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Self-doping n-type Polymer as Cathode Interface Layer Enables Efficient Organic Solar Cells by Increasing Built-in Electric Field and Boosting Interface Contact

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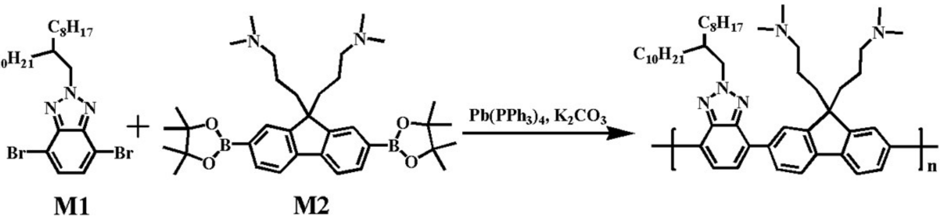
Synthesis of PBTA-FN

4,7-dibromo-2-(2-octyldodecyl)-2H-benzo[d][1,2,3]triazole (M1) [1] (55.7 mg, 0.1 mmol), 3,3'-(2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluorene-9,9-diyl)bis(N,N-dimethylpropan-1-amine) (M2) [2] (58.8 mg, 0.1 mmol), and tetrakis(triphenylphosphine) palladium [$(PPh_3)_4Pd$] (5 mg) were dissolved in a mixture of 10 mL of toluene, 3 mL of ethyl alcohol, and 1 mL of 2M K_2CO_3 aqueous solution in a 50 mL two-necked round-bottomed flask under argon. The mixture was refluxed with vigorous stirring for 24 h under an argon atmosphere. After the mixture was cooled to room temperature, 30 mL of methanol was added into the mixture. The precipitated material was recovered by filtration through a funnel. The resulting solid material was washed using acetone, n-hexane, trichloromethane in a Soxhlet apparatus, and the resulting material was concentrated, and precipitated from methanol to yield PBTA-FN as a yellow fiber solid (yield:72%).

M1: ^1H NMR (600 MHz, Chloroform-d): δ 7.42 (s, 2H), 4.67 (d, J = 7.3 Hz, 2H), 1.35-1.23 (m, 33H), 0.86 (d, J = 6.9 Hz, 6H). Elem. Anal. Calcd for $C_{26}H_{43}Br_2N_3$: C, 56.02; H, 7.77; N, 7.54. Found: C, 56.05; H, 7.72; N, 7.53.

M2: ^1H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, J = 6.6 Hz, 4H), 7.70 (d, J = 7.7 Hz, 2H), 2.07–2.02 (m, 4H), 1.96 (m, 16H), 1.38 (s, 24H), 0.73 (m, 4H). Elem. Anal. Calcd for $C_{35}H_{54}B_2N_2O_4$: C, 71.44; H, 9.25; N, 4.76. Found: C, 71.32; H, 9.23; N, 4.73.



Scheme 1. Synthesis route of PBTA-FN

Energy level Calculated of PBTA-FN

The optical band gap (E_g) of PBTA-FN was 2.53 eV obtained from the 490 nm of absorption edge (λedge) by using a equation S1. On the basic of relationship expression S2, [3] e is element charge and $E_{1/2ferrocene}$ stands for the onset redox potential of ferrocene/ferrocene+ (Fc/FC^+) was 0.16 V determined by electrochemical property curve (Fig. 2). Thus, the energy level of highest occupied molecular (E_{HOMO}) was calculated to be 5.35 eV and corresponding lowest unoccupied molecular energy level (E_{LUMO}) of PBTA-FN could be obtained from equation S3, 2.75 eV.

