Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

A thermoelectric copper-iodide composite from pyrolysis of a well-defined coordination polymer

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Materials and Methods

Copper iodide and acetonitrile were purchased from Sigma-Aldrich. Ethanol and diethyl ether (ACS grade) were purchased from VWR Chemicals and Tedia, respectively. Ligand L (L = bis(2-(cyclohexylthio)ethyl)amine)) was prepared by a literature procedure.(1) Electrospray ionization mass spectra (ESI-MS) were recorded in positive ion mode using a Shimadzu LCMS-IT-TOF mass spectrometer. Powder X-ray diffraction data were collected on a Bruker D8 Advance X-ray diffractometer with Cu-Kα radiation (λ = 1.5406 Å). The infrared spectrum was obtained on a Perkin Elmer Spectrum 2000 FT-IR spectrometer from a sample in KBr disc. Elemental analyses were performed on a thermo electron corporation flash EA 1112 series analyzer. Thermogravimetric analyses (TGA) were carried out under 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. Transmission electron microscopy (TEM) analyses were performed on a FEI Titan 80/300 high-resolution TEM (200 kV). Elemental distribution was obtained using energy-filtered TEM images. UV-vis diffuse reflectance spectroscopy was measured using a UV-3600 Shimadzu VIS-NIR spectrophotometer. Band gap energies were calculated based on the relationship E = hC/λ, here h is Planks constant, C is speed of light and λ is the cut off wavelength. 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 (λ = 0.71073 Å). Data integration and scaling were performed using Bruker SAINT software.(2) The empirical absorption correction was performed by SADABS.(3) The space group determination, structure solution and least-squares refinements were carried out with the Bruker SHELXL software.(4) Structure was solved by direct methods to locate the 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. The H atom of N1 was located from difference map and refined without restraints. One of the cyclohexane rings was disordered over two positions with an occupancy ratio of 60:40. CCDC reference number: 1586815 (**1**). Crystallographic data for **1**: formula $C_{16}H_{31}Cu_2I_2NS_2$, monoclinic crystal system, space group $P2_1/c$, a = 16.627(1), b = 10.6924(9), c = 13.171(1) Å, β = 110.243(2)°, V = 2197.0(3) Å^3, Z = 4, crystal size of 0.16 × 0.24 × 0.56 mm^3, GOF = 1.162, reflections collected: 14706, independent reflections of 5031 [R_{int} = 0.0386], R_1 = 0.0574 and wR_2 = 0.1576.

Synthesis of 1 and 2

Synthesis of $[L_2Cu_4I_4]_n$ (**1**). Ligand L (151 mg, 0.5 mmol) in acetonitrile (2 mL) was added to a acetonitrile solution (10 mL) of CuI (190 mg, 1 mmol) and the mixture was stirred for about one hour at room temperature. The resulting white precipitate was collected by filtration, washed with acetonitrile, ethanol, and diethyl ether and dried at 60 °C under vacuum for overnight. Yield: 275 mg, 80%. Crystals of **1** suitable for X-ray crystallography were grown by carefully layering of ligand solution (acetonitrile) onto a solution of CuI in the same solvent. Anal. Calcd. for $C_{16}H_{31}Cu_2I_2NS_2$(682.45): C, 28.16; H, 4.58; N, 2.05 %. Found: C, 28.31; H, 4.56; N, 2.08%. Main IR bands (cm^{-1}): 3219(m, N–H stretch), 2926(s, C–H stretch), 2850(m, C–H stretch), 1625(m, N–H bend), 1447(m), 1410(m), 1340(m), 1293(m), 1264(m), 1206(m), 1179(m), 1091(m), 1045(m), 1024(m), 998(m), 956(m), 930(m), 913(m), 888(m), 816(m), 789(m), 739(m) and 711(m). ESI-MS (m/z, %): $[CuL]^+$ (364, 16) and $[HL]^+$ (302, 100). A scale up experiment demonstrated that about

1.85 g of powder sample of **1** could be obtained from a single synthesis by stirring of ligand L (905 mg, 3 mmol) with CuI (1143 mg, 6 mmol) in acetonitrile (25 mL) at room temperature.

Synthesis of composite **2**. A powder sample of complex **1** (1.70 g) was heated at 350 °C in a tube furnace for one hour under an argon flow. The resulting black sample **2** (0.98 g) was scraped from the walls of the container. The pressed pellets of **2** were made under 10 bar of pressure. The average density of the composite pellets was 4.24 g/cm^3 (Fig. S1). Microanalysis indicated that composite **2** contained about 4.25 wt% of carbon, and trace amounts of nitrogen (~0.45 wt%), sulphur (~0.75 wt%) and hydrogen (0.25 wt%).

