FERROELECTRIC ION CONDUCTORS BASED ON METAL-CYANIDO COMPLEXES

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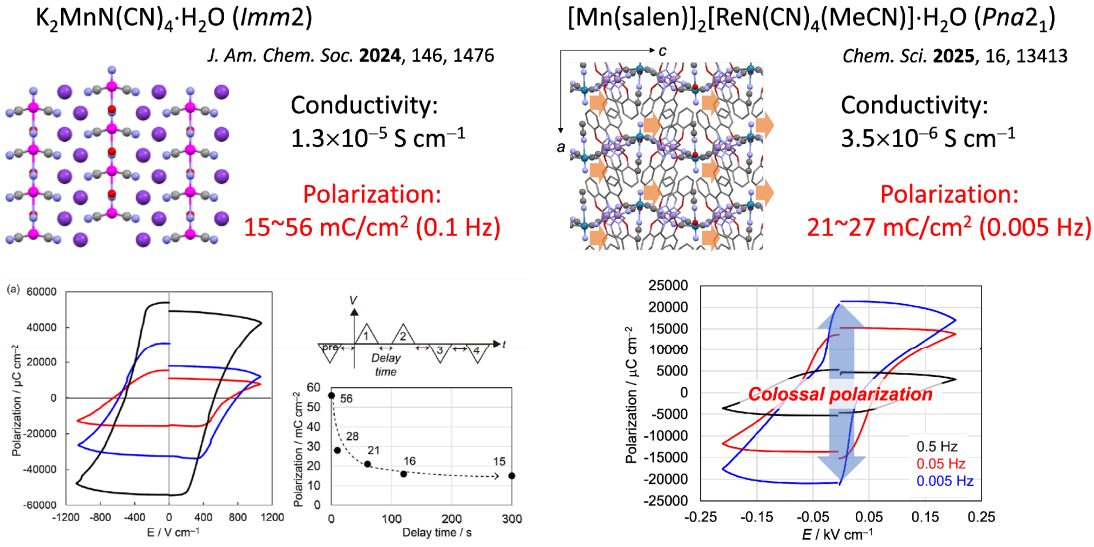
Ferroelectrics are actively researched as functional solid-state materials exhibiting various physical properties based on noncentrosymmetric structures. Conventional ferroelectrics are insulators. On the other hand, new functionalities that couple polarity and ionic conductivity have also been emerged recently. Our group is approaching such new type of ferroelectrics, named ferroelectric ion conductor, by cyanide (CN) based metal complexes. Metal cyanides such as the Prussian Blue Analogs consist of cyanide-bridged frameworks have been investigated actively as molecular based solid-state materials in the coordination chemistry area. Our group synthesizes the related but new-type compounds by penta-coordinate mixed-anion units $[MN(CN)_4]^{2-}$ (M = Mn, Re).[1,2] These units produce one-dimensional (1D) polar assemblies by combining with various cations, led to the ferroelectric ion conductor. For example, we reported the synthesis and ferroelectric nature of $K_2MnN(CN)_4 \cdot H_2O$.[2] This polar compound accommodates water molecules in noncentrosymmetric channels along the *c*-axis, which is responsible to proton conduction with 1.3×10^{-5} S/cm at 298 K and under 80% RH. Uniquly, the ferroelectricity correlated with the proton conduction was demonstrated by applying large voltages of 1kV/cm. Thus, this is the first example of ferroelectric proton conductor. The evaluated polarization value was 15 mC/cm^2 which is quite large comparing with the conventional ferroelectrics. Very recently, the second example of the ferroelectric proton conductor was also demonstrated by a cyanido-bridged 2D coordination polymer $[Mn(salen)]_2[ReN(CN)_4(MeCN)] \cdot H_2O$.[3]



[1] *Angew. Chem. Int. Ed.* 2023, 62, e202306853 [2] *J. Am. Chem. Soc.* 2024, 146, 1476-1483 [3] *Chem. Sci.* 2025, 16, 13413-13421