Molecular-based Antiferromagnetic Conductor: β”-(BEDT-TTF)$_3$[Cu$_2$(μ-C$_2$O$_4$)(C$_2$O$_4$)$_2$(CH$_3$OH)(H$_2$O)]

Bin Zhang[1], Yan Zhang[2], Zheming Wang[3], Takehiko Mori[4], Daoben Zhu[1]

[1] *BNLMS, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, P. R. China.*
[2] *Institute of Condensed Matter, College of Physics, Peking University, Beijing, 100871, China.*
[3] *College of Chemistry, Peking University, Beijing, 100871, P. R. China.*
[4] *Department of Materials Science and Engineering, Tokyo Institute of Technology, O-Okayama, Tokyo 152-8552, Japan*

The organic-inorganic hybrid β”-(BEDT-TTF)$_3$[Cu$_2$(μ-C$_2$O$_4$)(C$_2$O$_4$)$_2$(CH$_3$OH)(H$_2$O)] (BEDT-TTF = bis(ethylenedithio)tetrathia-fulvalene) composed of BEDT-TTF donor and the oxalate-bridged binuclear anion [Cu$_2$(μ-C$_2$O$_4$)(C$_2$O$_4$)$_2$(CH$_3$OH)(H$_2$O)]$^{2-}$ has been obtained by electrocrystallization. It crystallizes in the triclinic $P\bar{1}$ space group with cell parameters of a = 7.4803(3) Å, b = 9.3547(3) Å, c = 18.6711(7) Å, α = 95.797(3)°, β = 90.974(3)°, γ = 93.508(3)°, V = 1297.06(8) Å^3, and Z = 1 at 100 K. The donor arrangement belongs to the β″ phase. From the TTF core bond lengths and Raman spectroscopy, the oxidation state of BEDT-TTF is assigned to ~+2/3. CH$_3$OH or H$_2$O molecules bond to the metal atoms at the apical position of the square pyramid with occupancy of 0.5. A supramolecular square lattice forms through hydrogen bonds between the antiferromagnetically binuclear anions in the anion sheet. From band structure at 100 K, metallic conductivity is expected, which agrees with four-probe conductivity measurement: its conductivity is 11.5 S/cm at room temperature, increases to 160 S/cm at 7.6 K, then decreases to 150 S/cm at 2 K. From magnetic measurement, there is no long-range magnetic ordering, which is confirmed by specific heat measurement.

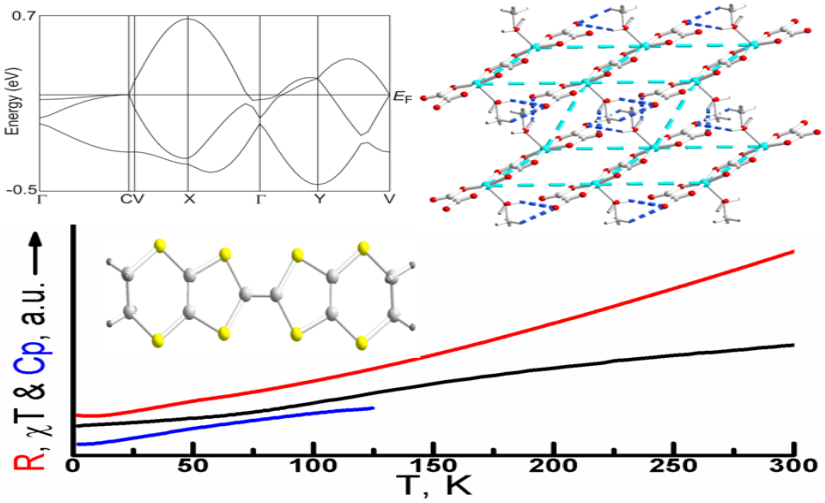

Figure 1. Band structure and anion arrangement in anionic sheet. Temperature-dependent R, χT and Cp.

References

[1] O. Kahn, *Angew. Chem.*, **24**, 834(1985).
[2] J. Cano, P. Alemany, S. Alvarez, M. Verdaguer, E. Ruiz, *Chem. Eur. J.*, **4**, 476(1998).
[3] B. Zhang, Y. Zhang, Z. Wang, D. Wang, D. Yang, Z. Gao, G. Chang, Y. Guo, T. Mori, Z. Zhao, Q. Li, D. Zhu, *J. Mater. Chem. C*, **10**, 2845(2022).

Acknowledgement : This work was supported by NSFC No. 22073106.