

## First-Principles Study of Spontaneous Polarization in Tetrathiafulvalene-*p*-Chloranil (TTF-CA)

Shoji Ishibashi<sup>1</sup>, and Kiyoyuki Terakura<sup>2</sup>

<sup>1</sup>*Research Institute for Computational Sciences (RICS),  
National Institute of Advanced Industrial Science and Technology (AIST), Japan*

<sup>2</sup>*Research Center for Integrated Science (RCIS),  
Japan Advanced Institute of Science and Technology (JAIST), Japan  
Email: shoji.ishibashi@aist.go.jp*

The organic compound tetrathiafulvalene-*p*-chloranil (TTF-CA: TTF = C<sub>6</sub>H<sub>4</sub>S<sub>4</sub>, CA = C<sub>6</sub>Cl<sub>4</sub>O<sub>2</sub>) has been attracting much attention because of its peculiar phase transition and related phenomena. TTF-CA belongs to a class of materials called mixed-stack compounds. They fall into two types depending on the balance between the ionization cost and the electrostatic energy. One is a neutral donor-acceptor complex whose constituent molecules are nominally neutral. The other is an ionic salt composed of donors and acceptors. Several mixed-stack compounds are located near the neutral-ionic phase boundary and undergo a phase transition by applying pressure or decreasing temperature. TTF-CA is a typical example. At room temperature and ambient pressure, TTF-CA is in the neutral (N) phase. The system becomes the ionic (I) phase above ~ 11 kbar at 300 K or below ~ 84 K at ambient pressure. In the I phase, donor-acceptor dimers with weak bond are formed along the stacking direction *a* and the inversion symmetry is lost for the crystal and for each molecule. As a result, the I phase is ferroelectric while the N phase is paraelectric.

In the present work, we have evaluated spontaneous polarization of TTF-CA by first-principles calculations using our in-house computational code QMAS (Quantum MAterials Simulator), which is based on the projector augmented-wave (PAW) method with the planewave basis set. Calculations were made not only on the experimental structure [1] but also on computationally optimized ones. The obtained electronic band structures are in good agreement with those reported by Oison *et al.* [2]. The spontaneous polarization for the experimental structure is estimated to be 0.10 C/m<sup>2</sup>, which is significantly larger than the experimental value of 0.4 × 10<sup>-2</sup> C/m<sup>2</sup> reported by Collet [3]. We discuss the origin of the large spontaneous polarization from the present calculation as well as possible sources for the discrepancy between the calculation and the experiment.

\* This research was partially supported by Grant-in-Aid for Scientific Research on Innovative Areas 20110003 from the Ministry of Education, Science, Sports and Culture .

[1] M. Le Cointe *et al.*, Phys. Rev. B 51 (1995).

[2] V. Oison *et al.*, Phys. Rev. B 67 (2003) 035120.

[3] E. Collet, Ph.D thesis, University of Rennes 1, (1999).