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Introduction

Thermoelectric materials have attracted global attention because of their unique ability of directly converting waste heat to electricity.^{1–3} Their clean energy conversion contributes to both local cooling and improves the energy conversion efficiency of electricity generation from fossil fuels.^{4–6} Significant effort has been devoted to the development of efficient thermoelectric materials such as Bi₂Te₃, PbTe, SnSe and BiCuSeO.⁷ Thermoelectric efficiency is evaluated based on the equation, $zT = S^2 \sigma T/\kappa$. The dimensionless figure of merit zTis reliant on the collective influence of electrical conductivity (σ), Seebeck coefficient (*S*), and thermal conductivity (κ). However, material performance optimisation is challenging as the interdependence of these parameters is complex and not well understood. Typically, inorganic thermoelectric materials show high zT values (up to about 3). However, most of these

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A new 3-D coordination polymer as a precursor for Cul-based thermoelectric composites[†]

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Two complexes, $[Cu_{6}l_{6}(L1)_{3}]_{n}$ (I) and $[Cu_{4}l_{4}(L2)_{2}]_{n}$ (II) (L1 = 1,4-bis(phenylthio)but-2-yne; L2 = 1,4-bis (phenylthio)butane), as precursors for thermoelectric composites were prepared using a literature procedure. During the preparation of I, an unexpected 3-D polymorph $[Cu_{4}l_{4}(L1)_{2}]_{n}$ (I) with a triclinic space group and an infinite $[Cul]_{n}$ staircase structure was obtained. This new polymorph (1) exhibited the same structure at both room temperature and 173 K. Complexes 1 and II were therefore pyrolysed to composites 2 and 3, respectively, at 400 °C under a nitrogen gas flow. Composite 3 was pale in color with a low carbon content (0.05 wt%) and easily disassembled during handling. By comparison, the high carbon containing (10.2 wt%) composite 2 can be compressed into a robust, light pellet (density 3.58 g cm⁻³), which showed a moderate to high Seebeck coefficient (543–1308 μ V K⁻¹) over the temperature range 70–240 °C.

materials either have complex structures or require laborious fabrication conditions.⁸⁻¹⁰ For example, high performance Bidoped PbSeTe/PbTe nanostructured materials are grown by molecular beam epitaxy⁹ whereas BiSbTe alloys are fabricated by melt spinning and a spark plasma sintering process.¹¹ The brittle nature and inherent toxicity of some materials may also limit their potential applications or large-scale fabrication. Organic polymer based thermoelectric materials have the advantage of easier fabrication using wet chemistry methods. However, they generally exhibit a low thermoelectric stability and efficiency (the highest *zT* value to date is ~0.42).¹²⁻¹⁶

The practical application of a material for thermoelectric current generation or cooling depends on its power factor (PF = $S^2\sigma$). The electron thermal diffusion rate is directly related to the electrical conductivity of a given material and is also crucial to the Seebeck coefficient. Hybrid thermoelectric materials could potentially show high values by having the advantages of both inorganic and organic components. Inspired by the design principle of "electron crystal and phonon glass",^{10,17} chemical modification and physical processes have been developed to prepare optimized and ecofriendly hybrid thermoelectric materials. Inorganic–organic hybridization, doping, nanocompositing and electrochemical deposition are recently developed fabrication methods for these composites.^{18–23}

Coordination compounds can exhibit fascinating topologies and polymorphism, with potential applications as porous, luminescent, electrical, magnetic or catalytic materials.^{24–29} They can be discrete small molecules, clusters, 1D chains, 2D

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layers, 3D frameworks or metal-organic frameworks (MOFs) depending on the type of ligand and metal centre. Synthetic conditions such as temperature, solvent, metal-ligand ratio etc. will also influence the product outcome. Recently, coordination compounds have been used as precursors for the preparation of nano- and composite materials for energy applications.³⁰⁻³³ In the quest for high performance supercapacitance, nitrogen-doped carbon/graphene has been fabricated from pyrolysis of a composite of graphene oxide and a nitrogen-ligand supported coordination polymer.³¹ Similarly, single-atom iron implanted N-doped porous carbon for efficient oxygen reduction catalysis has been prepared directly from Fe-porphyrin based MOFs.³² Pyrolysis of a Cu-based MOF has been used to fabricate a hollow CuO/C electrode material for lithium-ion batteries.33 Lanthanide dithiocarbamate complexes have also been used as pyrolytic precursors to form rare earth sulfides, which are potential n-type thermoelectric materials.34,35

