

A Brief Investigation on the Performance Variation and Shelf Lifetime in Polymer:Nonfullerene Solar Cells

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ABSTRACT: Polymer:nonfullerene solar cells with an inverted-type device structure were fabricated by employing the bulk heterojunction (BHJ) active layers, which are composed of poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophene-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione))] (PBDB-T) and 3,9-bis(6-methyl-2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3-d']-s-indaceno[1,2-b:5,6-b']dithiophene (IT-M). The BHJ layers were formed on a pre-patterned indium-tin oxide (ITO)-coated glass substrate by spin-coating using the blend solutions of PBDB-T and IT-M. The solar cell performances were investigated with respect to the cell position on the ITO-glass substrates. In addition, the short-term shelf lifetime of solar cells was tested by storing the PBDB-T:IT-M solar cells in a glovebox filled with inert gas. The results showed that the performance of solar cells was relatively higher for the cells close to the center of substrates, which was maintained even after storage for 24 h. In particular, the PCE of PBDB-T:IT-M solar cells was marginally decreased after storage for 24 h owing to the slightly reduced fill factor, even though the open circuit voltage was unchanged after 24 h.

Key words: Polymer:nonfullerene solar cells, PBDB-T, IT-M, Cell position, Shelf lifetime

1. Introduction

Due to the viable advantages including vacuum-free low temperature processes towards flexible/rollable solar modules, polymer-based organic solar cells (i.e., polymer solar cells) have been highlighted for the last two decades¹⁻⁹. The power conversion efficiency (PCE) of polymer solar cells with donor-acceptor bulk heterojunction (BHJ) structures was remarkably improved from ca. 2~5% in 2006 and ca. 6~9% in 2010 to ca. 10~15% in 2019, which can be attributed to the advanced technologies in materials and devices¹⁰⁻¹⁷. The PCE improvement from ca. 5% to ca. 10% could be realized by the introduction of new electron-donating (p-type) conjugated polymers, while new electron-accepting (n-type) small molecules (known as a nonfullerene acceptor) enabled further PCE improvement up to ca. 15%¹⁸⁻²³.

It is currently considered that the nonfullerene acceptors have successfully replaced conventional soluble fullerene acceptors

with demerits of easy crystallization and/or aggregation leading to poor device stability²⁴⁻²⁷. In addition, most nonfullerene acceptors have a merit in terms of light harvesting when it comes to the extended wavelengths up to ca. 900 nm. In particular, the nonfullerene acceptors possess a planar core group, which consists of five to seven heterocycles, so that the easy charge transport between planar core groups can be another benefit leading to the improved PCE.

Here it is noted that most results on such high PCEs in polymer:nonfullerene solar cells have been reported on the basis of small-sized devices fabricated by employing spin-coating techniques in university laboratory²⁸⁻³⁰. Such small-sized devices consist of several sub-cells that are normally separated by a fixed distance, which can induce position-sensitive cell performances such as fill factors and series resistance (R_s)³¹. Therefore, it is necessary to understand how much the performance of cells can be varied according to the position of each cell (device) in single substrates used for spin-coating. Additionally, investigating the short-term shelf lifetime of each cell (device) in the single substrates can contribute to securing confident data when such laboratory-sourced polymer:nonfullerene

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solar cells are stored for various measurements. In our previous work, it has been demonstrated that the short-term stability measurement can deliver simple but effective clues for pre-screening prior to initializing long-term stability measurement in laboratory scale⁵.

In this work, we have fabricated polymer:nonfullerene solar cells using indium-tin oxide (ITO)-coated glass substrates (area = 2.25 cm²) by spin-coating the BHJ layers that consist of poly [(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione))] (PBDB-T) and 3,9-bis(6-methyl-2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (IT-M). The performance of PBDB-T:IT-M solar cells was measured and characterized according to the position of each cell on the glass substrates. In particular, the shelf (storage) lifetime of each cell was measured after keeping whole devices in a nitrogen-filled glovebox for 24 h.

2. Experimental Section

2.1 Materials and solutions

PBDB-T (weight-average molecular weight = 18 kDa; polydispersity index = 2.5) and IT-M (formula molecular = 1.455 kDa) were received from Solarmer (USA) and used without further purification. Zinc acetate dehydrate (purity >99%) and o-chlorobenzene (CB) were purchased from Sigma-Aldrich (USA). Binary blend solutions of PBDB-T and IT-M were prepared using CB as a solvent, followed by addition of 1,8-diodooctane (DIO, 1 vol%) as an additive. The solid concentration of PBDB-T:IT-M blends (1:1 by weight) was kept as 20 mg/ml. All solutions were subjected to continuous stirring for better mixing at room temperature for 24 h prior to spin-coating processes. Precursor solutions of zinc oxide (ZnO) were prepared by adding zinc acetate dehydrate (100 mg) to the mixture of 2-methoxyethanol (1 ml) and ethanol amine (0.028 ml, stabilizer). The ZnO precursor solutions were vigorously stirred at 60°C for 3 h for sol-gel reactions and then gently stirred at room temperature for 12 h.

