Poster Presentation

MS83.P39

Semiconductors and Aperiodic Structures in Organocyanide-Based Materials

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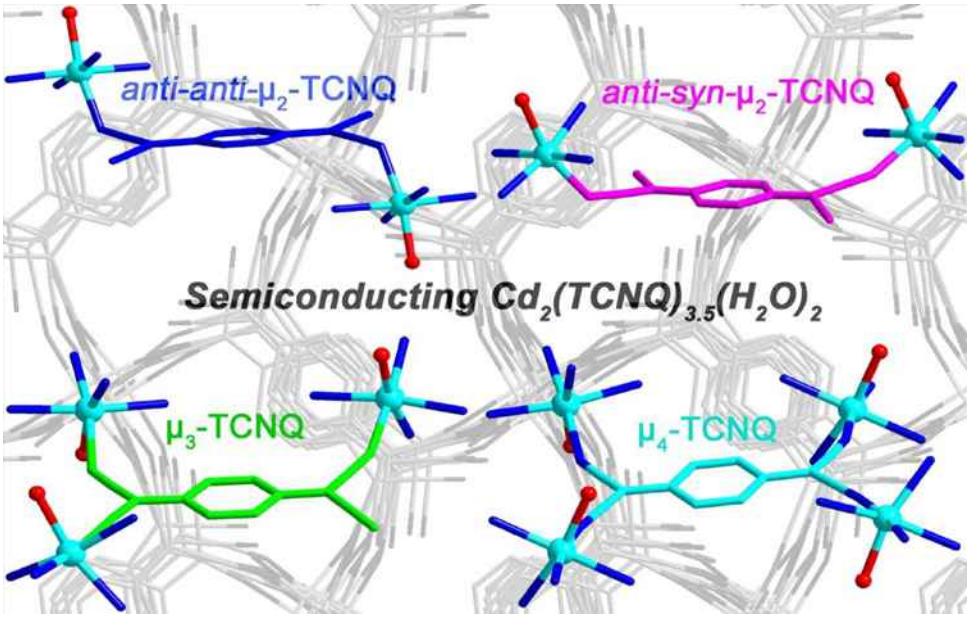
Organocyanides such as TCNQ (tetracyanoquinodimethane) and DCNQI (dicyanoquinodiimine) are excellent electron acceptors and have been extensively studied in electrically conducting/switching and magnetic materials. Supramolecular interactions such as π-stacking and hydrogen bonding in addition to coordination bonds with metal ions play an important role in the self-assembly of these functional inorganic materials. A novel semiconductor Cd2(TCNQ)3.5(H2O)2 with non-integer valences of TCNQ was synthesized and is the first example that exhibits four bridging modes of TCNQ in one structure (Figure 1). Despite the rather large stacking distance of 3.687(1) Å between the two μ3-TCNQ species, which constitute a "broken link" in the electron conducting pathway, the semiconductor exhibits a room temperature conductivity of 5.8×10-3 S·cm-1. The hydrogen bonding interactions between the coordinated water molecules and nitrogen atoms of the mu2- and mu3-TCNQ help to stabilize these coordinatively unsaturated TCNQ species. Another application of the chemistry of organocyanides in the context of this research is the study of reactions of the meta-dicyanamidobenzene dianion (DCYD2-) which was predicted by Ruiz and coworkers to facilitate ferromagnetic interactions between certain paramagnetic metal ions. The DCYD2- anion self-assembles with Mn(II) building blocks to afford a rare example of inorganic quadruple helices with an incommensurate modulated structure (Figure 2a). A supercell in the high symmetry space group P4/nnc is obtained with a c parameter five times that of the basic structure and a further 15-fold expansion in the space group of P1 along the c axis reveals that ~2% of Mn positions are disordered. The packing of these helical chains through π-stacking of pyridyl groups leads to 1D nanochannels with an estimated empty volume of 38.6% of the super cell volume (31,587Å3). However, in the presence of water, hydrogen bonding between the water molecules and the cyano-N atoms dominates and only zig-zag chains are formed (Figure 2b).

[1] *Zhang, X.; Zhang, Z.; Zhao, H.; Mao, J. G.; Dunbar, K. R. Chem Commun, 2014, 50, 1429.*



Keywords: Organocyanide, Semiconductor, Aperiodic structure