PRF# 56184-DNI10

Project Title: Experimental Realization of Organic Topological Insulators

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The thermoelectric properties of two-dimensional metal-organic frameworks belonging to the class of predicted organic topological insulators were studied during the reported time period of the project. A manuscript "Intrinsic and Extrinsic Thermoelectric Properties of Electrically Conductive, Polycrystalline Two-Dimensional Metal-Organic Frameworks" reporting these results is under preparation to be submitted for publication and one graduate student has been supported for a large fraction of the year working on this project toward her PhD (other graduate students were supported in for small fractions of time in support of this work).

Two-dimensional (2D) metal-organic frameworks (MOFs) – hybrid organic-inorganic materials with a 2D crystalline lattice of metal ions and coordinating organic ligands – are versatile new materials for designing properties such as metallic, semiconducting, magnetic and topological insulating behaviors with appropriate choice of metals and organic ligands. Previously, a 2D MOF nickel-benzenehexathiol (Ni-BHT)[1] had been predicted[2] to exhibit topological insulating properties, in that the bulk of the 2D MOF was predicted to host an inverted band gap while the edges of the sample are conducting. Prior to the start of this project, we had realized for the first time 2D MOFs made with a new organic ligand hexaaminobenzene (HAB) and studied the electrical conducting properties of a material Ni-HAB, which was also supposed to host the same topological properties. However, we found that Ni-HAB was a poor electrical conductor, as seen from the large (MΩ-GΩ) resistance of devices measured with this material[3].

The focus of this project has been specifically on the metal-benzenehexathiol (M-BHT) family of materials, with the bis(dithiolene) ligand coordinated with different metal ligands. At the beginning of this work, our chemist collaborator tried to reproduce the synthesis of ref. 1, but this was challenging due to problems of yield in the synthesis. As a result, we synthesized another compound of the same family namely Cu-BHT. At the time, Cu-BHT had been reported[4] by a group at the Chinese Academy of Science to have high electrical conductivity numbers in the 1000 S/cm range. We found that our samples as synthesized also yielded conductivity numbers in the same ballpark but more importantly, they showed a metallic temperature dependence (Fig. 1) in contrast to the results of ref. 4 which showed a decrease in conductivity with decreasing temperature. Buoyed with this result, we decided to take advantage of the strong metallicity of the samples in exploring a property of 2D MOFs which is strongly influenced by metallicity but has not been explored sufficiently, namely thermoelectricity. This property has major implications for thermoelectric energy conversion of waste heat into electricity. The energy conversion efficiency is related to $ZT = S^2\sigma T/\kappa$ (T: temperature, S: Seebeck coefficient, σ: electrical conductivity, κ: thermal conductivity) and can be improved by increasing S and σ, and decreasing κ. In general, organic materials are electrically insulating, resulting in a small power factor ($S^2\sigma$). However, Cu-BHT with its large conductivities σ (comparable to some of the best conductive organic polymers e.g. PEDOT), offered a unique opportunity as an organic thermoelectric (which are preferable to inorganic thermoelectrics due to the lower toxicity and manufacturing/processing costs of organics, among other factors). Furthermore, MOFs have large pores in their unit cells (which have previously found application in gas storage, gas separation and catalysis) which may offer a route to low thermal conductivity κ values[5], making them ideal for thermoelectric applications. However, the thermoelectric properties of Cu-BHT have not been studied and formed the focus of the rest of the reported time period.

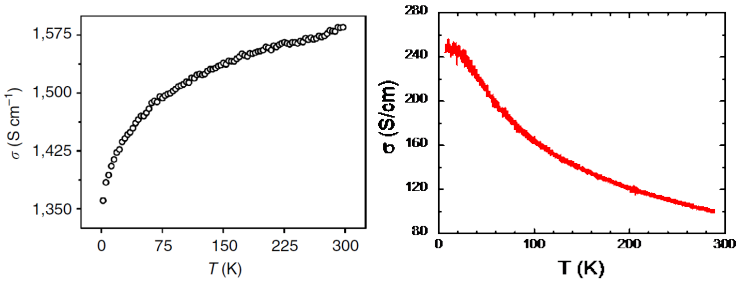

Figure 1. Temperature dependence of electrical conductivity of Cu-BHT as reported in ref. 4 (left) and in our sample (right, unpublished data). The increasing conductivity with decreasing temperature seen in our data (right) is a strong indicator of metallicity of our sample.

Cu-BHT was synthesized using a liquid-liquid interfacial synthesis as described by ref. 4. X-ray Photoelectron Spectroscopy (XPS) was used to characterize the material, which revealed the presence of copper, sulfur and carbon

as the only elements present. A hexagonal crystal structure was confirmed using Selected-Area Electron Diffraction (SAED), revealing a lattice constant of 0.76 nm (Figure 2), consistent with previously reported values. The Cu-BHT film was transferred onto PDMS stamps and exfoliated into thinner films to be transferred onto target substrates. The thickness of exfoliated films varied from 30 nm to 400 nm. We separately fabricated devices for thermal conductivity, electrical conductivity, and Seebeck effect. The electrical conductivity of our samples ranged from ~5 to 2000 S/cm at room temperature, depending on the synthesis batch, but largest values were consistent with previously reported value for Cu-BHT.

