Supporting Information for:

Fluorine functionalised Phosphine based solid additive for morphology control and achieving efficient organic solar cells

Jegadesan Subbiah, [a]* and David J. Jones [a] *

[a]School of Chemistry, Bio21 Institute, University of Melbourne, 30 Flemington Road, Victoria 3010, Australia.

*Email: jsubbiah@unimelb.edu.au, djjones@unimelb.edu.au,

Experimental Section

1. Materials

Photoactive materials PM6 and acceptor BTP-eC9 were purchased from Solarmer Material Inc. The interlayer material PFN-Br was purchased from 1-Material.

2. Device fabrication and characterisation

Organic solar cells were fabricated with a conventional geometry of ITO/PEDOT:PSS (40 nm)/PM6: BTP-eC9 /PFN-Br/Ag. A thin layer of PEDOT:PSS (poly-(3,4-ethylenedioxythiophene):poly(styrene sulfonate)) was spin-cast on pre-cleaned ITO glass from a PEDOT:P SS aqueous solution (Baytron P VP AI 4083 from H. C. Starck) at 6000 rpm and dried subsequently at 150 °C for 10 min in air. Then the device was immediately transferred to a glove box, where the active layer of the blend of the polymer (PM6) and nonfullerene acceptor (BTP-eC9) was spin−coated onto the PEDOT:PSS layer. The active layer was formed by spin-coating chloroform ($CHCl_3$) solution (1 ml) containing PM6 (8 mg): BTP-eC9 (9.6 mg) with various concentration additives TPFPP, at 3500 rpm. And the active layer films are annealed with 100 ºC for 10 minutes. Then, the methanol solution of poly9,9-bis6-(*N,N,N*-trimethylammonium) hexylfluorene-*alt-co*-phenylenebromide (PFN-Br) with a concentration of 0.5 mg/mL was spin-coated on the active layer at 4000 rpm for 30s. Finally, Ag top electrode was deposited in vacuum at a pressure of ca. 6.0×10^{-7} Pa.

The thickness of the active layer was measured as ~110 nm The active area of the device was 10 mm^2. The active layer thickness of the PSCs was determined by Dektak profilometer. Optical absorption was measured with an Agilent Cary spectrophotometer. Film thickness was determined by Veeco Dektak 150+Surface Profiler. The surface morphology of the blend films was acquired using an Asylum Research Cypher scanning probe microscope operated in tapping mode. Contact angle measurements were performed on a video-based optical contact angle measuring system (OCA20, Data physics Corp.). The current density-voltage measurements of the devices were carried out using a 1 kW Oriel solar simulator with an AM 1.5G filter as the light source in conjunction with a Keithley 2400 source measurement unit. Solar measurements were carried out under 1000 W/m^2 AM 1.5G illumination conditions. For accurate measurement, the light intensity was calibrated using a reference silicon

solar cell (PV Measurements Inc.) certified by the National Renewable Energy Laboratory. Device fabrication and characterizations were performed in a glove box without any encapsulation.

XPS data were acquired using a Kratos AXIS Supra X-ray photoelectron spectrometer equipped with a monochromated Al-Kα X-ray source (1486.7 eV) and a concentric hemispherical analyser. Depth profile XPS study was performed by etching the active layer surface by Ar ion beam for about 10 s repeatedly, and XPS spectra were taken after every etching cycle. Thermal gravimetric analysis (TGA) experiments were carried out with a Perkin Elmer TGA8000 and differential scanning calorimetry (DSC) experiments were performed on a Perkin Elmer Sapphire DSC at a ramp rate of 10 °C min^{-1}.

3. Optical and ATR-FTIR characterisation

ATR-FTIR measurements were carried out using FTIR Microscope (Lumos by Bruker, USA). The infrared analyses were performed using a germanium ATR crystal with a high refractive index (n_{Ge} = 4), which permits the analysis of films. We applied low contact pressure on the filk to avoid damaging the crystal and each spectrum was compiled from 16 scans with a resolution of 4.0 cm^{-1} in a range of 4000–600 cm^{-1}.

