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Supplemental Information for

Full electronic structure across a polymer heterojunction solar cell

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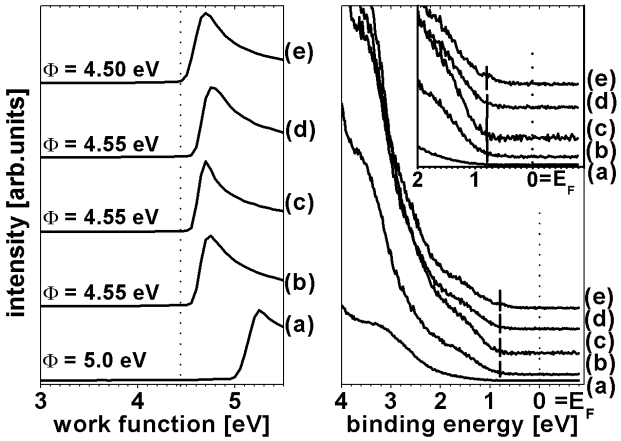
PEDT:PSS/PFTBTT and P3HT/PFTBTT interface

The pristine PEDT:PSS work function (ϕ) of 5.0 eV is decreased to 4.55 eV upon deposition of PFTBTT. The VB onset is located at 0.8 eV binding energy (BE). The resulting ionization energy is 5.35 eV. The PFTBTT film thickness on top of P3HT-IL presented here is much thicker as in Fig. 2 in the text. Whereas the film thickness here is ~25 nm, PFTBTT films in Fig. 2 are much thinner ~7 nm. In contrast to the thinner film in FigS.1 no change in the valance band onset can be seen after annealing. This indicates that annealing only affects the morphology directly at the P3HT/PFTBTT interface.



FigS. 1 Photoemission spectra of the valence region (right side) and secondary electron cutoff (left side) of a) pristine PEDT:PSS, b) PFTBTT spin coated on PEDTPSS as prepared and c) after annealing for 10 min at 140°C d) PFTBTT spin coated on top of P3HT-IL as prepared and e) after annealing for 10 min at 140°C. The inset shows a zoom of the valance band near the Fermi-energy. Vertical lines indicate the valance band onset.