

Supporting Information

Built-in voltage enhanced by in-situ electrochemical polymerized undoped conjugated hole-transporting modifier in organic solar cells

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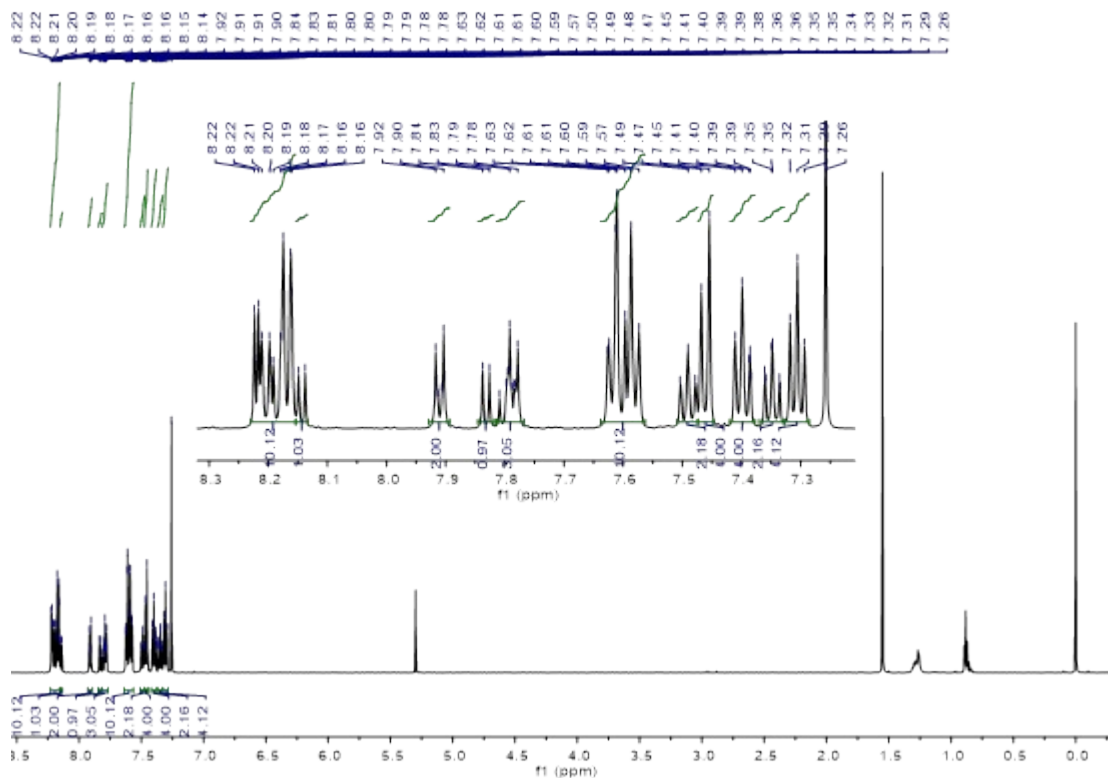


Fig. S1. The ^1H NMR spectrum of TPCF, conducted in Chloroform-*d*.

