REAL-SPACE IMAGING OF PHASE SEPARATION NEAR MOTT TRANSITION IN ORGANIC SUPERCONDUCTOR κ-(BEDT-TTF)$_2$Cu[N(CN)]$_2$Br

Microscopic spatially inhomogeneous electronic states have attracted much attention recently in many kinds of correlated electron systems. Materials with such intrinsic electronic inhomogeneity tend to have a criticality of changes in charge, spin, orbital, and lattice degrees of freedom in correlated electrons.

Organic charge transfer salts based on the BEDT-TTF molecule have been recognized as one of the highly correlated electron systems. Among them, κ-(BEDT-TTF)$_2$$X$ with X = Cu(NCS)$_2$, Cu[N(CN)$_2$]Y (Y = Br and Cl), etc. (Fig. 1(a)), have attracted considerable attention from the point of view of a strongly correlated electron system. The strong BEDT-TTF dimer structure effectively makes the conduction band half-filling. In such a strongly correlated electron system, several electronic phases appear and the transitions among these phases are controlled by the applied pressure and slight chemical substitution of the donor and anion molecules, as shown in Fig. 1(b), which must change the conduction bandwidth with respect to the effective Coulomb repulsion between two electrons on a dimer. The Mott first-order metal-insulator transition divides the superconducting and antiferromagnetic Mott insulator phases. Thus, the κ-(BEDT-TTF)$_2$$X$ family has been considered to be the bandwidth-controlled Mott system in contrast to the filling-controlled one in inorganic perovskites, such as high-T_c copper oxides. Therefore, an intrinsic electronic inhomogeneity has been expected to appear in the vicinity of the Mott transition.

Scanning microregion infrared reflectance spectroscopy (SMIS) was applied to perform a two-dimensional imaging of the local electronic state in the organic Mott system κ-[(h-BEDT-TTF)$_{1-x}$(d-BEDT-TTF)$_x$]$_2$Cu[N(CN)$_2$]Br [1], whose bandwidth is controlled by the substitution ratio x between the hydrogenated BEDT-TTF molecule (h-BEDT-TTF) and the deuterated one (d-BEDT-TTF). This deuterated molecule substitution makes it possible to control the bandwidth continuously at ambient pressure with minimal disorder effect. SMIS using synchrotron radiation were performed at beamline **BL43IR**. An IR microscope with a controlled precision x-y stage and a

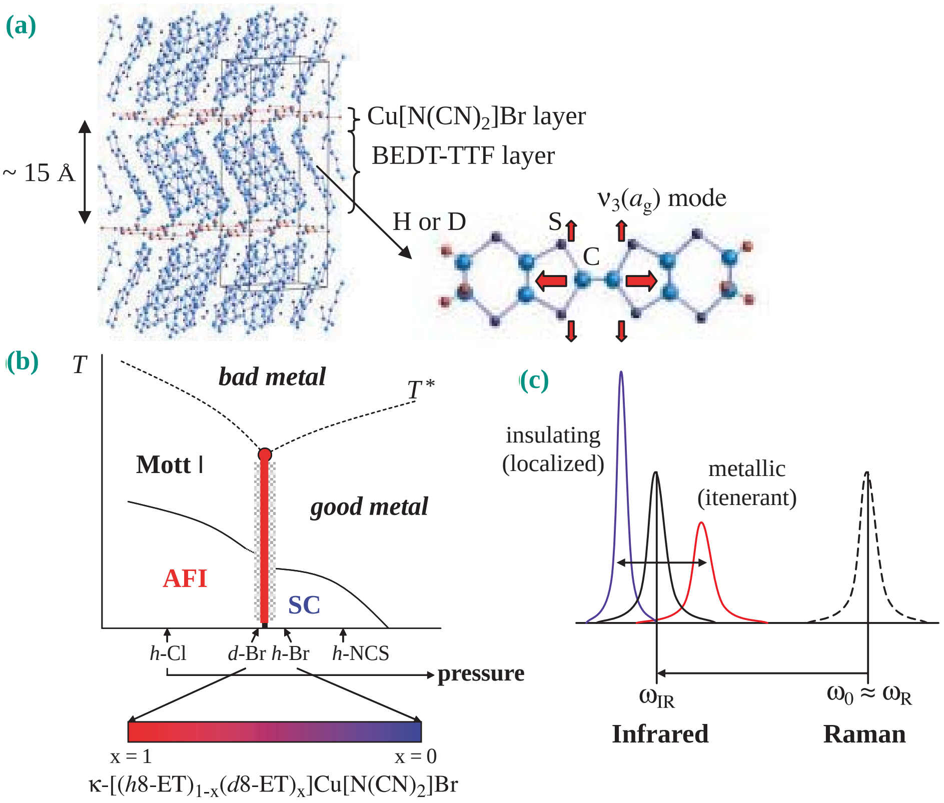

Fig. 1. **(a)** Crystal structures of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br and BEDT-TTF molecules. **(b)** Schematic phase diagram of κ-(BEDT-TTF)$_2$$X$. (c) IR molecular vibration shifted by EMV coupling.

