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

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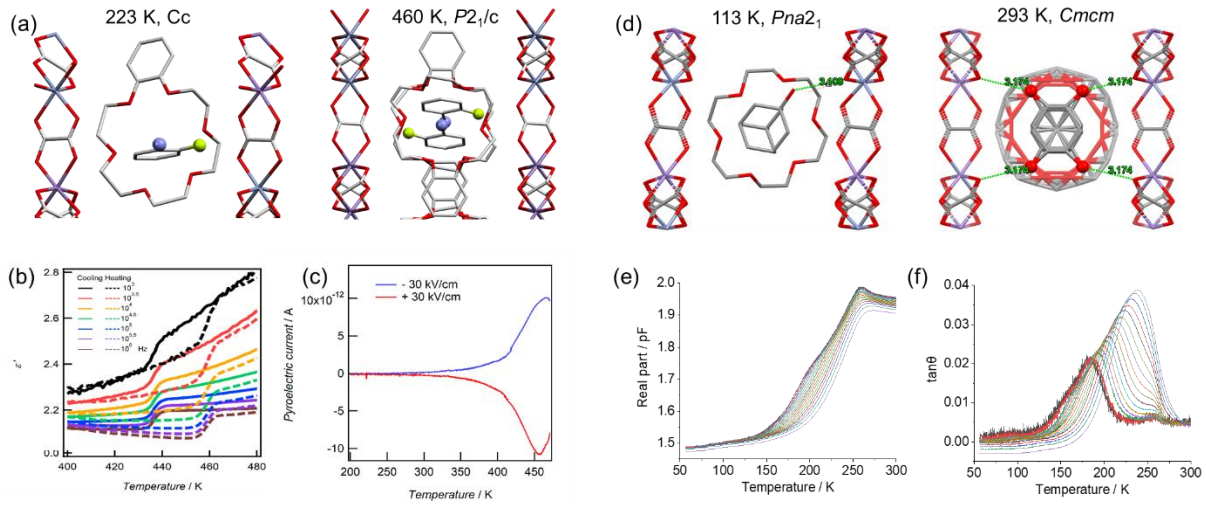
Multiferroics is one of the most focusing kinds in multi-functional materials due to its wide applications in sensor, actuators, memories, *etc*.[1] Recently, we are focusing on introducing ferroelectric supramolecular rotor into the ferromagnetic oxalate coordinates to achieve the type-I multiferroics in molecular materials.[2] Through precise control of the substitution of the supramolecular rotor, we obtain two candidates for molecular multi-ferroelectrics: [(*o*-FAni)(Bz18C6)][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 of **1** and **2** display similar ferromagnetic properties compare to our previous result of $[MnCr(oxalate)_3]^-$ salts.[2] By adapting polar Bz18C6 rather than nonpolar dibenzo-18C6, **1** undergoes a polar-nonpolar phase transition from *Cc* to $P2_1/c$ at around 450 K as shown in Figure a. At 223 K, oFAni 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. During phase transition, **1** display a step-like dielectric anomaly with a ~20 K hysteresis (Figure b). The ferroelectricity of **1** is confirmed by its reversible direction of pyroelectric current under reversed applied electric field.

By adapting round-shaped cation HADA, **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. The E_a of the relaxation is37.5 kJ mol^{-1}, which is comparable to the energy of hydrogen bond. The crystal **2** maybe a relaxor ferroelectric due to the slow-time ordering of hydrogen bonds.



References

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[2] Endo T. *et al*., *Dalton Transactions* **1491**, 40 (2011).