

Highest-Occupied-Molecular-Orbital Band Dispersion of Rubrene Single Crystals as Observed by Angle-Resolved Ultraviolet Photoelectron Spectroscopy

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The electronic structure of rubrene single crystals was studied by angle-resolved ultraviolet photoelectron spectroscopy. A clear energy dispersion of the highest occupied molecular orbital-derived band was observed, and the dispersion width was found to be 0.4 eV along the well-stacked direction. The effective mass of the holes was estimated to be $0.65(\pm 0.1)m_0$. The present results suggest that the carrier conduction mechanism in rubrene single crystals can be described within the framework of band transport.

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The charge carrier transport properties of organic semiconductors are the key to a fundamental understanding of actual device performance. Studies of single crystals (SCs) have been regarded as the best research subjects to focus on the intrinsic carrier dynamics of organic materials, because it is possible to control and reduce any extrinsic factors (e.g., impurities and grain boundaries) that dominate the electrical properties of most organic thin-film devices.

Rubrene (5,6,11,12-tetraphenyltetracene) SCs have been extensively studied to address carrier transport properties, since they show the highest hole mobility ($\mu_h = 40 \text{ cm}^2/\text{Vs}$ [1]) of all organic semiconductors reported so far. A strong anisotropy of conductivity was reported for rubrene SCs [2–4], and it has been proposed that the carrier motion would be described as band transport, rather than intermolecular hopping, based on the temperature dependence of μ_h and the Hall effect [5–7]. However, recent theoretical calculations have indicated that the band-transport-like behavior of the temperature dependence of μ_h as well as the absolute value of μ_h can be reproduced within an intermolecular hopping framework [8]. Thus, the mechanisms of the charge transport have not yet been fully clarified. Still, the nature of the effective mass of the holes m_h^* is under discussion. Some research groups have proposed that the holes behave as small polarons of $m_h^* > 2m_0$ [6,9,10] (m_0 is the electron rest mass), whereas others have claimed a light m_h^* ($= 0.8m_0$ [11]) and the insignificance of the polaronic effect. In order to address these controversies, it is essential to determine whether the band dispersion itself exists and, if it does, how large its width W and m_h^* are in a rubrene SC.

Angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) is a powerful technique for clarifying the band dispersion of materials since one can directly obtain W and m_h^* determining the transport characteristics. For less-conductive organic semiconductor crystals, however, UPS is considered to be unsuitable because of the sample charging problem. Photoemission-induced positive

charges left near the sample surface are trapped by defects or impurities. An undesirable electric field caused by these “trapped photoholes” distorts the spectrum, and in extreme cases photoemission itself is suppressed. In order to resolve this charging problem, oriented thin films, which are free from the charging effect, have been used for band dispersion measurements [12–23]. Several other tactics for canceling out the photoholes have been attempted, and a few successful photoelectron spectra have been obtained through the simultaneous illumination of low-energy light during measurements [24,25]. However, the observation of band dispersion in organic semiconductor crystals has not yet been achieved, probably because of incomplete suppression of sample charging [23].

In this study, we successfully observed the valence band structures of rubrene SCs by high-resolution ARUPS with simultaneous laser illumination whose energy is above the transport gap. The highest occupied molecular orbital (HOMO)-derived band clearly dispersed along the well-stacked direction, and a light m_h^* was directly ascertained.

Rubrene SCs were prepared using a physical vapor transport technique in a purified nitrogen stream. Platelets (typically $1 \text{ mm} \times 5 \text{ mm} \times 20 \mu\text{m}$) of the crystal were subsequently bound onto gold-coated Si substrates with silver paste in air. UPS measurements were conducted in an ultrahigh vacuum system (base pressure of $5 \times 10^{-8} \text{ Pa}$) with a photoelectron spectrometer (VG-Scienta, R3000) which provided the spatially or angle-resolving electron lens modes. He I radiation (21.22 eV) was adopted as the excitation light, and the incident angle was fixed at 65° from the sample surface for all emission angles. During the UPS measurements, the whole area of the sample was illuminated uniformly with a continuous-wave laser light [405 nm (3.06 eV); 14 mW; spot size of ca. 30 mm^2] unless otherwise noted. The orientation of the crystal lattice was decided from the anisotropic character of the crystal shape [4,26], and was also verified by the emission-angle dependence of the photoemission intensity.