Copper iodide (CuI) is an eco-friendly thermoelectric material possessing p-type semiconductivity with a broad band gap (~3.1 eV), high Earth abundance and relatively low toxicity.³⁶ A transparent thin film of CuI with room temperature *zT* value of 0.21 has been reported^{37,38} and a transparent thermoelectric module has recently been fabricated.³⁹ CuI has also been used as a dopant in polycrystalline $In_4Se_{3-\delta}(CuI)_x$ to improve the thermoelectric performance.⁴⁰ We have reported the synthesis of a robust and thermally stable thermoelectric CuI/C composite with a relatively high Seebeck coefficient value (~900 μ V K⁻¹ at 204 °C) prepared by pyrolysis of a well-defined 2D coordination polymer.⁴¹

In the current work, we have extended this study to other CuI-based coordination polymer precursors. We were interested in using two coordination polymers ($[Cu_6I_6(L1)_3]_n$ (I) and $[Cu_4I_4(L2)_2]_n$ (II)) to compare the effects of using a rigid dithioether spacer (L1) *versus* a flexible counterpart (L2), 3D

versus 2D polymeric structures, and hexagon prismatic $[Cu_6I_6]$ *versus* cubane $[Cu_4I_4]$ CuI-secondary building units (SBUs) (Scheme 1). They can be prepared easily in high yields (76 and 72%, respectively).⁴²

The synthesis of these coordination polymers followed a literature procedure. Typically, a mixture of ligand L1 and CuI (1:2 molar ratio) in acetonitrile was stirred for 30 min. The white precipitate was collected by vacuum filtration and washed with acetonitrile, ethanol and diethyl ether and dried at 60 °C. Microanalytical data of the powder sample matched well with the calculated formula of **I**. However, the powder XRD pattern (Fig. 1, **I**E) of bulk materials did not match the calculated pattern (Fig. 1, **I**T) based on the published single-crystal structure (173 K) of **I** (Fig. 1). The synthesis was



Fig. 1 Powder X-ray diffraction (XRD) patterns of I, II and 1 (T = theoretical profile referenced to the experimentally determined single-crystal XRD pattern; E = experimental data).



Scheme 1 Overview of this work including the formation of coordination polymers I, 1 and II from ligands L1 and L2 and Cul; the formation of composites 2 and 3 by pyrolysis with sample images; thermoelectric performance evaluation of composite 2.

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repeated with a reproducible powder XRD pattern (Fig. 1, 1E). This pointed to a different solid-state structure of the material that was prepared in our laboratory. We proceeded to grow single crystals of the coordination complex from CuI and ligand L1 to study the structure of the product. Colourless crystals were obtained from slow evaporation of a sample solution over a week at room temperature (Fig. 2). These singlecrystals were air stable and their X-ray diffraction data were collected at r.t. and refined. This study revealed a new 3-D coordination polymer $[Cu_4I_4(L1)_2]_n$ (1).⁴³ Its powder XRD patterns simulated from the single-crystal XRD data matched well with the powder XRD patterns of the bulk sample seen earlier (Fig. 1, 1T and 1E). The X-ray diffraction pattern of the same single crystal of 1 was measured at 173 K and gave similar unit cell parameters, thus suggesting no structural transformation. These results mean that the coordination polymer 1 does not undergo any solid-state phase transition between room temperature and 173 K. This structural analysis of 1 revealed that it is a new 3-D coordination polymer with an infinite 1-D $[CuI]_n$ ladder as the SBUs (Scheme 1). The spacer serves as a bridging ligand using its two sulfur donors. It is a polymorph of the previously reported compound I, which composes hexagonal [Cu₆I₆] SBUs. This form of polymorphic variation is fairly common in coordination polymers, and sometimes with unpredictable outcomes.44,45 The room temperature powder XRD pattern of a bulk sample of II obtained from ligand L2 and CuI matched well with its simulated powder XRD pattern from the single crystal structure data collected at 173 K (Fig. 1, IIT,E). We herein report the isolation and characterization of this new coordination polymer 1 and the pyrolysis of 1 and II to generate CuI/C composites with quite different properties.

Results and discussion

Ligands L1, L2 and compound **II** were synthesized using literature procedures for thioether formation^{42,46} (ESI[†]). Complex **1** was produced on a gram scale in reasonable yield (72%) using ligand L1 with CuI in a 1:2 molar ratio in acetonitrile. The infrared spectra of **1** revealed strong vibration peaks at 735 and 686 cm⁻¹, which correspond to C–S stretching. The room temperature spectrum of **1** at an excitation wavelength of 405 nm revealed broad luminescence at ~587 nm and ~633 nm with the latter as maxima (Fig. S1, ESI[†]). The highenergy peak at ~587 nm became dominant as the temperature reached 120 K and below (Fig. S1, ESI[†]).

