

Towards improved efficiency of polymer solar cells via chlorination on benzo[1,2-*b*:4,5-*b'*]dithiophene based polymer donor

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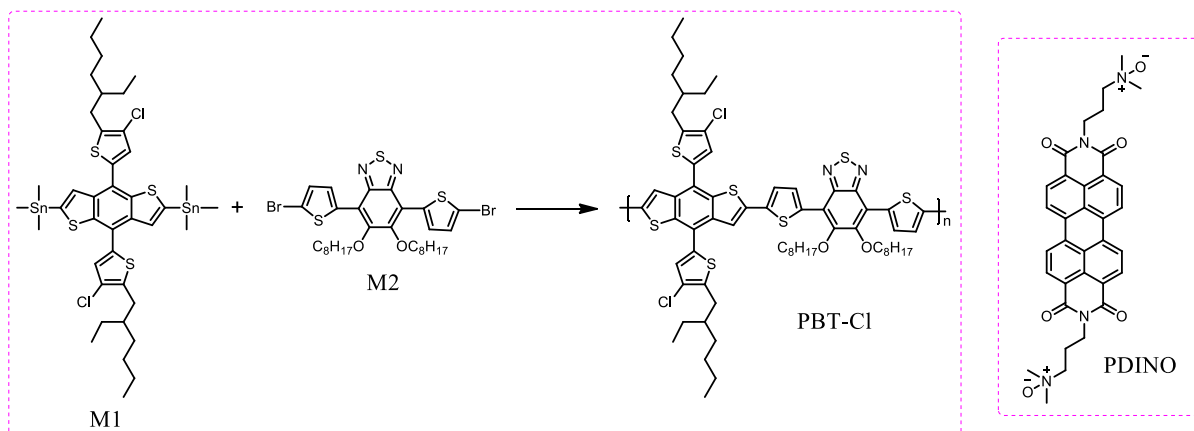
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Materials synthesis



Synthesis of PBT-Cl: In a 25 mL flask, monomers M1¹ (0.292 mg, 0.03 mmol) and M2² (0.271 mg, 0.03 mmol) were dissolved in 10 mL toluene, and the flask was flushed with argon for 10 min. Then 18 mg of Pd(PPh₃)₄ was added into the solution, and the mixture was flushed with argon for another 15 min. The solution was heated to reflux for 11 h under argon protection. After cooling to ambient temperature, the polymer was precipitated in 200 mL of methanol, filtered through a Soxhlet thimble. The precipitate was then subjected to Soxhlet extraction with methanol, hexane, and chloroform. The

polymer was precipitated from 100 mL of methanol. The precipitates were collected and dried under vacuum overnight to get polymer as solid.

PBT-Cl: $M_n = 15.3$ kDa, $M_w = 37.1$ kDa, PDI = 2.74.

Materials characterization

Cyclic voltammetry was performed on a Zahner IM6e electrochemical workstation with a three-electrode system in a solution of 0.1 M [Bu₄N]PF₆ acetonitrile solution at a scan rate of 100 mV s⁻¹. Glassy carbon disc coated with polymer film was used as the working electrode. A Pt wire was used the counter electrode and Ag/Ag⁺ was used as the reference electrode. Ferrocene/ferrocenium redox couple was used as the external standard and its redox potential is 0.06 V versus Ag/Ag⁺. The HOMO and LUMO energy levels were calculated from the onset of the oxidation and reduction potential of polymer using the following equations: HOMO = $-e(\varphi_{\text{ox}} + 4.74)$ (eV); LUMO = $-e(\varphi_{\text{red}} + 4.74)$ (eV), respectively.

Solar cells devices fabrication and characterization

The devices with a conventional architecture of glass/ITO/PDEOT:PSS/PBT-Cl:IT-4F/PDINO/Al were fabricated and characterized in an N₂-filled glove box. ZnO was used as cathode interlayer. 100 nm Al layer were subsequently evaporated through a shadow mask to define the active area of the devices and form a top anode. The current density-voltage (*J-V*) measurement of the PSCs were measured under a illumination of AM 1.5G (100 mW cm⁻²) using a SS-F5-3A solar simulator (AAA grade, 50 × 50 mm² photobeam size) of Enli Technology CO., Ltd.. The EQE was measured by using a Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Co., Ltd.). The light intensity at each wavelength was calibrated by a standard single-crystal Si solar cell.

Mobility Measurement: The hole and electron mobilities were calculated by using the space-charge-limited current (SCLC) method.³⁻⁴

$$J \cong (9/8)\epsilon\epsilon_0\mu_0V^2 \exp(0.89\sqrt{V/E_0L}) / L^3$$

where ε is the dielectric constant of the polymers, ε_0 is the permittivity of the vacuum, μ_0 is the zero-field mobility, E_0 is the characteristic field, J is the current density, and L is the thickness of the film.

