducting organic metal chalcogenides $\text{Cu}_x\text{BHT}$ (BHT = benzenehexathiol; $x = 3, 4, 5.5$ )

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#### Materials

Hexakis(benzylthio)benzene ( $\text{C}_6(\text{SCH}_2\text{Ph})_6$ ) was purchased from Linyi Technology Co. Ltd., methanol, ethanol, acetonitrile,  $\text{Cu}_2\text{O}$  were purchased from Acros Organics Co., tris(4-bromophenyl)aminium hexachloroantimonate ( $((4\text{-BrPh})_3\text{NSbCl}_6)$ ) was purchased from Sigma-aldrich. Boron tribromide, fluorobenzene were purchased from J&K. Water was purified using the Milli-Q purification system. The solvents were degassed by the Freeze-Thaw method before using. Benzenehexathiol (BHT) was synthesized according to the previous literature.<sup>1</sup>

**Component characterization and analysis.** The content of carbon and sulfur were analyzed using Flash EA 1112 (Thermo Fisher Scientific). The metal content was analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES, iCAP 6300 Radial, Thermo Scientific). For ICP-OES measurements, the samples were prepared by dissolving them into fuming nitric acid. Then the resulting solution was diluted to a known volume with Milli-Q water. NMR spectra was recorded at 400 MHz (Bruker). XPS and UPS were performed using AXIS Ultra-DLD ultrahigh vacuum photoemission spectroscopy system (Kratos Co.). A monochromatic Al K $\alpha$  source (1486.6 eV) and He I source (21.22 eV) was used for XPS and UPS characterizations in a base pressure of better than  $3 \times 10^{-9}$  Torr, respectively. And the pressed pellet samples (thickness =  $\sim 0.12$  mm) were used UPS measurements.

**Raman spectroscopic characterization.** Raman spectra were recorded on a LabRAM HR Evolution (HORIBA) Raman spectrometer with the excitation wavelength of 532 nm at room temperature. Moderate powder crushed sufficiently before the measurement.

**X-ray Characterization.** Experimental PXRD data were recorded on a PANalytical Empyrean II X-Ray diffractometer using Cu K $\alpha$  irradiation ( $\lambda = 1.5406 \text{ \AA}$ ), from  $2\theta = 5^\circ$  to  $60^\circ$  with  $0.026^\circ$  increment at room temperature. Before PXRD testing, the samples should be well-grounded.

**SEM and TEM Characterizations.** SEM images were obtained using a Toshiba SU8000-SEM with an acceleration voltage of 10 kV. For the pretreatment, the samples were fully dispersed in EtOH and transferred to conductive silicon substrates, then covered with a platinum with a thickness of several nanometers. TEM images and SAED patterns were gathered by using a JEOL 2100F-TEM with an accelerated voltage of 120 kV. About 1 mg samples were dispersed in 4 ml waterless ethanol, after sufficiently ultrasonic dispersion for 40 minutes, the supernatant was dripped on a copper grid coated with carbon film, then they can be used for TEM after drying.

**Electrical property measurement.** The electrical conductivities of Cu<sub>x</sub>BHT were measured on the pressed pellet samples via a four-probe method by using a KEITHLEY 2002 Multimeter (Keithley Instrument Inc.). The temperature of measurement environment for electrical conductivity was controlled by a CTI Cryogenics refrigerator. About 5 mg powder was compressed into a cuboid pellet under a pressure of 10 MPa. Then the pellets were connected with four probes by conductive silver paste. The Seebeck coefficient was measured by the SB-100 Seebeck Measurement System (MMR Tech.).

