Supporting Information for ***Acta Phys. -Chim. Sin.*** doi: 10.3866/PKU.WHXB201804098

基于无规三元共聚物的非卤溶液加工型高效聚合物太阳能电池

国霞[1]，凡群平[1]，崔超华[1]，张志国[2]，张茂杰[1,*]

[1] 苏州大学材料与化学化工学部，先进光电材料实验室，江苏 苏州 215123

[2] 中国科学院化学研究所，中国科学院有机固体重点实验室，北京 100190

Wide Bandgap Random Terpolymers for High Efficiency Halogen-Free Solvent Processed Polymer Solar Cells

GUO Xia [1], FAN Qunping [1], CUI Chaohua [1], ZHANG Zhiguo [2], ZHANG Maojie [1,*]

[1] Laboratory of Advanced Optoelectronic Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, Jiangsu Province, P. R. China.

[2] CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China.

*Corresponding author. Email: mjzhang@suda.edu.cn; Tel: +86-0512-65883576.

Materials

All chemicals and solvents were reagent grades and purchased from Alfa Aesar and TCI. BDTT-S [1], FBTz [2], TTz [3] and ITIC [4] were synthesized according to the procedure reported in the literatures.

Synthesis of PSBZ

In a dry 50 mL flask, $Pd(PPh_3)_4$ (15 mg) was added to a solution of BDTTS (324 mg, 0.30 mmol) and ffBTz (194 mg, 0.30 mmol) in 12 mL degassed toluene under nitrogen and stirred vigorously at 110 °C for *ca.* 6 h until the reaction system becomes a viscous state. Then the mixture was poured into methanol (100 mL) and the precipitation was occurred. The polymer was dissolved in chloroform and the solution was filtered through a silica gel column. The collected chloroform solution was concentrated and precipitated with methanol to get the dark-red solid (183 mg, 49%). Anal. Calcd for $C_{72}H_{95}F_2N_3S_8$: C, 66.01%; H, 7.46%. M_n = 20.6 kDa, PDI = 2.26.

Synthesis of PSBTZ-80

In a dry 50 mL flask, $Pd(PPh_3)_4$ (15 mg) was added to a solution of BDTTS (324 mg, 0.30 mmol), ffBTz (155 mg, 0.24 mmol) and TTz (42 mg, 0.06 mmol) in 12 mL degassed toluene under nitrogen and stirred vigorously at 110 °C for *ca.* 7 h until the reaction system becomes a viscous state. Then the mixture was poured into methanol (100 mL) and the precipitation was occurred. The polymer was dissolved in chloroform and the solution was filtered through a silica gel column. The collected chloroform solution was concentrated and precipitated with methanol to get the dark-red solid (213 mg, 55%). Anal. Calcd for $(C_{72}H_{95}F_2N_3S_8)_{0.8}(C_{70}H_{94}N_2S_{10})_{0.2}$: C, 65.77%; H, 7.47%. M_n = 21.8 kDa, PDI = 2.17.

Synthesis of PSBTZ-60

In a dry 50 mL flask, $Pd(PPh_3)_4$ (15 mg) was added to a solution of BDTTS (324 mg, 0.30 mmol), ffBTz (116 mg, 0.18 mmol) and TTz (83 mg, 0.12 mmol) in 12 mL degassed toluene under nitrogen and stirred vigorously at 110 °C for *ca.* 8 h until the reaction system becomes a viscous state. Then the mixture was poured into methanol (100 mL) and the precipitation was occurred. The polymer was dissolved in chloroform and the solution was filtered through a silica gel column. The collected chloroform solution was concentrated and precipitated with methanol to get the dark-red solid (225 mg, 53%). Anal. Calcd for $(C_{72}H_{95}F_2N_3S_8)_{0.6}(C_{70}H_{94}N_2S_{10})_{0.4}$: C, 65.53%; H, 7.48%. M_n = 21.3 kDa, PDI = 2.29.

