

Supporting Information

Experimental:

UV-Vis absorption spectra were measured with Agilent 8453. All thin film samples were deposited on the quartz substrate. The band gap of the separate layers (pentacene, Ta₂O₅, PVP and PMMA) were calculated by the following equation:

$$E_g \text{ (eV)} = hc / \lambda_{\text{onset}} \approx 1241 / \lambda_{\text{onset}} \text{ (nm)}$$

Vacuum-ultraviolet spectroscopy (PSY-202, Japan Sumitomo) was used to obtain the ionization potentials of the separate layers. The light source was Deuterium lamp and the photon energy ranged from 5.0 eV to 8.0 eV. The separate layers were deposited on the ITO substrate (the same process as stated in the **Experimental** part of the paper) and measured in the measurement chamber under a 1×10^{-2} Pa vacuum. With the increasing of photon energy, the outermost electrons would be excited to the vacuum level and then the threshold energy, which was the ionization potential, was attained. The ionization potential was consistent with the definition of the HOMO level of organic materials and the valence band (VB) of inorganic materials. Then the LUMO level or the conduction band (CB) could be estimated by the following equation:

$$E_{\text{LUMO}} = E_{\text{HOMO}} + E_g$$

$$E_{\text{CB}} = E_{\text{VB}} + E_g$$

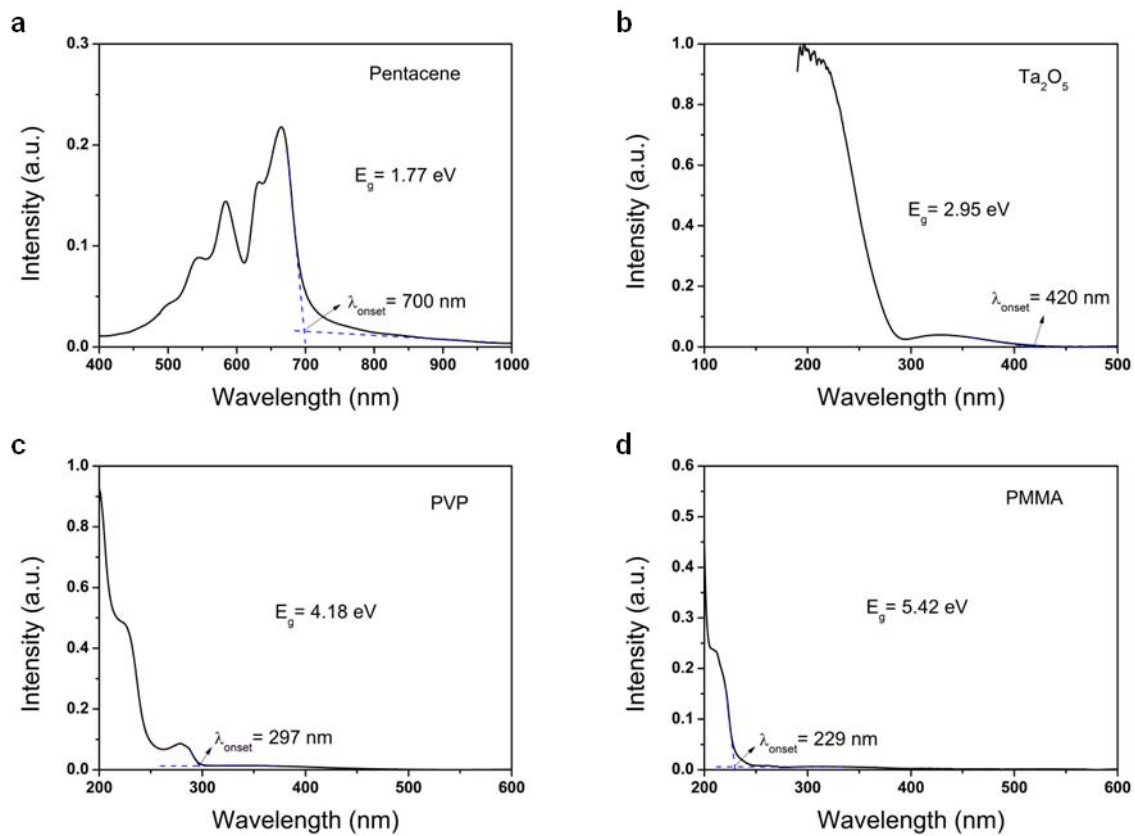


Figure S1. UV-Vis absorption spectra of (a) pentacene, (b) Ta_2O_5 , (c) PVP and (d) PMMA.

