

Translational symmetry-breaking in the quasiparticle band structure of organic semiconductor rubrene

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As the sustainability of our global resources and energy-harvesting rapidly becomes a central issue in navigating our technological advancements, the development of quantum devices made of organic molecular semiconductor materials, which combine the low fabrication cost, abundance of the constituent elements and high bio-degradability, while maintaining their high performance is of paramount importance.

Among such organic semiconductors, single crystalline rubrene (C₄₂H₂₈) is known to exhibit exceptionally high carrier mobility (~40 cm²/Vs [1]), and is at the heart of current organic electronic devices. At room temperature, rubrene crystal is known to support partially coherent polaron-band transport through the itinerant holes. Clearly, in such case, the understanding on the nature of these carriers in wavevector space is a prerequisite for any first-principle-based, strategic developments utilizing this material, such as direct band-structure engineering. However, despite the extensive efforts devoted to uncover the entirety of electronic band structure of rubrene crystal for more than a decade, both experimentally [2] and theoretically [3], there remain multiple major discrepancies, even at qualitative levels, between the theoretically predicted band structures and those identified in the experimental studies, leaving the true nature of the charge carriers highly elusive.

In order to resolve these issues, we have utilized photon-energy- and polarization-dependent angle-resolved photoemission spectroscopy (ARPES) to investigate the valence band structure of highly single-crystalline rubrene. Our results, elucidating the valence band structures in terms of their quasiparticle spectral functions over the multiple Brillouin zones (BZs), clearly reveal the mismatched periodicities in the band structure between the single-particle and quasiparticle pictures, which had hindered the observations of the full band structures in the previous studies. Taking proper accounts for these translational-symmetry breaking in rubrene crystal, we fully uncover its band structure, in agreement with theoretical simulations, thereby resolving the long-standing controversies on the rubrene's electronic structures.

Keywords: Organic molecular semiconductors, Angle-resolved photoelectron spectroscopy, Quasiparticle spectral functions, Low-energy electron diffraction

¹ J. Takeya et al., Appl. Phys. Lett. **90**, 102120 (2007). ² S. Machida et al., Phys. Rev. Lett. **104**, 156401 (2010) etc. ³ D. A. da Silva Filho et al., Adv. Mater. **17**, 1072 (2005) etc.