**Raw Data and Data processing**

Raw data for ultraviolet–visible spectroscopy, photoluminescent and ultraviolet photoelectron spectroscopy has been uploaded for data transparency. All the data was plotted using Origin 9.1. The project files for data processing and data plotting have also been uploaded. To combine the plotted data into a manuscript figure, Adobe Illustrators were used for adjusting the layout. Below shows some important information for data processing in this work:

**Data for Fig1(b):**

Ultraviolet–visible spectroscopy data was taken using Perkin Elmer UV-VIS-NIR Spectrometer on P3HT, BBL and bulk heterojunction sample. Raw data from this instrument is an absorption intensity vs wavelength. For this instrument, two types of detectors were used for collecting the data range from 400nm to 1500nm. When the detector passed through 860nm, the signal may produce a spike (instrument error)

**Data processing for UV-vis data containing two steps:**

* Converted absorption into transmittance by using:
* Removed the spike generated by instrument.

1. Take the transmittance difference between 860nm and 865nm
2. Add the difference on the transmittance of 860nm-400nm data points