Synthesis of PSBTZ-40

In a dry 50 mL flask, $Pd(PPh_3)_4$ (15 mg) was added to a solution of BDTTS (324 mg, 0.30 mmol), ffBTz (77 mg, 0.12 mmol) and TTz (124 mg, 0.18 mmol) in 12 mL degassed toluene under nitrogen and stirred vigorously at 110 °C for *ca.* 8 h until the reaction system becomes a viscous state. Then the mixture was poured into methanol (100 mL) and the precipitation was occurred. The polymer was dissolved in chloroform and the solution was filtered through a silica gel column. The collected chloroform solution was concentrated and precipitated with methanol to get the dark-red solid (244 mg, 57%). Anal. Calcd for $(C_{72}H_{95}F_2N_3S_8)_{0.4}(C_{70}H_{94}N_2S_{10})_{0.6}$: C, 65.29%; H, 7.42%. Mn = 22.2 kDa, PDI = 2.11.

Synthesis of PSTZ

In a dry 50 mL flask, $Pd(PPh_3)_4$ (15 mg) was added to a solution of BDTTS (324 mg, 0.30 mmol) and TTz (207 mg, 0.30 mmol) in 12 mL degassed toluene under nitrogen and stirred vigorously at 110 °C for *ca.* 7 h until the reaction system becomes a viscous state. Then the mixture was poured into methanol (100 mL) and the precipitation was occurred. The polymer was dissolved in chloroform and the solution was filtered through a silica gel column. The collected chloroform solution was concentrated and precipitated with methanol to get the dark-red solid (196 mg, 57%). Anal. Calcd for $C_{70}H_{94}N_2S_{10}$: C, 64.81%; H, 7.45%. M_n = 19.9 kDa, PDI = 2.28.

Experimental Section

Measurements: Elemental analysis was carried out on a flash EA1112 analyzer. Gel Permeation Chromatography (GPC) was carried out on Agilent Technologies PL-GPC-220 at 160 °C, where 1,2,4-tricholorobenzene as the eluent and polystyrene as the standard. UV-vis absorption spectra were taken on an Agilent Technologies Cary Series UV-Vis-NIR Spectrophotometer. Photoluminescence (PL) spectra were taken on an Edinburgh Instrument FLS 980. Atomic force microscopy (AFM) measurements were performed on a Dimension 3100 (Veeco) Atomic Force Microscope in the tapping mode. Transmission electron microscopy (TEM) was performed using a Tecnai G2 F20 S-TWIN instrument at 200 kV accelerating voltage. TEM was performed using a Tecnai G2 F20 S-TWIN instrument at 200 kV accelerating voltage, in which the blend films were prepared using a processing technique, as following: first, the blend films were spin-cast on the ITO/PEDOT:PSS substrates; second, the resulting

ITO/PEDOT:PSS/blend film substrates were submerged in deionized water to make these blend films float onto the air-water interface; finally, the floated blend films were taken up on unsupported 200 mesh copper grids for a TEM measurement.

