Bulk-Sensitive Angle-Resolved Photoemission Spectroscopy on TTF-TCNQ

Kenji Koizumi$^{1,2}$, Kyoko Ishizaka$^2$, Takayuki Kuss$^{1,2}$, Mario Okawa$^3$, Reizo Kato$^3$, and Shik Shiu$^4$

$^1$ISSP, University of Tokyo, Kashiwa, Chiba 277-8581, Japan
$^2$Department of Applied Physics, University of Tokyo, Bunkyo, Tokyo 113-8656, Japan
$^3$RIKEN-ASI, Wako, Saitama 351-0198, Japan
$^4$RIKEN Spring-8, Sayo, Hyogo 679-5143, Japan

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TTF-TCNQ is a quasi-1D molecular conductor exhibiting metal-insulator transition at 54 K accompanied by charge-density-wave (CDW) formation. Its electronic properties in relation to the Peierls instability and CDW transitions are well investigated through the several decades.\textsuperscript{1–7} Past ARPES studies indicate the band dispersion consisting of TCNQ molecules (namely the TCNQ-band) shows the signature of spin–charge separation, together with the suppression of the quasiparticle excitation at the Fermi level.\textsuperscript{8–10} These observations have been discussed in terms of the 1D character of TTF-TCNQ, nevertheless, there are several mysteries remained. One is the band dispensions obtained by ARPES commonly indicating the band-width (or the band group velocity) larger by a factor of $\sim$2 with respect to band theory.\textsuperscript{8} To account for this discrepancy, the possibility of relaxed tilting of the topmost molecules and/or strong correlation effect have been raised until now.\textsuperscript{8,11} The second is the anomalous suppression of the spectral weight near the Fermi level ($E_F$), which gives negligible amount of spectral intensity at $E_F$ even in the highly-conductive state above $>$60 K.\textsuperscript{9,10} The electronic structure of the metallic quasi-1D state has been thus remained to be elucidated.

To investigate the precise electronic structure of TTF-TCNQ, here we utilized the laser-excited ARPES with $h\nu = 6.994$ eV.\textsuperscript{15} Owing to the relatively low photon-energy as compared with past ARPES studies ($h\nu = 20–40$ eV), the bulk-sensitive measurement becomes available. The effect of photoirradiation-induced damage peculiar to molecular compounds is also considered to be weaker compared to the measurements using higher-energy photons. The high cross section of $s$ and $p$ electrons for this photon-energy provides some advantage in studying the light-element based organic conductors.

ARPES measurements were performed using a system constructed with VG-Scienta R4000 electron analyzer and an ultraviolet ($h\nu = 6.994$ eV) laser.\textsuperscript{12} He I $\alpha$ ($h\nu = 40.8$ eV) light source was also used to check the correspondence with past reports. Single crystals of TTF-TCNQ grown by the diffusion method were cleaved in-situ to obtain fresh surfaces. The pressure was below $5 \times 10^{-11}$ Torr throughout all the measurements. The energy resolution was $\Delta E = 4.0$ meV. The Fermi level $E_F$ of the sample was referred to that of a Au film evaporated on the sample substrate, with an accuracy of $\pm 0.1$ meV.

