Towards molecular multiferroics by supramolecular rotor and ferromagnetic $[MnCr(oxalate)_3]^-$ salts

([1] *Research Institute for Electronic Science, Hokkaido University, Sapporo, 001-0021, Japan*, [2] *Graduate School of Environmental Science, Hokkaido University, Sapporo, 001-0021, Japan*)
○Rui-Kang Huang,[1,2] Jiabing Wu[1], Kiyonori Takahashi,[1,2] Takayoshi Nakamura[1,2]
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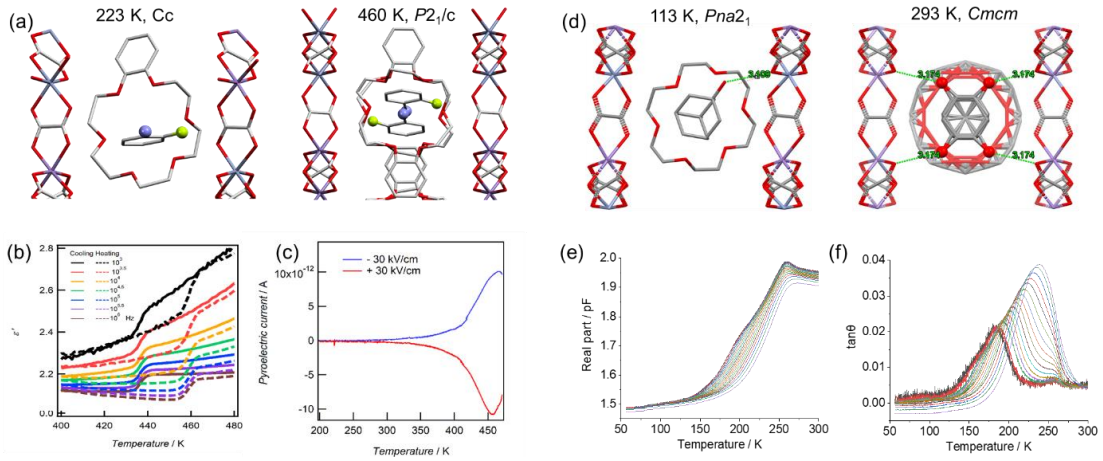
Multiferroics is one of the most focusing kinds in multi-functional materials due to its wide applications in sensors, actuators, memories, etc.[1] Recently, we are focusing on introducing ferroelectric supramolecular rotors into the ferromagnetic oxalate coordinates to achieve multiferroics in molecular materials.[2] We obtain two candidates for molecular multi-ferroelectrics: [(*o*-fluoroanilinium)(benzo-18-crown-6)][MnCr(oxalate)$_3$] (**1**, *o*FAni = *o*-fluoroanilinium, Bz18C6 = benzo-18-crown-6) and [(HADA)(18C6)][MnCr(oxalate)$_3$] (**2**, HADA = 3-hydroxy-1-adamantylammonium, 18C6 = 18-crown-6).

Both **1** and **2** display similar ferromagnetic properties compare to the previous result.[2] **1** undergoes a polar-nonpolar phase transition from *Cc* to $P2_1/c$ at around 450 K (**Figure a**). At 223 K, *o*FAni is aligned and Bz18C6 is anti-aligned while both of *o*FAni and Bz18C6 are disordered thanks to their in-plane rotation at 460 K. **1** displays a step-like dielectric anomaly during phase transition (**Figure b**). The ferroelectricity of **1** is confirmed by its reversible direction of pyroelectric current under reversed applied electric field.

2 undergoes a polar-nonpolar phase transition from $Pna2_1$ to *Cmcm* due to order−4-fold-disorder transition of $(HADA)(18C6)^+$ as shown in **Figure d**. During phase transition, **2** displays a dielectric relaxation in a board range from 120 K to 270 K (**Figure e**). The relaxation of real part is similar to relaxor ferroelectrics. And E_a of this relaxation is calculated by imagery part (37.5 kJ mol^{-1}), which is comparable to the E_a of hydrogen bond.



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