

## Direct observation of molecular orbital distribution by synchrotron X-ray diffraction

Molecular conductors exhibit various electronic states upon a small change in external field because the quantum parameters (transition integrals and electronic correlation energies) of substances are small and antagonistic. In order to understand physical properties correctly, it is necessary to clarify what type of interaction is cooperating/competing in a system. For that, precise information of the crystal structure and electron distribution state is indispensable.

In the case of molecular crystals, the observation of the molecular orbital distribution is considered to be very important in providing guidelines for material design. Today, quantum chemistry calculations play a major role in molecular design owing to the development of computational science. However, in the case of molecular crystals, since the number of constituent atoms is large and the number of independent parameters becomes enormous, it is difficult to experimentally obtain accurate crystallographic information including the electronic state.

The typical quasi-one-dimensional system  $(\text{TMTTF})_2\text{PF}_6$  consists of weak dimers of TMTTF stacked in the *a*-axis direction (Fig. 1(a)) and exhibits low-dimensional electronic properties and relatively strong electron-electron correlations. This compound shows a phase transition from the dimer-Mott phase

to the charge ordering phase at approximately 67 K, which is called the mysterious “structureless transition” because the structural parameters are hardly affected by the transition [1]. Some experiments have been performed in an attempt to solve this mystery [2,3].

We first revealed the microstructural changes accompanying the charge ordering of  $(\text{TMTTF})_2\text{PF}_6$  by careful analysis using a device at SPRING-8 BL02B1, where it is possible to collect diffraction data with high luminance and high resolution. Furthermore, using this high-quality data, we showed that direct observation of the molecular orbital distribution state is possible by electron density analysis by the core differential Fourier synthesis (CDFS) method [4].

Figure 1(d) shows the total electron density distribution of a TMTTF molecule calculated by a normal inverse Fourier transform of the high resolution data obtained at BL02B1. Even if short-wavelength ( $\sim 0.35 \text{ \AA}$ ) X-ray diffraction data is used, a marked truncation effect due to the inverse Fourier transform appears around atoms, meaning that atomic electron clouds cannot be identified.

Therefore, we used the CDFS method to separate the information of the core electrons that do not contribute to the bonding of atoms and the valence electrons that form the frontier orbital. Figure 1(e) shows the valence electron density distribution of a

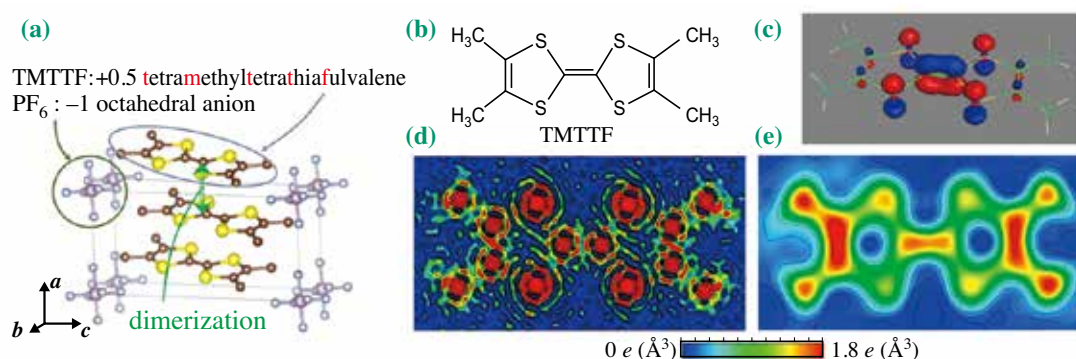


Fig. 1. (a) Crystal structure of  $(\text{TMTTF})_2\text{PF}_6$ . (b) Molecular structure of a TMTTF molecule. (c) Molecular orbital obtained by quantum chemistry calculation of isolated molecules. Molecular orbitals do not represent the electron density and are painted red and blue depending on the sign of the quantum phase. The electron density of the square of the absolute value of the orbital was experimentally observed. (d), (e) Total electron density distribution and valence electron density distribution of a TMTTF molecule, respectively.

TMTTF molecule obtained by the CDFS method. Both the smooth electron density of the bonding orbital on the C=C bond and the electron density node of the anti-bonding orbital of the C–S bond (Figs. 1(b) and 1(c)) are clearly shown.

By comparing the valence electron number of the two TMTTF molecules in the dimer obtained by the CDFS analysis in the atomic basins calculated by Bader's topological analysis, the amount of charge transfer was found to be  $\delta_{CO}=0.20e$ . We directly revealed that the spatial charge ordering pattern

formed a two-dimensional Wigner crystal state from the electron density distribution in the charge ordering phase called the "structureless transition" (Fig. 2).

This CDFS method can be applied not only to determine molecular orbitals in molecular crystals but also to determine the localized *d* orbitals of transition metals in inorganic crystals. By using the CDFS method, it becomes possible to discuss the detailed electronic state of a wider range of materials and to provide information for the development of functional materials.

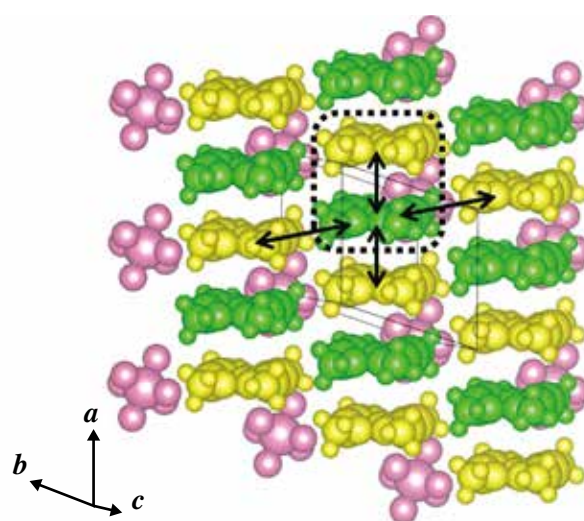


Fig. 2. Charge ordering patterns of hole-rich (yellow) and hole-poor (green) molecules, which indicate a two-dimensional Wigner crystal state. The region surrounded by the dotted line shows a TMTTF molecule dimer.

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