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Detailed Analysis of Humidity Dependent Properties of a Polymer Matrix Enabled Molecular Conductor

Comparing to the number of studies on the responses of molecular conductors to thermodynamic and/or electromagnetic fields, the effects of the modulation of chemical composition have not been appreciably investigated except for the doping processes of polycyclic aromatics, fullerenes and some other conducting components. Especially, the structural modulations corresponding to the compositional changes were difficult to examine due to the deterioration of sample crystallinity in general.

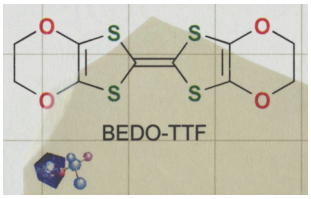

Fig. 1: The chemical structure of BEDO-TTF, which is partly covered with the transparent RDP film.

On the other hand, BEDO-TTF (Fig. 1) exhibits the self-assembling nature to construct conducting layers with the specified crystal structure in the charge-transfer complexes. The metallic complex, $(BEDO\text{-}TTF)_2Br(H_2O)_3$ (Fig. 2) showed a quasi-reversible conductivity change corresponding to humidity. The details have not yet been investigated due to the sever degradation of the crystallinity under desiccated conditions, though the self-assembling property was regarded to play an important role in this repetitiveness.

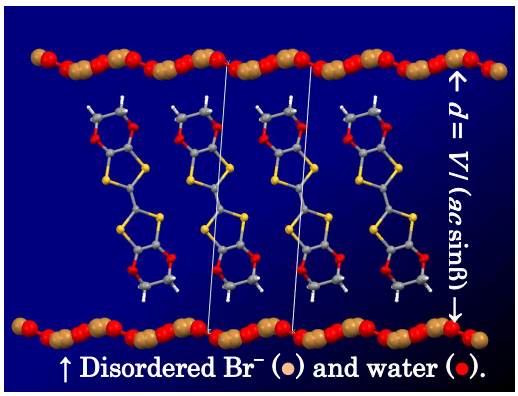

Fig. 2: The *c*-axis projection of the crystal structure of $(BEDO\text{-}TTF)_2Br(H_2O)_3$ along with the definition of interlayer spaceing (*d*).

Recently, the researchers in Kyoto, Nagoya and Łódź (Poland) cooperated to investigate the details of this complex.

By applying so-called two step method of RDP technique, the surface doped polycarbonate films were prepared. The micro-crystals of $(BEDO\text{-}TTF)_2Br(H_2O)_3$ were embedded to align the conducting layer parallel to the film surface. Thanks to this configuration, the surface conductivity and x-ray diffraction pattern of the film corresponded to the conductivity parallel to the conducting layer and inter-conducting-layer distance (*d* in Fig. 2) of micro-crystals, respectively. The simultaneous measurements of humidity dependences of them resulted in that the film exhibited the maximum conductivity at *ca*. 10% of relative humidity (RH) with the significant decrement in drier conditions, while the *d*-value showed the monotonous variation according to RH. The most striking feature was the concurrently observed two (001) diffraction peaks under 5.4-8.6% RH (indicated in red in Fig. 3). This means that two kinds of crystal structures coexisted in this RH range and the crystal structures in dry (RH < 5.4%) and ambient conditions should be significantly different to each other. This material should be the first TTF based molecular conductor for which both continuous and discontinuous structural modulations corresponding to the composition are proved.

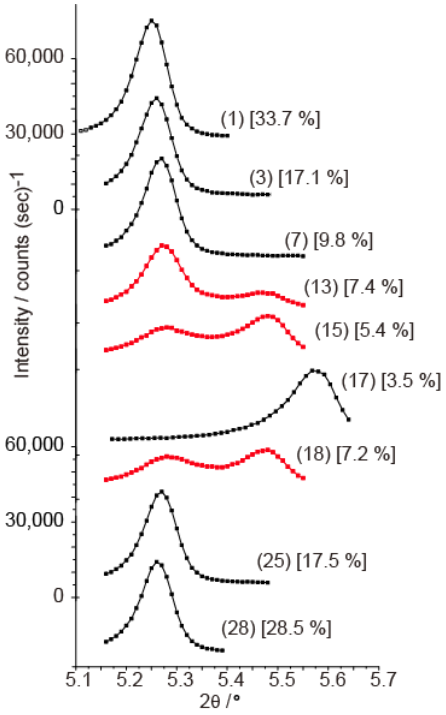

Fig. 3: Humidity dependence of X-ray (001) diffraction pattern of $(BEDO\text{-}TTF)_2Br(H_2O)_3$. The measurement run number and humidity are indicated in the parentheses and blankets, respectively.

This study revealed some details of water release/intake of the BEDO-TTF complex. Also, the film formation was proved to be important not only for applications but also for basic researches.

For details, see an article, "Continuous and discontinuous water release/intake of $(BEDOTTF)_2Br(H_2O)_3$ micro-crystals embedded in polymer film", *J. Mater. Chem.*, **21**(5), 1621-1626 (2011) by T. Haneda, A. Tracz, G. Saito and H. Yamochi (A05)