

## Infrared Optical Probe of Carrier Doping by X-Ray Irradiation in Organic Dimer Mott Insulator $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl

Organic charge transfer salts based on the BEDT-TTF molecule have been recognized as a highly correlated electron system. Among them,  $\kappa$ -(BEDT-TTF)<sub>2</sub>X with X=Cu(NCS)<sub>2</sub>, and Cu[N(CN)<sub>2</sub>]Y (Y=Br and Cl) (Fig. 1) have attracted considerable attention from the point of view of the strongly correlated electron system. The strong BEDT-TTF dimer structure makes the conduction band effectively half-filling. In such strongly correlated electron systems, the Mott insulating phase appears and the first-order Mott insulator – metal transition takes place with the application of hydrostatic pressure, which must broaden the conduction bandwidth with respect to the effective Coulomb repulsion energy on the dimer. Thus, the  $\kappa$ -(BEDT-TTF)<sub>2</sub>X family has been considered to be the bandwidth controlled Mott system in comparison to the filling controlled one in inorganic perovskites such as high-*T<sub>c</sub>* copper oxides.

X-ray irradiation usually induces disorders in a crystal, for example, the displacement of the atomic position. In the case of molecular materials, the irradiation produces molecular defects, which are

generated by radiolysis under ionizing radiation. These molecular defects permanently remain; in contrast, the irradiation damage in inorganic materials is only due to atomic displacements and can be restored with proper heat treatment. These defects and disorders decrease electrical conductivity in general because of enhanced electron scattering [1]. An increase in conductivity by X-ray irradiation, however, has been observed in the organic Mott insulator  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl, as shown in Fig. 2 [2]. The irradiation-induced defects expected at the donor and/or anion molecule sites might cause a local imbalance in the charge transfer in the crystal. Such local modulation of the charge transfer becomes an effective mean of doping carriers into half-filling Mott insulators. In order to investigate the change in the electronic state caused by possible carrier doping induced by X-ray irradiation into organic dimer-Mott insulators, infrared optical reflectivity spectra were measured in a typical bandwidth controlled Mott insulator,  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl [3]. Synchrotron irradiation light was used for infrared

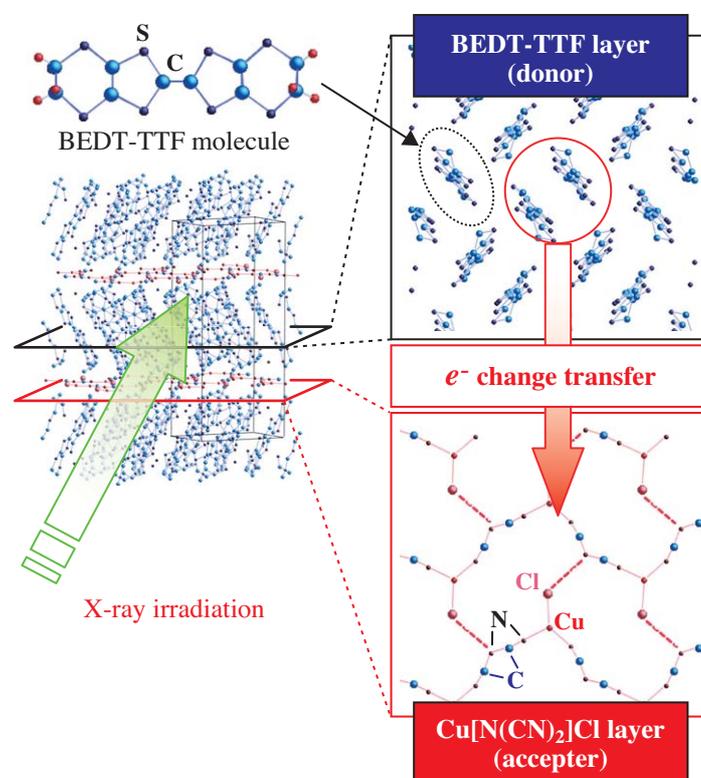


Fig. 1. Crystal structure of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl. The two-dimensional conduction plane consists of BEDT-TTF donor molecules, which is sandwiched by insulating Cu[N(CN)<sub>2</sub>]Cl anion molecule layers.

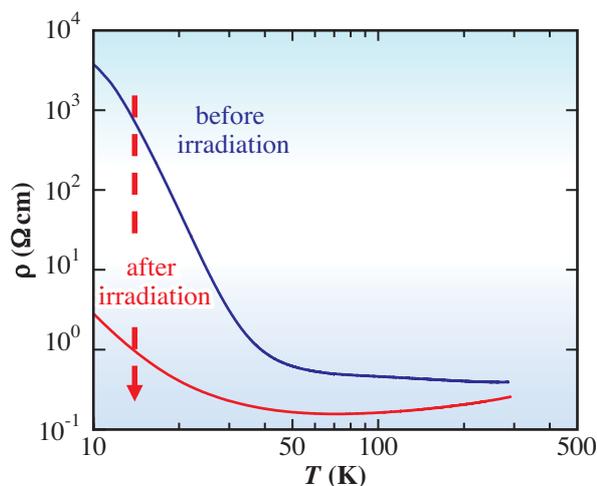


Fig. 2. Temperature dependence of the resistivity of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl before and after 350 hours of X-ray irradiation.

reflectivity measurement at beamline BL431R.

In the optical reflectivity spectra (Fig. 3) of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl obtained after X-ray irradiation using a tungsten tube (40 kV, 20 mA), it was observed that the spectral weight was transferred from the high-energy region to low-energy region. This means that the interband transitions in dimer bands and Hubbard bands in the mid-infrared region are suppressed drastically and the low-energy Drude-like part is enhanced by compensation. The

observed optical spectra suggest that the Mott insulator changes into essentially a metal due to small shift of the carrier number from the half-filling in the conduction band by X-ray irradiation.

As for the future application of this X-ray irradiation technique, a conductive circuit and dots can be made artificially on molecular crystals by controlling the local irradiated position, which will be useful for fabricating organic electronic devices.

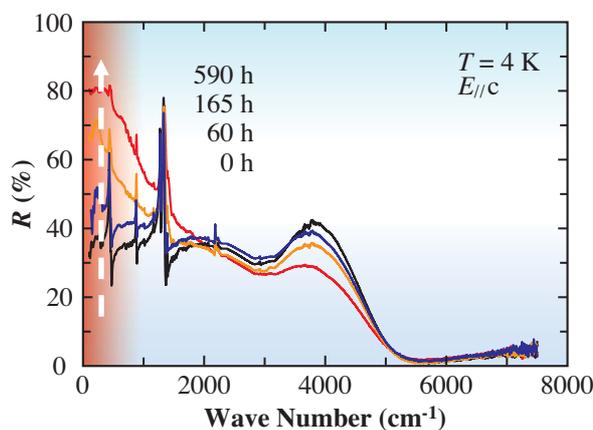


Fig. 3. Optical reflectivity spectra of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl at 4 K. Reflectivity in far-infrared region increases with increasing X-ray irradiation time. Concurrently, we observe a decrease in the magnitude of the interband transition in the mid-infrared region at around 3500-4000 cm<sup>-1</sup>.

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#### References

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