2.2 Device fabrication and measurement

For the fabrication of PBDB-T:IT-M solar cells, the ITO-coated glass substrates were pre-patterned and cleaned using acetone and isopropyl alcohol by employing an ultrasonic cleaner. The cleaned ITO-glass substrates were irradiated by a

UV-ozone for 20 min in order to remove any organic residues. Next, the ZnO precursor films were spin-coated using corresponding solutions, followed by thermal annealing at 200°C for 1 h in air ambient condition. On top of the ZnO layers, the BHJ (PBDB-T:IT-M) layers were spin-coated inside a nitrogen-filled glovebox system equipped with a spin-coater and hot-plate, etc. These samples were shifted to a vacuum chamber equipped inside an argon-filled glove box. When the base pressure of chamber reached ca. 1.0×10^{-6} torr, molybdenum oxide (MoO₃, 10 nm) and silver (Ag, 80 nm) electrodes were thermally evaporated on the BHJ layers by controlling the evaporation rate. The current density-applied voltage (J - V_{APP}) curves of devices, which were mounted inside a sample holder, were measured using a specialized solar cell measurement system equipped with a solar simulator (92250A-1000, Newport Oriel) and an electrometer (Keithley 2400). The incident light intensity from the solar simulator was fixed to 100 mW/cm² (air mass 1.5G) for all devices. In order to investigate the short-term shelf lifetime, one set of devices was stored inside the argon-filled glovebox for 24 h. Then the same measurement was applied for the stored devices.

3. Results and Discussion

The present PBDB-T:IT-M solar cells have a typical inverted-type structure that contains the active (BHJ) layers coated on the ZnO electron-collecting buffer layers (see the chemical structures in Fig. 1a and the cross-sectional view of cell in Fig. 1b top). The surface part of the PBDB-T:IT-M layers contact the MoO₃ hole-collecting buffer layers (see Fig. 1b top). Therefore, electrons and holes are extracted from the BHJ layers to the bottom and top directions of devices, respectively. As displayed in Fig. 1b (bottom), one glass substrate possesses each device cell in parallel. Upon spin-coating, the blend solutions might be spread out from the center point (0). As a consequence, the active layers at each cell could have slightly different states including composition, thickness, chain alignment, etc. Hence, it is useful to briefly investigate the performance of each cell according to the cell position.

As shown in Fig. 2a, the light (100 mW/cm²) current density-applied voltage (J - V_{APP}) curves of as-fabricated devices seem to be typical for high PCE solar cells when it comes to their shapes leading to high short circuit current density (J_{SC}) and open circuit voltage (V_{OC}). However, a close look finds that four cells show slightly different J - V_{APP} curves which is relatively

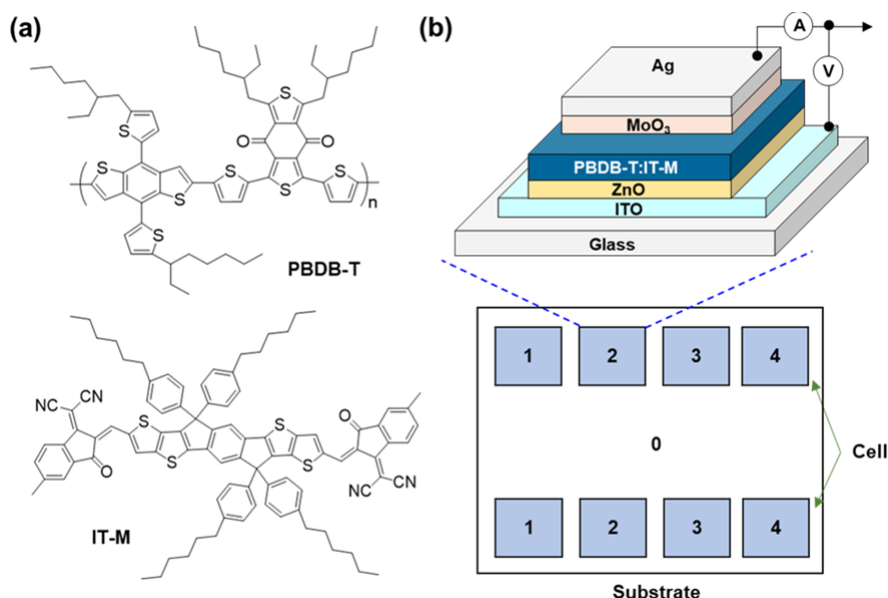


Fig. 1. (a) Chemical structure of materials used for the active (BHJ) layers for the PBDB-T:IT-M solar cells. (b) Device structure (top) for the PBDB-T:IT-M solar cells and cell positions (1-4) on the ITO-glass substrate (note that "0" is the center point of substrate)