high brilliance SR light enable us to obtain a two-dimensional reflectance spectrum map with a spatial resolution of ~10 μm with no apertures. To obtain the real space image of the electronic states by SMIS, we use the shift in the frequency ω_3 of a molecular vibration mode, $\nu_3(a_g)$. The specific $\nu_3(a_g)$ mode, which is a symmetric stretching mode of the central double-bonded carbon atoms of the BEDT-TTF molecule (Fig. 1(a)), has been found to be very sensitive to the difference between metallic and insulating states due to the large electron-molecular vibration (EMV) coupling [2]. The peak of the $\nu_3(a_g)$ mode should shift to a lower frequency and exhibit a sharper shape in the insulating state, while it should show an opposite shift in the metallic state (Fig. 1(c)).

Figure 2 shows the two-dimensional contour maps of the reflectivity peak frequency ω_3 of the $\nu_3(a_g)$ mode at 4 K. In the contour maps, a bright region indicates the higher frequency of ω_3 which demonstrates a metallic feature. In the samples with small substitution ratios of $x = 0$ and 0.2, an almost homogeneous metallic state is realized in their entire area. In contrast, the sample of the opposite end member $x = 1$ shows a homogeneous insulating state. In the intermediate substitution, however, an inhomogeneous feature, that is, phase separation on a micrometer scale can be found in the maps. The insulating domains appear on the dominant metallic background in the $x = 0.5$ sample. Such insulating domains have a tendency to grow with increasing x. In the $x = 0.8$ sample, the insulating region becomes dominant and the metallic domains are found to remain.

Experimental evidence of the electronic phase separation is obtained in the organic Mott system using the real space imaging technique. SMIS using SR enables us to show the macroscopic size of the domain structure of the insulating and metallic regions. The observation of the micrometer scale phase separation is different from the recent findings of nanoscale electronic inhomogeneity in a strongly correlated inorganic system. The origin of the phase separation must be the strong electronic correlation near the Mott transition.

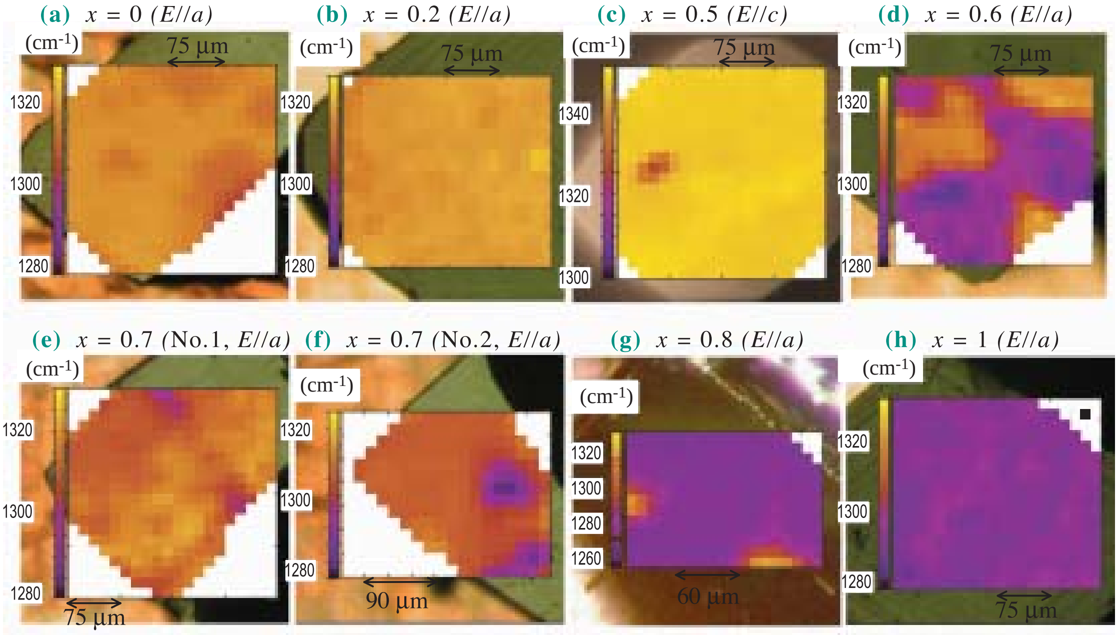

Fig. 2 Two-dimensional contour maps of peak frequency of $\nu_3(a_g)$ for various substitution ratios x in κ-[(*h*-BEDT-TTF)$_{1-x}$(*d*-BEDT-TTF)$_x$]$_2$Cu[N(CN)$_2$]Br. The left colored bar corresponds to the peak frequency.

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