

Supporting Information

Enhancing the power conversion efficiency of polymer solar cells to 9.26% by a positive synergistic effect of fluoro and carboxylate substitution

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Experiment Part

1.1 Material and Instruments.

Unless otherwise noted, all chemicals were purchased from aldrich or Acros and used without further purification. The catalyst precursor Pd(PPh₃)₄ was prepared according to the literature and stored in a Schlenk tube under nitrogen atmosphere. Dichloromethane (DCM) was distilled from CaH₂ under nitrogen atmosphere. N,N-Dimethylformamide (DMF) was distilled from CaH₂ under reduced pressure. Unless otherwise noted, all reactions were performed under an atmosphere of nitrogen and monitored by thin layer chromatography (TLC) on silica gel. Column chromatography was carried out on silica gel (200-300 mesh). ¹H and ¹³C NMR spectra were recorded on a Bruker AV 400 spectrometer. UV-visible absorption spectra were obtained on a PerkinElmer UV-vis spectrometer model Lambda 750. Elemental analyses were performed on a Flash EA 1112 analyzer. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on TA2100 and Perkin-Elmer Diamond DSC instrument, respectively, under a nitrogen atmosphere at a heating rate of 10 °C/min to record TGA and DSC curves. The gel permeation chromatography (GPC) measurements were performed at 80 °C on a PL-220 (Polymer Laboratories) chromatography connected to a differential refractometer with chlorobenzene as an eluent. Atomic force microscopy (AFM) measurements were performed under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA operating in the tapping mode. The thickness of the blend films was determined by a Dektak 6 M surface profilometer. The powder X-ray diffraction (XRD) patterns were collected using a PANalytical X'Pert PRO MPD diffractometer with Cu KR

radiation. The electrochemical behavior of the polymers was investigated using cyclic voltammetry (CHI 630A Electrochemical Analyzer) with a standard three-electrode electrochemical cell in a 0.1 M Bu_4NPF_6 solution in CH_3CN at room temperature under an atmosphere of nitrogen with a scanning rate of 0.1 V/S. A Pt plate working electrode, a Pt wire counter electrode, and an Ag/AgNO_3 (0.01 M in CH_3CN) reference electrode were used. The experiments were calibrated with the standard ferrocene/ferrocenium (F_c) redox system and assumption that the energy level of F_c is 4.8 eV below vacuum.

1.2 Polymer Solar Cells Fabrication and Characterization

PSCs were fabricated with the device configuration of ITO/PEDOT:PSS (40 nm)/polymer:PC₇₁BM/LiF (Ca)/Al (100 nm). The conductivity of ITO is 20 Ω . PEDOT:PSS (Baytron Al 4083 from H.C. Starck) was filtered with a 0.45 μm polyvinylidene difluoride (PVDF) film before use. A PEDOT:PSS thin layer was spin-coated on top of the cleaned ITO substrate at 3000 rpm/s for 60 s and dried subsequently at 130 $^\circ\text{C}$ for 20 min on a hotplate. The thickness of the PEDOT:PSS layer is about 30 nm. A mixture solution of polymer and PC₇₁BM in 1,2-dichlorobenzene (DCB) was stirred at 75 $^\circ\text{C}$ for more than 3 hours with a concentration of 8 mg/mL (**P1** or **P2**) to ensure complete dissolution, then the blend solution was spin-coated onto the PEDOT:PSS layer to form the active layer. Due to good solubility of P1, the blend solution was prepared at room temperature and spin coated onto the substrate of ambient temperature at a speed of 700 r/min. For **P2**, the active layers were fabricated in the same condition but with warm (75 $^\circ\text{C}$) polymer solutions. On one substrate five cells with an effective area of 0.04 cm^2 for each were fabricated. Current-voltage (I-V) and external quantum efficiency (EQE) measurements were conducted in air without encapsulation. I-V characteristics were recorded at room temperature using an Agilent B2902A Source Meter under the illumination of an AM1.5G AAA class solar simulator (model XES-301S, SAN-EI) with an intensity of 100 mW cm^{-2} and the white light intensity was calibrated with a standard single-crystal Si solar cell.

1.3 Space-Charge Limited Current Measurement

Hole/electron devices with a structure of ITO/PEDOT:PSS (30 nm)/polymer:PC₇₁BM/Au (Al) were fabricated. The blend solution of polymer and PC₇₁BM in 1,2-dichlorobenzene (DCB) was spin-coated onto PEDOT:PSS layer to form active layer like PSC devices, and Au (Al) was thermally evaporated at a pressure of 10^{-4} Pa through a shadow mask. Dark J-V curves of the hole/electron devices were measured by the space-charge limited current (SCLC) method.

