

Cooperative Supramolecular Motion in Magnetic Crystals for Multifunctional Materials

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Molecular machines have been widely studied, and a variety of artificial molecular machines have already been reported. We are developing supramolecular systems that show molecular motion in crystals. In a crystal, molecules are fixed in position forming directional and high-density array. The cooperative motion of individual molecules through intermolecular interactions enables various functions in crystals, such as polarity conversion and mass transport, to be realized as a consequence of the periodicity of the crystals. In this study, we introduced supramolecular systems with dibenzo[24]crown-8 into magnetic $[\text{Ni}(\text{dmit})_2]^-$ crystals. Type-I multiferroic was also realized by combining a ferromagnetic two-dimensional honeycomb layer of $[\text{Mn}^{\text{II}}\text{Cr}^{\text{III}}(\text{oxalate})_3]^-$ and ferroelectric supramolecular rotators.

Dibenzo[24]crown-8 has large cavities in which heteroaromatic cations can be encapsulated. The π - π interactions between phenylene rings of neighboring molecules form channel structures in $[\text{Ni}(\text{dmit})_2]^-$ crystal.¹ Within the channel, heteroaromatic cations exhibit large amplitude motions such as translation, rotation, and inversion. Pyridazinium was introduced into the dibenzo[24]crown-8 channel structure. The crystals exhibited negative thermal expansion due to entropy gain by molecular rotation. The rotation of pyridazinium also affected the magnetic properties of $[\text{Ni}(\text{dmit})_2]^-$, and the temperature dependence of the susceptibility was described by a modified singlet-triplet thermal excitation model.

4-Aminopyridinium (4-ApyH^+) with two hydrogen bonding sites, a pyridyl group and an amino group, was introduced into the one-dimensional channel of dibenzo[24]crown-8. Water molecule captured *via* hydrogen bonding at the pyridinium moiety moves to the adjacent pyridinium moiety *via* 4-ApyH^+ rotation. Water molecules moved through the channel *via* the cooperative motion of 4-ApyH^+ water wheels in $[\text{Ni}(\text{dmit})_2]^-$ crystal.

Dibenzo[24]crown-8 can form pseudo-rotaxane structures with dialkylammonium cations. We introduced $(\text{ClCH}_2\text{CH}_2)_2\text{NH}_2^+$ into dibenzo[24]crown-8 cavity to form one-dimensional supramolecular structures in $[\text{Ni}(\text{dmit})_2]^-$ crystals. The crystal exhibited a relaxor ferroelectric-like dielectric response due to the cooperative motion of $(\text{ClCH}_2\text{CH}_2)_2\text{NH}_2^+$ in the one-dimensional structure.

Type I ferroelectric was developed by combining the two-dimensional ferromagnet $[\text{Mn}^{\text{II}}\text{Cr}^{\text{III}}(\text{oxalate})_3]^-$ with a ferroelectric molecular rotator structure. $[\text{Mn}^{\text{II}}\text{Cr}^{\text{III}}(\text{oxalate})_3]^-$ exhibits a ferromagnetic transition around 5 K and incorporates various cations between two-dimensional honeycomb sheets.² We introduced the supramolecular structure of (*o*-fluoroanilinium)(benzo[18]crown-6) between the layers. The crystal exhibits a ferroelectric transition with large hysteresis around 450 K. The *M-H* behaviour implied a strong coupling between ferroic properties.

References

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- [2] J. Wu *et al.*, *Dalton Trans.*, **51**, 10595-10600 (2022).