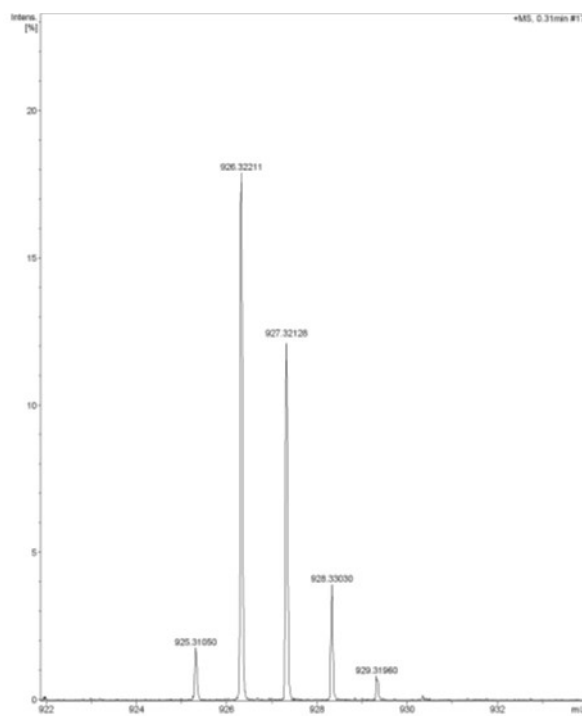


Fig. S2. The HR-MS spectrum of TPCF

^1H NMR (600 MHz, Chloroform-*d*, which was exhibited in Figure S1) δ 8.24 – 8.15 (m, 10H, ArH), 8.14 (d, $J = 6.7$ Hz, 1H, ArH), 7.93 – 7.89 (m, 2H, ArH), 7.83 (d, $J = 7.0$ Hz, 1H, ArH), 7.81 – 7.77 (m, 3H, ArH), 7.64 – 7.56 (m, 10H, ArH), 7.49 (dd, $J =$

8.2, 7.0 Hz, 2H, ArH), 7.46 (d, $J = 8.1$ Hz, 4H, ArH), 7.42 – 7.38 (m, 4H, ArH), 7.37 – 7.33 (m, 2H, ArH), 7.31 (t, $J = 7.4$ Hz, 4H, ArH). ^{13}C NMR (101 MHz, CDCl_3 , which was shown in Figure S2) δ 141.01, 140.85, 139.71, 139.51, 139.44, 139.27, 139.06, 138.75, 137.18, 136.80, 136.35, 136.20, 133.58, 133.44, 131.70, 131.58, 129.07, 128.60, 128.50, 126.98, 126.69, 126.07, 126.04, 125.90, 123.71, 123.66, 123.54, 123.44, 120.63, 120.51, 120.41, 120.35, 120.12, 120.00, 109.88, 109.67. HRMS (ESI): $(\text{M}+\text{H})^+ = 926.3221$ (calcd for $\text{C}_{70}\text{H}_{44}\text{N}_3^+$, 926.3530).

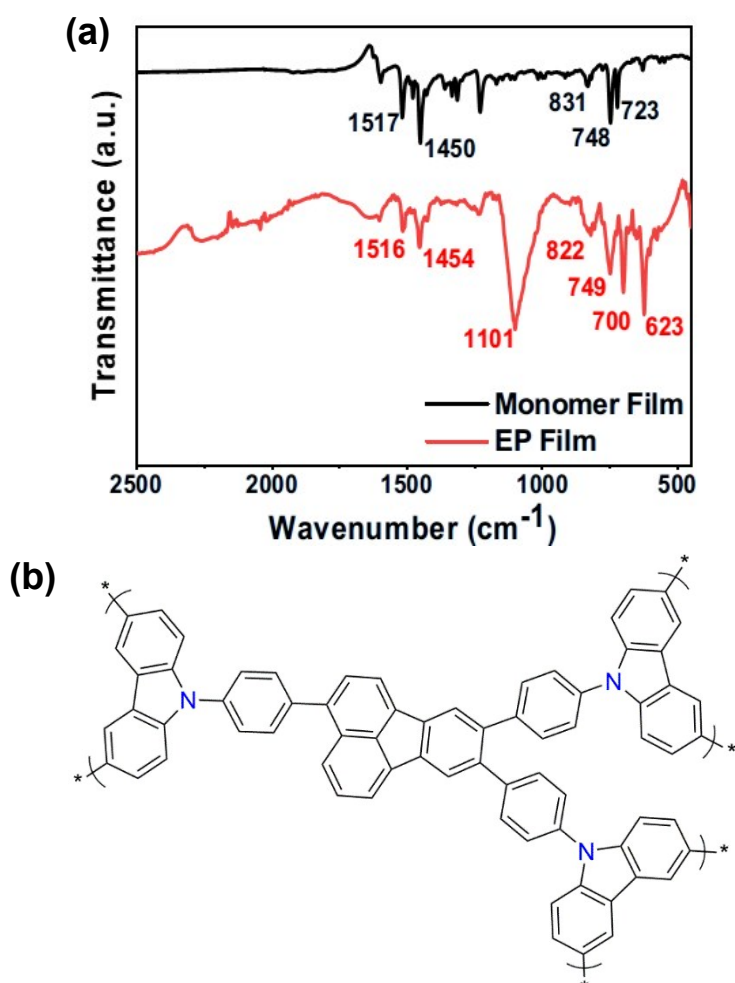


Fig. S3. a) Fourier transform infrared spectra of monomer film (the black one) and EP film (the red one). b) The chemical structure of p-TPCF.