Room-temperature, single-crystal X-ray diffractometry revealed that 1 crystallized in the triclinic centrosymmetric space group $P\bar{1}$ with two Cu(I) centres in the asymmetric unit (Fig. 2). The cell volume was 928.7 Å³ at 173 K and no phase transition with temperature was observed. Complex 1 is a neutral three-dimensional coordination polymer incorporating infinite $[CuI]_n$ staircases along the *a* direction (Fig. 2). Each $[CuI]_n$ ladder is linked to four neighbouring ladders through bridging ligand L1 using the two thioether sulfur (S-S) donors (Scheme 1, Fig. 2). The coordination polymers 1 and I are polymorphs with different crystalline space groups ($P\bar{1}$ and $R\bar{3}$) and secondary building units ($[CuI]_n$ staircase in 1 and $[Cu_6I_6]$ cluster in I). The Cu-S bond lengths in 1 are 2.34 and 2.36 Å, which are similar to 2.37 Å recorded in I. There is no chemical interaction between the copper centers and the triple bond (C≡C) of L1. The neighboring Cu…Cu separations within each $[CuI]_n$ staircase are 2.70, 3.14 and 2.78 Å. The Cu···Cu distance from the neighboring $[CuI]_n$ staircases separated by ligand L1 is about 10.4 Å.

Thermogravimetric analysis (TGA) of **1** was conducted from room temperature to 900 °C under air and nitrogen flows with a heating rate of 30 °C per min (Fig. 3). Coordination polymer **1** was stable up to about 180 °C in both air and nitrogen. The first weight loss stages between 180–565 °C (in air) and 180–615 °C (in N₂) correspond to the loss of ligand L1. Compound **1** then loses iodide at higher temperature and probably converts to CuO in air and remains as metallic



Fig. 2 (a) Molecular structure of 1. (b) Single-crystal of 1 with orientation directions. (c) Three-dimensional structure of 1.



Fig. 3 Thermal stability of coordination polymer 1 in both air and nitrogen gas flows.

(a)

copper in nitrogen. Guided by its TGA data, a white powder sample of 1 was thermally treated at 400 °C for 1 h in a box furnace under a nitrogen flow. The pyrolysis gave black composite 2 containing 10.17 wt% of carbon, and no sulfur (microanalysis). The pyrolysis of coordination polymer II using the same conditions as for 1 afforded pale composite 3 with only a trace amount of carbon (0.05 wt%). The density of a pellet of sample 2 formed under 10 bar pressure was 3.58 g cm^{-3} , which is slightly lower than a CuI/C composite (4.24 g cm^{-3}) with about 4.25 wt% of carbon recently fabricated by us from a 2-D coordination polymer.⁴¹ The pellet of composite 3 formed under the same pressure disassembled easily, which is similar to that of pure copper iodide.⁴¹ These results indicate that the residue (mainly carbon) may act as a binder and that the amount of binder may be crucial to stabilizing the pellet. Both composites 2 and 3 exhibited dominant CuI X-ray diffraction peaks, which are consistent with the standard pattern for

cubic phase CuI (PDF No. 00-006-0246) (Fig. 4a). No carbon diffraction peaks were detected in composite 2 which has a high amount (~10 wt%) of carbon, indicating the amorphous nature of this carbon. The thermal stabilities of composites 2, 3 and pure CuI were evaluated in a flow of N_2 . Composites 2 and 3 were less thermally stable than the control sample CuI, and composite 2 was less stable than 3 (Fig. S2, ESI[†]). The higher weight percentage of carbon in 2 was also reflected in the reduced density of a pellet formed at 10 bar. This pellet was robust, compared to the corresponding pellet of 3 which easily disassembled during handling and no further characterization was conducted. Composite 2 was conductive and reflectance UV-vis spectroscopy revealed a moderate band gap energy (2.93 eV) (Fig. 4b), calculated using the cut-off wavelength. This value indicated that composite 2 is a semiconductor and within the band gap range reported for CuI based materials.36



Fig. 4 (a) Powder XRD patterns of composites 2 and 3. (b) UV-vis reflectance spectroscopy of composite 2.



Fig. 5 Low-magnification field emission scanning electron microscopy (FESEM) images of composite 2 (a, b). Elemental mapping of iodine and copper in composite 2 (c-e).

