Electronic Supplementary Information (ESI)

Synthesis of a highly conductive coordination polymers film via a vapor-solid phase chemical conversion process

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Materials

Hexakis(benzylthio)benzene ($C_6(SCH_2Ph)_6$) was purchased from Linyi Technology Co. Ltd. Ag_2O was purchased from Acros Organics Co. Water was purified using the Milli-Q purification system. The solvents were degassed by the Freeze-Thaw method before using. Benzenehexathiol was synthesized according to the previous literature[1]

Synthesis of Ag_5BHT powder.

The powder sample of Ag_5BHT was synthesized via a simple inhomogeneous solution reaction of Ag_2O and H_6BHT[(21)]. In an argon atmosphere, H_6BHT (27 mg, 0.1 mmol) and silver oxide (Ag_2O) (58 mg, 0.25 mmol) were suspended in degassed isopropanol (40mL). The mixture was ultrasonic dispersed at 0 °C for 10 min, and then heated to 50 °C and reacted overnight. After stirring for 24 hours and the suspension will turn dark green. A dark green powder was obtained by filtration and washed three times with water, methanol and acetone, respectively. And the solvents were removed under vacuum. The yield of Ag_5BHT was 79mg (98%)

Synthesis of Ag_5BHT films.

Firstly, an inert substrate was coated with Ag films through thermal evaporation; subsequently, a high-quality flat Ag_2O films were achieved through plasma oxidation. Then, H_6BHT was deposited onto the surface of the Ag_2O films using thermal evaporation technique at a ratio of 1.3:1 relative to the thickness of Ag_2O films. The resulting Ag_2O-H_6BHT films were placed within a closed container filled with an atmosphere containing vaporized isopropanol. This setup undergone heating at temperatures ranging from 90-120 ℃ for several days to yield Ag_5BHT thin films. The time largely depended on both the thickness of the Ag_2O films and H_6BHT films; increasing these parameters will correspondingly increase reaction time duration. For instance, when using Ag_2O films with thickness of 50nm combined with H_6BHT films with thickness of 65nm, it takes approximately two days for completion, whereas employing Ag_2O films (100nm) along with H_6BHT films(130nm) extends this duration to five days.

Device Fabrication.

The heavily doped n-type Si wafers with a 300 nm thick SiO_2 layer were used as substrates of OFETs, which were cleaned with deionized water, piranha solution (70/30 vol./vol. H_2SO_4/H_2O_2), deionized water, isopropanol and blow-dried by N_2. Evaporating 100 nm thick Au or Pt source and drain electrodes onto a SiO_2/Si / Ag_5BHT films to fabricate the bottom-gate top-contact devices.

Characterization.

Thermogravimetric analysis. TGA date was performed on a PerkinElmer TGA 8000 instrument under nitrogen atmosphere.

X-ray characterization. Experimental PXRD data was collected on a PANalytical Empyrean II X-Ray diffractometer using Cu Ka irradiation (λ=1.5406 Å). The generator was operated at 40 kV and 40 mA. Samples were scanned at diffraction angles ranging between 2° and 60° at a scanning rate of 0.026°/s.

SEM and TEM Characterizations. The SEM and EDS images were obtained using a Toshiba SU8000-SEM with an acceleration voltage of 10 kV. The TEM images and HR-TEM images and SAED patterns were obtained by using a JEOL 2100F TEM with an accelerated voltage of 120 kV.

The step profiler tests. The date was performed on a Bruker DektakXT. The Scan type was Standard Scan, scan duration was 6s, scan length was 300μm, and scan resolution was 0.166482 μm.

The X-ray photon spectrum (XPS) characterizations. XPS was performed with a monochromatic magnesium Ka source (1253.8 eV) using AXIS Ultra-DLD ultrahigh vacuum photoemission spectroscopy system (Kratos Co.).

The Fourier transform infrared (FT-IR) spectroscopy characterizations. The spectra data was collected on VERTEX 70v vacuum micro-Fourier infrared spectrometer.

