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Organic solar cells fabrication

All materials for device fabrication were purchased from Ossila Ltd. and used without further treatment. The device architecture was glass substrate/ITO/hole transporting layer (HTL)/polymer:6,6)-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$)/calcium (Ca)/aluminium (Al). PCDTBT:$PC_{71}BM$ (1:4 by weight, 20 mg/ml) or P3HT:PCBM (1:0.8 by weight, 25 mg/ml) were used as active layer materials. Pre-patterned ITO glass substrates were washed with Hellmanex solution, iso-propyl alcohol (IPA), and deionised water in ultrasonic bath for 10 min each. The substrates were dump rinsed twice in hot deionised water and once in cold deionised water. HTL2, HTL5, HTL8 was made by addition of PSFP-DTBTP 2 mg, 5 mg, and 8 mg respectively into the 1 ml of PEDOT:PSS Al4083. The HTL solution was filtered by PVDF filter (0.45 µm) and was spin-coated on the ITO substrate at 6000 rpm then annealed at 150 °C on a hot plate for 15 min. For the PCDTBT solar cells, a blended mixture of PCDTBT:$PC_{71}BM$ was spin coated on the HTL at 700 rpm to achieve a thickness of ~75 nm. For the P3HT solar cell, a blended mixture of P3HT:PCBM was spin coated on the HTL at 2000 rpm to give a thickness of ~70 nm. Calcium (2.5 nm) and aluminium (100 nm) cathodes (for PCDTBT solar cell) or aluminium (100nm) cathode (for P3HT solar cells) were deposited onto the active layer in a vacuum evaporator. The base pressure of evaporation chamber was less than 1 x 10^{-6} mbar. Devices were thermally annealed on a hot plate at 80 °C (for PCDTBT solar cells) or 150 °C (for P3HT solar cells) for 15 min. All devices were encapsulated by uv-epoxy resin with cover slide.

Preparation of films for characterisation

In general, conjugated polyelectrolytes with sulfonyl side chains attached cannot be measured by GPC due to inaccurate results. However, we can estimate their molecular weight through dialysis membrane cut off. The dialysis membrane cut-off was 12,400. Therefore this polymer has a molecular weight over 12,400.

In order to measure UV-vis absorption, thickness, AFM, and PL of HTL, PEDOT:PSS or PEDOT:PSS:PSFP-DTBTP thin films they were spin-coated at 6000 rpm for 40 s on glass substrates, silicon wafer or ITO patterned glass substrates. The cleaning steps of glass substrates were the same procedure used to ITO substrates and the thin films were thermally annealed on a hotplate at 150 °C for 15 min. For the PL measurement of PSFP-DTBTP and PCDTBT, PSFP-DTBTP solution of 15 mg/ml in water were spin-coated at 6000 rpm for 40 s on glass substrates and thermally annealed at 150 °C for 15 min then, PCDTBT (4 mg/ml in chlorobenzene) was spin-coated at 700 rpm for 30 s and thermally annealed at 80 °C for 15 min.