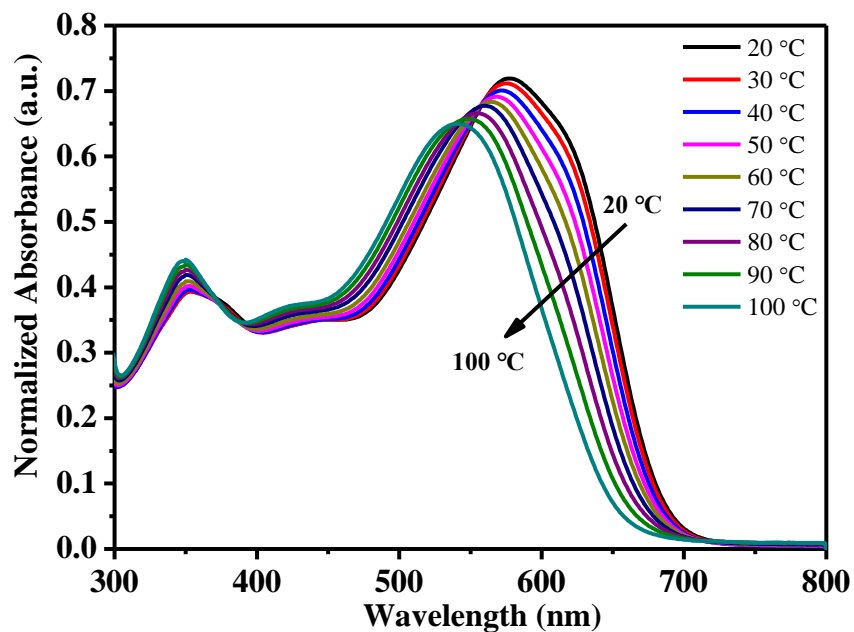


Fig. S1 UV-vis absorption spectra of PBT-Cl in chlorobenzene solution under different temperature.

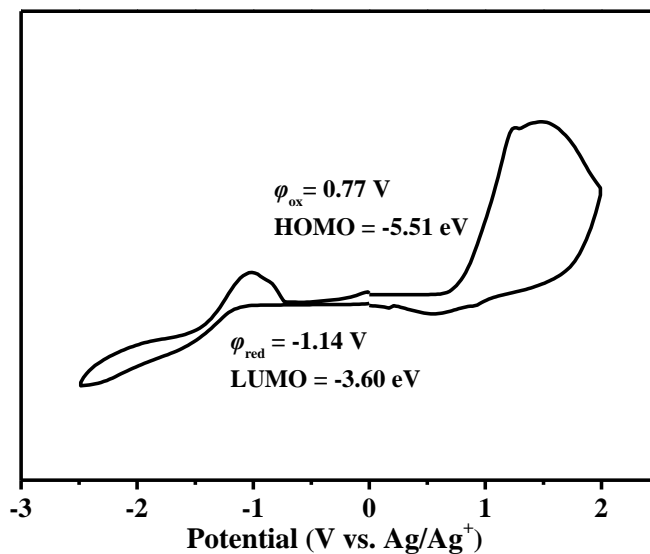


Fig. S2 Cyclic voltammograms of PBT-Cl film on a glassy carbon electrode in 0.1 mol L⁻¹ Bu₄NPF₆ acetonitrile solution at a scan rate of 100 mV s⁻¹.

Table S1 Photovoltaic performance of the PBT-Cl:IT-4F based PSCs with different D/A ratio and post-treatment under the illumination of AM 1.5 G at 100 mW cm⁻².

D/A ratio	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE ^a [%]
1:0.5	0.811	14.39	36.6	4.26
	[0.811 ± 0.04]	[14.36 ± 0.24]	[36.6 ± 0.30]	[4.22 ± 0.08]
1:1	0.813	18.20	52.1	7.72
	[0.811 ± 0.04]	[18.13 ± 0.34]	[51.7 ± 0.54]	[7.60 ± 0.08]
1:1.5	0.818	17.95	56.0	8.21
	[0.820 ± 0.002]	[18.03 ± 0.06]	[54.8 ± 0.70]	[8.10 ± 0.07]
1:2	0.814	13.88	60.4	6.83
	[0.814 ± 0.04]	[13.71 ± 0.38]	[59.4 ± 0.92]	[6.63 ± 0.17]

^aThe statistical values in square bracket are the average PCE obtained from 12 devices.

Table S2 Photovoltaic performance of the PBT-Cl:IT-4F (1:1.5, w/w) based PSCs with different D/A post-treatment under the illumination of AM 1.5 G at 100 mW cm⁻².