### Synthesis of Cu<sub>3</sub>BHT

Cu<sub>3</sub>BHT was prepared by mixing BHT (30 mg, 0.11 mmol) and Cu<sub>2</sub>O (23.6 mg, 0.165 mmol) in the 30 ml degassed ethanol under argon atmosphere. The suspension was heated to 80 °C for 72 hours with constant stirring to give a black powder, followed by natural cooling to room temperature. Then the powder was filtered, washed with water, EtOH, acetone and diethyl ether in sequence, and dry at 60 °C under vacuum conditions for 24 h. Yield: 46 mg (92%). Elem. Anal. Calcd. for Cu<sub>3</sub>C<sub>6</sub>S<sub>6</sub>: C, 15.84; S, 42.27; Cu, 41.89. Found: C, 16.46; S, 41.82; Cu, 41.45.

### Synthesis of Cu<sub>4</sub>BHT

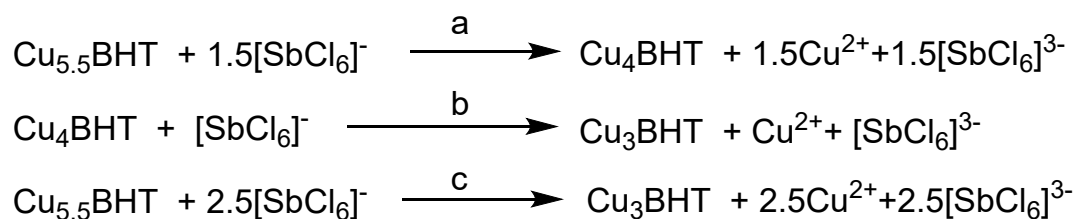
Cu<sub>4</sub>BHT was prepared by mixing BHT (30 mg, 0.11 mmol) and Cu<sub>2</sub>O (31.5 mg, 0.22 mmol) in the 30 ml degassed ethanol under argon atmosphere. The suspension was heated to 80 °C for 48 hours with constant stirring to give a dark blue powder. After cooling to room temperature, the powder was filtered, washed with water, EtOH, acetone and diethyl ether in sequence, and then dry at 60 °C under dynamic vacuum for 24 h. Yield: 52 mg (91%). Elem. Anal. Calcd. for Cu<sub>4</sub>C<sub>6</sub>S<sub>6</sub>: C, 13.9; S, 37.09; Cu, 49.01. Found: C, 14.64; S, 37.13; Cu, 48.16.

### Synthesis of Cu<sub>5.5</sub>BHT

Cu<sub>5.5</sub>BHT was prepared by mixing BHT (30 mg, 0.11 mmol) and Cu<sub>2</sub>O (43.3 mg, 0.303 mmol) in the 30 ml degassed acetonitrile under argon atmosphere. The suspension was heated to 80 °C for 48 hours with constant stirring to give a dark green powder. After cooling to room temperature, the powder was filtered, washed with water, EtOH, acetone and diethyl ether in sequence, and then dry at 60 °C under vacuum conditions for 24 h. Yield: 61 mg (90%). Elem. Anal. Calcd. for Cu<sub>5.5</sub>C<sub>6</sub>S<sub>6</sub>: C, 11.74; S, 31.33; Cu, 56.93. Found: C, 12.39; S, 30.89; Cu, 56.43.

### Oxidation regulation

From the view of charge balance, the equation of oxidation conversion can be described as below when (4-BrPh)<sub>3</sub>NSbCl<sub>6</sub> acts as the oxidant:

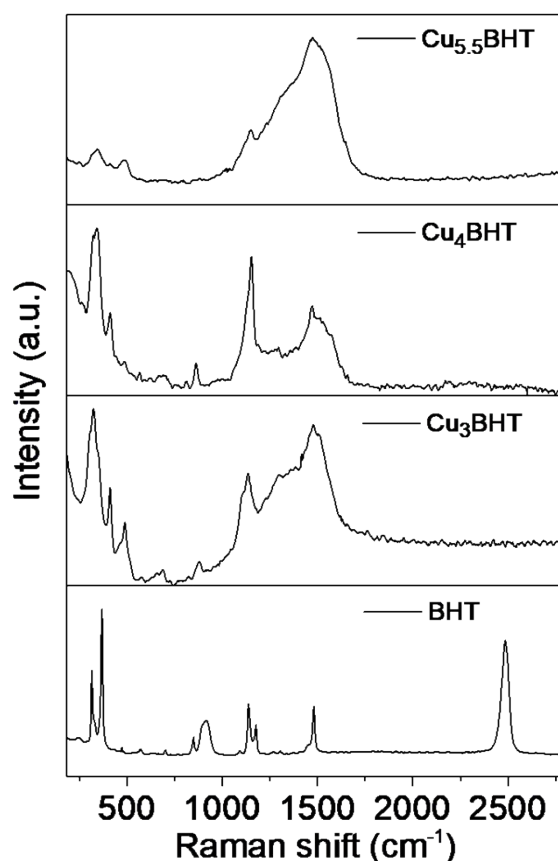


**Ox-Cu<sub>5.5</sub>BHT-a.** Under an Ar atmosphere, Cu<sub>5.5</sub>BHT (15 mg, 0.024mmol) and (4-BrPh)<sub>3</sub>NSbCl<sub>6</sub> (29.4 mg, 0.036mmol) were added to CH<sub>3</sub>OH (25 ml). The solution was stirred at room temperature for 12 h. Then the mixture was filtered. The resultant powder was washed with H<sub>2</sub>O, EtOH, dichloromethane until the filtrate became colorless. After drying at 60 °C under vacuum, the dark blue solid was obtained. The filtrate was collected and dried under a dynamic vacuum and denoted

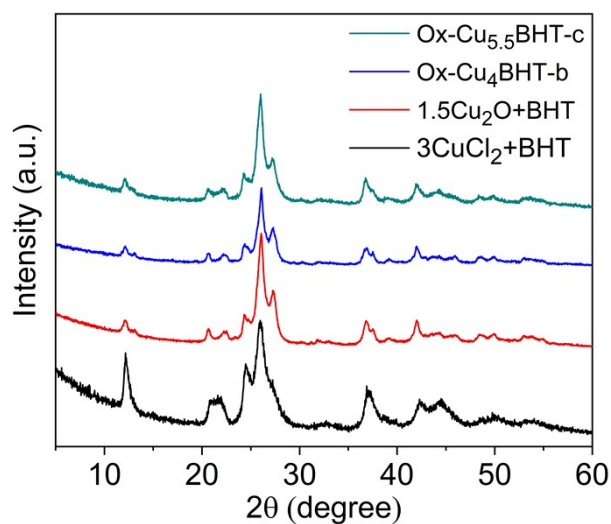
as pro-a. Yield: 10 mg (81%). Elem. Anal. found for Ox-Cu<sub>5.5</sub>BHT-a: C, 15.83; S, 36.23; Cu, 47.94, which is close to the compositional analysis of Cu<sub>4</sub>BHT.

**Ox-Cu<sub>4</sub>BHT-b.** Under an Ar atmosphere, Cu<sub>4</sub>BHT (15 mg, 0.029mmol) and (4-BrPh)<sub>3</sub>NSbCl<sub>6</sub> (24mg, 0.029mmol) were added to CH<sub>3</sub>OH (25 ml). The solution was stirred at room temperature for 24 h. The resultant powder was washed with H<sub>2</sub>O, EtOH, dichloromethane until the filtrate became colorless. After drying at 60 °C under vacuum, the black solid was obtained. Yield: 11 mg (84%). The filtrate was collected and dried under a dynamic vacuum and denoted as pro-b. Elem. Anal. found for Ox-Cu<sub>4</sub>BHT-b: C, 16.25; S, 40.92; Cu, 42.83, which is close to the compositional analysis of Cu<sub>3</sub>BHT.