FT-IR spectra of CPE and HTL layers

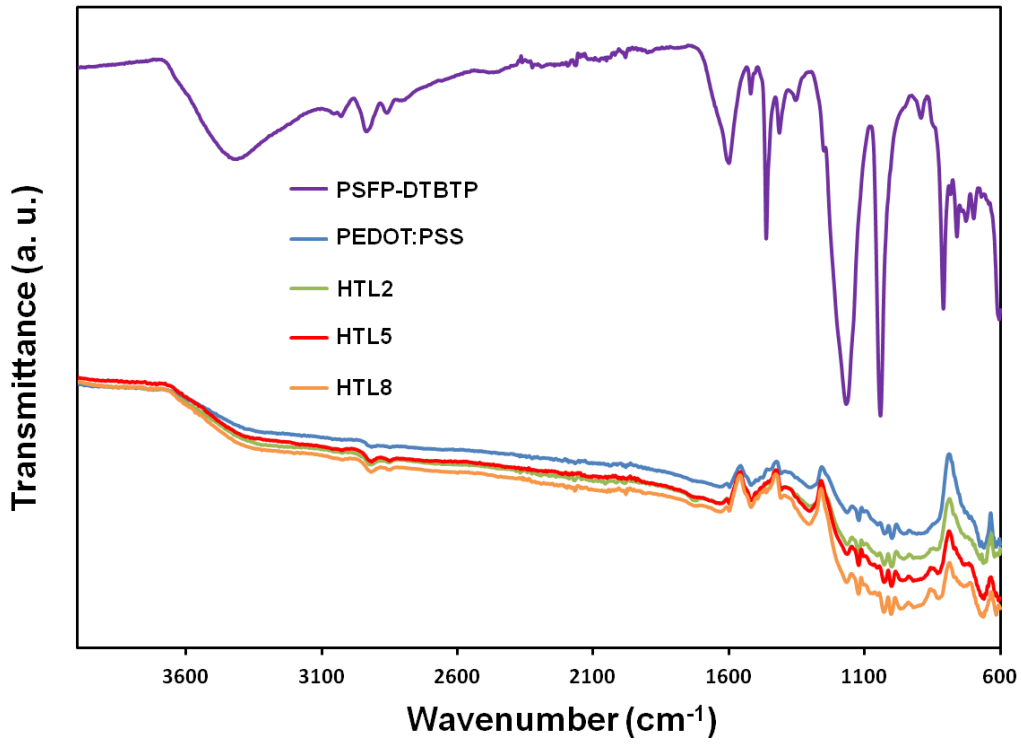

Figure S1 ATR FT-IR transmittance of PSFP-DTBTP (purple), PEDOT:PSS (blue), HTL2 (green), HTL5 (red), and HTL8 (orange)

To understand the components of HTL, the FT-IR spectra of polymer, PEDOT:PSS, HTL2, HTL5, and HTL8 are shown in Figure S1. The PSFP-DTBTP showed strong SO_3 peaks at 1167 cm^{-1} and 1042 cm^{-1}. This is corresponding peak approximately at 1300-1000 cm^{-1} with previous reports. [1, 2] Compared with the spectra of PEDOT:PSS and PSFP-DTBTP, it is hard to define that PSFP-DTBTP was left in the films due to PEDOT:PSS having similar SO_3 peaks. As shown in Figure 5, however, the spectra were showing increase of absorption around 1300-1000 cm^{-1} when PSFP-DTBTP concentration was increased and the spectra was normalised for comparison. C-H stretch peak of alkyl chain in polyelectrolyte was slightly appeared at 2870 cm^{-1} in HTL peaks.