Electrical property measurement. The electrical conductivities were measured 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. The films were connected with four probes by conductive silver paste.

Characterizations of field-effect transistors (FETs). The device characteristics were measured at room temperature by Agilent 1500A. The mobility was calculated in the linear regime form the equation $I_{DS}=(W\mu C_i/L)(V_{GS}-V_T)V_{DS}$, where I_{DS} is the drain-source current, μ is the filed-effect mobility, W and L are the channel width and length, respectively, C_i is the capacitance per unit of the dielectric layer, V_T is the threshold voltage, and V_{GS} and V_{DS} are the gate voltage and drain-source voltage, respectively.

Results and Discussion

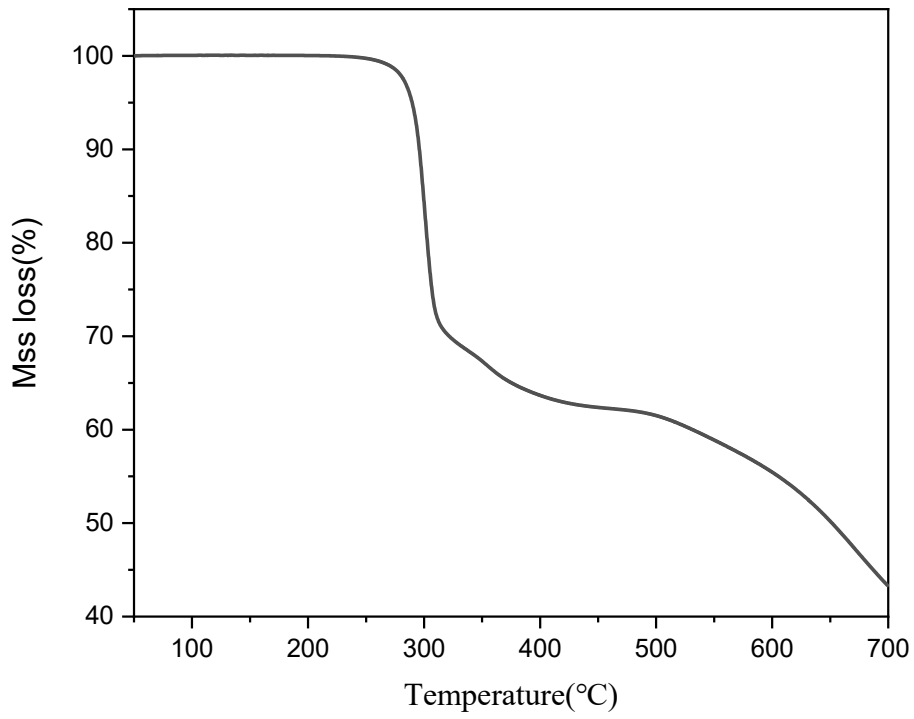

Fig. S1 TGA profile of H_6BHT under nitrogen atmosphere showing that it is stable at the sublimation temperature range.

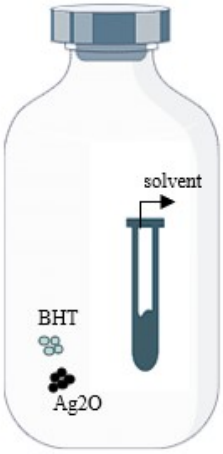

Fig. S2 Schematic of a reaction performed by heating Ag_2O powder and H_6BHT powder in a closed reaction bottle filled with isopropanol vapor atmosphere.

