Syntheses and Physical Properties of Robust Porous Molecular Conductors with 1,2,4-Triazole Group

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Molecular conductors with one-dimensional (1D) electron system are very promising as switching materials, because they can change their conducting, magnetic and optical properties by external stimuli such as light, pressure and temperature. However, chemical stimuli such as molecular desorption/adsorption have rarely been applied to these materials, because the dense molecular packing disturbs the response to the chemical stimuli. To solve this problem, we recently proposed porous molecular conductors (PMCs) as the fusion of metal-organic frameworks (MOFs) and molecular conductors. The reported PMCs consist of 1D coordination polymer with π-stacking columns among them.[1,2)] Thus, the framework was fragile and the removal of solvent molecules in the pores gave irreversible structural change.

In this work, we chose *N*,*N'*-bis-(1,2,4-triazolyl)naphthalenediimide (NDI-trz) as the organic linker, because terminal 1,2,4-triazolyl group was used to construct three-dimensional (3D) MOFs compatible with the periodicity of π-stacking array.[3)] The solvothermal reaction with $CdCl_2$ afforded the complicated mixture, whereas we found tiny black single crystals therein. The X-ray structure analysis exhibited that two 3D frameworks were interpenetrated with forming infinite π-stacking columns (Fig. 1). The pure polycrystalline compounds was obtained by electrocrystallization. This PMC was more robust than the previously reported PMCs due to the 3D framework. The electrical conductivity of the single crystal was 2×10^{-4} S cm^{-1} at 300 K. The semiconducting behavior was observed in the temperature-dependence conductivity measurement.

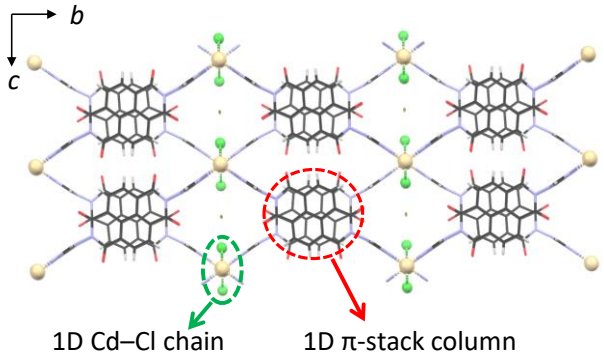

Fig. 1 Crystal structure of the new PMC with interpenetrated 3D frameworks

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