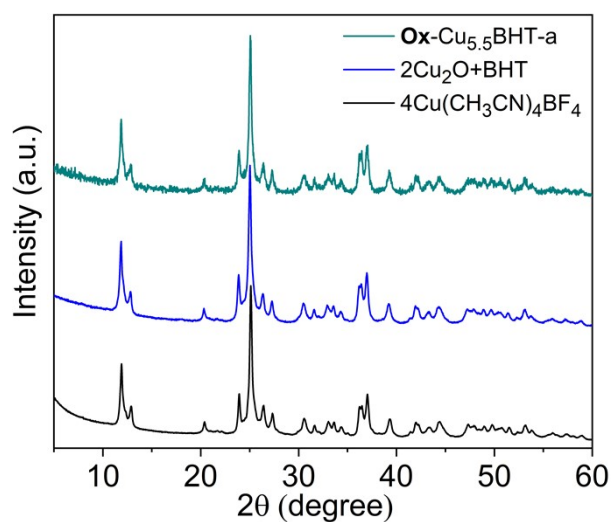
**Ox-Cu<sub>5.5</sub>BHT-c.** Under an Ar atmosphere, Cu<sub>5.5</sub>BHT (15 mg, 0.024mmol) and (4-BrPh)<sub>3</sub>NSbCl<sub>6</sub> (49mg, 0.06mmol) were added to CH<sub>3</sub>OH (25 ml). The solution was stirred at room temperature for 24 h. Then the mixture was filtered. The resultant powder was washed with H<sub>2</sub>O, EtOH, dichloromethane until the filtrate became colorless. After drying at 60 °C under vacuum, the black solid was obtained. The filtrate was collected and dried under a dynamic vacuum and denoted as pro-c. Yield: 9 mg (82%). Elem. Anal. found for Ox-Cu<sub>5.5</sub>BHT-c: C, 17.32; S, 42.67; Cu, 40.01, which is close to the compositional analysis of Cu<sub>3</sub>BHT.



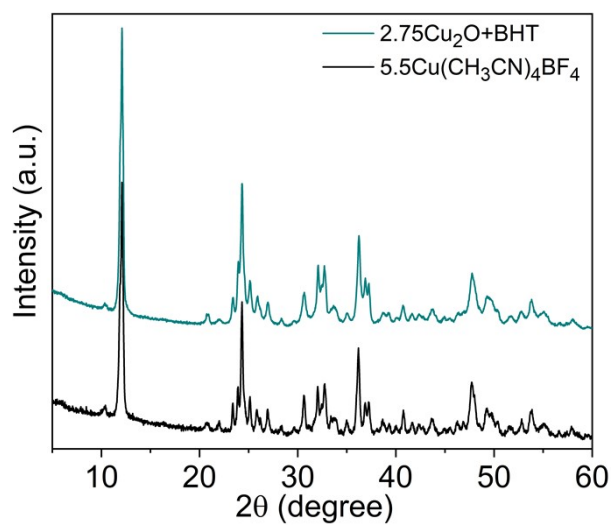
**Fig. S1** Raman spectrum of BHT and Cu<sub>x</sub>BHT.



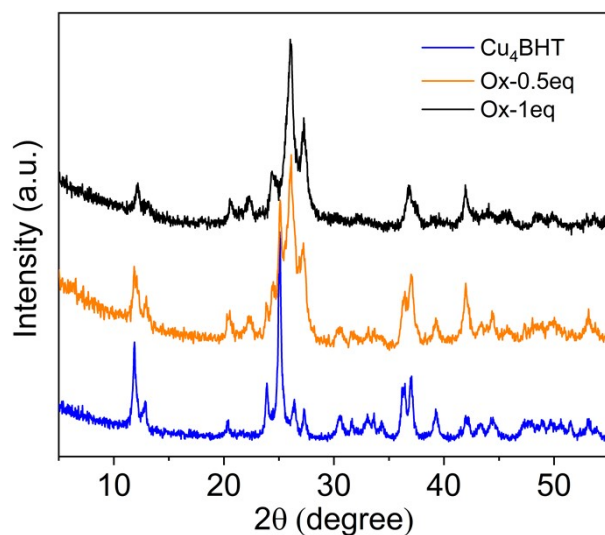
**Fig. S2** PXRD patterns of Cu<sub>3</sub>BHT product synthesized under different reaction conditions.