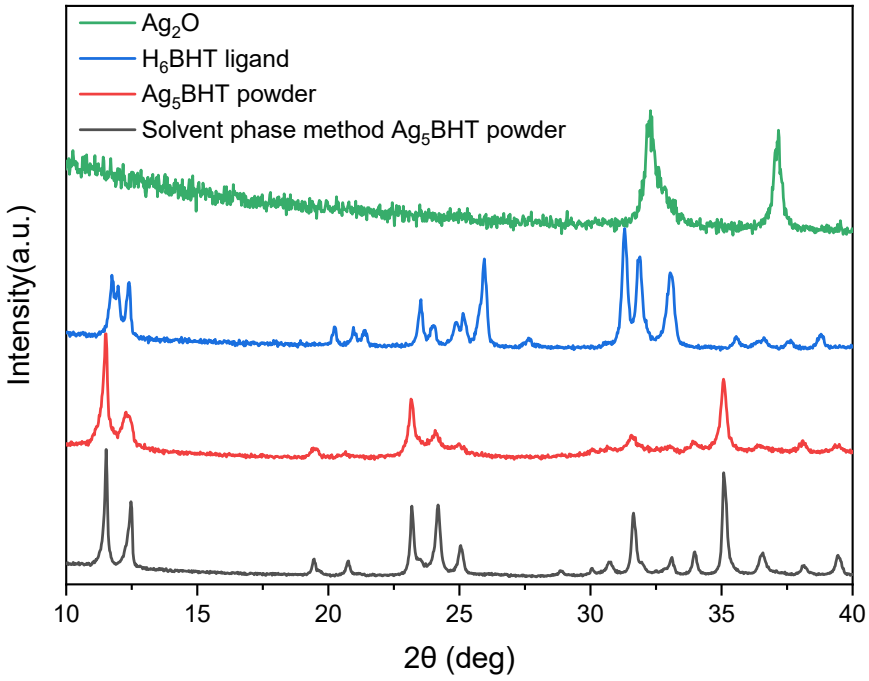

Fig. S3 PXRD pattern of solvent phase method-Ag_5BHT powder (black) and crystalline Ag_5BHT powder prepared by the vapor-solid phase chemical conversion method (red) and H_6BHT ligand (blue) and Ag_2O (green).

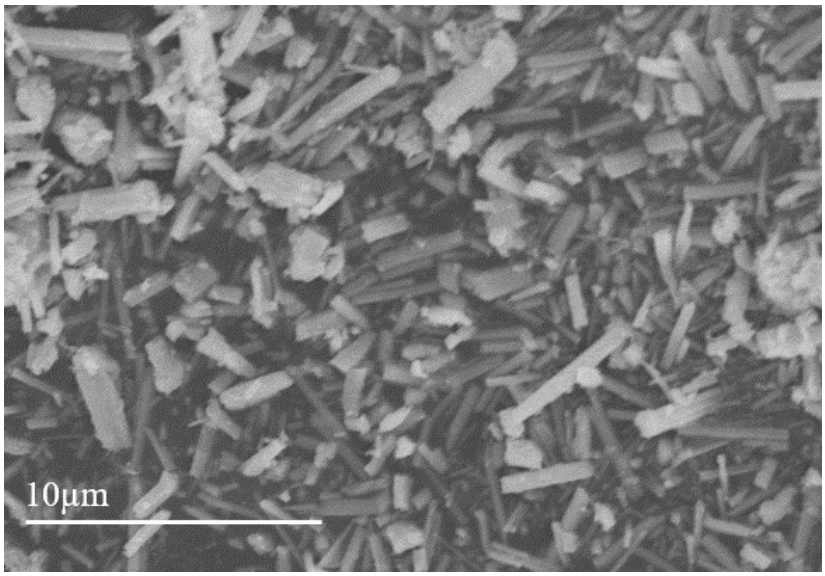

Fig. S4 SEM images of crystalline Ag_5BHT powder prepared by the vapor-solid phase chemical conversion method.

