Supplementary Information

**Anisotropic valence band dispersion of single crystal pentacene as measured by angle-resolved ultraviolet photoelectron spectroscopy**

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**1. Geometries of the ARUPS measurements**

FIG. S1: Molecular arrangement of the Pn-SC(001) surface indicating the measurement orientations of ARUPS in the real space. The directions of the present ARUPS measurements are illustrated as blue arrows. The corresponding SBZ is superimposed.

**2. Spectral changes by irradiation damage**

FIG. S2: (a) ARUPS spectral image of a *fresh* Pn-SC sample taken in the Γ-M’ direction around the Γ point before long-term measurements. (b) ARUPS spectral image of an *aged* Pn-SC sample taken in the Γ-M’ direction around the Γ point after repeated ARUPS measurements (in the Γ-Y and Γ-X directions shown in Figs. 4(a) and (b)). (c) Angle-integrated UPS spectra of the *fresh* and *aged* Pn-SC samples. The spectra are normalized at each intensity of the top valence band peak. Emergence of the additional component X on the high energy side of the valence band peak for the *aged* sample is ascribed to irradiation damage induced by repeated ARUPS measurements.