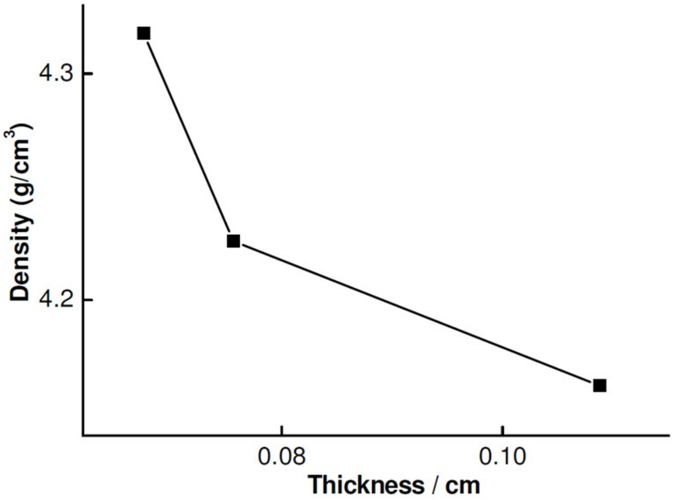

Fig. S1 Density of pellets of composite **2** at different thickness.

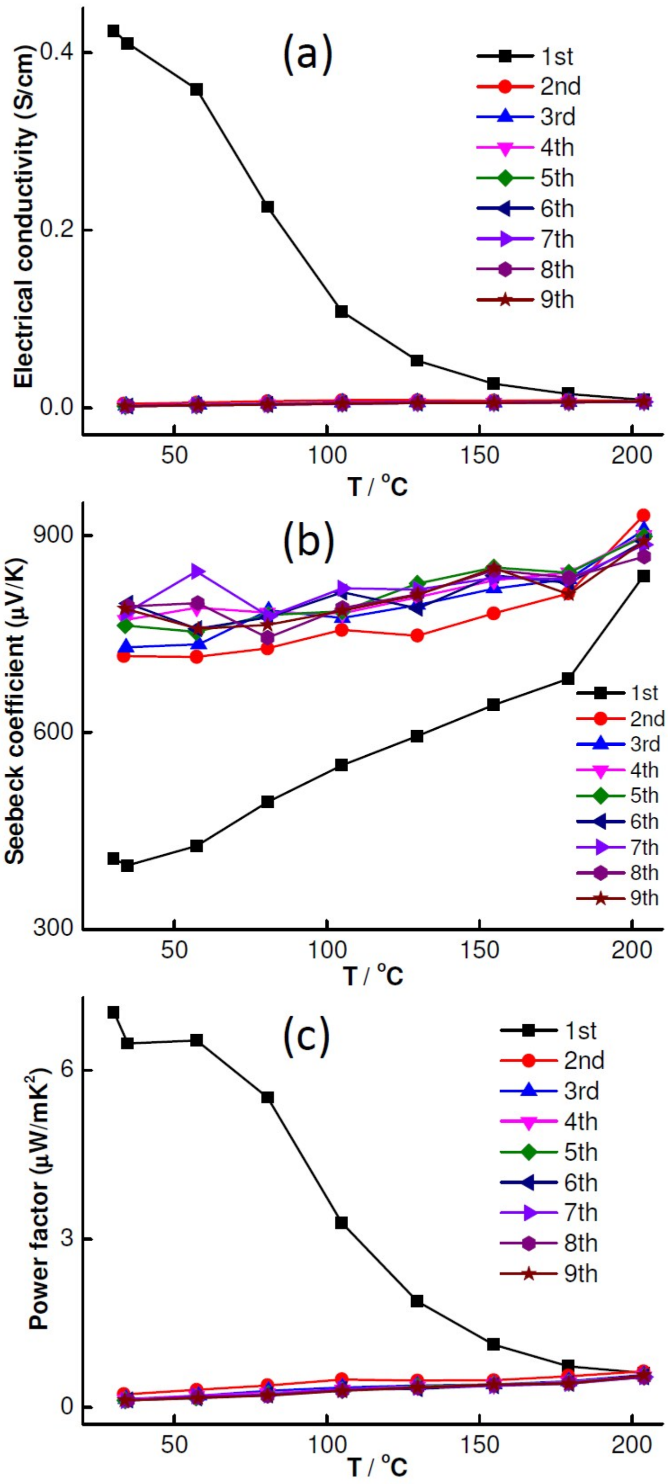

Fig. S2 Temperature-dependent thermoelectric properties of composite **2** (pellet B, density: 4.23 g/cm^3) evaluated from nine-cycle measurements: (a) electrical conductivity, (b) Seebeck coefficient, and (c) power factor.

Citations

(1) M. Konrad, F. Meyer, K. Heinze and L. Zsolnai, *J. Chem. Soc., Dalton Trans.*, 1998, 199–205.

(2) Version 6.0, SAINT Software Reference Manual, Bruker AXS Inc., 2003.

(3) L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Cryst.*, 2015, **48**, 3–10.

(4) G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3–8.