$$E_g = 1240 / \lambda_{edge} \tag{S1}$$

$$E_{HOMO} = -e(E_{ox} + 4.8 - E_{1/2\,ferrocene}) \tag{S2}$$

$$E_{LUMO} = E_{HOMO} - E_g \tag{S3}$$

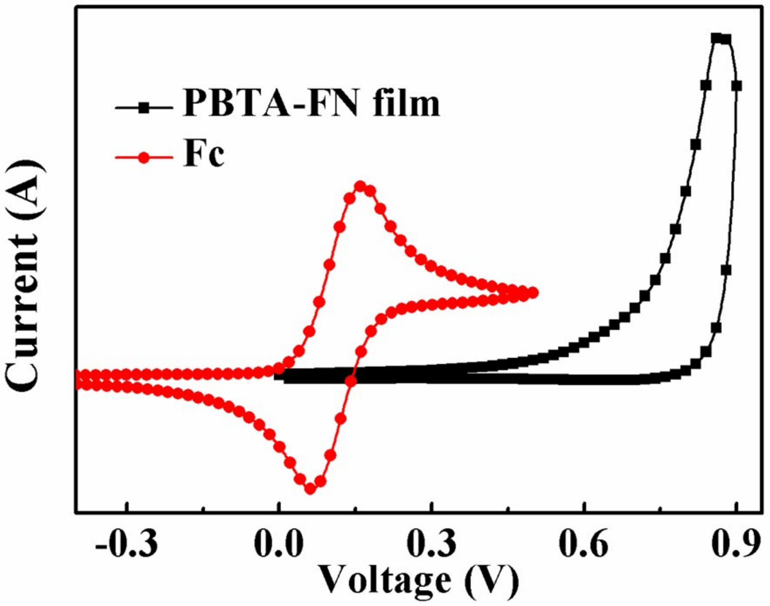


Fig. S1 Electrochemical property curve of PBTA-FN film.

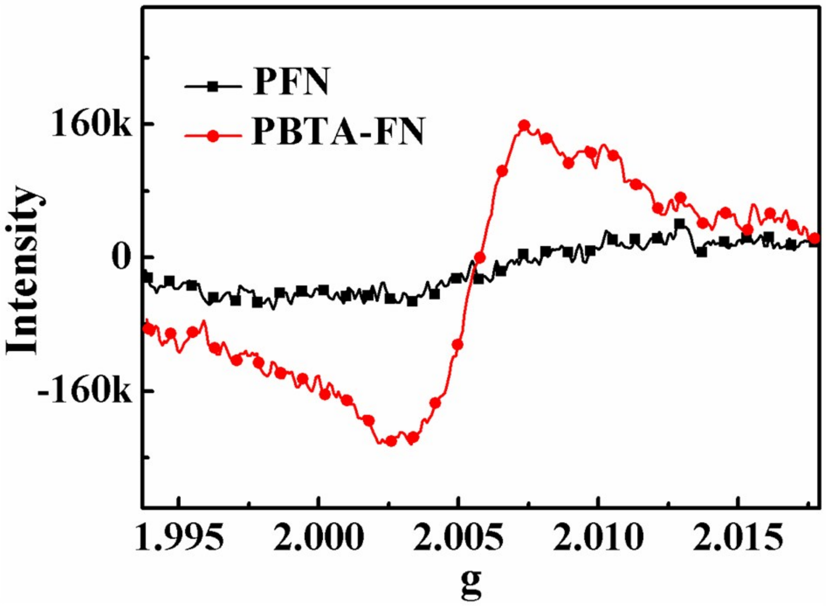


Fig. S2 EPR spectra Intensity-g values of PFN and PBTA-FN under solid state.