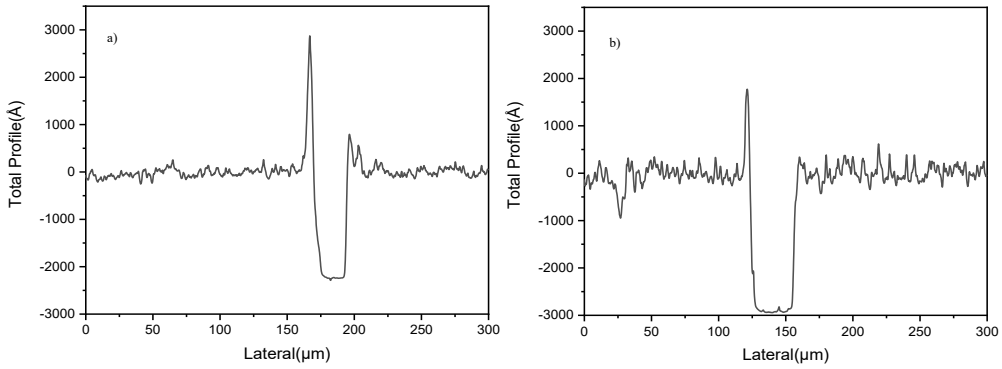

Fig. S5 The step profiler test results before and after reaction between 100nm Ag_2O and 130nm H_6BHT films. a) Ag_2O/H_6BHT films before reaction b) Ag_5BHT thin films after reaction.

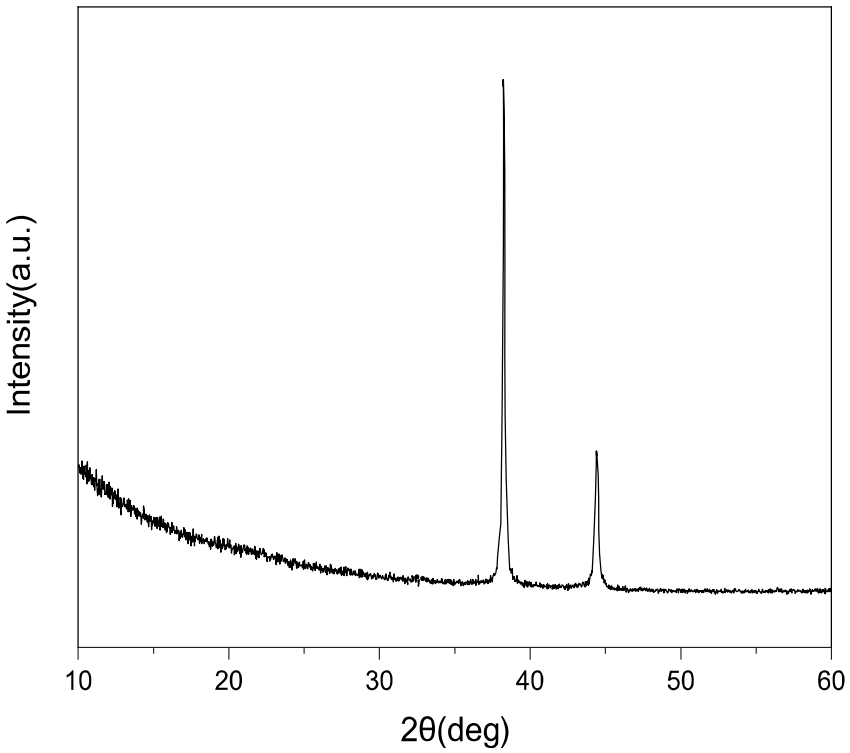

Fig. S6 PXRD pattern of Ag_2O films reduced to Ag films.