The measurement setup is displayed in Fig. 1(a). The total energy resolution of the present system was estimated to be less than 100 meV from the Fermi edge of the silver paste. In addition to UPS measurements, the ionization energy (I_s) of rubrene SCs was also separately determined using photoelectron yield spectroscopy (PYS), which probes the total photoemission current as a function of the incident photon energy. This technique is fundamentally unhampered by sample charging [27]. Details of the experimental procedure of PYS can be found elsewhere [28]. All measurements were carried out at room temperature.

The normal emission UPS spectrum (taken by the spatially resolving lens mode) of a rubrene SC under laser illumination is shown in Fig. 1(a). The line shape of the spectrum is in good accordance with previous UPS results of rubrene thin films [29,30]. As shown in the bottom spectrum in Fig. 1(b), the absence of laser illumination resulted in significant broadening of the HOMO peak and a shift to the high E_B side. This behavior is a typical sign of sample charging. By increasing the illumination intensity, the peak was narrowed and shifted to the low E_B side, reflecting the suppression of charging. The shift finally saturated at a laser power of 7 mW [Fig. 1(c)]. In contrast, the sample charging was not resolved under 455 nm (2.73 eV) laser light illumination even though the power was 20 mW. Taking into consideration that the calculated electronic band gap of rubrene SCs is 2.8 eV (443 nm) [31], the generation of free photocarriers should be essential to suppress sample charging. Further, the photovoltaic effect, if there is one in this case, does not disturb the observation of the band dispersion. Figure 1(d) shows the magnified UPS spectrum of the HOMO peak plotted with respect to

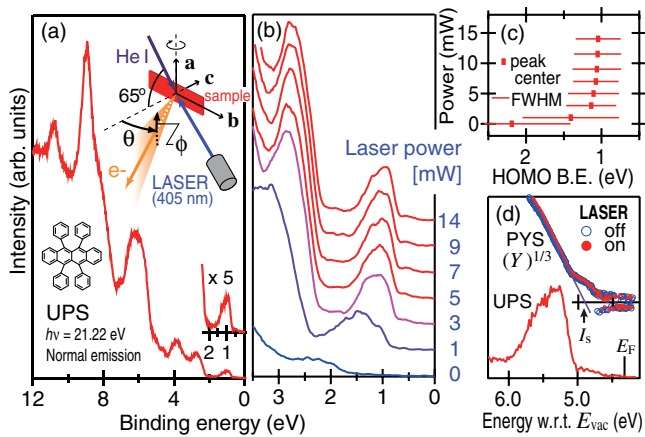


FIG. 1 (color online). (a) ARUPS spectrum of a rubrene SC taken at normal emission angle. (Inset) A schematic drawing of the experimental setup. The b axis is parallel to the long side of the crystal. (b) UPS spectra of the HOMO region taken under various laser power. (c) Laser power dependence of the HOMO peak position and its FWHM. (d) The magnified UPS spectrum around the HOMO peak and PYS spectra (with and without laser illumination). Binding energy (BE) with respect to the vacuum level (w.r.t. E_{vac}) is taken as the abscissa.

the vacuum level (E_{vac}), as determined from the secondary-electron cutoff position (spectra not shown). Good accordance of the HOMO onset with the threshold energy of PYS spectra (I_s) also confirms the successful suppression of sample charging, as PYS is fundamentally charging-durable [27]. The small feature observed up to 0.3 eV above the HOMO onset may be attributed to the so-called “oxygen-related gap states” which have previously been proposed to occur on rubrene SCs after air exposure [32,33]. The laser illumination did not generate significant changes in the PYS spectra. This indicates that the laser illumination does not disturb the observation of “intrinsic” electronic structures in the present case.

ARUPS spectra (taken by the angle-resolving lens mode) along the Γ - Y direction are shown in Fig. 2(a). Although spectral contribution of silver paste was overlapped on each spectrum due to a reduced spatial resolution of this lens mode operation, the line shape around the HOMO region was not interfered, because there was no feature at the HOMO region in the spectrum of silver paste [the bottom spectrum in Fig. 2(a)]. At normal emission ($\theta = 0^\circ$), one can find a clear peak at $E_B \sim 0.9$ eV. The main peak clearly shifted toward higher E_B side with increase of θ , reaching the maximum E_B of ~ 1.2 eV at $\theta = 12^\circ$. Further increase of θ resulted in turning back of

