

Supporting Information for

A new 3-D coordination polymer as a precursor for CuI-based thermoelectric composites

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Materials and Methods

Copper iodide and acetonitrile were purchased from Sigma-Aldrich. Ethanol, diethyl ether and hexane (ACS reagent) were purchased from VWR, Tedia and J.T.Baker Chemicals, respectively. Powder X-ray diffraction data were collected on a Bruker D8 Advance X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). The infrared spectrum was obtained on a Perkin Elmer Spectrum 2000 FT-IR spectrometer from a sample in KBr. Elemental analyses were performed on a thermo electron corporation flash EA 1112 series analyzer. Photoluminescence spectrum of solid sample was measured with excitation from a pulsed laser diode operating at 405 nm. The Photoluminescence was dispersed by a monochromator (Acton, SpectroPro 2300i) and detected with a liquid-nitrogen-cooled charge-coupled device detector. The spot size 0.4 μm , $400 \pm 10\text{nm}$ knock out filter was used to remove laser effects. Thermogravimetric analyses (TGA) were carried out in air or nitrogen streams using a TA Instruments TGA Q500 analyzer with a heating

rate of 30 °C/min. FESEM images were collected using a JEOL 7600 SEM system. UV-vis diffuse reflectance spectroscopy was measured using a UV-3600 Shimadzu VIS-NIR spectrophotometer. X-ray photoelectron spectroscopy measurement was performed using a Thermo Scientific Theta Probe system with a monochromatic Al_{Kα} X-ray source ($h\nu = 1486.7$ eV). Electrical conductivity and Seebeck coefficients were optimized and evaluated using an Advance Riko ZEM-3 HR Seebeck coefficient / electric resistance measurement system. The single-crystal x-ray diffraction data were collected using a Bruker AXS SMART APEX diffractometer, equipped with a CCD area-detector using Mo-K_α radiation ($\lambda = 0.71073$ Å). Data integration and scaling were performed using Bruker SAINT software.⁽¹⁾ The absorption correction was performed by SADABS.⁽²⁾ Space group determination, structure solution and least-squares refinements were carried out with Bruker SHELXL software.⁽³⁾ The structure was solved by direct methods to locate heavy atoms, followed by difference maps for the light non-hydrogen atoms. Anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms.

Synthesis of ligands L1 and L2

The ligands L1 (1,4-bis(phenylthio)but-2-yne) and L2 (1,4-bis(phenylthio)butane) were synthesized according to a literature procedure for thioethers.⁽⁴⁾ 1,4-Dichloro-2-butyne (4.9 g, 40 mmol, for L1) or 1,4-dibromobutane (8.6 g, 40 mmol, for L2) was added to a solution of NaOH (3.2 g, 80 mmol) and benzenethiol (8.8 g, 80 mmol) in ethanol (150 mL) at 0 °C. The mixture was stirred for 6 h and concentrated to about 50 mL under vacuum. The resulting precipitate was filtered and washed with DI water and hexane to give a crystalline solid. Yield: 6.2 g, 57 % (L1) or 6.6 g, 60 % (L2). For ligand L1: ¹H NMR (CDCl₃, 500.2 MHz) δ : 7.41–7.39 (m, 4H), 7.31–7.28 (m, 4H), 7.25–7.22 (m, 2H) and 3.62 (s, 4H, CH₂). ¹³C NMR (CDCl₃, 125.8 MHz): 135.4, 129.9, 129.0, 126.8, 79.4 (C≡C), 23.1 (CH₂). For ligand L2: ¹H NMR (CDCl₃, 500.2 MHz) δ : 7.35–7.28 (m, 8H), 7.21–7.18 (m, 2H), 2.95–2.93 (m, 4H) and 1.82–1.79 (m, 4H). ¹³C NMR (CDCl₃, 125.8 MHz): 136.5, 129.3, 129.0, 126.0, 33.3 and 28.2.

Synthesis of coordination polymer 1

Complex **1** was synthesized by mixing acetonitrile solutions of ligand L1 (1 mmol, 270 mg) (3 mL) and CuI (2 mmol, 380 mg) (7 mL). Colorless single crystals were obtained by slow evaporation of the solvent over one week at room temperature. The bulk sample of **1** was obtained by mixing the ligand L1 (3 mmol, 810 mg) and CuI (6 mmol, 1140 mg) at room temperature. Yield: 1.4 g, 72%. Anal. Calcd. for C₃₂H₂₈Cu₄I₄S₄ (1302.62): C, 29.51; H, 2.17; S, 9.84%. Found: C, 29.52; H, 2.18; S, 9.83%. Main IR bands (cm⁻¹): 3070(m), 3042(m), 2993(m), 2912(m), 1964(m), 1939(m),

1876(m), 1853(m), 1719(m), 1638(m), 1577(m), 1480(m), 1440(m), 1406(m), 1239(m), 1230(m), 1166(m), 1148(m), 1078(m), 1026(m), 999(m), 896(m), 868(m), 827(m), 735(s, ν_{C-S}), 712(m), 686(s, ν_{C-S}), 485(m) and 459(m).

