Supporting Information:

## Competition between morphological attributes in the thermal annealing and additive

## processing of polymer solar cells

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**Figure S1**. EQE and UV absorption curves of the organic solar cells based on thermal annealed QxO or QxT blend with  $PC_{71}BM$ .



**Figure S2** Contrast function between pairs of materials or vacuum: polymer:fullerene (QxO:PC<sub>71</sub>BM and QxT:PC<sub>71</sub>BM and materials:vacuum (QxO:vacuum, QxT:vacuum, PC<sub>71</sub>BM:vacuum) (where  $\delta$  and  $\beta$  describe dispersion and absorption properties in the complex index of refraction  $n = 1 - \delta + i\beta$ )).



Figure S3, Fitted R-SoXS profiles with log-normal distribution functions for QxT-annealed, QxO-annealed, QxT-DIO and QxO-DIO blend samples. In the q-range were the R-SoXS can not be fitted with log-normal function, an additional power law function was utilized.

Total scattering intensity (TSI) is calculated by two different ways:

- The first one is integrating the scattering intensity in the q range we measured. This method gives us relative purity of 0.43, 0.78, 0.93, and 1 for QxO-annealed, QxTannealed, and QxT-DIO and QxO-DIO, respectively. Due to the q range limitation, TSI of QxT-annealed is underestimated.
- The second one is by fitting scattering profiles with log-normal function and extend it to higher q range. Then, calculate the area of the fitted the curve. The results are 0.47, 0.68, 0.89 and 1 for for QxO-annealed, QxT-annealed, and QxT-DIO and QxO-DIO, respectively.

The final results are the average of method 1) and 2). Note that the ranking is not changing between the two methods and that the results are very similar for all, but the QxT-annealed sample.

## Crystallinity

Polymer/fullerene blend thin films were characterized using grazing incidence wide-angle xray scattering (GIWAXS) to acquire crystallinity information. Both QxO and QxT polymers were blended with PC<sub>71</sub>BM, cast with DCB, and annealed under the same conditions as used for devices. Thin films were spin-cast on PSS-treated Si substrates and had thicknesses ~125 nm and ~80 nm for QxO and QxT based films. 2D GIWAXS patterns along with out-of plane (q<sub>z</sub>) and in plane (q<sub>xy</sub>) profiles are shown in **Figure S4**. Both GIWAXS patterns show broad (100) polymer lamellar reflections between q = 0.3 – 0.4 Å<sup>-1</sup>. QxO-based blends films show diffraction peaks (100) at q  $\approx$  0.3 Å<sup>-1</sup>, while QxT-based blends films exhibit a (100) peak near q  $\approx$  0.35 Å<sup>-1</sup>. This indicates that QxT blend film shows larger lamellar stacking than QxO based film. Furthermore, (010) peaks at q = 1.6 - 1.7 Å<sup>-1</sup> suggest that some  $\pi$ - $\pi$  stacking is observed for both QxO and QxT-based blend films. By fitting  $\pi$ - $\pi$  stacking peak by Gaussian function, we find QxT exhibits larger  $\pi$ - $\pi$  stacking size (see Supporting information Figure S5). This indicates that QxT-based polymers have stronger  $\pi$ - $\pi$  stacking than QxO-based polymers. Meanwhile, the location of  $\pi$ - $\pi$  stacking peak demonstrates the  $\pi$ - $\pi$  stacking distance. QxT exhibits  $\pi$ - $\pi$  stacking peak at 1.66 Å<sup>-1</sup> suggesting a distance of 3.78 Å. QxO shows a broad peak at 1.62 Å<sup>-1</sup>, indicating a larger distance 3.87 Å. It is known that smaller  $\pi$ - $\pi$  stacking distance is more favorable for charge transfer. It should also be noted that (010) peaks are present in the out-of plane direction, which indicates a face-on crystal orientation in thin films. The predominant face-on orientation, larger lamellar stacking and stronger  $\pi$ - $\pi$ stacking of QxT based polymers in blend films may allow for efficient hole transport in BHJ organic solar cells, which could be the reasons that OxT-based solar cells exhibits higher  $J_{sc}$ . Concerning their chemical structure, the QxT-based polymer has an extending  $\pi$  conjugated alkythienyl substitution. However, ordering in these systems as observed by WAXS is rather week when compared to other materials. The ordering in the DIO processed films should be even weaker. Polymer-polymer ordering is thus unlikely to play a significant roll in the device performance.



**Figure S4**. (a) GIWAXS 2D scattering pattern corrected for the missing wedge of blend films of the thermal annealed  $QxO:PC_{71}BM$  and  $QxT:PC_{71}BM$ ; (b) Out-of plane (OOP) and inplane (IP) sector averages of blend films extracted from Figure 2(a); GIWAXS profiles have been shifted vertically for comparation.



**Figure S5**: Fitted (010) peaks for GIWAXS profiles in out-of plane direction for (a) QxO:PC<sub>71</sub>BM and (b) QxT: PC<sub>71</sub>BM.

The full width at half maximum (**FWHM**) and the location of (010) peak were determined by fitting GIWAXS profiles with Gaussian function. The FWHM of GIWAXS peaks are corrected by instrumental resolution. The coherence length of  $\pi$ - $\pi$  stacking of 1.8 nm for QxO based device, 2.5 nm for QxT based device were obtained. The  $\pi$ - $\pi$  stacking spacing is 0.387 nm and 0.378 for QxO and QxT based device, respectively.