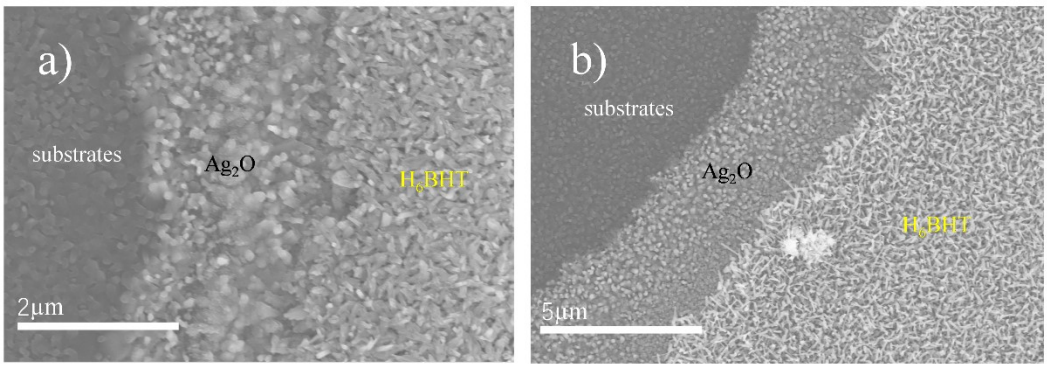

Fig. S7 SEM images of the Ag_2O/H_6BHT films.

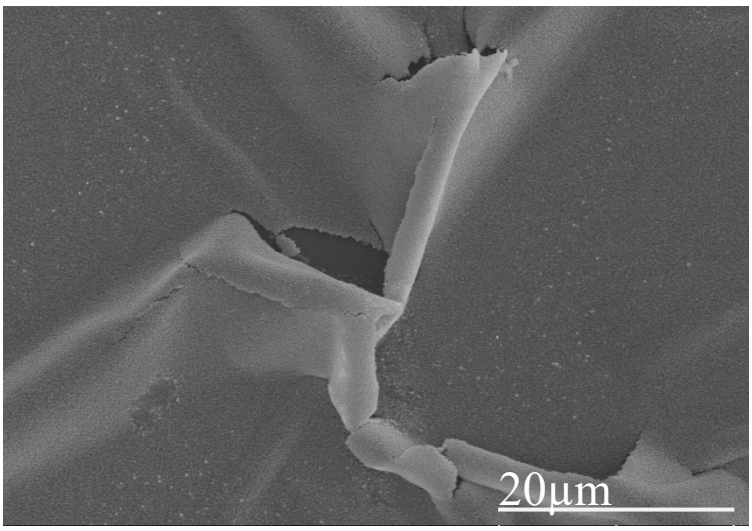

Fig. S8 SEM images of the fold of Ag_5BHT thin films.

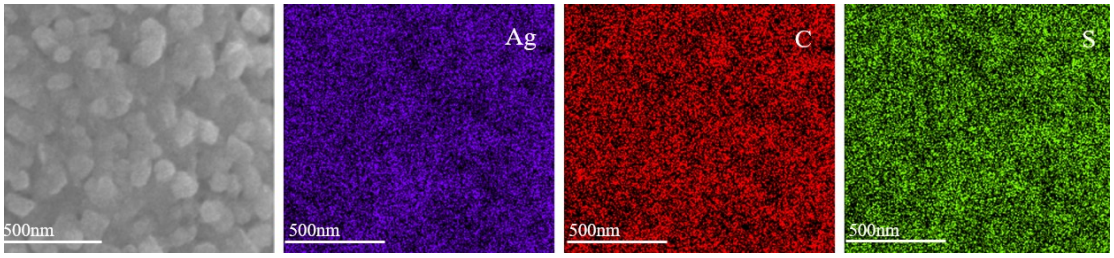

Fig. S9 SEM and the corresponding EDS mapping images of Ag_5BHT thin films.