DFT calculated

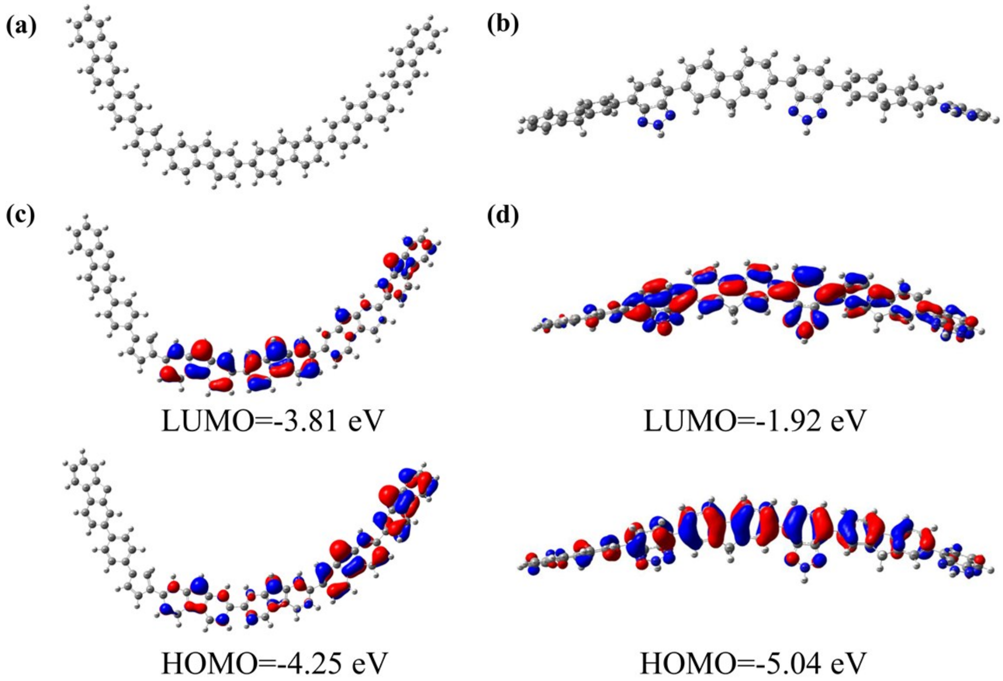


Fig. S3 Front view of the optimized geometries (a) PFN and (b) PBTA-FN, electronic state density distributions at LUMO and HOMO of (c) PFN and (d) PBTA-FN. These DFT calculations were performed in three repeat units at the B3LYP-D3(BJ)/6-31G level and the effect of side chain was ignored.

Calculation of electron mobility

The only-electron device with ITO/ZnO/PBDB-T-2F:IT-4F/CILs/Al were prepared and measured with space charge limiting current (SCLC) mode in the dark condition. The *I-V* curves of devices with different conditions were displayed in Fig. S5 and the related electron mobility was calculated using a comparison expression:

$$J = \frac{9}{8}\varepsilon_0 \varepsilon_r \mu \frac{(V_{appl} - V_{bi})^2}{L^3} \qquad \text{(S4)}$$

where J is referred current density, ε_r stands for the relative dielectric constant in the organic photoactive layer (≈3.00), ε_0 represents the vacuum permittivity of of 8.85×10^{-12} F/m, *L* is the active layer thickness (100 nm), V_{app}l is the applied voltage, and V_{bi} is the built-in voltage since the difference in the work function of the cathode and the anode, μ expresses mobility. [4-5] Noted that $V_{bi} = 0.7$ V for the electron-only devices.