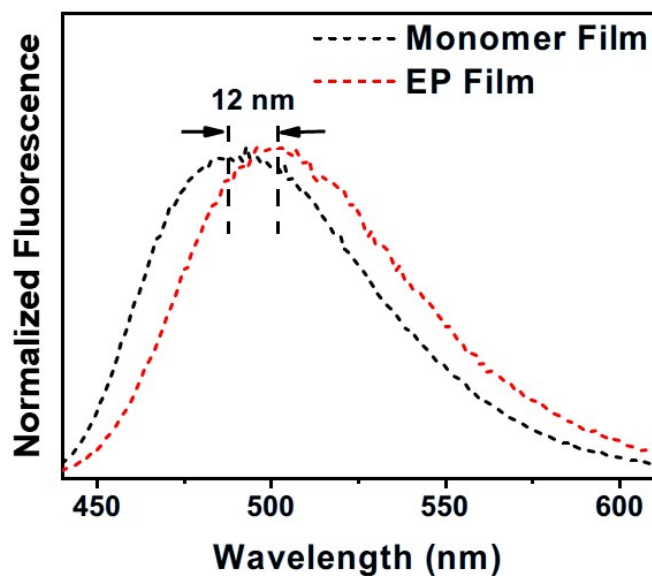


Fig. S4. Fluorescence spectrum of Electro-polymerization film (Red line) and monomer film (Black line).

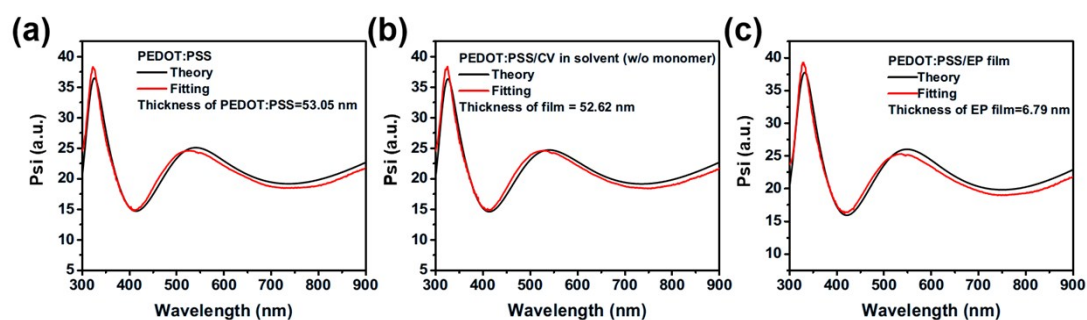


Fig. S5. Thickness data of a) PEDOT:PSS film, b) PEDOT:PSS film experienced CV process in solvent without monomer and c) PEDOT:PSS/EP film obtained by ellipsometer.

Table S1. The thickness parameters measured by ellipsometer.

HTL	Thickness (nm)
PEDOT:PSS	53.05
PEDOT:PSS/ CV (w/o EP film) ^a	52.62
PEDOT:PSS/EP film	53.05 / 6.79 ^b

^a. The PEDOT:PSS film treated by CV process in solvent ($\text{CH}_3\text{CN}:\text{CH}_2\text{Cl}_2=1:4$) without monomer.

^b. PEDOT:PSS thickness/EP film thickness.