Fabrication and characterization of polymer solar cells. Polymer solar cell devices with a inverted device structure of ITO/ZnO/PFN/polymers:ITIC/MoO_3/Al were fabricated under conditions as follows: patterned indium tin oxide (ITO)-coated glass with a sheet resistance of 10–15 $\Omega\cdot\square^{-1}$ was cleaned by a surfactant scrub and then underwent a wet-cleaning process inside an ultrasonic bath, beginning with deionized water followed by acetone and isopropanol. After oxygen plasma cleaning for 10 min, then the ZnO layer with a thickness of 30 nm was deposited by spin-coating under 2000 r·min^{-1} for 60 s on top of the ITO substrate. ZnO nanoparticles were synthesized followed the literature [5]. The poly[(9,9-bis(3'-(*N*,*N*-dimethyl)-nethylammoinium-propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)] (PFN) was then deposited on top of the ZnO layer by spin-coating an methanol solution with a concentration of 0.2 mg·mL^{-1} under 2000 r·min^{-1} for 60 s. The active layer was then deposited on top of the PFN layer by spin-coating a toluene solution or a blend solution of toluene and diphenyl ether (DPE) (10 mg mL^{-1}, dissolved 10 h under 60 °C) of polymers:ITIC. The thicknesses of the active layers are *ca.* 100 nm and measured on a KLA Tencor D-100 profilometer. Finally, 10 nm MoO_3 and 80 nm Al were successively deposited on the photosensitive layer under vacuum at a pressure of ca. 4×10^{-4} Pa, and through a shadow mask to determine the active area of the devices (~0.2 cm^2). For the PSC devices, the detail testing processes of the thermal stability as follows: firstly, the PSCs are prepared according to the optimal device conditions; secondly, in the N_2-filled glovebox, these devices are transferred to the heat plate with a typical temperature of 100 °C; finally, the photovoltaic performances of the PSCs with different annealing time were measured. The PCE values 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 mm × 50 mm photobeam size) of Enli Technology CO., Ltd. A 2 cm × 2 cm monocrystalline silicon reference cell (SRC-00019) was purchased from Enli Technology CO., Ltd. PCE statistics were obtained using 10 individual devices fabricated under the same conditions. The EQE was measured by Solar Cell Spectral Response Measurement System QE-R3011 of Enli Technology CO., Ltd. The light intensity at each wavelength was calibrated with a standard single crystal Si photovoltaic cell. To study the charge generation and dissociation processes of the PSCs, plots of the photocurrent (J_{ph}) *versus* effective voltage (V_{eff}) of the PSCs were measured. Here, J_{ph} and V_{eff} are defined as $J_{ph} = J_L - J_D$ and $V_{eff} = V_0 - V_{appl}$, respectively, where J_D and J_L are the photocurrent densities in the dark and under the illumination, and V_{appl} is the applied bias voltage and V_0 is the voltage at which $J_{ph} = 0$, respectively [6]. The J_{ph} reaches the saturation current density (J_{sat}) at high V_{eff} (≥ 2 V in this case).

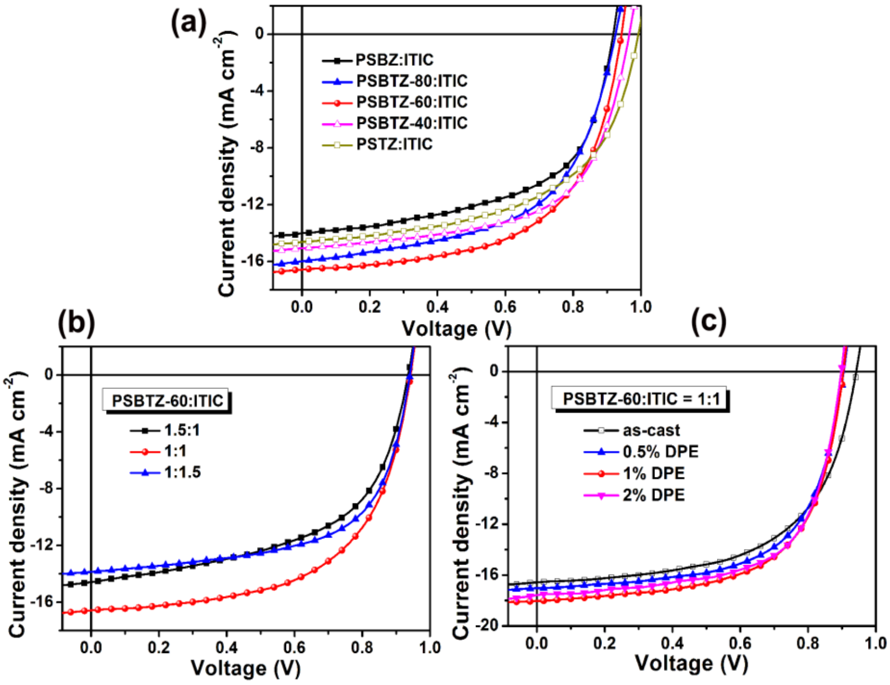

Fig. S1 The *J–V* plots of (a) the PSCs based on a D/A (1 : 1) pair of ITIC as acceptor and different polymers as donors, (b) the PSCs based on PSBTZ-60:ITIC with different D/A weight ratios, (c) the PSCs based on PSBTZ-60:ITIC (1 : 1) with different DPE contents.

Table S1 Photovoltaic date of the PSCs based on a D/A (1 : 1) pair of ITIC as acceptor and different polymers as donors.

Polymer:ITIC	V_{oc}/V	J_{sc}/(mA·cm^{-2})	FF/%	PCE/% [a]
PSBZ	0.92	14.0	56.3	7.3 (7.0)
PSBTZ-80	0.93	16.0	56.4	8.3 (8.1)
PSBTZ-60	0.94	16.5	58.5	9.1 (8.9)
PSBTZ-40	0.96	15.1	60.6	8.8 (8.5)
PSTZ	0.99	14.6	55.4	8.0 (7.6)

[a] The average PCEs in parentheses from 10 devices.

Table S2 Photovoltaic date of the PSCs based on PSBTZ-60:ITIC with different D/A weight ratios.

D/A	V_{oc}/V	J_{sc}/(mA·cm^{-2})	FF/%	PCE/% [a]
1.5 : 1	0.94	14.6	54.6	7.4 (7.1)
1 : 1	0.94	16.5	58.5	9.1 (8.9)
1 : 1.5	0.93	13.8	59.0	7.6 (7.4)

[a] The average PCEs in parentheses from 10 devices.

Table S3 Photovoltaic date of the PSCs based on PSBTZ-60:ITIC (1:1) with different DPE contents.

DPE	V_{oc}/V	J_{sc}/(mA·cm^{-2})	FF/%	PCE/% [a]
as-cast	0.94	16.5	58.5	9.1 (8.9)
0.5%	0.91	17.0	62.6	9.7 (9.5)
1%	0.91	18.0	62.7	10.3 (10.0)
2%	0.90	17.6	64.3	8.0 (7.7)

[a] The average PCEs in parentheses from 10 devices.

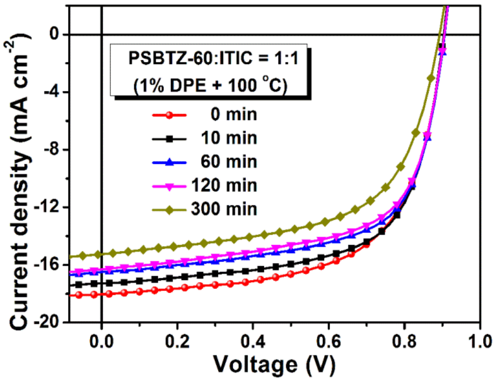

Fig. S2 The *J–V* curves the PSBTZ-60:ITIC-based PSCs processed with 1% DPE and different annealing times at 100 °C.

Table S4 Photovoltaic date of the PSCs based on PSBTZ-60:ITIC (1:1) with 1% DPE and different annealing times at 120 °C.

Temperatures/min	V_{oc}/V	J_{sc}/(mA·cm^{-2})	FF/%	PCE/% [a]
0	0.91	18.0	62.7	10.3 (10.0)
10	0.91	17.3	64.9	10.1 (9.8)
60	0.91	16.5	64.4	9.7 (9.3)
120	0.91	16.3	63.6	9.4 (8.9)
300	0.89	15.4	60.6	8.3 (7.7)

[a] The average PCEs in parentheses from 10 devices.