Thermal conductivity was measured in a suspended device configuration as shown in Figure 3a. Cu-BHT was transferred onto an undoped silicon substrate after exfoliation, followed by patterning electrodes with electron beam lithography and deposition of Cr/Cu. Then the silicon underneath was dry-etched with XeF_2 gas, resulting in a suspended Cu-BHT device. We adopted the scheme of thermal conductivity measurement used previously for graphene. The thermal conductivity of Cu-BHT was calculated using the simple definition, $\kappa \equiv (Q/\Delta T)\cdot(l/wd)$, where l is sample length and w is width. The heat transported through Cu-BHT, Q, was measured by applying a temperature gradient ΔT using the metal heater and measuring voltage drop across sensor leads. Figure 3b shows the temperature dependence of in-plane κ of Cu-BHT. The low values of thermal conductivity obtained are promising for application in thermoelectrics. Future work consists of measurement of Seebeck coefficient, its temperature dependence and estimation of thermoelectric figure of merit ZT. Further, temperature dependence data such as obtained in this project is also extremely helpful in proposing mechanisms of electrical, thermal and thermoelectric transports and is the focus of our manuscript under preparation. Finally, 2D MOFs apart from Cu-BHT will be synthesized and studied which may host topological properties.

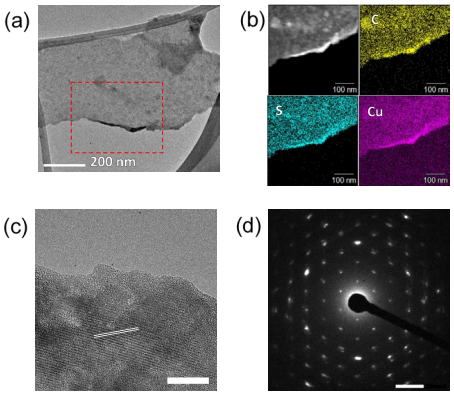

Figure 2. TEM images of Cu-BHT: (a) TEM image of a Cu-BHT flake. (b) STEM-DF image of Cu-BHT in the region indicated by the red dashed line box in (a), and its mapping of carbon, sulfur and copper elemental distributions using STEM-EDS. (c) HR-TEM image showing a Cu-BHT lattice with a lattice spacing of 0.76 nm. Scale bar: 20 nm. (d) Selected Area Diffraction (SAED) image highlighting the hexagonal lattice structure of the material. Scale bar: 2 nm^{-1}.

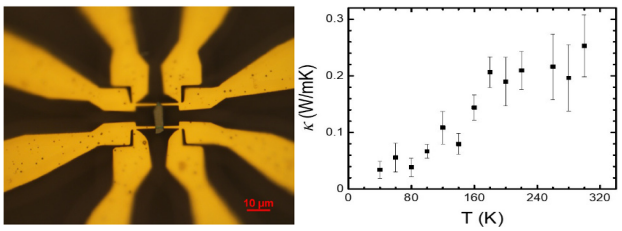

Figure 3. Thermal conductivity measurement of Cu-BHT. (a) An optical image of a device for the thermal conductivity measurement. The heater/sensor leads are connected to the large metal pads to measure the change in the resistance in four-terminal configuration. Cu-BHT sample is suspended between these leads. Scale bar: 10 µm. (b) Measured thermal conductivity of Cu-BHT as a function of temperature.

As a result of this work, we have made our first foray into a new area of research for the group viz. organic thermoelectrics. 2D MOFs seem to be well-suited for this application and this is likely to provide valuable experience in applied research & publications for the students involved in the project and new opportunities of funding for the PI.

[1] Kambe, T. *et al.* π-Conjugated Nickel Bis(dithiolene) Complex Nanosheet. *J. Am. Chem. Soc.* **135**, 2462–2465 (2013).

[2] Wang, Z. F., Su, N. & Liu, F. Prediction of a Two-Dimensional Organic Topological Insulator. *Nano Lett.* **13**, 2842–2845 (2013).

[3] Lahiri, N., Lotfizadeh, N., Tsuchikawa, R., Deshpande, V. V. & Louie, J. Hexaaminobenzene as a building block for a Family of 2D Coordination Polymers. *J. Am. Chem. Soc.* **139**, 19–22 (2017).

[4] Huang, X. *et al.* A two-dimensional *π–d* conjugated coordination polymer with extremely high electrical conductivity and ambipolar transport behaviour. *Nature Communications* **6**, 7408 (2015).

[5] Sun, L. *et al.* A Microporous and Naturally Nanostructured Thermoelectric Metal-Organic Framework with Ultralow Thermal Conductivity. *Joule* **1**, 168–177 (2017).