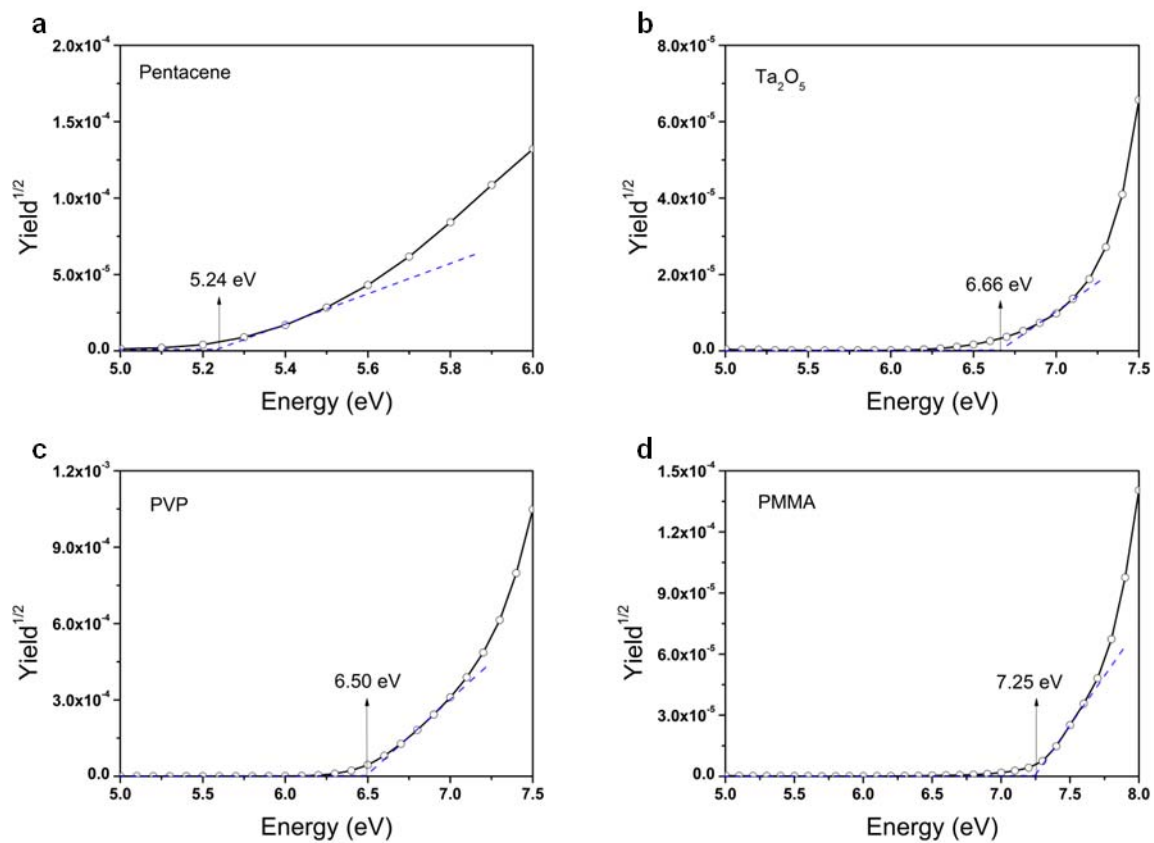


Figure S2. The vacuum-ultraviolet spectroscopy of (a) pentacene, (b) Ta₂O₅, (c) PVP and (d) PMMA.