The optical images of the samples are acquired using FTIR Microscope before carried out ATR-FTIR measurement.
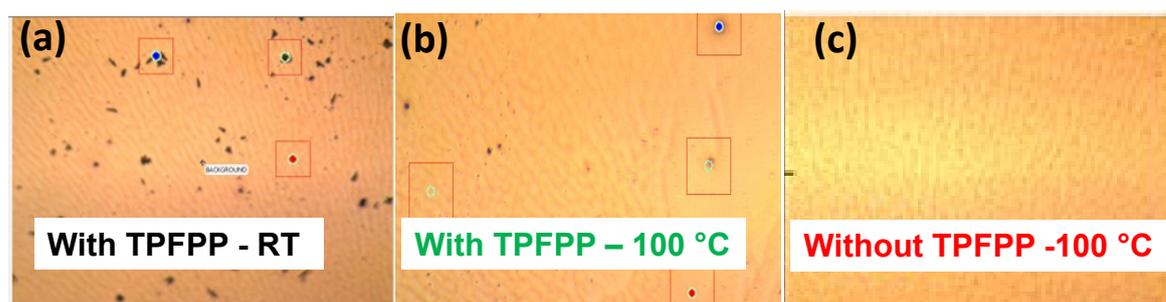
Figure S1. Optical images of photoactive layer blend of PM6:BTP-eC9 with TPFPP additive, processed at room temperature (RT) (b) 100 °C and (c) without TPFPP additive

4. Water contact angle characterisation

w/o TPFPP additives − 103.5⁰

with TPFPP additives → 106.1⁰
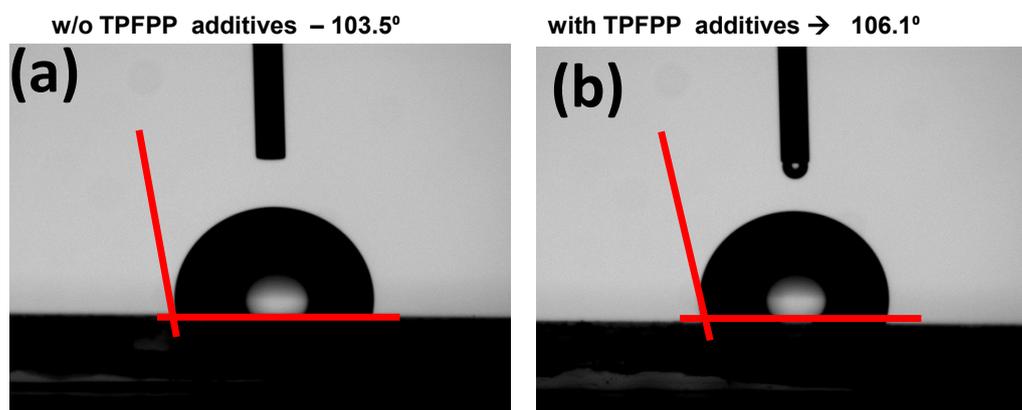
Figure S2. Water contact angles of the annealed PM6:BTP-eC9 film (a) without and (b) with 10 mg/ml TPFPP additive.