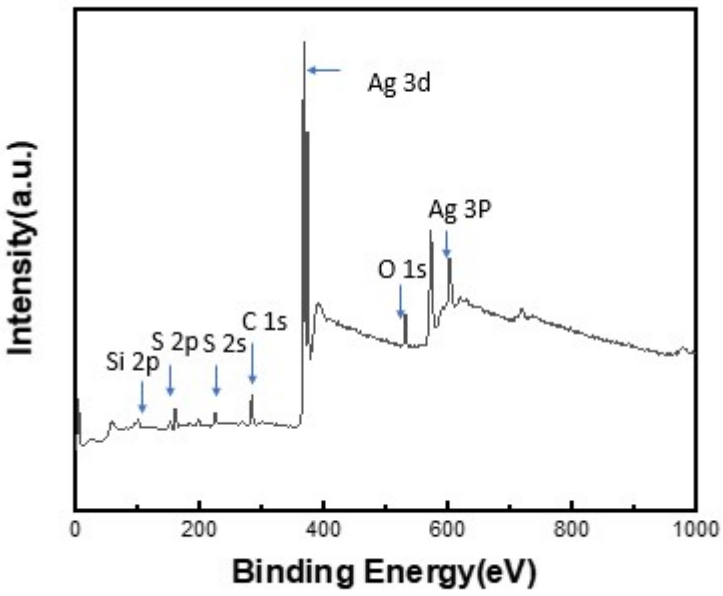

Fig. S10 The full XPS spectrum of Ag_5BHT thin films.

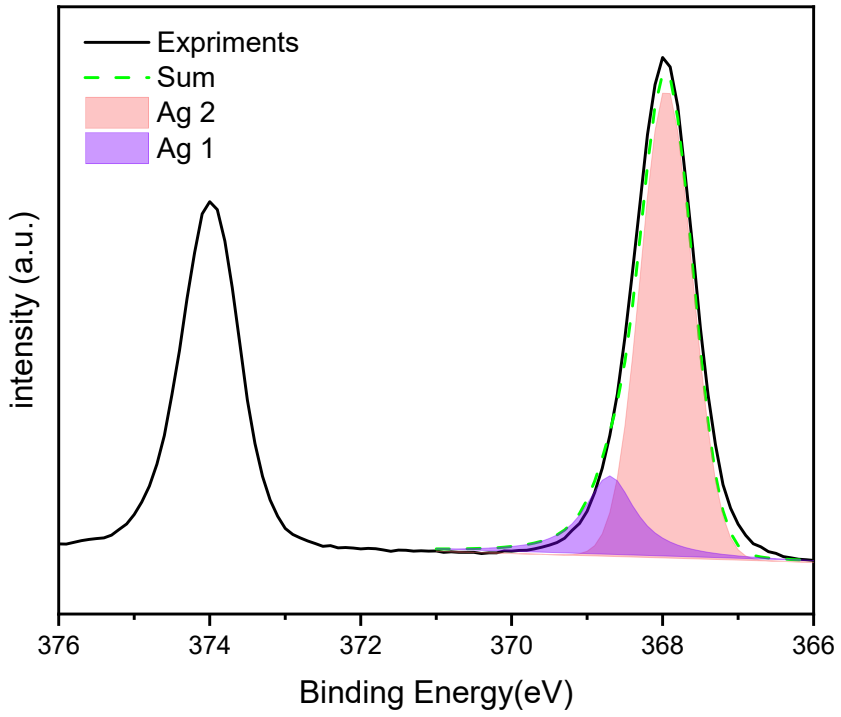

Fig. S11 The XPS of Ag_5BHT thin films focusing on Ag 3d region.

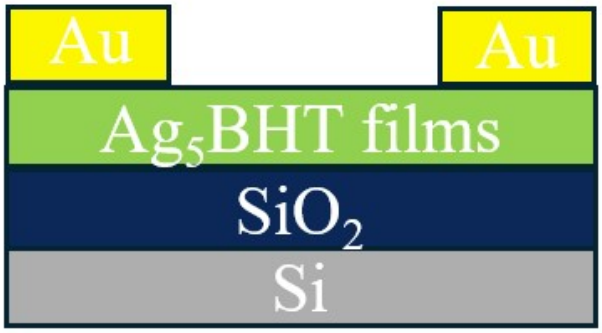

Fig. S12 Illustrative schematic of Ag_5BHT films-based field-effect transistors.

	1	2	3	average value
S/Ag atom ratio	1.41:1	1.58:1	1.66:1	1.55:1

Table S1. S/Ag atomic ratio calculated from EDS data.

Supplementary Reference

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