Electronic Supplementary Material (ESI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2016

Supplementary material

Table S1: Photovoltaic parameters of PTB7:$PC_{71}BM$ and P3HT:$PC_{71}BM$ devices.

	J_{sc} [mA/cm^2]	V_{oc} [mV]	FF [%]	PCE [%]
PTB7:$PC_{71}BM$ devices	17.68	729.98	56.04	7.23
P3HT:$PC_{71}BM$ devices	9.83	618.60	45.33	2.80

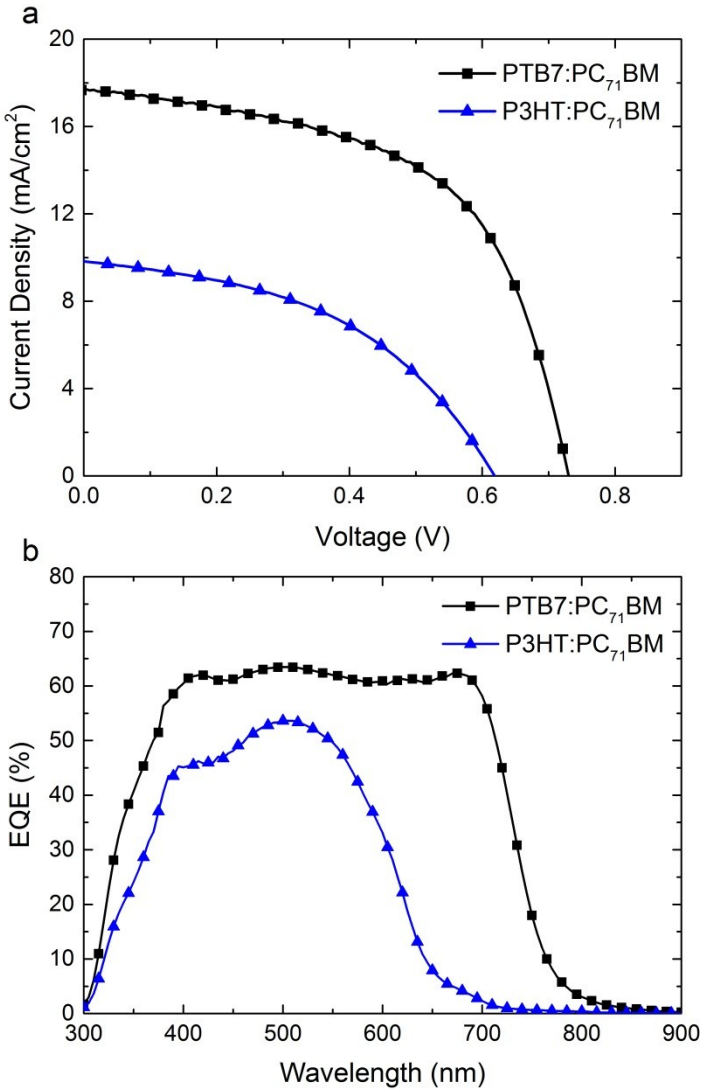

FIG. S1. (a) J-V characteristics curves and (b) EQE curves for PTB7:$PC_{71}BM$ and P3HT:$PC_{71}BM$ fresh devices.