5. Thermal characterisation
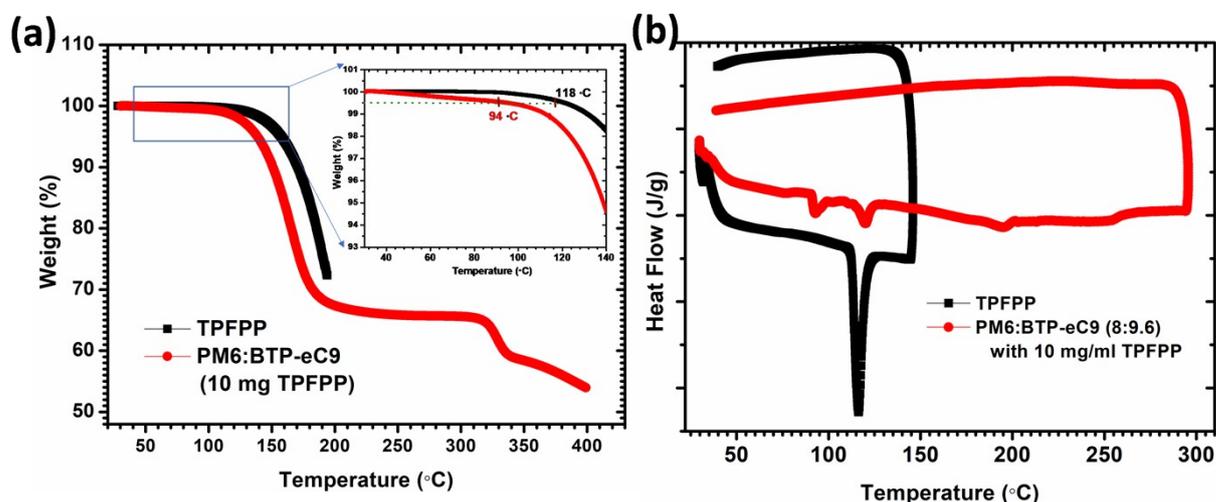
Figure S3. (a) Thermo gravimetric analysis (TGA) and (b) Differential scanning calorimetry (DSC) thermograms (the first heating cycle, a ramp rate of 10 ºC min^{-1}, nitrogen) of TPFPP and PM6;BTD-eC9:TPFPP (8.9.6:10, w/w), the mixtures were prepared by solution-cast method (dissolving the mixture of TPFPP, PM6 and BTD-eC9 in chloroform and then removing the solvent). The lower trace of TGA is from the heating cycle and the upper trace is from the cooling cycle. The TGA plot shows that the evaporation/decomposition start at 94 ºC (99.5% at 94 ºC) during annealing process.

6. SCLC Mobility Measurements

The space charge limited current (SCLC) of PM6;BTP-eC9 (with and w/o 10 mg /ml TPFPP additive) were studied using Hole-only and Electron-only devices. The SCLC devices are fabricated as shown in figure S2 to find the charge-carrier mobilities. From the current density as a function of voltage data, the hole mobility and electron mobility in the space-charge limited current (SCLC) region can be estimated using the Mott-Gurney equation, $J = 9\,(\varepsilon_r\varepsilon_0\mu)/8 \times (V^2/d^3)$, where J is the current density, $V = V_{appl} - V_{bi}$, V_{appl} is the applied potential, V_{bi} is the built-in potential resulting from work function difference between two electrodes, ε_r is the dielectric constant of the polymer, ε_0 is the permittivity of vacuum, μ is the hole mobility, d is the sample thickness.
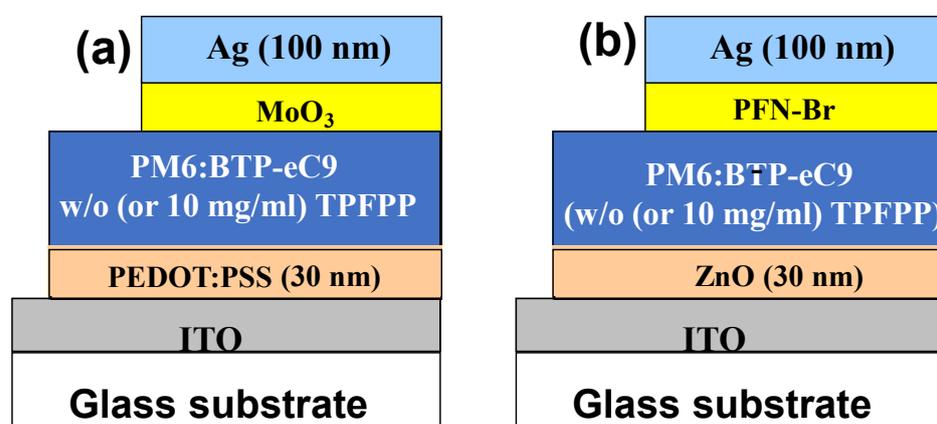
Figure S4. The device structure of (a) Hole-only and (b) Electron-only device.

Active layer	Hole mobility (μ_h)	Electron mobility (μ_e)
PM6:BTP-eC9 (0 mg ml TPFPP)	2.62×10^{-4} cm^2 V^{-1} s^{-1}	7.56×10^{-4} cm^2 V^{-1} s^{-1}
PM6:BTP-eC9 (10 mg ml TPFPP)	8.31×10^{-4} cm^2 V^{-1} s^{-1}	1.88×10^{-3} cm^2 V^{-1} s^{-1}

Table S1. Charge transport characteristics of hole-only and electron-only devices.