1.4 XPS measurement

The blend solution of P2 and PC₇₁BM was spin coated on the ITO substrate with PEDOT:PSS layer. Then the substrate was carefully immersed into water. Due to the good water solubility of PEDOT:PSS, the active blend films were easily to come off from ITO substrate and rose to the water surface. This facilitated flexible transfer of these films by tweezer onto Si substrates in face-up or face-down direction, respectively. Element content of the bottom and top surface was investigated with XPS (ESCSLAB 250Xi).

1.5 molecular effect on the photovoltaic performance

| | M_n (kg/mol) | M_w (kg/mol) | PDI |
|-------------------|----------------|----------------|-----|
| P1 | 16.3 | 39.9 | 2.5 |
| P1-H ^a | 96.6 | 158.9 | 2.7 |
| P2 | 42.2 | 154.4 | 3.7 |

^a) MW reaction condition: 180 °C, 270 Watt, 2h. (*Adv. Mater.* 2013, 25, 2445-2451)

| Polymer | D : A | V_{oc} (V) | J_{sc} (mA/cm ²) | FF(%) | PCE (%) | thickness (nm) |
|-------------|-------|--------------|--------------------------------|-------|-------------|----------------|
| P1 | 1:1.5 | 0.85 | 2.79 | 60 | 1.42 (1.33) | 84 |
| P1-H | 1:1.5 | 0.84 | 4.99 | 67 | 2.81 (2.52) | 90 |
| P2 | 1:1.5 | 0.87 | 12.53 | 67 | 7.30 (7.24) | 184 |

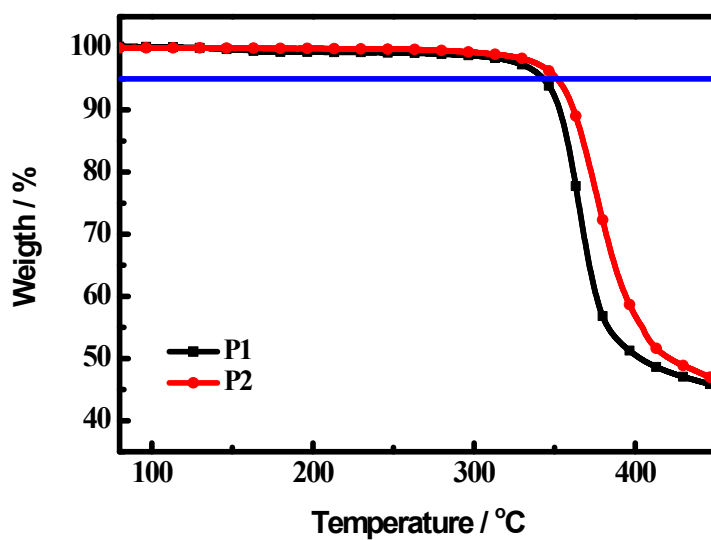


Figure S1. TGA curves of P1 and P2 under nitrogen at a heating rate of 10 °C/min.

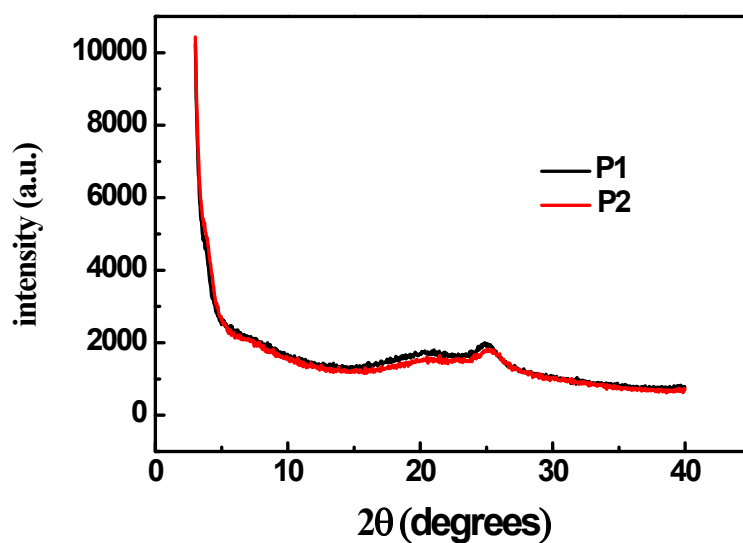


Figure S2. X-ray diffraction of P1 and P2 powdery sample.

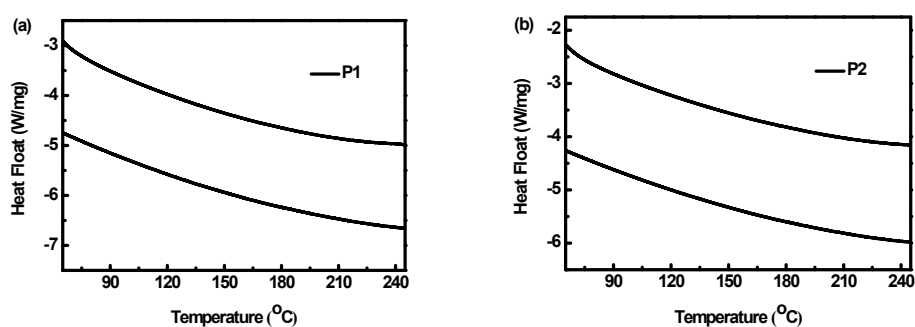


Figure S3. DSC curves of a) P1 and b) P2 with a scanning rate of 10 °C/min.