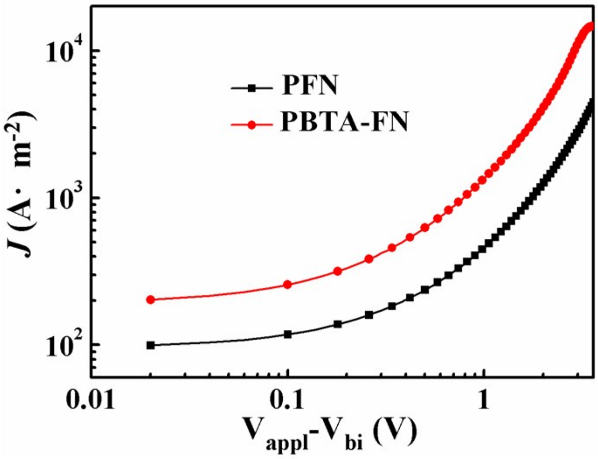


Fig. S4 *I-V* curves of electron-only devices

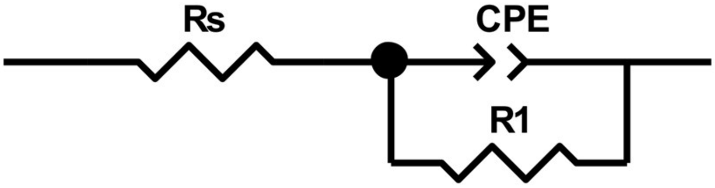


Fig. S5 Equivalent circuit for fitting Nyquist plots.

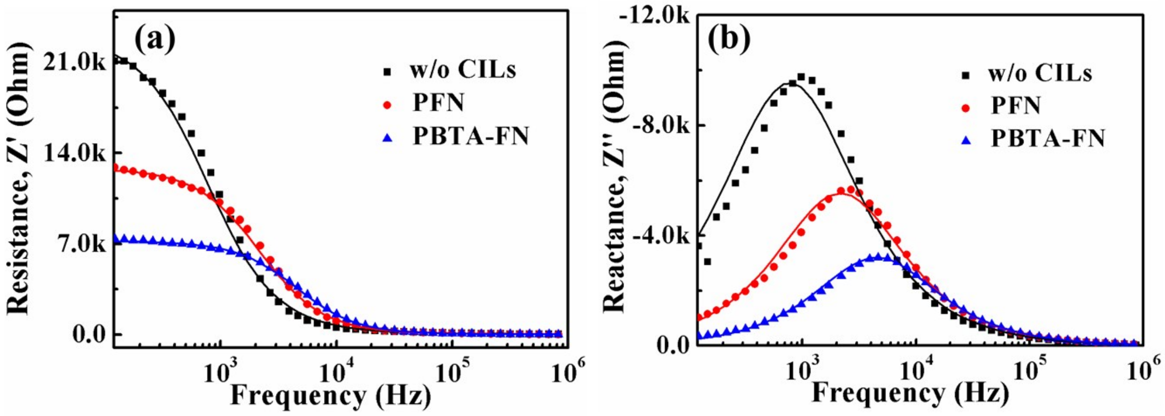


Fig. S6 (a) Resistance vs frequency and (b) reactance vs frequency of OSCs with different CILs

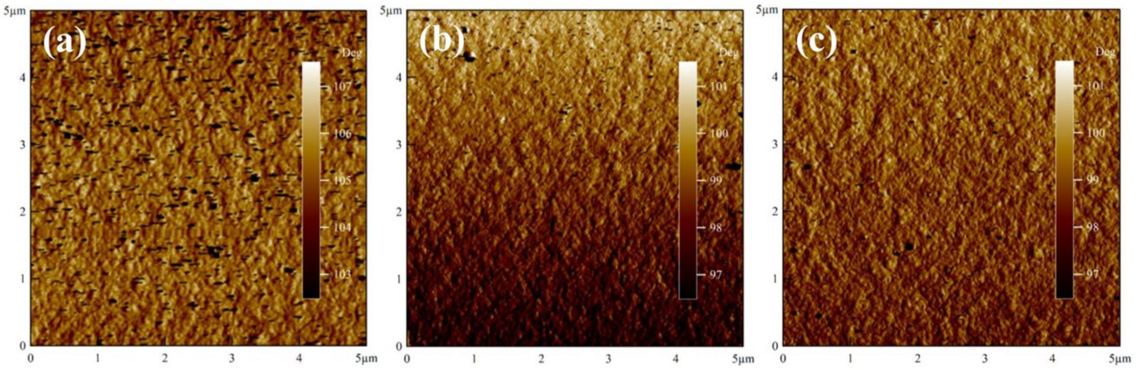


Fig. S7 AFM phase images of PBDB-T-2F:IT-4F films with different CILs (a) w/o CILs, (b) PFN,

(c) PBTA-FN

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