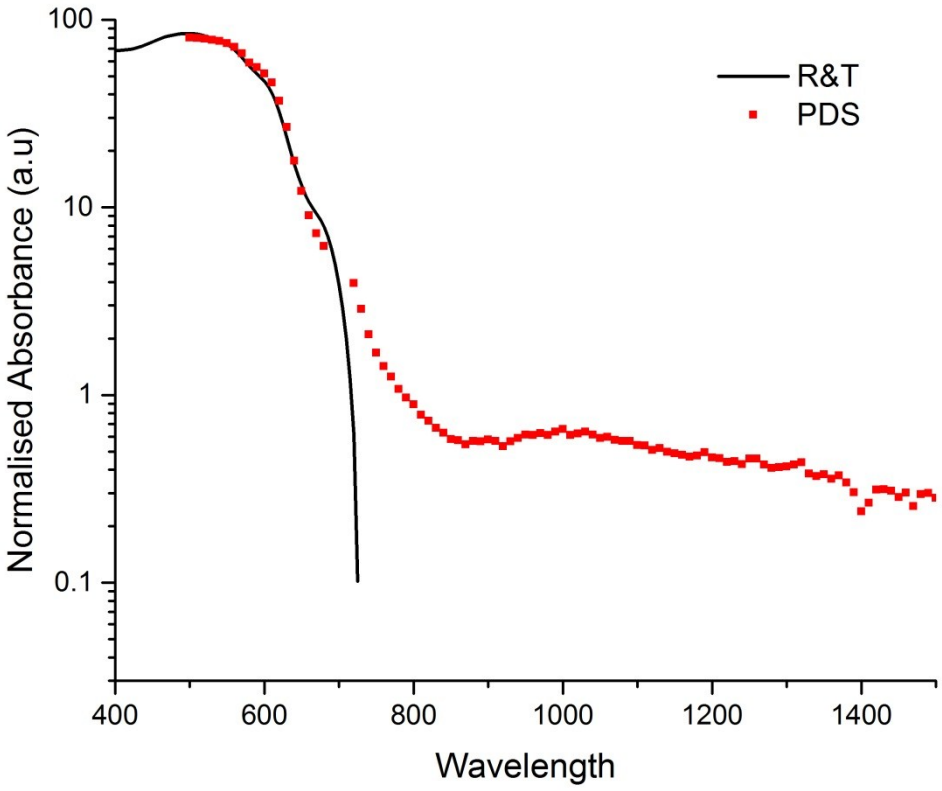

FIG. S2. A comparison of absorbance of fresh P3HT:$PCB_{71}M$ film measured using R&T and PDS techniques is shown in the figure above. Whilst the measured absorbance from R&T method drops off very quickly beyond 650nm due to its low sensitivity, the detailed sub-bandgap features are observed using PDS, which is 2 orders of magnitude more sensitive than the R&T method.

Urbach energy calculation:

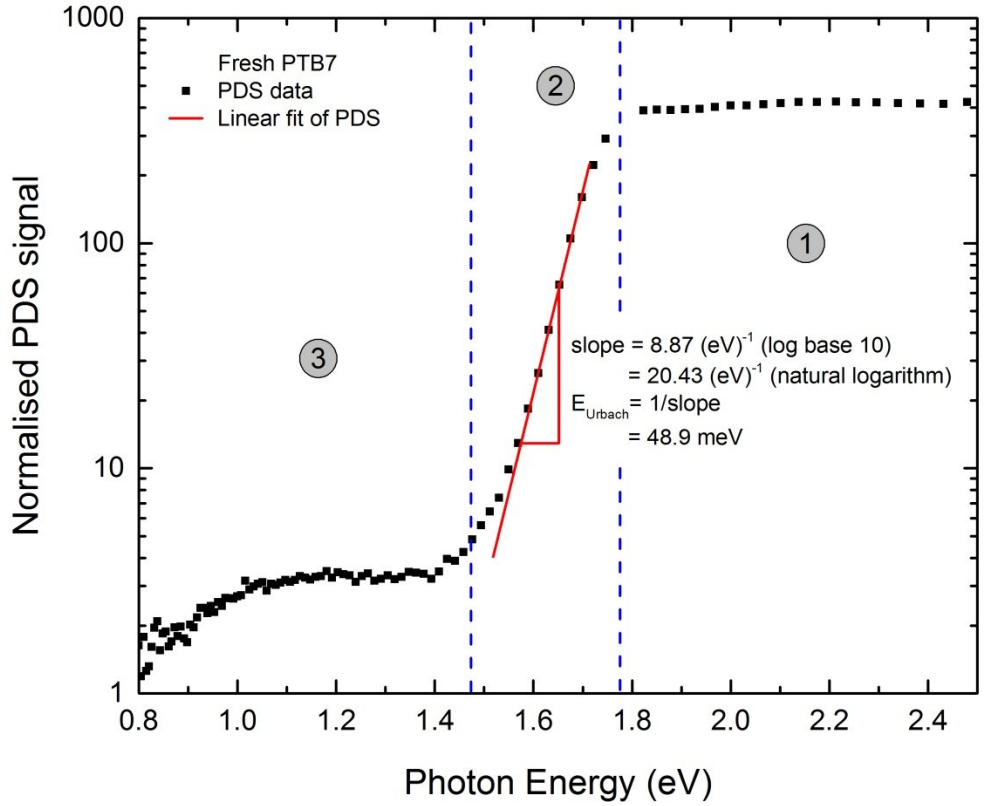

FIG. S3. Calculation of Urbach energy of fresh PTB7:$PC_{71}BM$ film from the slope of the linear region of normalized PDS signal is shown in the figure above. The Urbach energy of PTB7:$PC_{71}BM$ and P3HT:$PC_{71}BM$ (both fresh and aged) is summarized in the following table:

Film Description	Urbach Energy (meV)
Fresh P3HT:$PC_{71}BM$	109.9
Aged P3HT:$PC_{71}BM$	109.8
Fresh PTB7:$PC_{71}BM$	48.9
Aged PTB7:$PC_{71}BM$	71.1

Sub-bandgap absorption co-efficient (α cm^{-1}) in region-3:

The area under the PDS curve in region 3, ∫α.dE, is directly related to the density of defect states [1]. To calculate this area, we first need to isolate the absorption in region 3, and fit this region with a Gaussian function. For example, the Gaussian expression used to fit the PTB7:$PC_{71}BM$ fresh film is as follows:

$$y = y_0 + \frac{A}{w \times \sqrt{\frac{\pi}{4 \times ln(2)}}} \times e^{\frac{-4 \times ln(2) \times (x - x_c)^2}{w^2}}$$

The Gaussian fits for all four samples are shown in Fig. S5.

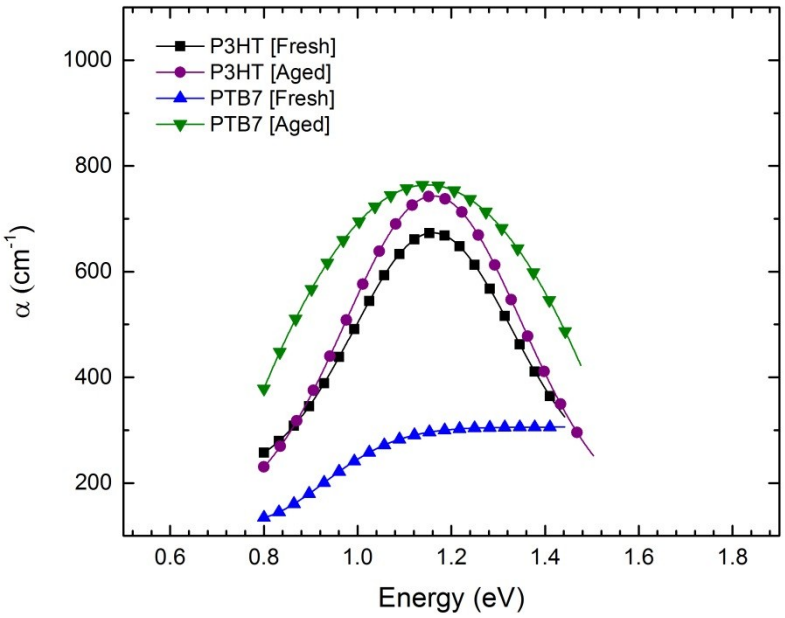

FIG. S4. Gaussian fits of absorption coefficient in region 3 (low energy region).

These functions were then integrated over the displayed energy range. From this, we can compare the area under the curve for fresh and aged films, as shown below. The ratio for PTB7 is considerably higher.