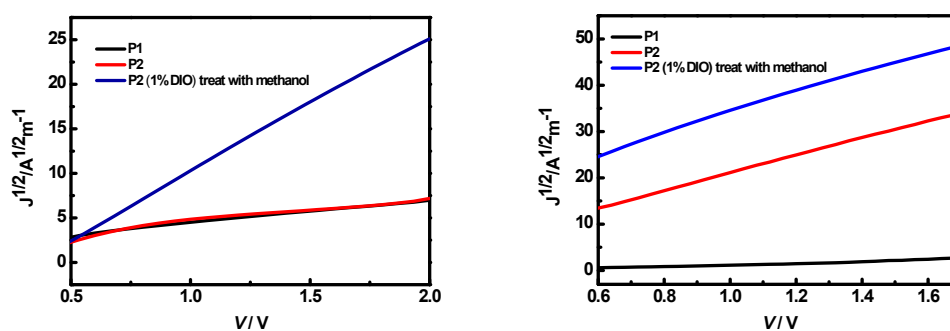


Figure S4. a) the hole mobility and b) electron mobility of blend film based on **P1** and **P2**.

| Polymer | Solvent | D : A | V_{oc} (V) | J_{sc} (mA/cm ²) | FF (%) | PCE (%) | thickness (nm) |
|-----------|---------|-------|--------------|--------------------------------|--------|-------------|----------------|
| | | 1:1 | 0.84 | 2.51 | 63 | 1.33 (1.21) | 80 |
| P1 | DCB | 1:1.5 | 0.85 | 2.79 | 60 | 1.42 (1.33) | 84 |

| | | | | | | | |
|-----------|-----|-------|------|-------|----|-------------|-----|
| | | 1:2 | 0.84 | 2.57 | 61 | 1.32 (1.23) | 85 |
| | | 1:1 | 0.87 | 11.34 | 68 | 6.71 (6.47) | 180 |
| P2 | DCB | 1:1.5 | 0.87 | 12.53 | 67 | 7.30 (7.24) | 184 |
| | | 1:2 | 0.88 | 11.11 | 66 | 6.45 (6.35) | 185 |

Table S1. Photovoltaic Parameter of polymers:PC₇₁BM fabricated from ODCB with different D/A ratio.

| | Hole mobility | Electron mobility |
|--------------------------------|-----------------------|----------------------|
| P1 | 1.97×10^{-6} | 1×10^{-6} |
| P2 | 3.38×10^{-5} | 9.5×10^{-4} |
| P2(1% DIO) treat with methanol | 6.42×10^{-4} | 1.2×10^{-3} |

Table S2. Hole and electron mobility values of **P1** and **P2**.

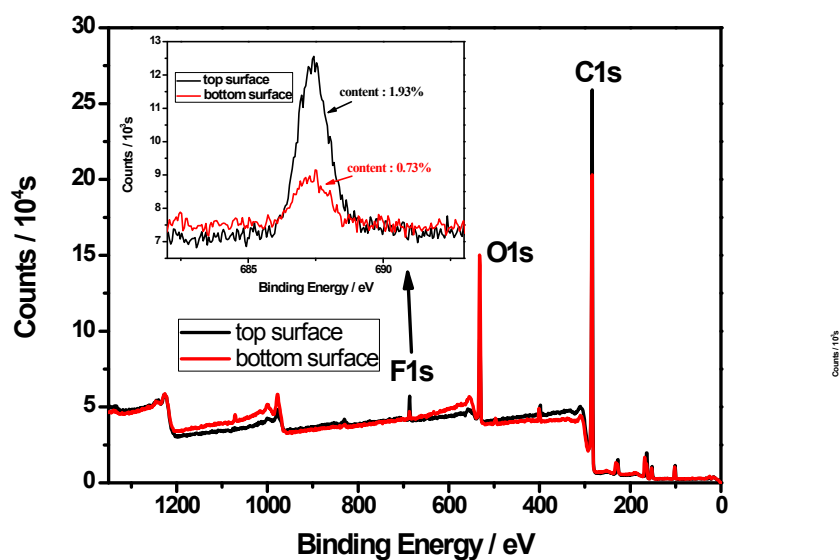


Figure S5. The XPS spectra of the P2:PC₇₁BM blend film processed with DCB (1%DIO) mixed solvents and treated with methanol.