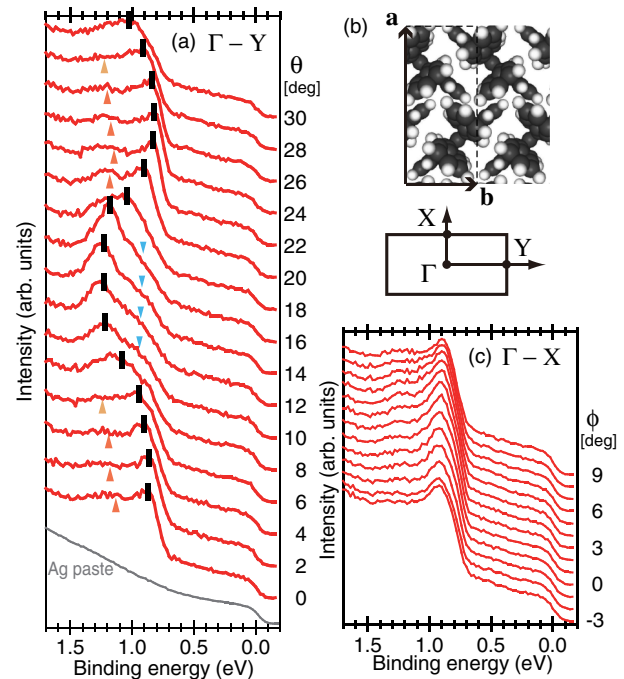


FIG. 2 (color online). (a) ARUPS spectra of a rubrene SC along the Γ - Y direction. The main peak position at each θ is marked with a thick bar. The upward and downward triangles indicate the high- and low-BE shoulders, respectively. The bottom curve represents a spectrum of the silver paste. (b) Schematics of molecular orientation of the crystalline a - b plane ($a = 1.44$ nm, $b = 0.72$ nm [35]) and corresponding reciprocal lattice. (c) ARUPS spectra along the Γ - X direction.

the main peak, and it finally returned to $E_B \sim 0.8$ eV at $\theta = 24^\circ$. This behavior represents an energy dispersion of the HOMO band. The dispersion width W is 0.4 eV, which is in good agreement with the value predicted by the calculations [11,34]. In addition to the main peak, a shoulder component was observed at its high E_B side for the spectra taken around normal and 24° emission angle. This component seemed to shift slightly along the main peak. Since splitting of the HOMO band at the Γ point is expected from band calculations [11,34], reflecting two inequivalent molecules in the unit cell, the high E_B shoulder could be attributed to the second band derived from the HOMO. Around $\theta = 12^\circ$, another shoulder appeared at the low E_B side, which may be ascribed to indirect transitions via phonons because it did not show any energy dispersion.

In contrast to the Γ - Y direction, the HOMO peak hardly dispersed ($W < 0.05$ eV) along the Γ - X direction, as shown in Fig. 2(c). Such a relatively anisotropic dispersion is also in agreement with the band structure calculations [11,34] and should be associated with the reported anisotropic mobility [2–4].

Figure 3(a) shows the mapping of the observed dispersion along the Γ - Y direction plotted as a function of the parallel component of the electron wave vector k_{\parallel} . The observed period of the dispersion is consistent with the expected size of the Brillouin zone (BZ) [35]. As shown in Fig. 3(b), the E - k_{\parallel} relation of the main peak derived from the HOMO reproduces the first band in the previous band calculation [34] fairly well. Under the one-dimensional tight-binding (TB) approximation, the energy dispersion is explained as $E_B = E_c - 2t \cos(bk_{\parallel})$ [23], where E_c , t , and b represent the energy of the band center, transfer

integral, and lattice constant of the corresponding crystal axis, respectively. The present E - k_{\parallel} relation shows excellent accordance with this formulation, and t is estimated to be 0.11 eV from the least-squares fitting with cosine curve. The m_h^* at the HOMO band is given by $m_h^* = \hbar^2/2tb^2$ around the Γ points in the TB approximation, and the present results lead to an estimation of $m_h^* = 0.65(\pm 0.1)m_0$. This is extremely light compared with other molecules that show intermolecular band dispersion [23]. Fitting by a parabolic function also gives the equivalent m_h^* .