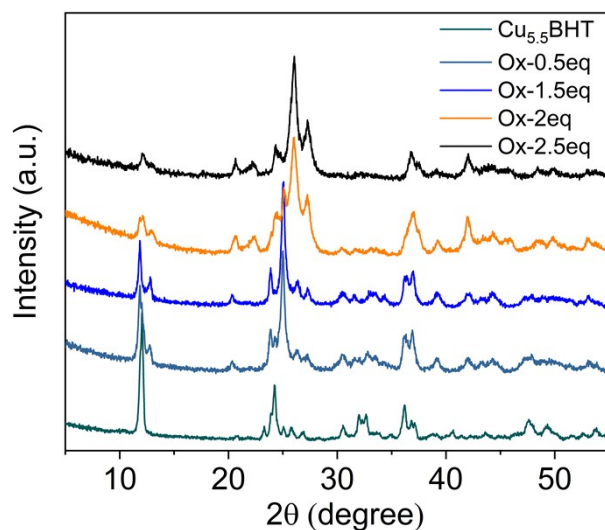
**Fig. S3** PXRD patterns of Cu<sub>4</sub>BHT product synthesized under different reaction conditions.



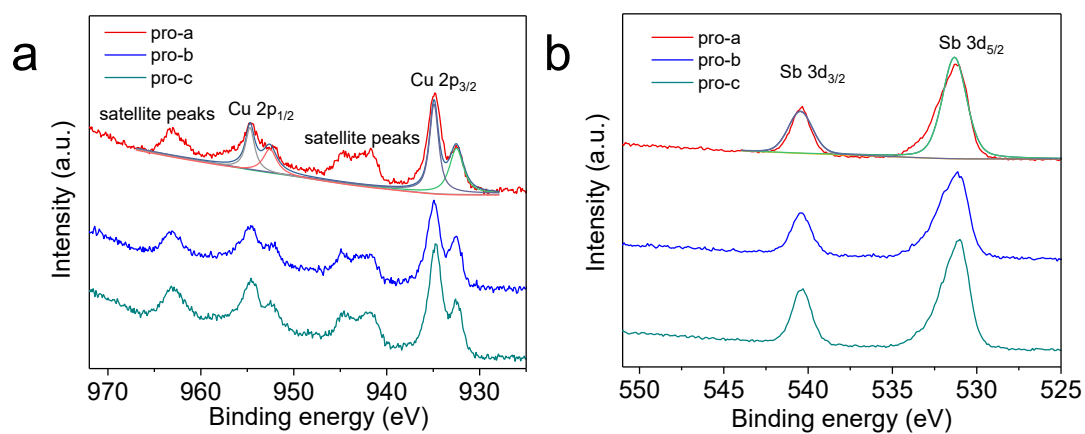
**Fig. S4** PXRD patterns of Cu<sub>5.5</sub>BHT product synthesized under different reaction conditions.



**Fig. S5** XRD patterns of the oxidized products of Cu<sub>4</sub>BHT using different equivalents of (4-BrPh)<sub>3</sub>NSbCl<sub>6</sub>.



**Fig. S6** XRD patterns of the oxidized products of Cu<sub>5.5</sub>BHT using different equivalents of (4-BrPh)<sub>3</sub>NSbCl<sub>6</sub>.



**Fig. S7** XPS spectra of Cu and Sb in the remaining filtrate after the oxidized process (a, b, c).

**Supplementary reference**

1 H. K. Yip, A. Schier, J. Riede, H. Schmidbaur, *Journal of the Chemical Society, Dalton Transactions* 1994, 2333-2334.