Electronic Supplementary Information

The ionization energy of α -sexithiophene and p-sexiphenyl in 2D and 3D thin films grown on silicon oxide surfaces

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1. Influence of irradiation on the PY spectra and morphology of the α -6T thin films



Fig. S1 (a) PY spectra of the α -6T thin film (0.74 ML) measured at different regions. The intensity of the PY spectrum in the 1st scan in Region B was close to that in the 6th scan in Region A, indicating that the decrease in the intensity of PY spectra was mainly due to exposure to air. AFM images of the α -6T thin film (0.66 ML) taken (b) before and (c) after irradiation. No significant change in morphology was observed.

2. Variation of the PY spectra during data acquisition and derived IE values



Fig. S2 (a) $PY^{1/3}$ spectra of the α -6T thin film (0.65 ML) obtained by six consecutive scans. (b) The IE values derived from each spectra.

3. Histogram of the height distribution of the α -6T domains and terraces



Fig. S3 Histogram of the height distribution of the α -6T domains and terraces in the (a) monolayer and (b) multilayer regimes. The average values of the height were 2.58 ± 0.04 nm and 2.50 ± 0.03 nm for the monolayer and multilayer, respectively.

4. Histogram of the height distribution of the p-6P domains and terraces



Fig. S4 Histogram of the height distribution of the *p*-6P domains and terraces in (a) monolayer and (b) multilayer regimes. The average values of the height were 2.80 ± 0.04 nm and 2.94 ± 0.04 nm for the monolayer and multilayer, respectively.

5. AFM topography image of a p-6P thin film (2 ML) prepared at a substrate temperature of 85 °C



Fig. S5 AFM image of a *p*-6P thin film (2 ML) prepared at a substrate temperature of 85 °C. The size of the AFM images is $5 \ \mu\text{m} \times 5 \ \mu\text{m}$.

6. PY spectra of α -6T thin films measured in a wide photon energy rage



Fig. S6 PY spectra of α -6T thin films normalized at the peak top intensity. An offset to each PY spectrum was added for easy viewing.

7. AFM topography images of p-6P thin films (~0.3 ML) prepared at different substrate temperatures



Fig. S7 AFM topography images of *p*-6P thin films (~0.3 ML) prepared at different substrate temperatures: 60 °C, 80 °C, 85 °C, 92 °C, 100 °C, 120 °C, and 185 °C. The size of the AFM images is 5 μ m × 5 μ m.

8. The IE values of p-6P thin films (~0.3 ML) prepared at different substrate temperatures



Fig. S8 PY^{1/3} spectra of *p*-6P thin films (~0.3 ML) prepared at different substrate temperatures (T_s): (a) 60 °C, (b) 80 °C, (c) 85 °C, (d) 92 °C, (e) 100 °C, (f) 120 °C, and (g) 185 °C. (h) The IE of the *p*-6P thin films (~0.3 ML) extracted from the PY^{1/3} spectra is shown in panels (a–g).

9. AFM topography image and PY spectrum of a *p*-6P thin film (10 ML) prepared at 185 °C



Fig. S9 AFM topography images of *p*-6P thin films prepared at substrate temperatures (T_s) of (a) 120 °C and (b) 185 °C. The size of the AFM images is 20 µm × 20 µm. (c) PY^{1/3} spectra of *p*-6P thin films prepared at $T_s =$ 120 °C and 185 °C. The IE values of the *p*-6P thin films were estimated to be 5.63 eV ($T_s = 120$ °C) and 5.64 eV ($T_s = 185$ °C).

10. $PY^{1/3}$ spectra of p-6P (1 ML)/ α -6T (1 ML) and p-6P (2 ML)/ α -6T (1 ML) thin films



Fig. S10 (a) PY^{1/3} spectra of α -6T (1 ML), *p*-6P (1 ML), *p*-6P (1 ML)/ α -6T (1 ML), and *p*-6P (2 ML)/ α -6T (1 ML) thin films grown on SiO₂ surfaces. The IE values of the α -6T (1 ML) layers in the *p*-6P (1 ML)/ α -6T (1 ML) and *p*-6P (2 ML)/ α -6T (1 ML) thin films were estimated to be 4.95 eV and 4.97 eV, respectively. (b) AFM images of the *p*-6P (1 ML)/ α -6T (1 ML) and *p*-6P (2 ML)/ α -6T (1 ML) thin films. The size of the AFM images is 20 µm × 20 µm.