Figure 1(a) shows the mapping of the ARPES intensity ($h\nu = 6.994$ eV) at the Fermi level, obtained by integrating the ARPES intensity in the energy window of $\pm 50$ meV. The shape of the Fermi surface thus observed makes a straight line at $k_F = 0.24 \pm 0.01$ Å$^{-1}$ = (0.29 $\pm$ 0.01)$b^*$, indicative of 1D electronic structure. The image of band dispersions along $\Gamma$–Z direction, obtained by $h\nu = 6.994$ and 40.8 eV is shown in Fig. 1(b,c). The peak positions of the ARPES intensity estimated from momentum distribution curve (MDC) and energy distribution curve (EDC) are plotted by circle and cross markers, respectively. The red and blue curves, on the other hand, represent the band dispersions consisting of TTF and TCNQ molecules, obtained by the first-principles calculation.\textsuperscript{13} By comparing with the band calculation, we can notice that the $h\nu = 6.994$ eV data is dominated by the signal from TTF bands, whereas the $h\nu = 40.8$ eV data shows both TTF and TCNQ bands that are well in accord with past reports. This $h\nu$-dependence, which should be due to the photoionization cross section and/or matrix element effect, also explains the slight difference of the present “Fermi-surface” shape from that previously reported.\textsuperscript{14} The Fermi momentum obtained by ARPES, $k_F = 0.24 \pm 0.01$ Å$^{-1}$, is somewhat smaller compared with the band calculation, reflecting the overestimation of the charge transfer between TTF and TCNQ inevitably arising in the calculated data.

Here, let us focus on the gradient of the TTF band dispersion. In the $h\nu = 40.8$ eV ARPES spectrum, the gradient of the TTF band dispersion is about 2 times larger as compared to the calculation. It shows that the observed
band-width of the TTF band is significantly larger than that expected by calculation. On the contrary, the $h \nu = 6.994$ eV data shows that the gradient of the TTF band dispersion is much smaller compared to $h \nu = 40.8$ eV, and almost equivalent to the calculation. Since the $k_z$-dependence of the corresponding band dispersion is very small, it can be understood by the difference of the bulk sensitivity between $h \nu = 6.994$ and 40.8 eV ARPES, of which probing depths are known to be >80 Å and several Å, respectively. This result indicates that the long-standing inconsistency of the band-width is due to the surface effect, not the correlation effect. The tilting of topmost molecules, however, has been experimentally ruled out in Ref. 11. The precise mechanism of band-width enhancement at the surface remains to be further investigated.

Next we show the temperature-dependent EDC at the Fermi momentum in Fig. 2(a), obtained by $h \nu = 6.994$ eV ARPES. With lowering the temperature from 200 to 60 K, the spectral weight near the Fermi level increases and forms a broad peak at $\sim$0.2 eV. At the Fermi level, the spectral weight is suppressed and shows no quasiparticle peak or clear Fermi-edge cutoff even in the metallic phase ($>60$ K). By closely looking at the Fermi-level, nevertheless, a very small but finite intensity is found at high temperatures. The ARPES intensity $I(k, \omega, T)$ at momentum $k$, energy $\omega$, and temperature $T$ is practically given by $I(k, \omega, T) = MA(k, \omega, T)f_{FD}(\omega, T)$, where $M$ is the matrix element, $A(k, \omega, T)$ is the single-particle spectral function, and $f_{FD}(\omega, T)$ is the Fermi–Dirac distribution function. To see the temperature dependence of the spectral function itself, we divided the EDCs by the Fermi–Dirac distribution function convolved by the gaussian energy-resolution function, as shown in Fig. 2(b). Here we can see that there is a finite intensity at the Fermi level at 200 K, which slightly increases on cooling down to 60 K, the most conductive temperature. On further cooling down to 6 K, the long-range 2$k_F$-CDW formation occurs at 54 K, which opens a CDW gap at the Fermi level, observed as the leading edge shift of about $\sim$30 meV. This value of gap is mostly consistent with that obtained by optical spectroscopy.

In conclusion, we investigated the electronic structure of TTF-TCNQ by using laser-excited ARPES. The observed TTF band shows that the band-width agrees well with the band theory, and small but finite spectral intensity exists in the metallic state. These results show the effectiveness of the bulk-sensitive laser ARPES measurement for studying the variety of organic conductors.

Fig. 2. (Color) (a) Temperature-dependent EDC at the Fermi momentum of TTF-TCNQ, obtained by $h \nu = 6.994$ eV. (b) EDC in (a) divided by the Fermi–Dirac function convolved by the energy-resolution gaussian function.

References


*koizumi@issp.u-tokyo.ac.jp*