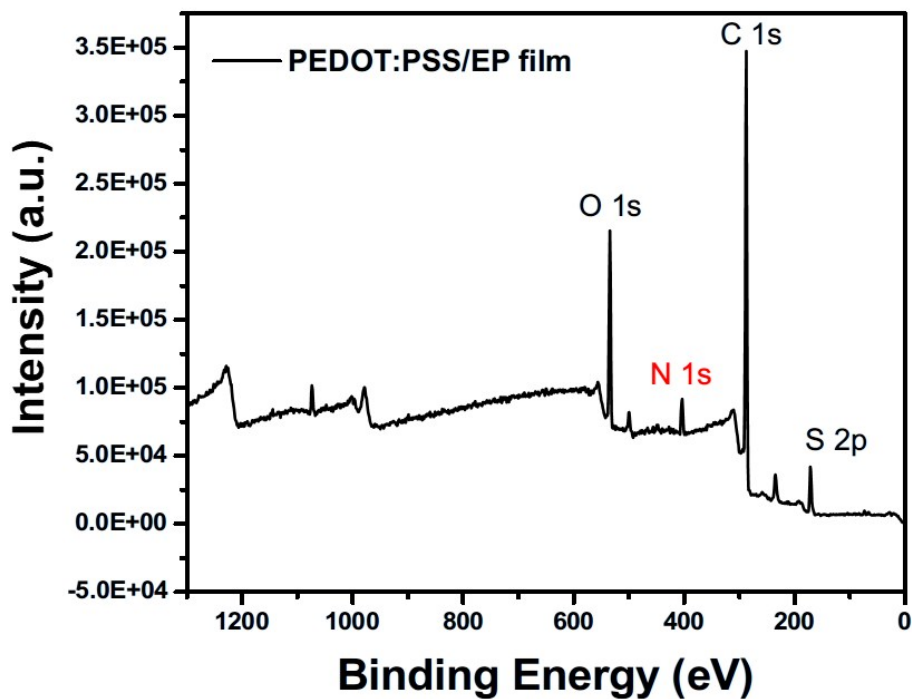


Fig. S6. XPS survey of PEDOT:PSS/EP film.

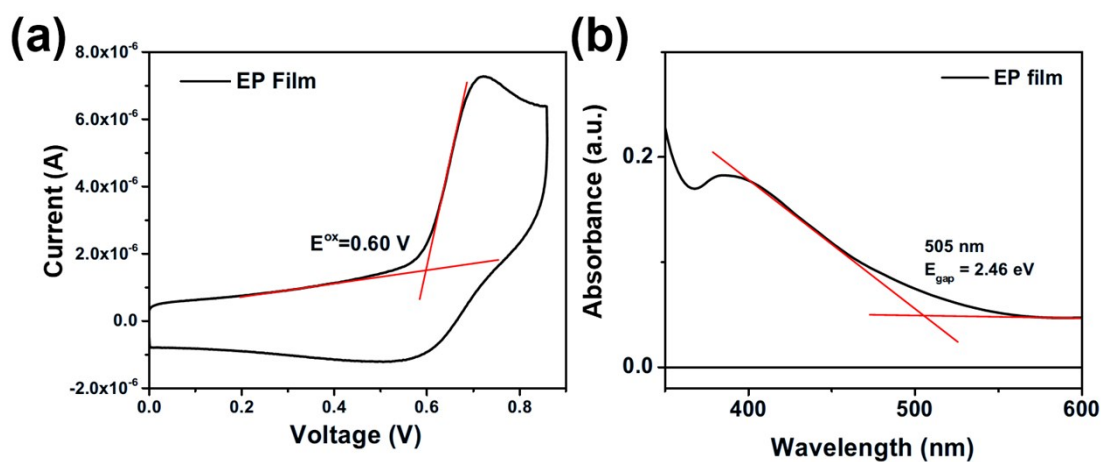


Fig. S7. a) CV test of p-TPCF EP film. In this test, ferrocene is applied as calibration.

b) UV-Vis absorbance spectra of EP-film. $E_{\text{gap}} = 1240/\lambda$ ($\lambda = 505 \text{ nm}$)

Table S2. Parameters of p-TPCF including E_{gap} , HOMO and LUMO.

Film	E_{gap} (eV)	HOMO (eV)	LUMO (eV)
p-TPCF	2.46	-5.3	-2.84

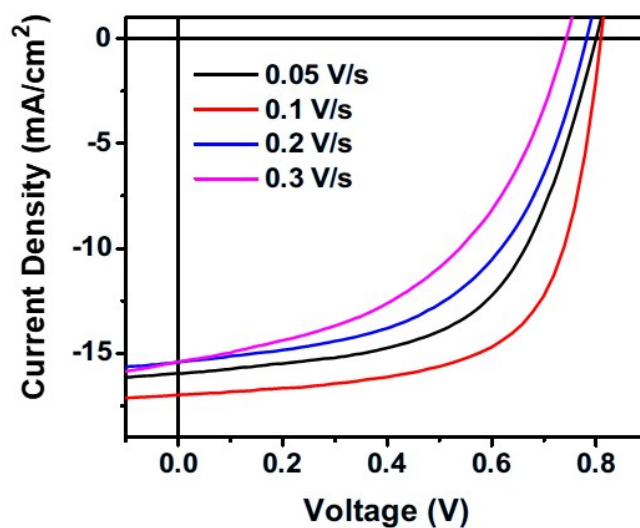


Fig. S8. J-V curves of devices with EP film polymerized on PEDOT:PSS in different scan rate.

