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Determination of Energy Level Alignment at Interfaces of Hybrid and Organic Solar Cells under Ambient Environment

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Supporting Information

The IP's of P3HT, TIPS-pentacene and PCBM films was measured by PESA in air. PESA spectra of these organic films on glass substrates are shown in **Fig. S1** along with the response for bare glass. For organic semiconductors the threshold energy for yield of electrons from the surface corresponds to the IP of the film.[12,13] These IP's are listed in Table 1.

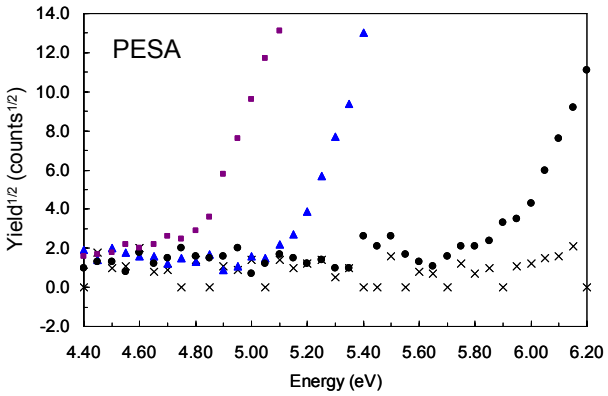

Fig. S1 PESA spectra measured in dry air for thin films of P3HT (■), TIPS-pentacene (▲), and PCBM (●) on glass. The instrument response from a bare glass substrate (**X**) is shown for comparison.

X-ray diffraction (XRD) spectra (**Fig. S2A**) were collected for spin-cast TIPS-pentacene and 1:1 P3HT:TIPS-pentacene films annealed at 150°C on Si in order to access the crystallinity of TIPS-pentacene in these films. This data was collected with a Philips X'Pert MPD X-ray Diffractometer using a Cu anode and a Θ/2Θ (incident beam angle/detected beam angle) configuration. XRD of the spin-cast TIPS-pentacene films shows peaks at 5.4, 10.7, 12.7 and 16.1° consistent with molecular ordering similar to that reported for bulk TIPS-pentacene crystals[31] XRD of the mixed 1:1 P3HT:TIPS-pentacene film shows less order with only two, less intense peaks present at 10.7 and 16.0° despite similar quantities of TIPS-pentacene in the films.

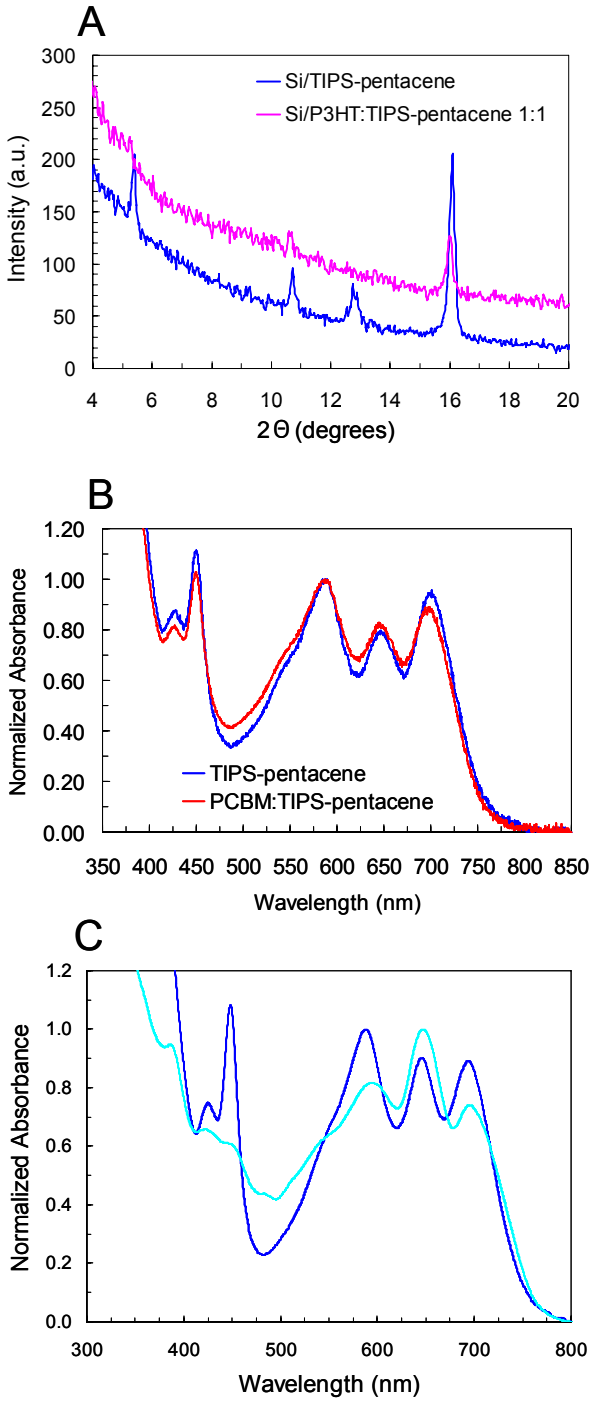

Fig. S2 (A) XRD of a spun cast TIPS-pentacene film and a spun cast 1:1 P3HT:TIPS-pentacene film annealed at 150oC, and (B) Normalized UV-Vis spectra of a TIPS-pentacene film and a mixed 1:1 PCBM:TIPS-pentacene film, (C) Normalized UV/Vis spectra for drop cast (light blue) and spun cast (dark blue) thin films of TIPS-pentacene on ZnO

A comparison of the normalized UV-Vis spectra of ZnO/TIPS-pentacene and ZnO/PCBM:TIPS-pentacene films are depicted in **Fig. S2B**, corresponding to the devices shown in **Fig. 5**. Both the TIPS-pentacene and PCBM:TIPS-pentacene films show the characteristic absorption peaks at 425 and 450 nm noted above to correspond to disordered TIPS-pentacene. Comparison of the position and peak intensity of the absorption peaks at 425, 450, 600, 650 and 700 nm for these two films confirms that TIPS-pentacene is present in both. These results confirm that TIPS-pentacene does not entirely react with PCBM in a solution of chlorobenzene prior to film deposition, although it should be noted that even a small amount of adduct formation between TIPS-pentacene and PCBM may significantly alter device performance without being readily measurable by UV-Vis.

In order to access the degree of molecular order of spin-cast TIPS-pentacene films used in this study, TIPS-pentacene films were prepared by drop casting and spin coating (at 1000 rpm for 1 min) from a solution of 20 g/L TIPS-pentacene in toluene onto cleaned glass substrates. Normalized UV-Vis spectra for these TIPS-pentacene films are shown in **Fig. S2C**. Drop-cast TIPS-pentacene films prepared by this method have been reported to be highly crystalline.[31] The onset of absorption for spin-cast TIPS-pentacene films is very slightly blue shifted compared to that for the drop-cast film, consistent with lower molecular order in the spin-cast film. In addition sharp peaks appear at 425 and 450 nm in the more disordered spin-cast film, along with a change in the relative intensities of the peaks at 600, 650 and 700 nm. These changes in the absorption characteristics of the spin-cast TIPS-pentacene film suggest that it is less crystalline than the drop-cast film which likely leads to reduced mobility.