PL properties of HTL and active layer

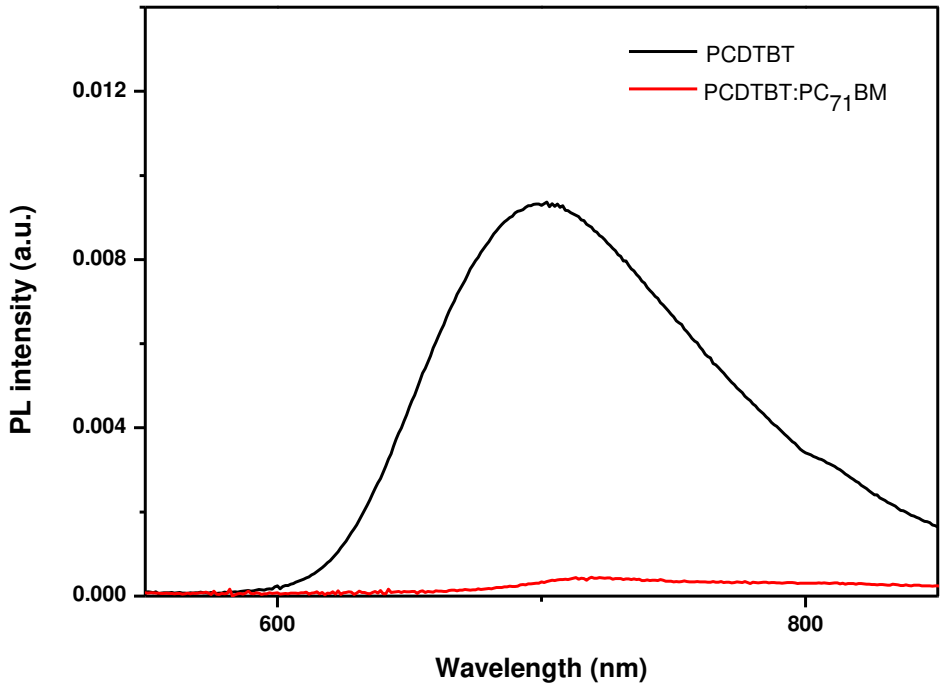

Figure S2 PL spectra of PCDTBT (black) and PCDTBT:PC71BM in a blend ratio of 1:4 (red).

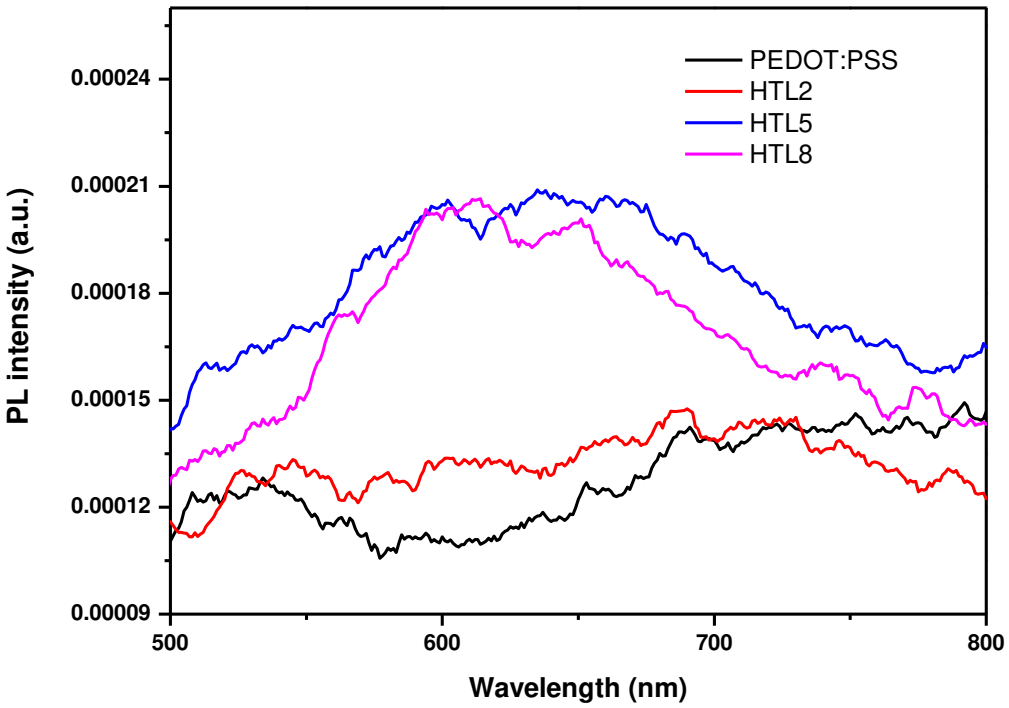

Figure S3 PL spectra of PEDOT:PSS (black), HTL2 (red), HTL5 (blue), and HTL8 (pink).