Film	Ratio of area under sub-bandgap absorption curve of aged and fresh films, ∫α.dE
P3HT:$PC_{71}BM$	1.14
PTB7:$PC_{71}BM$	2.60

REF:

[1] W.B. Jackson, N.M. Amer, Direct measurement of gap-state absorption in hydrogenated amorphous silicon by photothermal deflection spectroscopy, Physical Review B, 25 (1982) 5559-5562.

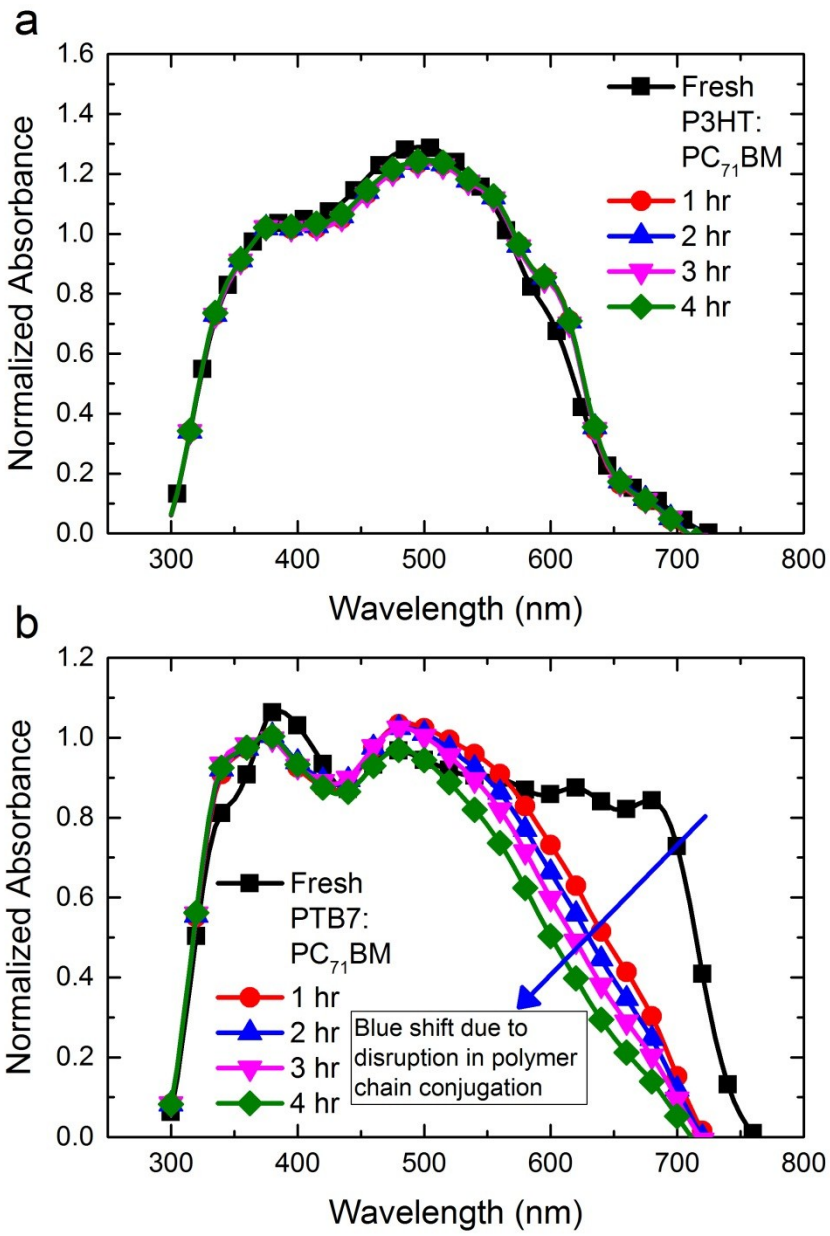

FIG. S5. Hourly absorption spectra of (a) P3HT:$PC_{71}BM$ and (b) PTB7:$PC_{71}BM$ films under continuous 1-sun illumination. All spectra was normalised to the absorption at 370 nm.

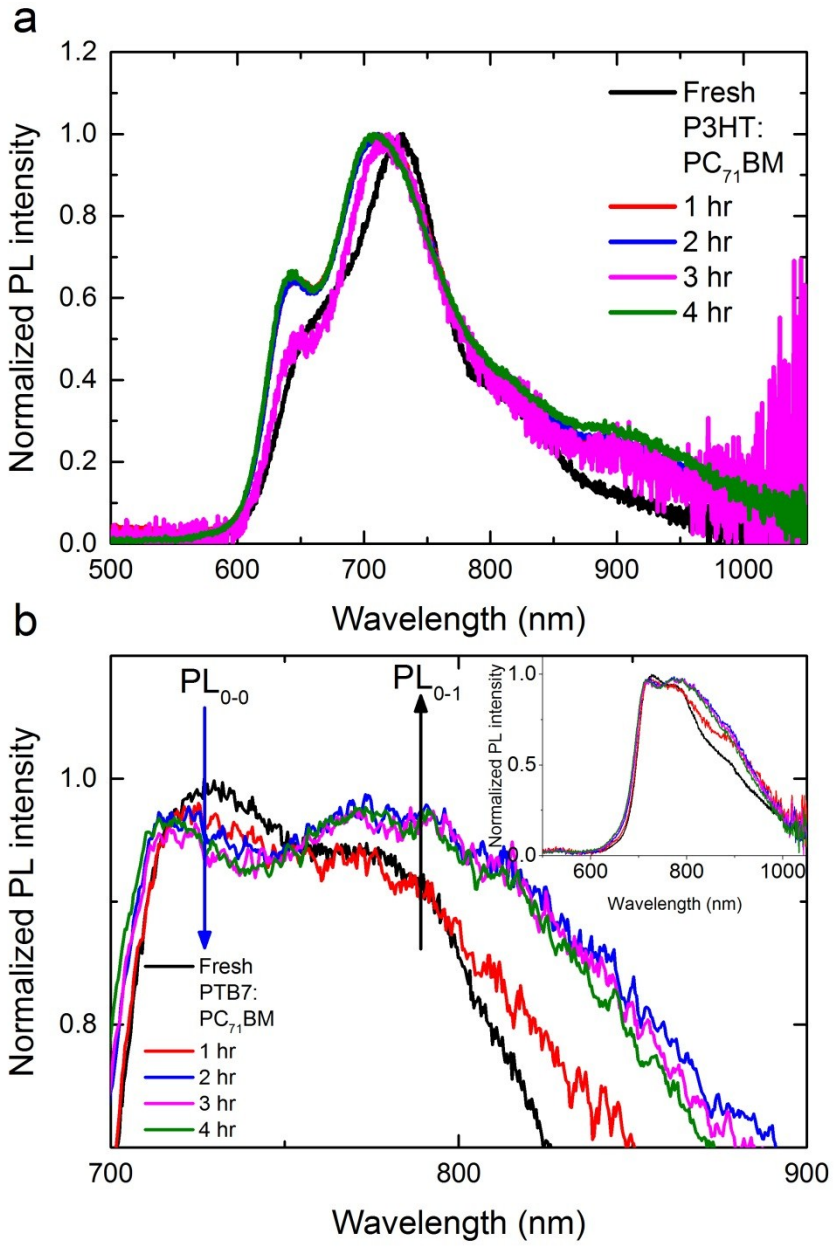

FIG. S6. Hourly PL spectra of (a) P3HT:$PC_{71}BM$ and (b) PTB7:$PC_{71}BM$ films under continuous 1-sun illumination.

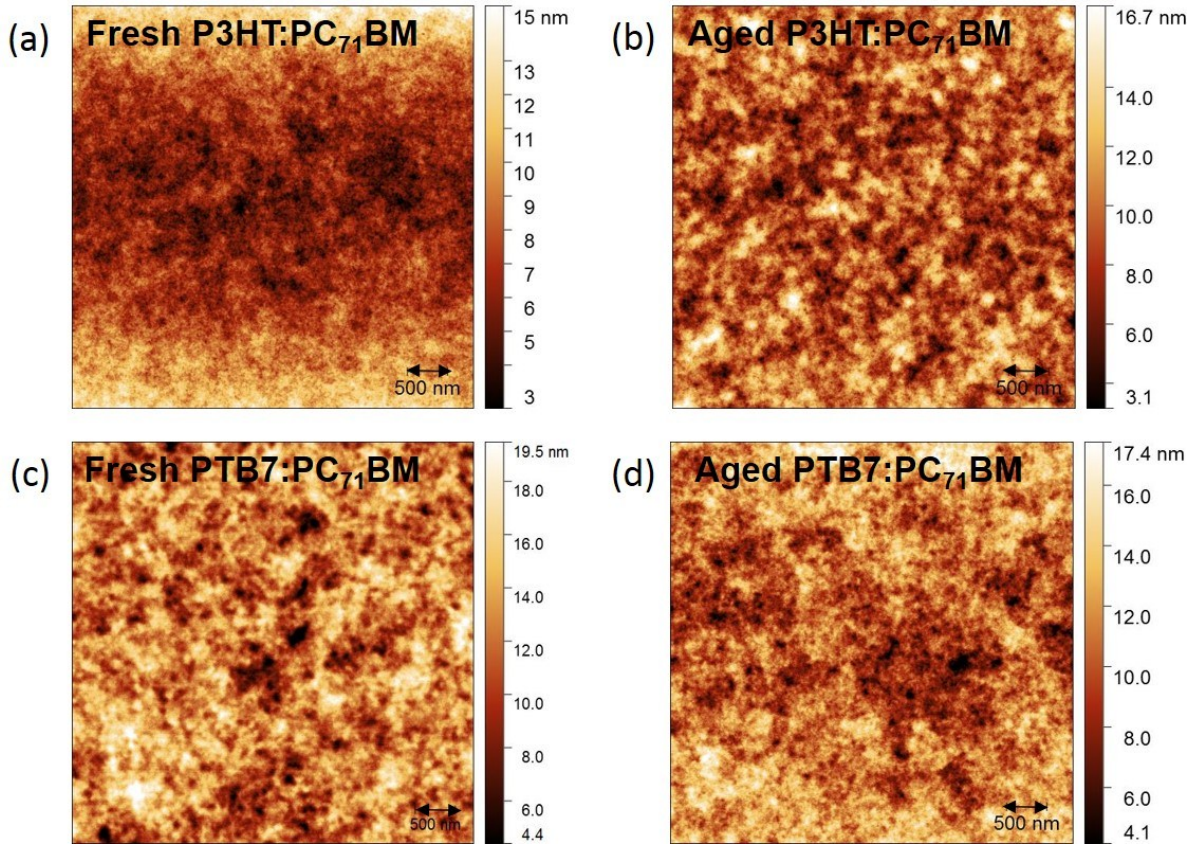

FIG. S7. AFM images (5 µm x 5 µm) of P3HT:PC_{71}BM and PTB7:PC_{71}BM films under both fresh and aged conditions. The RMS surface roughness extracted from AFM images are summarized in the following table:

Film Description	**RMS Surface Roughness (in nm) from AFM**
Fresh P3HT:PC_{71}BM	2.27
Aged P3HT:PC_{71}BM	2.24
Fresh PTB7:PC_{71}BM	2.74
Aged PTB7:PC_{71}BM	2.27

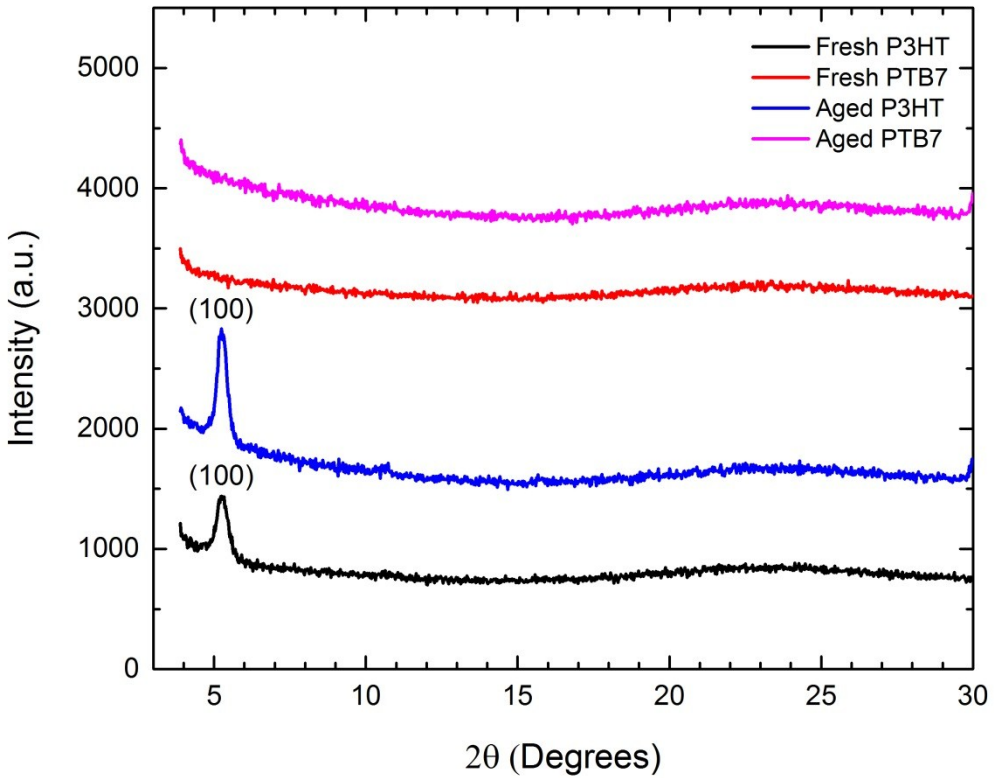

FIG. S8. X-ray diffraction patterns of P3HT:$PC_{71}BM$ and PTB7:$PC_{71}BM$ films under both fresh and aged conditions

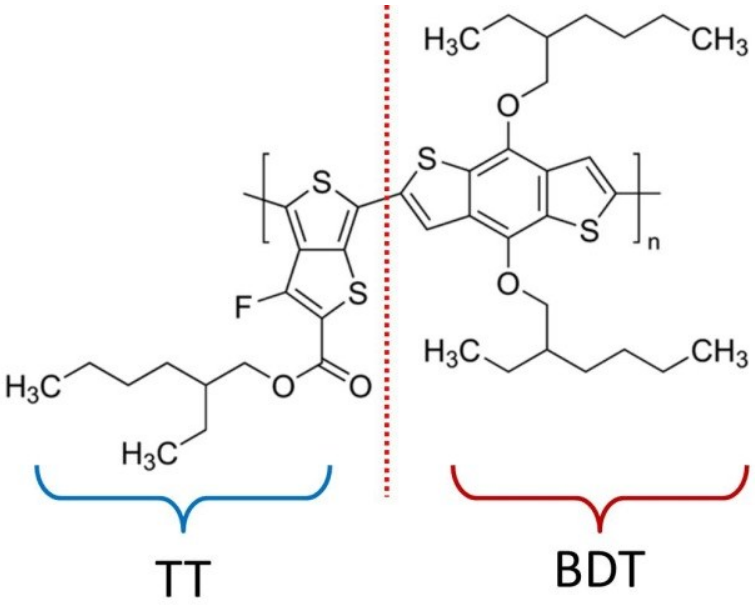

FIG. S9. Chemical structures of the repeat unit consisting BDT and TT for the polymer donor PTB7