## Microsymposium

## Electronically wired polyoxometalate-based networks in the crystalline states

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Polyoxometalates (POMs) are anionic metal oxide molecules with a transition metal such as Mo, W and V. Structural diversities of these cluster family as well as their unique physical and chemical characteristics has been explored and developed for molecular scaled nano-structure and which emergent nanomolecular and supramolecular chemistry are opened by POM-based materials, for example catalysis, complex self-assembly process, molecular scaled electronics/spintronics and life sciences.1-3 Morphology and composition of POMs are controlled uniformly where POMs are given by structurally well-defined inorganic nanostructures. POM clusters are able to employ a stable mixed-valence state between MV and MVI. An electron of this intramolecular charge fluctuation is delocalized over several M sites with low activation energy. This is because of a low ability in inter-cluster interactions that involve electrostatic interaction, hydrogen bond and vdW interaction.

We have been interested in these electronic systems for macroscopic conduction. Electronic conduction through polyoxometalates in the crystalline state has been investigated with several subsets of organic cations. Mixed valence POMs are arrayed with dimers of TTFPyH2+ with alternative packing manner, giving (TTFPyH)2[PMoVMoVI11040]. Even though TTFPyH2+ were isolated by POMs where they did not form conductive columns as is well-seen in TTF-based molecular conductors, conductivity of the single crystals was comparable to that of Si (~106 S/cm). Electron transport characteristics were suggested to represent electron hopping through interactions between cluster and cationic  $\pi$ -molecules.[4] Here, we discuss electron transport properties of the crystalline salt based on POMs through structure of other counter cations.

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Keywords: polyoxometalate