Treatment	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE ^a [%]
0.5% DIO	0.782	21.03	68.3	11.18
	[0.778 ± 0.002]	[20.82 ± 0.28]	[68.2 ± 0.71]	[11.04 ± 0.11]
1% DIO	0.790	21.45	67.8	11.49
	[0.789 ± 0.02]	[21.27 ± 0.19]	[68.0 ± 0.49]	[11.42 ± 0.07]
2% DIO	0.765	18.46	68.3	9.64
	[0.763 ± 0.002]	[18.39 ± 0.07]	[68.0 ± 0.50]	[9.55 ± 0.10]
1% DIO + TA 100 °C	0.788	21.25	67.8	11.35
	[0.787 ± 0.002]	[21.14 ± 0.11]	[68.0 ± 0.31]	[11.30 ± 0.05]
1% DIO + TA 120 °C	0.782	21.03	70.0	11.60
	[0.784 ± 0.003]	[20.99 ± 0.19]	[70.0 ± 0.78]	[11.53 ± 0.06]

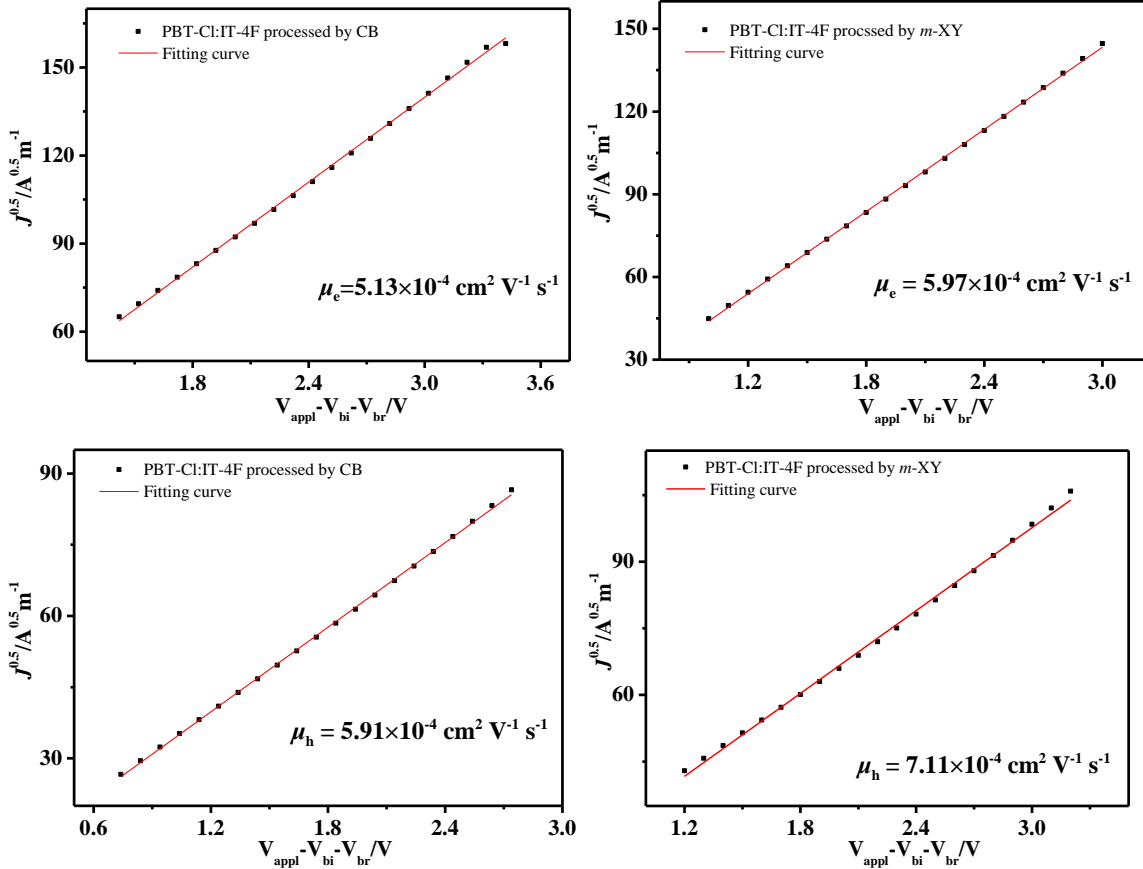


Fig. S3 $J^{0.5}$ vs $(V_{\text{app}} - V_{\text{bi}} - V_{\text{br}})$ plots of electron-only devices of PBT-Cl:IT-4F (1:1.5, w/w) processed by (a) CB and (b) *m*-XY. $J^{0.5}$ vs $(V_{\text{app}} - V_{\text{bi}} - V_{\text{br}})$ plots of hole-only devices of PBT-Cl:IT-4F (1:1.5, w/w) processed by (c) CB and (d) *m*-XY.

References

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