

Supplementary Information

The Band Energy Diagram of PCBM-DH6T Bulk Heterojunction Solar Cells: Synchrotron-Induced Photoelectron Spectroscopy on Solution Processed DH6T:PCBM Blends and *In-situ* Prepared PCBM/DH6T Interfaces.

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To section **Interface Experiment:**

To retrace the deposition of DH6T also for the first evaporation steps from the C1s emission, difference spectra have been calculated. These show the DH6T C1s emission during the step-wise evaporation of DH6T on PCBM (see **Figure S1**).

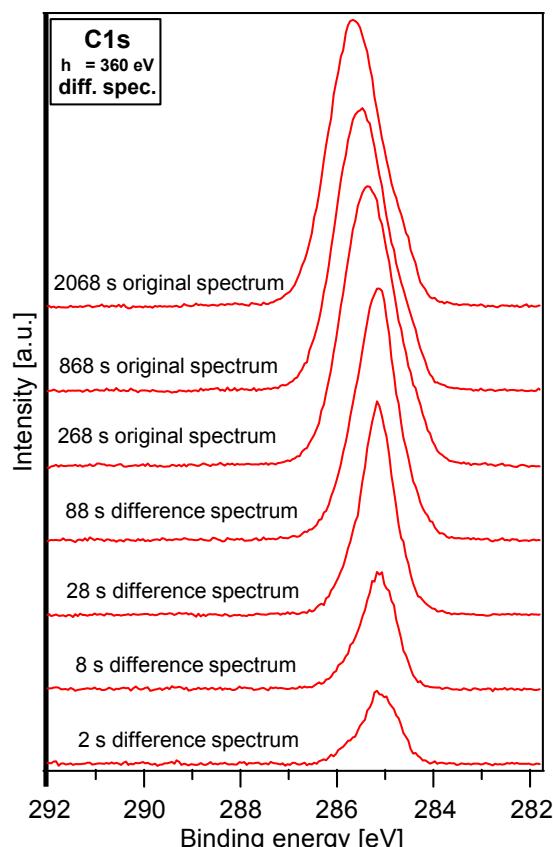


Figure S1: Difference spectra of the C1s emission of the evaporation experiment. For the first deposition steps, the PCBM spectrum has been subtracted to reveal an additional carbon emission attributed to DH6T.

To section **Blends**

Difference spectra of the valence regions for the blend films have been calculated in order to evaluate HOMO positions for the individual blend components, namely PCBM and DH6T (see **Figure S2, S3, and S4**).

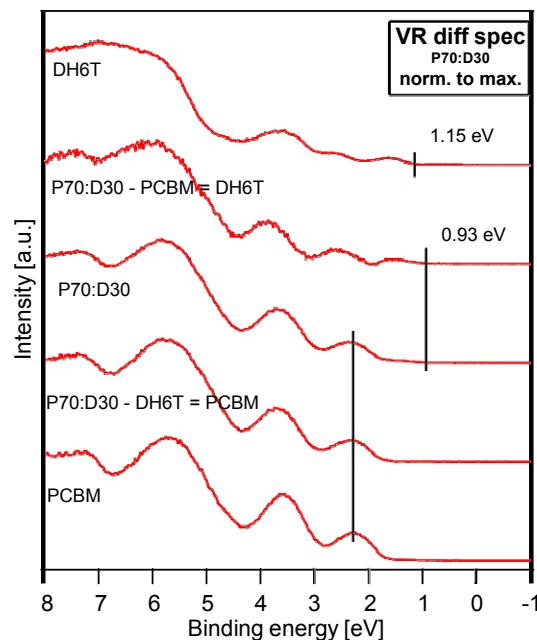


Figure S2: Valence region difference spectra for the P70:D30 blend.

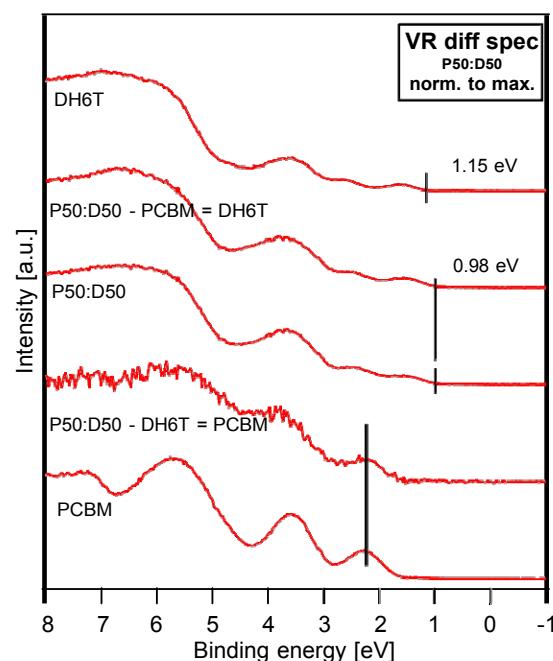


Figure S3: Valence region difference spectra for the P50:D50 blend.

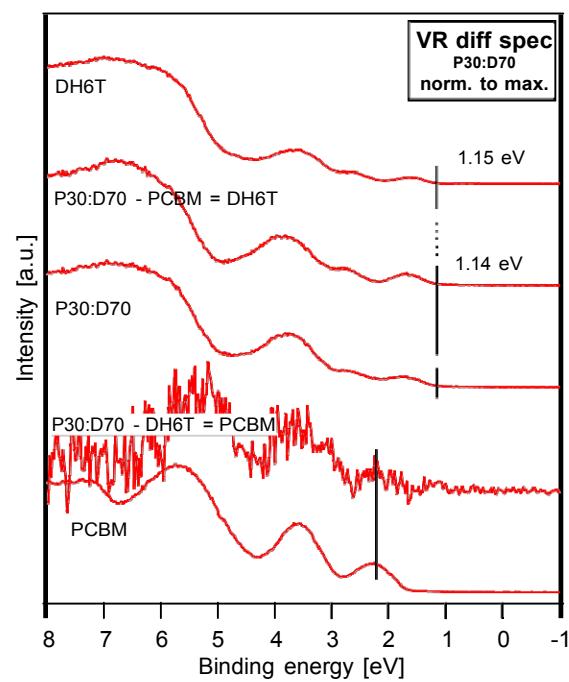


Figure S4: Valence region difference spectra for the P30:D70 blend.