Chemical modification and pressure effect of small-sized single-component molecular conductors

H. B. Cui a *, T. Tsumuraya b, H. Yeung c, C. Coates c, and R. Kato a

a Condensed Molecular Materials Laboratory RIKEN, 2-1 Hirosawa, Wako-shi, Saitama, 351-0198, Japan

b Priority Organization for Innovation and Excellence (POIE), Kumamoto University, 2-39-1, Kurokami, Chuoku, Kumamoto, 860-8555, Japan

c Inorganic Chemistry Oxford University, South Parks Road, Oxford OX1 3QR, UK.

hcui@riken.jp

In the development of single-component molecular conductors, metal dithiolene complexes, with a small energy gap between HOMO and LUMO, have formed an important category.1,2 Among them, due to the simple synthesis and easiness to obtain large single crystals, small-sized metal dithiolene complexes have attracted considerable attention. At ambient pressure, they are semiconducting or insulating. We modified the four-probe resistivity measurement technique by using a Diamond Anvil Cell (DAC), and successfully found that the single-component molecular crystal \([\text{Ni}(\text{dmit})_2]\) (dmit = 1,3-dithiole-2-thione-4,5-dithiolate) turns metallic at 15.9 GPa.3

We also found that the single-component molecular crystal \([\text{Pd}(\text{dddt})_2]\) (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate) exhibits temperature-independent resistivity at 12.6 GPa. The density functional theory (DFT) calculations indicate that Dirac cones emerge in \([\text{Pd}(\text{dddt})_2]\) under high pressure.4 To understand the central metal and ligand effect on properties of \([\text{M}(\text{dddt})_2]\), we synthesized \([\text{M}(\text{dddt})_2]\) (M = Ni, Au, Pt) and \([\text{Ni}(\text{ddds})_2]\) (ddds = 5,6-dihydro-1,4-dithiin-2,3-diselenolate), \([\text{Ni}(\text{edo})_2]\) (edo = 5,6-dihydro-1,4-dioxine-2,3-dithiolate), and \([\text{Ni}(\text{ddt})_2]\) (ddt = 1,4-dithiiin-2,3-dithiolato). High-pressure transport measurements, crystal structure analyses, and theoretical calculations were also performed.


Figure 1 Molecular structures