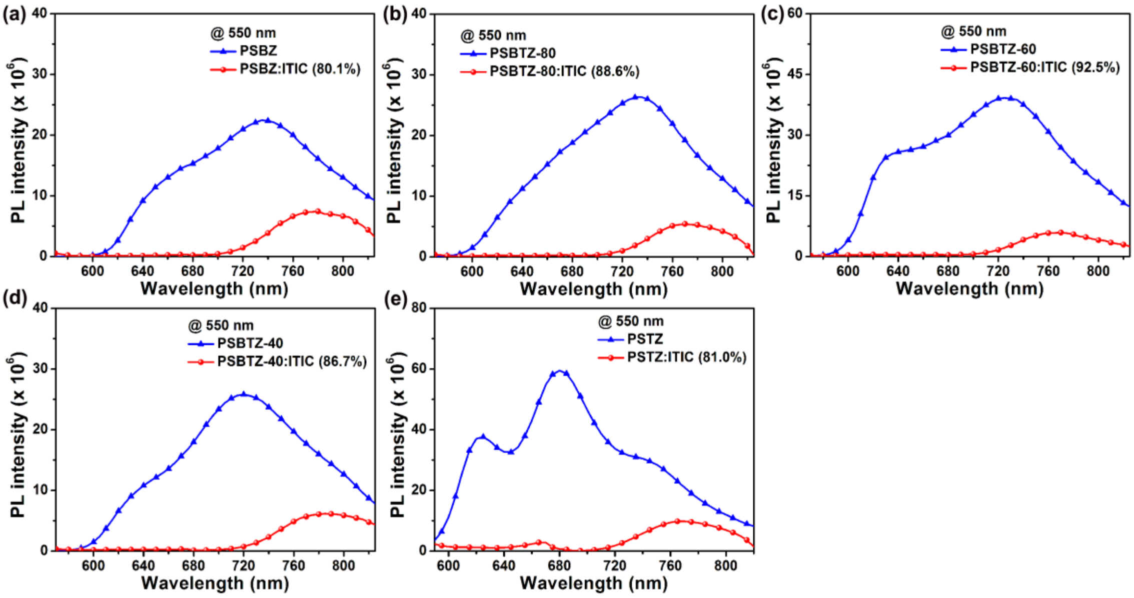

Fig. S3 The PL spectra of pure PSBZ, PSBTZ-80, PSBTZ-60, PSBTZ-40 and PSTZ films, and the related blend films at an excitation wavelength of 580 nm.

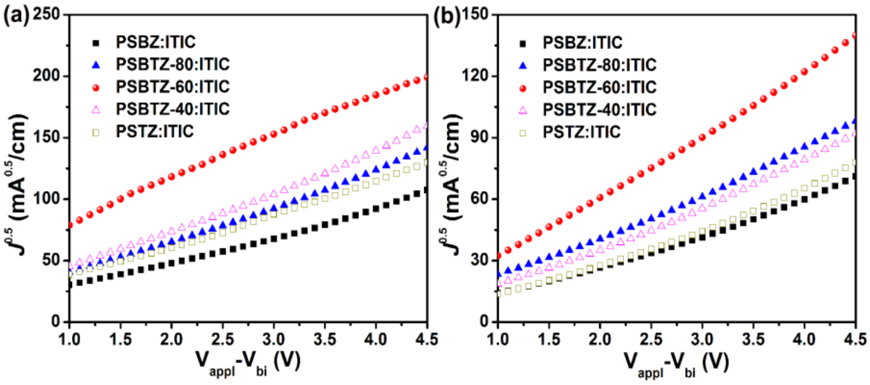

Fig. S4 The *J–V* curves of (a) the hole-only devices with the structure of ITO/PEDOT:PSS/polymers:ITIC/MoO_3/Al; and (b) the electron-only devices with the structure of ITO/ZnO/polymers:ITIC/Ca/Al according to the SCLC model.

References

(1) Fan, Q.; Su, W.; Guo, X.; Wang, Y.; Chen, J.; Ye, C.; Zhang, M.; Li, Y. *J. Mater. Chem. A* **2017,** *5*, 9204. doi: 10.1039/c7ta02075a

(2) Bin, H.; Zhang, Z. -G.; Gao, L.; Chen, S.; Zhong, L.; Xue, L.; Yang, C.; Li, Y. *J. Am. Chem. Soc.* **2016,** *138*, 4657. doi: 10.1021/jacs.6b01744

(3) Su, W.; Fan, Q.; Guo, X.; Meng, X.; Bi, Z.; Ma, W.; Zhang, M.; Li, Y. *Nano Energy* **2017,** *38*, 510. doi: 10.1016/j.nanoen.2017.05.060

(4) Lin, Y.; Wang, J.; Zhang, Z. -G.; Bai, H.; Li, Y.; Zhu, D.; Zhan, X. *Adv. Mater.* **2015,** *27*, 1170. doi: 10.1002/adma.201404317

(5) Beek, W. J. E.; Wienk, M. M.; Kemerink, M.; Yang, X.; Janssen, R. A. J. *J. Phys. Chem. B* **2005,** *109*, 9505. doi: 10.1021/jp050745x

(6) Blom, P. W.; Mihailetchi, V. D.; Koster, L. J.; Markov. D. E. *Adv. Mater.* **2007,** *19*, 1551. doi: 10.1002/adma.200601093