In the case of $W > k_B T$, the lower limit of μ_h along the Γ - Y direction at room temperature is estimated as $\mu_h > 29$ cm²/V s according to the formula $\mu_h > 20(m_0/m_h^*) \times (300/T)$ [36]. The reported largest value for μ_h in rubrene SCs (40 cm²/V s [1]) is actually larger than this lower limit. Drift mobility can be expressed as $\mu_h = e\tau/m_h^*$, where τ is the scattering time. In the adoption of that highest value for μ_h , the present m_h^* gives $\tau = 15$ fs. Taking into consideration that the μ_h of a trap-free rubrene SC will not be smaller than this value, τ should be longer than the present estimation. The energy uncertainty for this time scale is 10 times lower than W and therefore will not violate the description of band transport. The mean free path of holes l_h is explained with the mean speed of holes \bar{v} by $l_h = \bar{v}\tau$. Assuming that the speeds of the holes follow the Maxwell-Boltzmann distribution, where \bar{v} is given as $\bar{v} = \sqrt{3k_B T/m_h^*}$, the present τ leads to an estimation of $l_h = 2.1$ nm or longer. This distance is a few times longer than the lattice constant, suggesting that the transport behavior in the HOMO band of the rubrene SCs can be described with holes delocalized over a few molecules that behave as nearly free carriers. Of course, the transport properties of the practical devices may be more complicated because of interfacial characteristics between the gate dielectrics and rubrene [37]. It should, however, be emphasized that the intrinsic transport properties along the b direction in a single crystalline rubrene can be described by band transport even at room temperature. In the Marcus electron transfer model, which is applicable at high temperature, the hopping mobility can be described as a function of temperature, b , t , and intermolecular reorganization energy λ [38]. If we make a trial estimation of μ_h by the Marcus model, the expected μ_h at room temperature is estimated to be 26 cm²/V s, by adopting obtained value (0.11 eV = $W/4$) for t and 145 meV for λ [38]. It is still insufficient to reproduce the reported high mobility.

In conclusion, we succeeded in observing the HOMO band dispersion of rubrene SCs directly by means of ARUPS for the first time, assisted by simultaneous laser illumination to suppress sample charging. A large HOMO band dispersion of 0.4 eV was revealed, and the estimated effective mass of holes was found to be as light as $0.65m_0$ at the top of the HOMO band along the Γ - Y direction.

This light m_h^* is achieved mainly due to the effective intermolecular interaction and the small size of BZ.

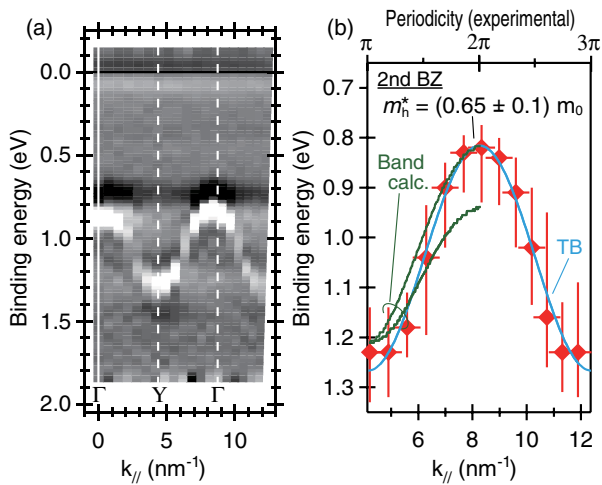


FIG. 3 (color online). (a) Second derivative of the ARUPS spectra mapped on the E - k_{\parallel} plane. Center and boundary of the Brillouin zone are also indicated. (b) E - k_{\parallel} diagram of the main peaks along the Γ - Y direction in the second BZ. Theoretical curves obtained by the band calculation [34] and a fitting curve obtained by the TB approximation are also shown.

Generally, enhancement of the transfer integral t has been recognized as the most crucial factor to obtain a light effective mass (i.e., large mobility) of carriers. However, the period of the dispersion curve, which is related to the BZ size (i.e., inverse lattice constant), also controls the effective mass. For instance, crystalline thin films of BTQBT [bis[1,2,5]thiadiazolo-*p*-quinobis(1,3-dithiole)], the BZ size of which is less than half that of rubrene SCs, revealed a significantly heavier m_h^* than the present result despite comparable t [12,39]. We would like to point out that the light m_h^* of the rubrene SC is realized due to concomitance of the sufficiently small BZ size and large t .

The present results strongly suggest that the carrier transport nature of the rubrene SCs should be described in the band transport framework of delocalized HOMO holes, rather than the hopping motion of localized holes within the molecules. The next scientific target will be aimed at investigating the effect of the molecular vibration and λ to the valence band dispersion, which may be associated with the polaronic effect [40].

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