

Structural and Physical Properties of Molecular Conductors Derived from Bis(methylthio)-Substituted π -Electron Donors

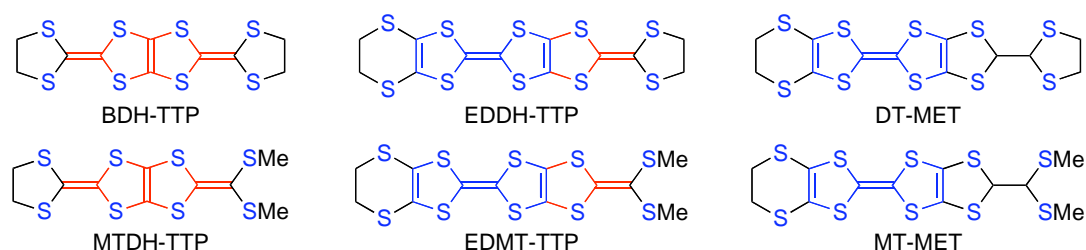
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Control of the electron correlation (U/W , U , the on-site Coulomb repulsion, W , the bandwidth) in molecular conductors is essential to the occurrence of various phase transitions such as MI (metal–insulator) transitions and superconducting transitions. We have been investigating chemical modifications to π -electron donors capable of generating a stable metallic state with the aim of increasing the electron correlation. For instance, we have found that the π -donor BDH-TTP forms many metallic salts stable to low temperatures ($> ca. 2$ K) [1], whereas MTDH-TTP, in which the outer dithiolane ring of BDH-TTP is replaced with two methylthio groups, gives semiconducting salts with activation energies ranging from 22 to 114 meV, a metallic salt with an MM (metal–metal) transition, and a stable metallic salt with a slight resistance upturn around 12 K. This chemical modification to BDH-TTP is thought to lead to an increase in structural flexibility (or a diversity in conformations) because the two methylthio groups of MTDH-TTP can be spatially situated in various positions. Meanwhile, we have found that metallic salts are obtainable from EDDH-TTP and DT-MET [1]. Our next attention was thus focused on bis(methylthio)-substituted analogs of EDDH-TTP and DT-MET, that is, EDMT-TTP and MT-MET. In this paper, we report on the synthesis, electrochemical properties, and molecular structures of EDMT-TTP and MT-MET, and also on the crystal structures and conductivity of their salts.



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[1] J. Yamada *et al.*, *Chem. Rev.*, 104, 5057–5083 (2004).