

Molecular Charge Analysis in α -(ET)₂I₃ with STM

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Scanning tunneling microscopy (STM) was utilized to observe the charge disproportion at RT in α -(ET)₂I₃, where ET represents bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF). According to the X-ray diffraction study [1], the title compound shows charge disproportion in the metallic phase above $T_C = 135$ K, and so-called horizontal stripe type charge ordering in the insulating phase below T_C .

All the measurements were performed in the constant current mode with the mechanically sharpened Pt-Ir wire under the ambient condition

Figure 1 represents the image of ET layer in the a - b surface of the title compound with the scan range of about 2.8×2.6 nm². This image allows us to assign A, A', B, and C sites in the unit cell. Analysis was based on the assumption that STM observed $3p$ orbitals of end sulfur atoms in HOMO of each ET molecule, ET(i).

The molecular charge at each site was estimated as follows.

- 1, The relation between the $3p$ orbital and molecular charges of ET(i) were formulated.
- 2, The ratio of molecular charges at ET(i) against ET(B) were expressed in terms of the topographic height difference of ET(i) against ET(B).
- 3, The absolute value of the charge number was estimated from the total hole charge number of two which were transferred from two I₃ ions to four molecules in the unit cell.

The obtained charge distribution in the unit cell was not consistent with the X-ray results reported at RT. On the contrary, the charge distribution in the surface ET layer is rather similar to that of the so-called horizontal stripe pattern of charge ordered state at 20 K. This suggests that charge ordered states are stabilized even at RT in the surface ET layer. This surface reconstruction might be induced by the lack of the surface I₃ layer. This fact provides important information for us to proceed to further research on the electronic states of the strongly correlated organic crystals.

Reference

- [1] T. Kakiuchi, Y. Wakabayashi, H. Sawa, T. Takahashi, and T. Nakamura : J. Phys. Soc. Jpn. 76(2007)113702

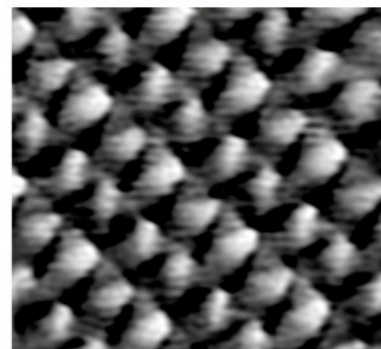


Figure 1 : STM image of α -(ET)₂I₃