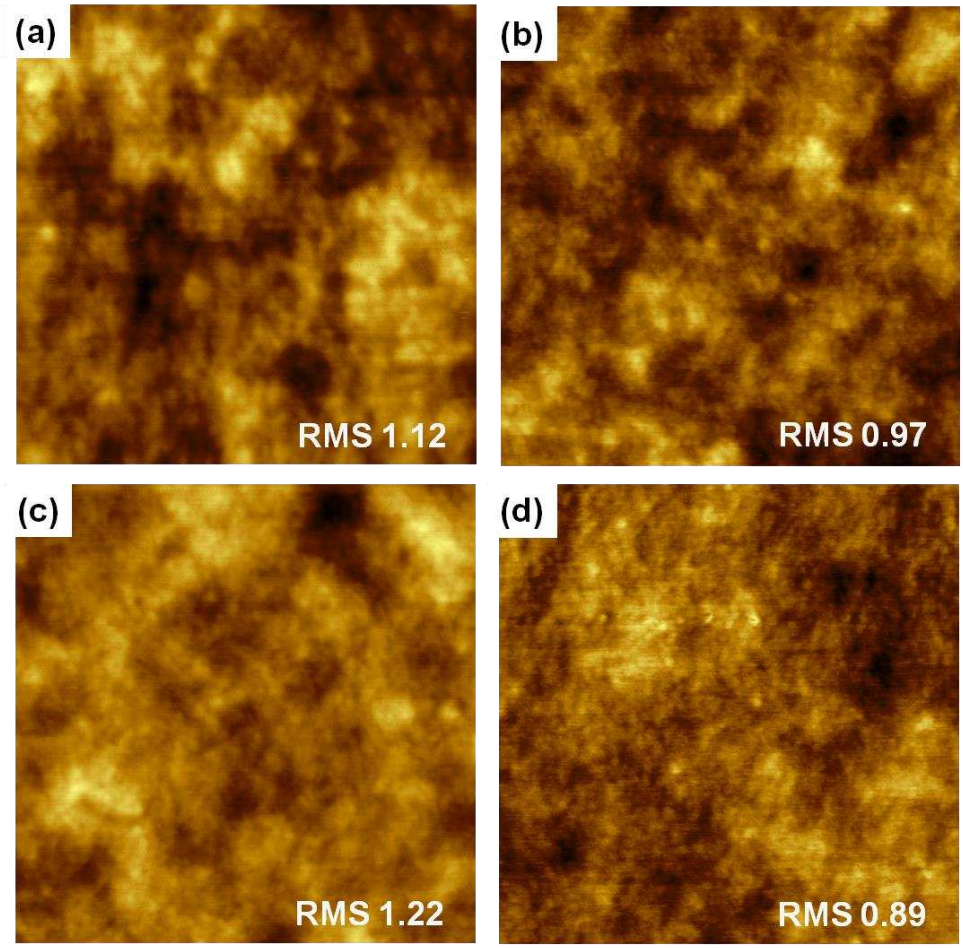

Figure S4 AFM images (1 x 1 µm) of hole transporting layer (a) PEDOT:PSS, (b) HTL2, (c) HTL5, and (d) HTL8.

The changes of HTL surface morphology between ITO and active layer were imaged by atomic force microscopy (AFM) tapping mode. The HTL was spin-coated on the ITO surface. The height images are illustrated in Figure S4. The height images (Figure S4 (b), (c), and (d)) of HTL2, HTL5 and HTL8 were not visibly different with pristine PEDOT:PSS (Figure S4 (a)). However their root-mean-square (RMS) roughness values showed small changes. RMS of pristine PEDOT:PSS was 1.12 nm and RMS was reduced when the PSFP-DTBTP were added into the PEDOT:PSS (HTL2 and HTL8). On the other hand, RMS of HTL5 was increased 1.22 nm. The correlation of RMS of all HTL and PCE of devices are briefly appeared by graph Figure S5 and RMS is coincident trend with PCE. The PCE of HTL5 based device was showed the highest value and it corresponded with the highest RMS of HTL5 surface. Other HTL2 and HTL8 based devices were appeared lower PCE than pristine PEDOT:PSS based device and also showed lower RMS.

