

MS34-P03**Pressure-induced metal-metal bond formation and HOMO-LUMO inversion in a single component Pt-based molecular crystal**

Hamish Yeung¹, Chloe Coates¹, Andrew Goodwin¹, Hengbo Cui², Reizo Kato², Takao Tsumuraya³, Mark Warren⁴, David Allan⁴, Dominik Daisenberger⁴

1. Inorganic Chemistry Laboratory, University of Oxford, Oxford, United Kingdom
2. Condensed Molecular Materials Laboratory, Riken, Wako-shi, Japan
3. Magnesium Research Center, Kumamoto University, Kumamoto, Japan
4. Diamond Light Source Ltd, Harwell Science and Innovation Campus, Didcot, United Kingdom

email: hamish.yeung@chem.ox.ac.uk

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.

References:

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MS35- From 0- to 3-dimensional porous systems

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MS35-P01**Negative compressibility of a metal-organic framework?**

Szymon Sobczak¹, Andrzej Katrusiak¹

1. Department of Materials Chemistry, Adam Mickiewicz University, Poznań, Poland

email: szymon.sobczak@amu.edu.pl

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)(H₂O)₂ · H₂O · CH₃OH · 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 Å³ 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 guests induced by external stimulus of pressure has been described as a 'zone-collapse' effect.³