# Prediction of properties of organic ferroelectrics and piezoelectrics by first-principles calculation

Shoji ISHIBASHI
*Research Center for Computational Design of Advanced Functional Materials (CD-FMat), National Institute of Advanced Industrial Science and Technology (AIST) Tsukuba, Ibaraki 305-8565*

Organic ferroelectrics and piezoelectrics are promising materials since they contain neither toxic nor rare elements. In addition, they are flexible and printable. Recently, we have experimentally found that organic antiferroelectrics undergo the antiferroelectric-to-ferroelectric transition by applying a electric field for squaric acid (SQA), [H-55dmbp][Hca] (55dmbp = 5,5'-dimethyl-2,2'-bipyridine; H2ca = chloranilic acid) [1], and 2-Trifluoromethylnaphthimidazole (TFMNI) [2]. Usually, an antiferroelectric consists of two sublattices oppositely polarized. We evaluated the total polarization values for ferroelectric SQA and [H-55dmbp][Hca] by calculating polarization of one sublattice and doubling it for each compound. We used the experimentally obtained sublattice structures for the antiferroelectric phases. As for the hydrogen positions, they were computationally optimized. The obtained polarization values are in good agreement with the experimental results [1]. As for TFMNI, the crystal structure of the ferroelectric phase under a electric field has been successfully obtained [2]. We evaluated the spontaneous polarization using the experimental structure of the ferroelectric phase with the hydrogen positions computationally optimized. The obtained value is in good agreement with the experimental result.

The above calculations have been done with the GGA-PBE functional on the experimental structures with only the hydrogen positions computationally optimized. For SQA, we have tried to optimize computationally the whole of the crystal structure. In addition to the standard LDA and GGA-PBE functionals, we applied the vdW-DF-cx and rvv10 functionals, which are recent versions of the van der Waals DFT. Among the four functionals, the rvv10 reproduces the low-temperature structure of SQA best. We, therefore, applied the rvv10 for further calculations. By computationally applying a electric field, we have succeeded in simulating the antiferroelectric-to-ferroelectric transition in SQA [3]. Depending on the electric-field direction, two different ferroelectric phases have been obtained. One of them is thought to correspond to the experimentally-obtained phase [1] while the other is yet to be experimentally confirmed.

We utilized the System B of the Supercomputer Center, the Institute for Solid State Physics, the University of Tokyo for some calculations.

## References

[1] S. Horiuchi, R. Kumai, and S. Ishibashi: Chem. Sci. **9** (2018) 425.

[2] K. Kobayashi, S. Horiuchi, S. Ishibashi, Y. Murakami, and R. Kumai: J. Am. Chem. Soc. **140** (2018) 3842.

[3] S. Ishibashi, S. Horiuchi, and R. Kumai: submitted to Phys. Rev. B.