MS34-P03

Pressure-induced metal-metal bond formation and HOMO-LUMO inversion in a single component Pt-based molecular crystal

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The discovery of the first organic metal based on tetrathiafulvalene (TTF) in the 1970's resulted in an explosion of interest in the exotic electronic properties of molecular materials.[1] In these charge transfer salts, electronic properties are governed by the interactions between frontier molecular orbitals (HOMO and LUMO interactions), which control the band gap and charge carrier generation. Design of single-component molecular conductors is difficult, however, because the HOMO-based and LUMO-based bands tend to be well-separated from each other, leading to insulating behaviour. We and others have found that application of pressure can be a useful tool with which to alter the HOMO-LUMO overlap and broadening of the bands, resulting in metallic[2] or even superconducting behaviour.[3]

We report a combined experimental and computational study of the single component molecular crystal $[Pt(dddt)_2]$ (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate), which undergoes a remarkable first-order single-crystal to single-crystal transition under pressure. X-ray diffraction measurements show that the ambient pressure offset-dimer structure converts to a face-to-face dimer above 5 GPa, accompanied by a dramatic reversal in the lengths of the crystal *b*- and *c*-axes. First principal electronic structure calculations show that the change in dimer geometry causes an inversion of the energies of the HOMO and LUMO bands. This enables the formation of a rare unsupported Pt-Pt bond that drives the transition and gives rise to metallic conductivity at pressures above 10 GPa.

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Keywords: High pressure, Molecular metal, Phase transition

MS35- From 0- to 3-dimensional porous systems

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MS35-P01

Negative compressibility of a metal-organic framework?

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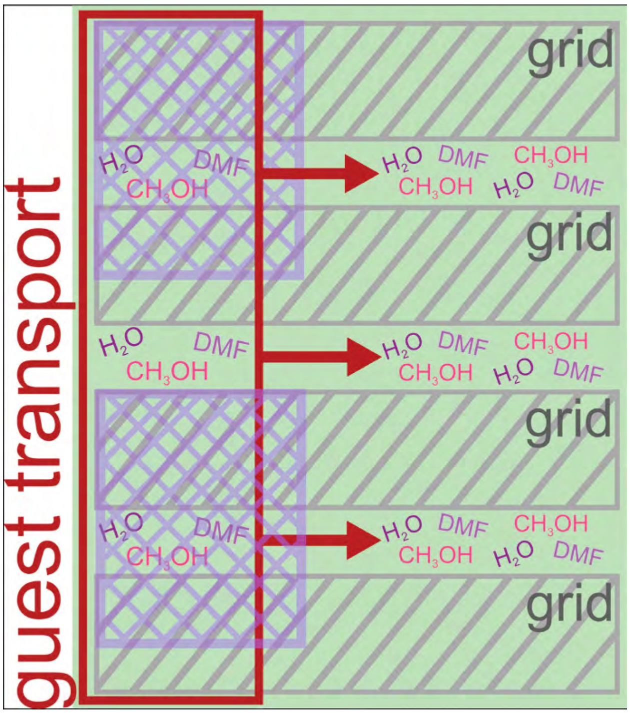
Fundamental thermodynamics requires that all materials reduce their volume at high pressure. Owing to specific anisotropic features, originating from various structural motifs, some compounds can elongate in one or two directions, which is termed as negative linear and area compressibility.[1] The volume compression restriction applies to constant composition materials (*i.e.* closed systems). It was evidenced that zeolites and other porous materials can uptake the guest molecules from gaseous and liquid surrounding, which can increase the crystal volume despite the increasing pressure.[2] These are so called open systems. In those high-pressure experiments, various simple molecular fluids (water, methanol, ethanol, *etc.*) and their mixtures were used. The transport of guest molecules can be eliminated by compressing the sample in liquids composed of molecules much larger than the dimensions of pores, for example in oils.

We have performed a series of such experiments for a newly synthesized 2D metal-organic framework $Ni(hip)(bipy)(H_2O)_2 \cdot H_2O \cdot CH_3OH \cdot DMF$, denoted as AMU-2 (where AMU abbreviates Adam Mickiewicz University). Its flexible structure is built of 4,4'-bipyridines (bipy) and 5-hydroxyisophthalic acid anions (hip) into grids further connected by H-bonds. The compression of AMU-2 revealed its unprecedented elastic and sorption-elastic properties. Hydrostatic compression performed in three different large-molecule liquids (oils Daphne 7373 and NVH or Fluorinert FC-77) result in a significant volume expansion of about 120 Å^3 at 0.2 GPa. This counterintuitive effect mimicking the negative volume compression was observed by X-ray diffraction for several samples. We have shown that this porous material, when compressed in oils, partially collapses and becomes amorphous, which triggers a transport of guest molecules present in the pores to the crystalline parts of the sample. This mechanism of transport of gests induced be external stimulus of pressure has been described as a 'zone-collapse' effect.[3]



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Keywords: metal-organic framework, high-pressure, volume compression, amorphization

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MS35-P02

A novel bismuth-containing metal-organic framework: the first example of a flexible bismuth MOF

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Despite the large number of published metal-organic frameworks (MOFs), only a handful of microporous structures which contain bismuth have been published so far [1, 2]. Unlike coordination polymers synthesized from other metal cations, bismuth cations have rather high coordination numbers and unusual coordination geometries, leading to highly unpredictable and unique structures. Additionally, bismuth is interesting for potential pharmaceutical applications as it has been shown to be biologically active and potentially a future aid in relieving problems with multi-resistant bacterial strains [3].

In order to achieve a better understanding of the chemistry of bismuth in inorganic-organic hybrid structures, four new bismuth-containing structures have been synthesized. The reagents used where bismuth and a tritopic organic linker. One of the acquired phases proved to be a porous metal-organic framework, which undergoes reversible structural changes upon activation of the framework, thus being the first example of a flexible bismuth MOF. The structures were solved using single crystal X-ray diffraction (SCXRD), X-ray powder diffraction (XRPD) and continuous rotation electron diffraction (ED). Continuous rotation ED may greatly aid in the characterization of microcrystalline materials, which are often acquired when synthesizing bismuth-containing compounds. The structural changes occurring have been inferred from Rietveld refinement against XRPD data and will be discussed extensively.

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Keywords: metal-organic frameworks, Rietveld refinement, hydrothermal synthesis