The low-magnification scanning electron microscopy images of 2 revealed crystalline nano-/micro-sized particles (Fig. 5a and b). Elemental mapping indicated dominant iodide and copper in the composite (Fig. 5c–e). X-ray photoelectron spectroscopy (XPS) confirmed the presence of C, Cu and I (Fig. 6). A high-resolution Cu 2p spectrum (Fig. 6a) shows two relatively strong peaks centred at 932.6 and 952.5 eV corresponding to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively. Similarly, the I 3d spectrum (Fig. 6b) contained two peaks centred at 619.8 and 631.5 eV, which correspond to I $3d_{5/2}$ and I $3d_{3/2}$, respectively. These values are consistent with the binding energies of CuI nanoparticles and composite materials.^{47–49}

A pressed pellet sample of composite 2 was evaluated for its electrical conductivity and Seebeck coefficient using a ZEM3 system. Six cycle measurement experiments were conducted for stability and reproducibility (Fig. 7). Each cycle included eight relative high temperature points (75, 100, 125, 150, 175, 200, 225 and 250 °C) together with four temperature gradients (5, 10, 15 and 20 °C). The thermoelectric behaviour in the first cycle was quite different from that observed in the 2nd to 6th cycles. We observed a similar pattern in our previous study and regard the first cycle as sample optimization. Overall, the electrical conductivity values were low and increased with temperature over a very narrow range (0.000045-0.00035 S cm⁻¹) from 70 to 240 °C during the 2nd and 6th cycles (Fig. 7a). Likewise, the Seebeck coefficients values between 70 and 240 °C were constant in a relatively narrow range (543-1308 $\mu V K^{-1}$). The highest Seebeck coefficient (1308 $\mu V K^{-1}$) was observed at 94 °C from the 6th cycle (Fig. 7b). The power factor





Fig. 7 Temperature-dependent thermoelectric properties of composite 2 evaluated using six-cycle measurements: (a) electrical conductivity, (b) Seebeck coefficient, and (c) power factor.

was calculated from the equation PF = $S^2 \sigma$ over the temperature range 70 to 240 °C and found to be in a relatively narrow range (0.006–0.03 μ W m⁻¹ K⁻²) (Fig. 7c).

There are few CuI-based thermoelectric materials reported in the literature, despite the potential advantages of this substance. Molten CuI demonstrates constant electrical conductivity (~1 S cm⁻¹) and high Seebeck coefficients (620–890 μ V K⁻¹) over the range ~900–1150 K.⁵⁰ Transparent CuI thin films exhibit good electrical conductivity (283 S cm⁻¹) with a moderate room temperature Seebeck coefficient value (~237 μ V K⁻¹).^{37–39} Moreover, CuI has also been doped into Se vacancies of polycrystalline In₄Se_{3– δ}(CuI)_x to improve its electrical conductivity.^{40,51} Although our CuI-based composites obtained from coordination polymers demonstrated relatively low electrical conductivity due to the high proportion of amorphous carbon,⁴¹ they have relatively high Seebeck coefficient values (>1300 μ V K⁻¹) over a moderate temperature range. Moreover, this coordination polymer precursor approach offers the possibility of tuning the carbon concentration of the thermoelectric composites formed under relatively mild conditions.

The pellet of composite 2 was robust during the multicycle measurements, whereas composite 3 obtained from the 2D coordination polymer II readily disassembled. By comparison, pyrolysis of a 2D coordination polymer [Cu₄I₄(L3)₂]_n formed from a flexible SNS ligand (L3 = bis(2-(cyclohexylthio)ethyl) amine) and CuI afforded a robust composite pellet with 4 wt% of carbon.⁴¹ Of the various structural parameters, including the ligand, CuI SBU motif and dimensionality (0-3D), the ligand could play the most important role in controlling the nature of the resulting composite. We have extensively studied and reported the use of chemically related spacers and metals to generate structurally distinctive soft materials, mainly coordination oligomers and polymers.44,45,52-54 Carbon species have previously been used for tuning the thermoelectric performance of core-shell C@PbTe. The amorphous carbon sphere was reported to enhance the thermoelectric performance.55 A reduced Seebeck coefficient was previously observed for carbon nanotubes and amorphous carbon doped Bi₂Te₃ composites. By comparison, amorphous carbon can have a positive influence on p-type materials.⁵⁶

Conclusions

We have produced gram-scale quantities of air stable and triclinic 3D coordination polymer 1 possessing a $[CuI]_n$ staircase structure. Complex 1 is a polymorph of known 3D coordination polymer I that crystallises in the highly-symmetric space group $R\bar{3}$ and contains $[Cu_6I_6]$ SBUs. Complex 1 does not undergo a solid-state phase transition at low temperature (173 K). The thermogravimetric analysis of 1 indicated a relatively broad ligand decomposition temperature range (180-615 °C) under nitrogen. The direct pyrolysis of 1 at a moderate temperature (400 °C) gave a robust, semi-conductive, thermoelectric composite 2 with a relatively high Seebeck coefficient. This work bridges the fields of coordination polymer self-assembly, polymorphism and the application of well-defined coordination polymer precursors to the synthesis of thermoelectric composite materials. The different behaviour of composites derived from different coordination compound precursors indicates that ligand composition significantly influences the nature of the resulting CuI-based composite.

Conflicts of interest

There are no conflicts of interest to declare.

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