Table S3. Parameters of EP film polymerized on PEDOT:PSS in different scan rate.

Scan rate of CV (V/s)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
0.05	0.80	15.96	57.97	7.40
0.10	0.80	16.98	66.21	8.99
0.20	0.78	15.40	53.99	6.48
0.30	0.74	15.42	47.96	5.47

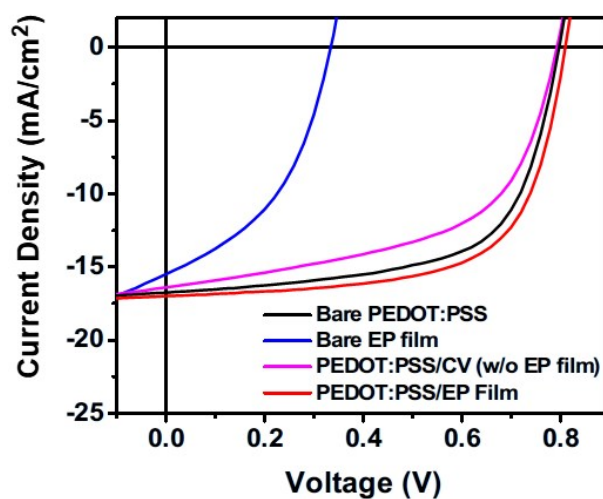


Fig. S9. J-V characteristics of devices with bare PEDOT:PSS (black), PEDOT:PSS/CV (w/o EP film) (pink), bare EP film (blue) and PEDOT:PSS/EP film (red).

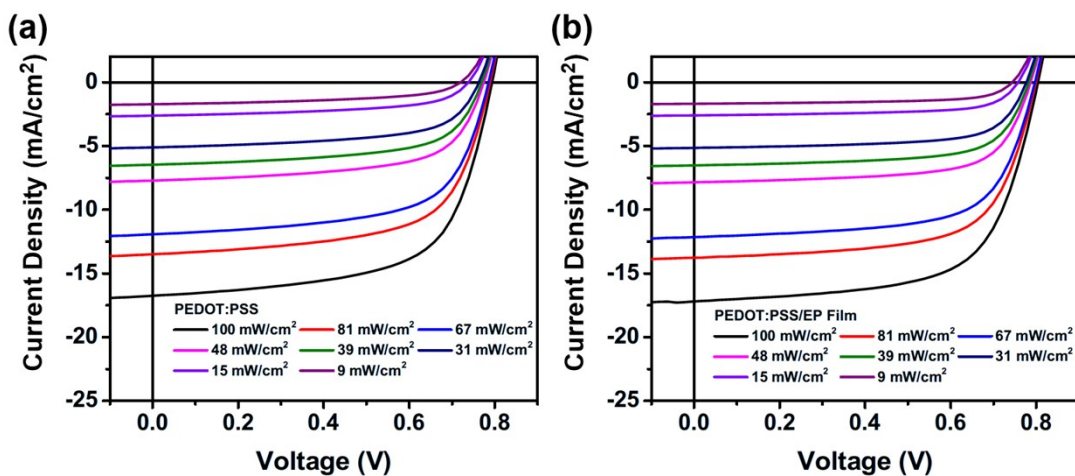


Fig. S10. J-V characteristics at different light intensities of organic solar cells a) without EP-film modified and b) with EP-film modified.

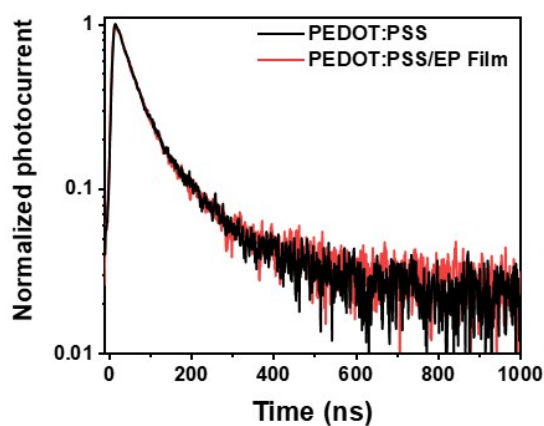


Fig. S11. Transient photocurrent characterization of devices with various HTLs.