Preparation of composite 2

A white powder sample of **1** (5g) was placed in a box-furnace under nitrogen-gas flow. The temperature was increased from room temperature to 400 °C at a rate of 5 °C per minute and held at that temperature for 1 hour, before cooling to room temperature. Yield: ~3.3 g, 66%. Elemental analysis: C, 10.17 wt%. Pellet sample was made using a hydraulic press under 10 bar pressure. Thermoelectric performance was evaluated using pellet sample and multicycle measurements from 75–250 °C.

Preparation of composite 3

Coordination polymer **II** was prepared based on a literature procedure.⁽⁵⁾ A white powder sample of **II** (5g) was placed in a box-furnace under nitrogen-gas flow. The temperature was increased from room temperature to 400 °C at a rate of 5 °C per minute and held at that temperature for 1 hour, before being allowed to cool to room temperature. Yield: ~2.9 g, 58 %. Elemental analysis: C, 0.05 wt%. The Pellet sample formed using a hydraulic press under 10 bar pressure easily disassembled on handling.

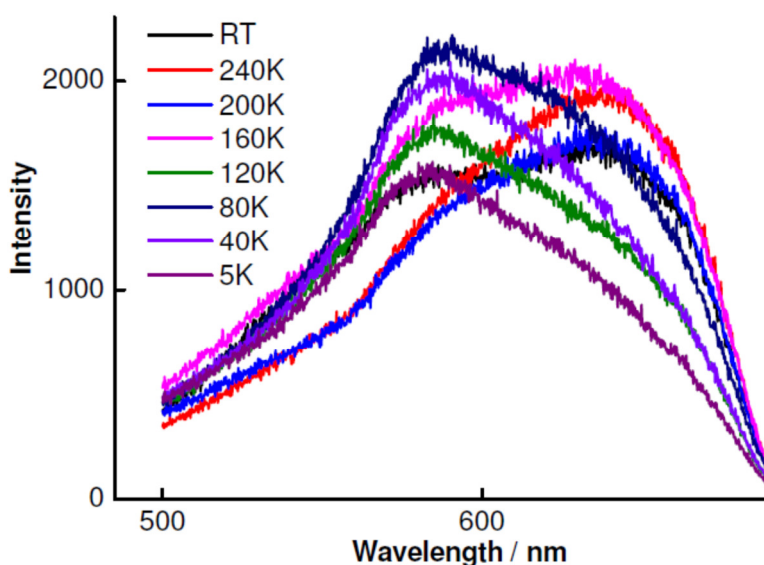


Fig. S1 Photoluminescent spectra of **1**.

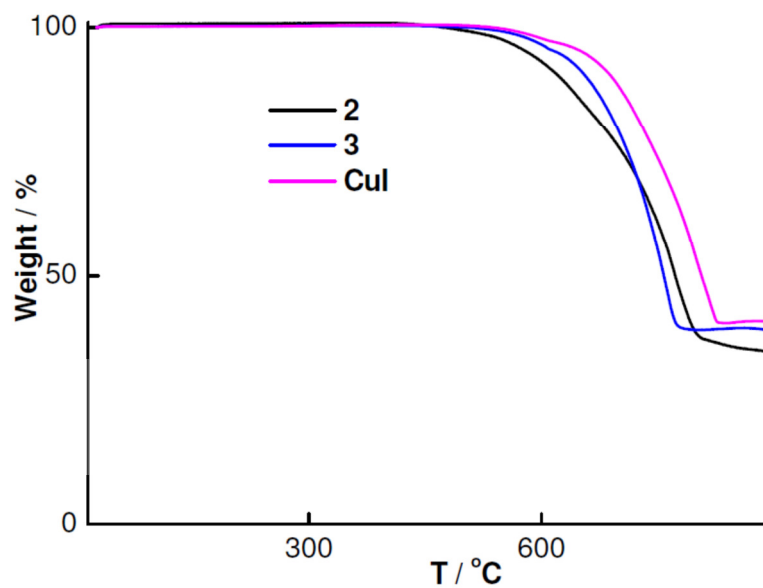


Fig. S2 TGA curves of composites 2, 3 and control sample Cul.

References

- (1) Version 6.0, SAINT Software Reference Manual, Bruker AXS Inc., 2003.
- (2) L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Cryst.*, 2015, **48**, 3–10.
- (3) G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3–8.
- (4) M. Konrad, F. Meyer, K. Heinze and L. Zsolnai, *J. Chem. Soc., Dalton Trans.*, 1998, 199–205.
- (5) M. Knorr, F. Guyon, A. Khatyr, C. Däschlein, C. Strohmam, S. M. Aly, A. S. Abd-El-Aziz, D. Fortin and P. D. Harvey, *Dalton Trans.*, 2009, 948–955.