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

Authors:
Hamish Yeung, Chloe Coates, Andrew Goodwin (Oxford University)
Hengbo Cui, Reizo Kato (RIKEN)
Takao Tsumuraya (Kumamoto University)
Mark Warren, David Allen, Dominik Daisenberger (Diamond Light Source)

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:

