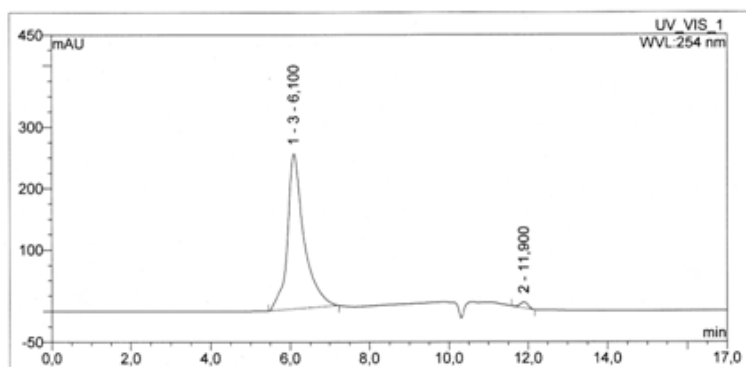
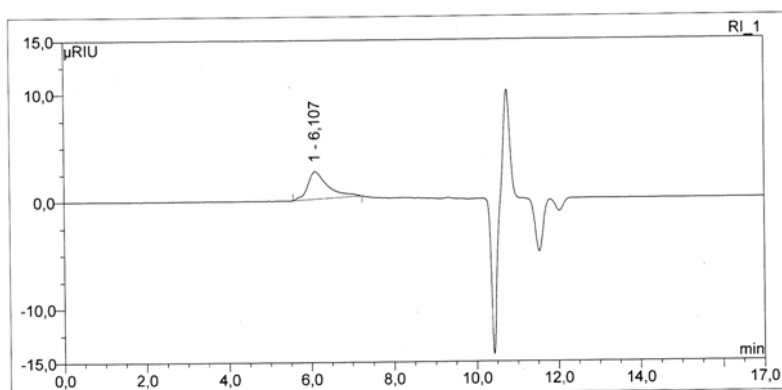


Supplementary Information

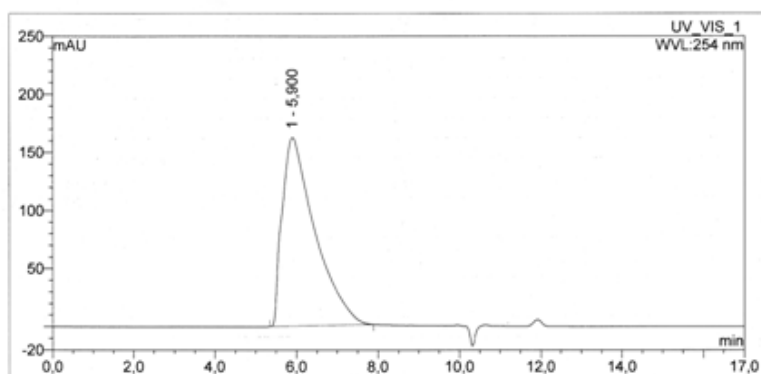
Figure S1 SEC chromatograms of **P3HT-co-P3EtPT**, **P3HT-b-P3EtPT** and **P3HT-b-P3BrPT**, respectively, recorded at 40 °C, using RI and UV-visible detector, and THF as eluent.



SEC chromatogram of **P3HT-co-P3EtPT**.



SEC chromatogram of **P3HT-b-P3EtPT**.



SEC chromatogram of **P3HT-b-P3BrPT**.

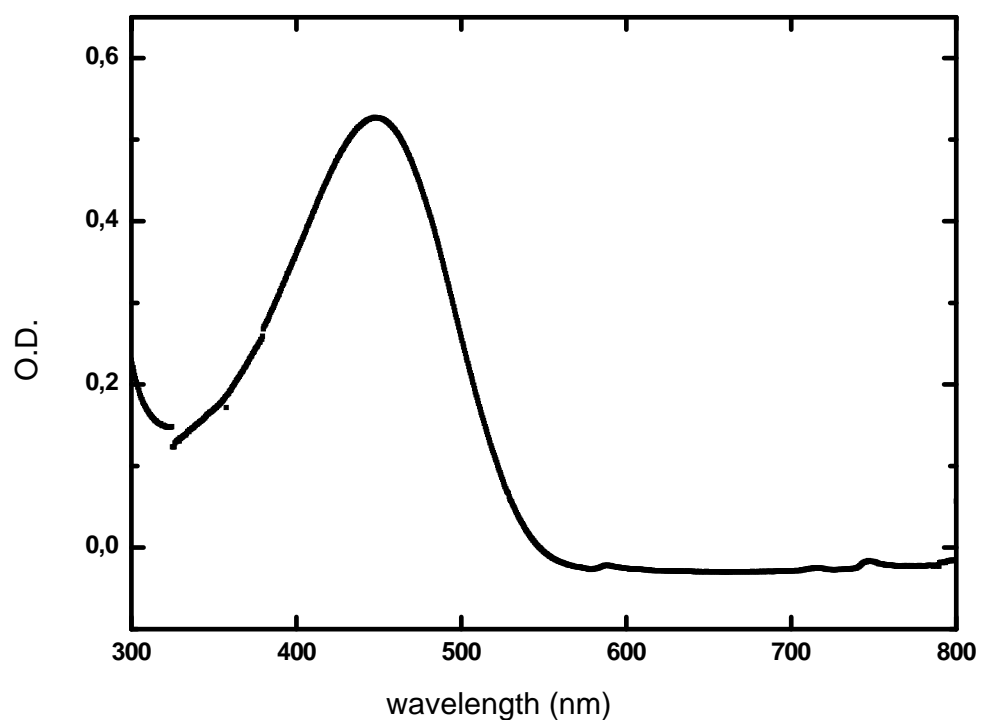


Figure S2 (a) The absorption spectrum of **P3HT-b-P3AcidHT** in toluene solution.

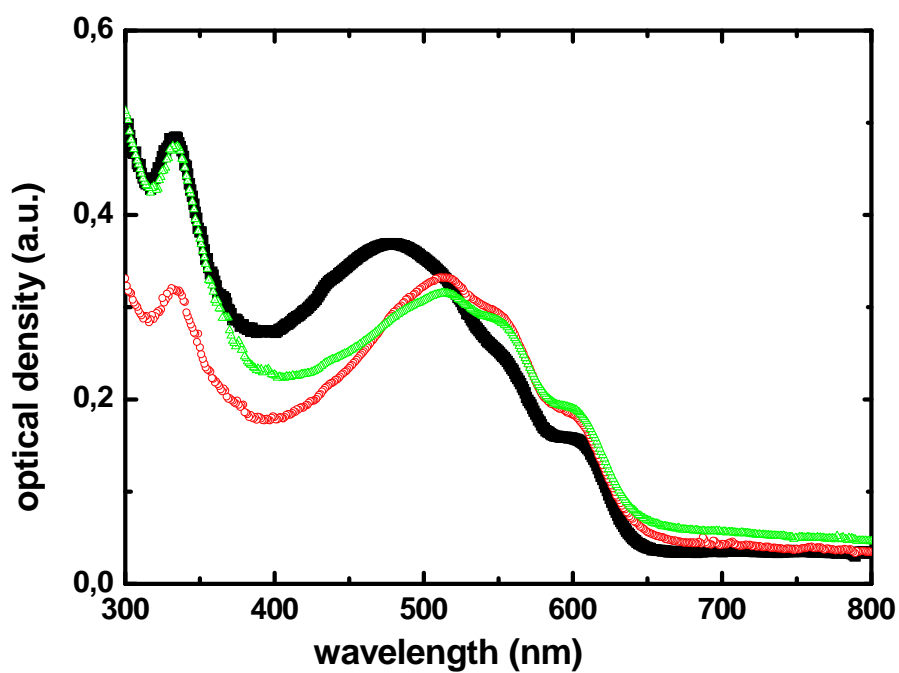


Figure S2 (b) The absorption spectra of blend films of **P3HT:PC₆₁BM** (red), **P3HT-b-P3AcidHT:PC₆₁BM** and **P3HT-co-P3EtPT:PC₆₁BM** (black).

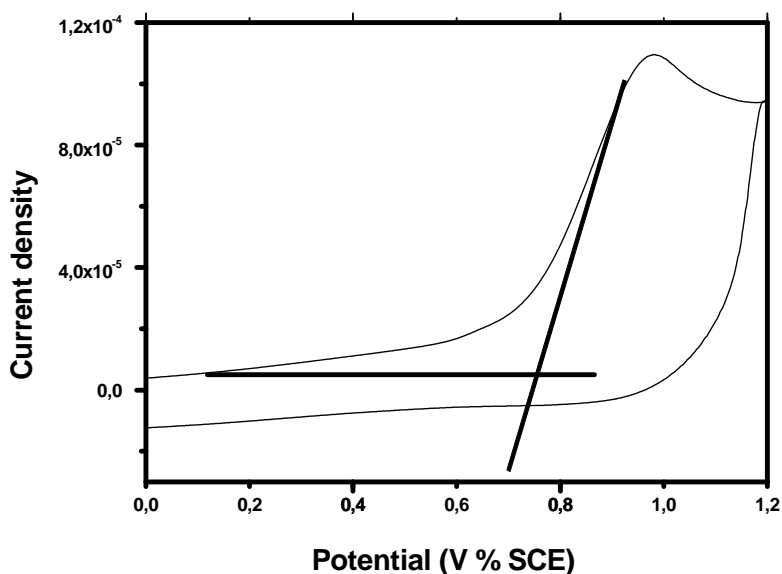


Figure S3 Example of cyclic voltammogram of the synthesized copolymers.

The electrochemical behaviors of the copolymers were examined by cyclic voltammetry (CV). The HOMO levels are calculated from the onset of the oxidation peak and referenced to the HOMO of ferrocene (-4.8 eV, below the vacuum level), using the following equation.¹

$$E^{\text{HOMO}} = [-e(E_{\text{onset (vs SEC)}} - E_{\text{onset (Fc/Fc+ vs SEC)}})] - 4.8 \text{ eV}.$$

Figure S3 shows an example of cyclic voltammogram of the synthesized copolymers. According to this expression, the HOMO level of the copolymer was -5.11 eV. The electrochemical measurements showed that All the copolymers have, LUMO and HOMO levels and band gap similar to those of P3HT.²

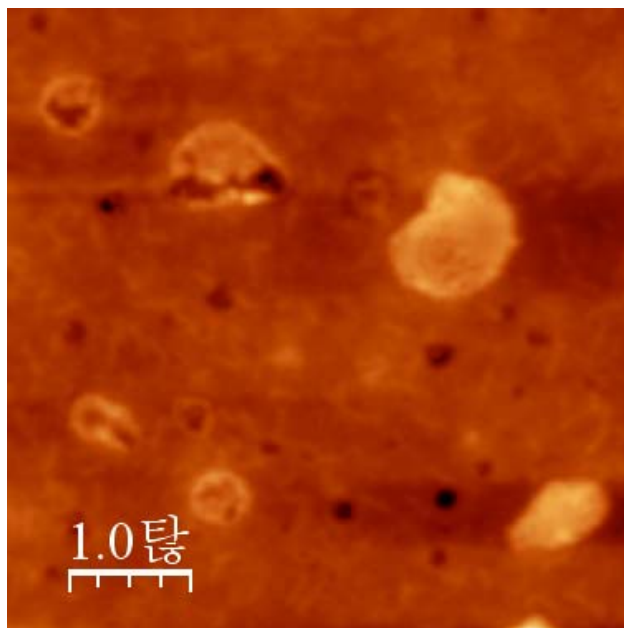


Figure S4 phase image of P3HT-co-P3EtPT: PC61BM (1:1) blend annealed at 120°C.

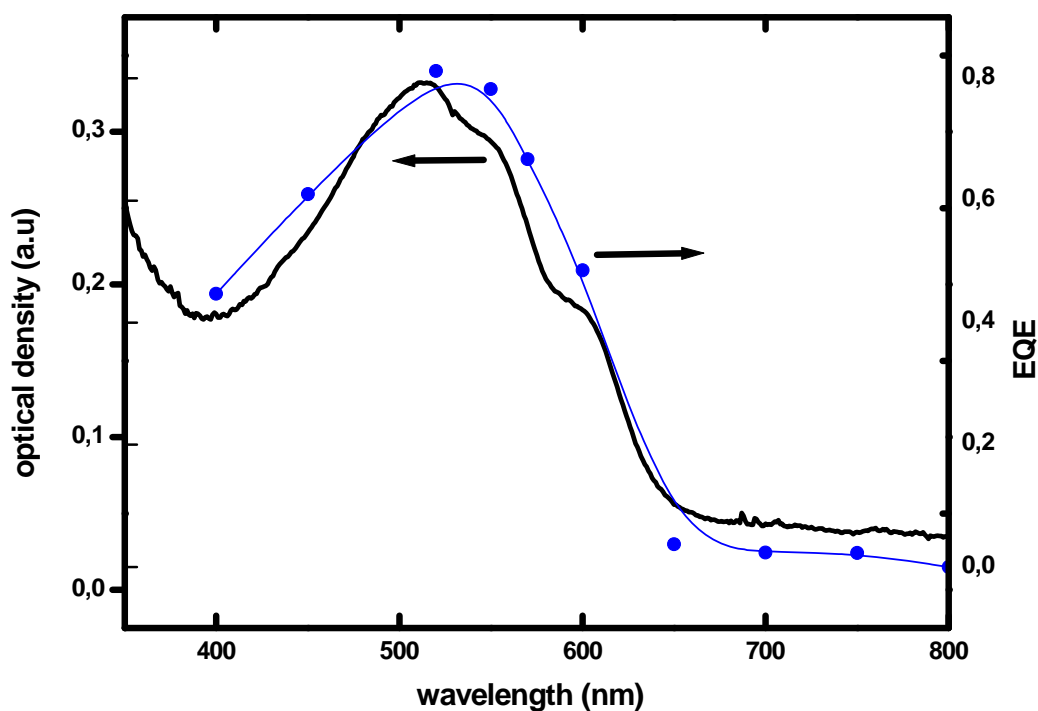


Figure S5 Example of the absorption spectra of copolymer:PC₆₁BM and the external quantum efficiency of the device of ITO/PEDOT/copolymer:PC₆₁BM/Li/ Al, the active layer is 100 nm.

1. Y. Liu, M. S. Liu and A. K. Y. Jen, *Acta Polym.*, 1999, **50**, 105-108.
2. M. Al-Ibrahim, H. K. Roth, U. Zhokhavets, G. Gobsch and S. Sensfuss, *Sol. Energy Mater. Sol. Cells*, 2005, **85**, 13-20.