

Figure S1. GIWAXS radial integration profiles along  $q_z$  for the different F8TBT loading. The numbers on the top of each profiles indicate the F8TBT weight fraction,  $f$ . The nearly unchanged positions (as a function of the F8TBT loading) of the edge-on (100), (200) and (300) scattering peaks of P3HT are indicated and labeled with the corresponding  $d$ -spacing, at  $q_z \approx 0.39 \text{ \AA}^{-1}$ ,  $0.78 \text{ \AA}^{-1}$  and  $1.17 \text{ \AA}^{-1}$ , respectively. Secondary scattering peaks at lower F8TBT concentrations, as well as intensity dropping at higher  $q_z$  values are due to the Kapton windows used for some of these experiments. The curves are shifted vertically. The profile of F8TBT it is shown for reference.

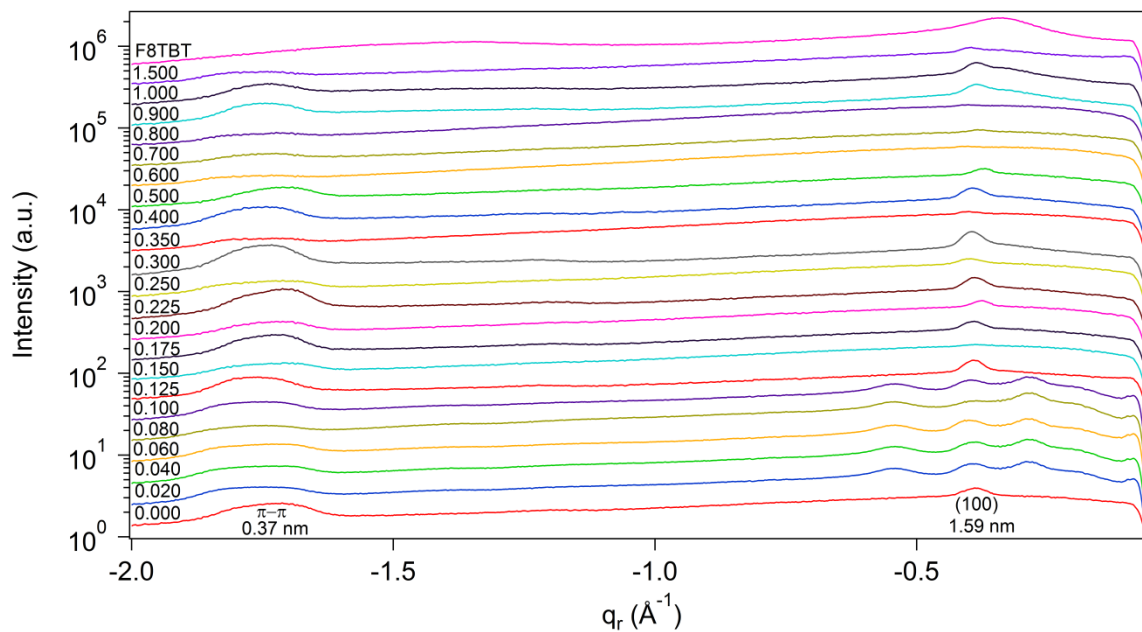


Figure S2. GIWAXS radial integration profiles along  $q_r$  for the different F8TBT loading. The nearly unchanged positions (as a function of the F8TBT loading) of the edge-on  $\pi$ - $\pi$  stacking and face-on (100) scattering peaks of P3HT are indicated and labeled with the corresponding  $d$ -spacing, at  $q_r \approx 1.72 \text{ \AA}^{-1}$  and  $0.39 \text{ \AA}^{-1}$  respectively. Secondary scattering peaks at lower F8TBT concentrations are due to the Kapton windows used for some of these experiments. Same notation as in Fig. S1.

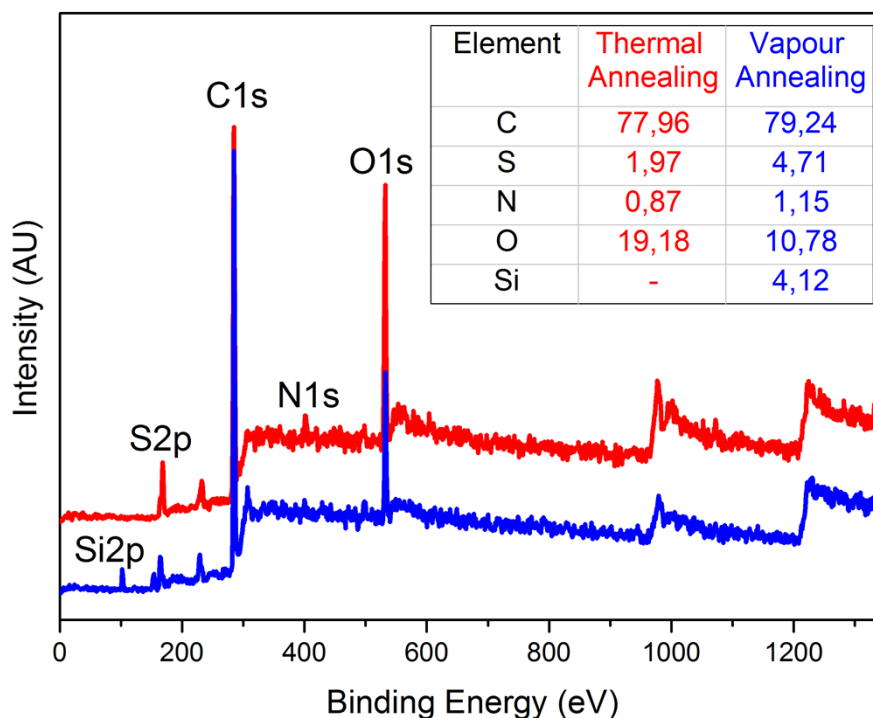


Figure S3. X-ray photoemission spectra of the bottom surface of thermally and vapour annealed films. For these measurements, P3HT/F8TBT films were spin-cast on PEDOT:PSS and thermally or vapour annealed. The films were then floated off onto DI water, inverted and placed on a Si substrate with the initial substrate surface facing up. Inset: atomic composition of each sample.

	Thermal Annealing	Vapour Annealing
S/N ratio	2.26	4.09
F8TBT % (before correction)	77%	50%
<b>F8TBT % (after correction)</b>	<b>87%</b>	<b>58%</b>

In our previous XPS studies on P3HT/F8TBT films, we have observed that the amount of N measured with XPS is consistently lower by 20% than the theoretical composition of the F8TBT polymer. [Vaynzof *et al*, **Compositional and Morphological Studies of Polythiophene/Polyflorene Blends in Inverted Architecture Hybrid Solar Cells**, *Adv. Funct. Mater.* 2012, 22, 2418–2424] Taking this into account we can apply a correction to compensate for this in calculating the % of F8TBT on the film surface.