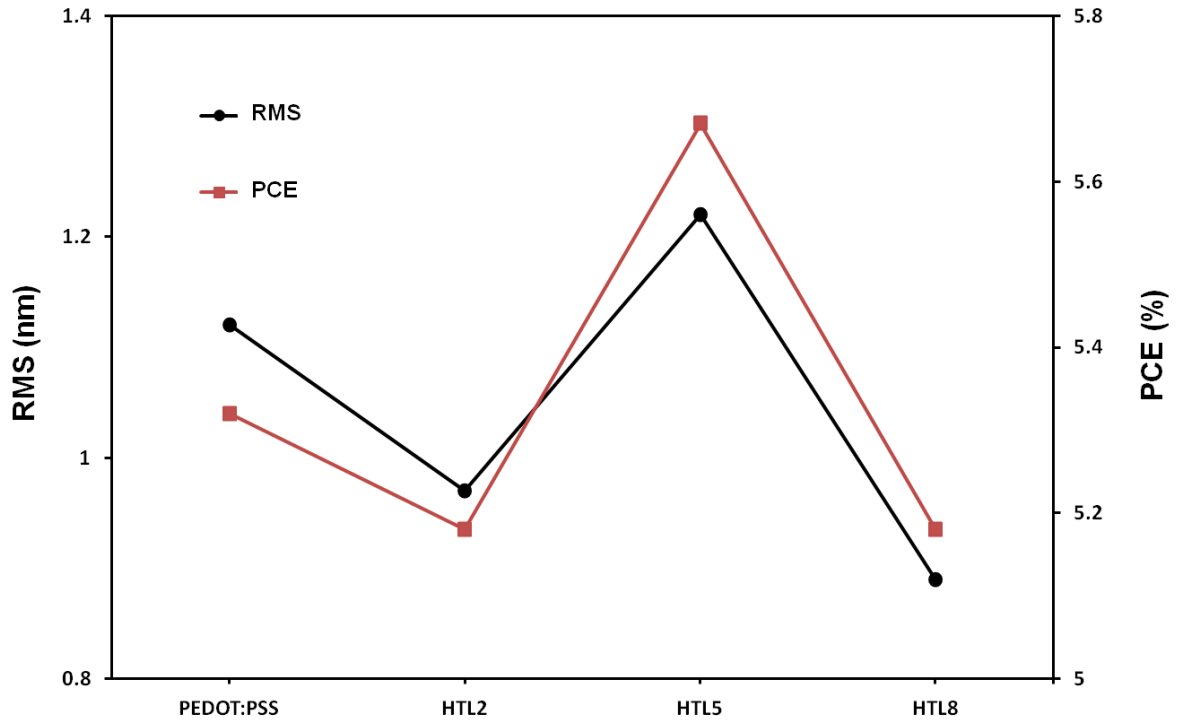

Figure S5 RMS values and the best device PCE of each hole transporting layers.

When the PSFP-DTBTP was used without any PEDOT:PSS as the HTL (i.e. replacing the PEDOT:PSS), it showed a lower PCE (about 2%) than reference devices.

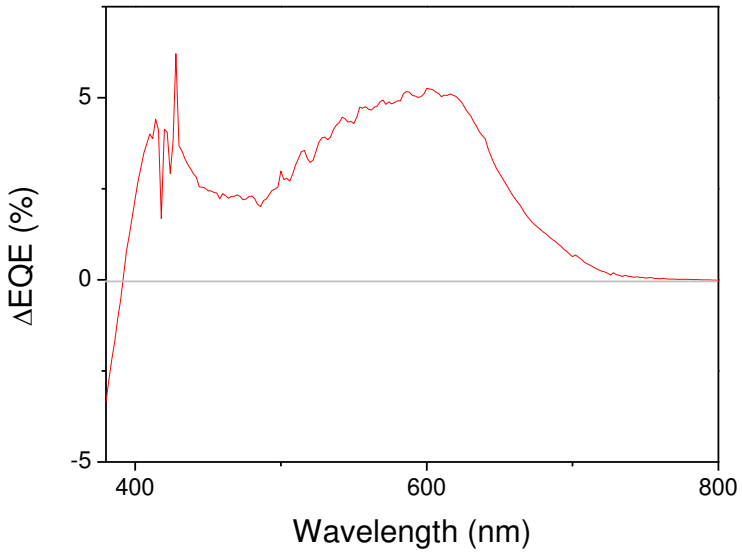

Figure S6 The change in EQE upon replacing the PEDOT:PSS HTL with the HTL5, calculated by subtracting the two curves plotted in Figure 5(b)

Reference

1. O. Borozenko, V. Machado, W. G. Skene and S. Giasson, *Polym Chem-Uk*, 2014, **5**, 5740-5750.
2. C. R. Martins, G. Ruggeri and M. A. De Paoli, *J Brazil Chem Soc*, 2003, **14**, 797-802.