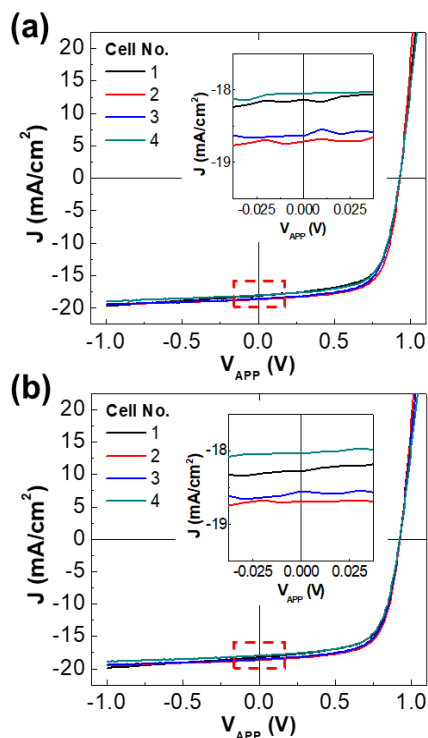


Fig. 2. Light $J-V_{APP}$ curves according to the cell number for the PBDB-T:IT-M solar cells (see inset for the enlarged curves focusing on the short circuit region as marked with red box)

pronounced at the high photocurrent regions ($J > 15$ mA/cm²). In contrast, almost no difference could be observed on the open circuit region ($V_{APP} = \text{ca. } 0.9$). The inset graph delivers that the

current density of cell 1 and cell 4 is very similar but relatively lower than that of cell 2 and cell 3 (note very similar current density between cell 2 and cell 3 as well). This result informs that the current density can be relatively lower for the cells far from the center of substrate but the cells at the same distance from the center can give very similar current density.

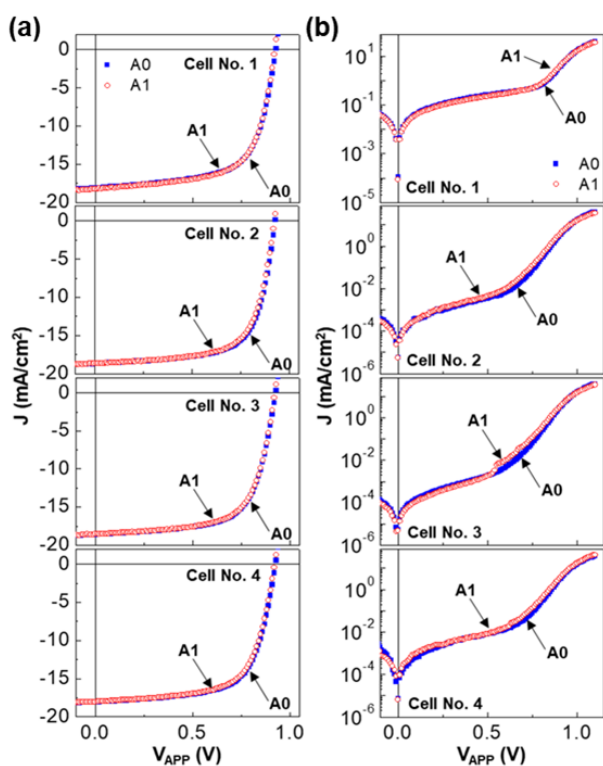
After storage for 24 h, the cells also delivered good $J-V_{APP}$ curves as shown in Fig. 2b. Interestingly, the open circuit region was still identical for all cells even after storage but the similar difference was observed for the short circuit region. As compared in the inset graph of Fig. 2b, the current density gap between cell 1 and cell 4 was marginally increased after storage for 24 h even though it was still well maintained in the case of cell 2 and cell 3. This result implies that the performance stability during storage might be relatively better for the cells close to the center point of substrate.

In order to further understand the influence of storage for 24 h on the device performance, the light $J-V_{APP}$ curve of each cell was enlarged and directly compared in Fig. 3a. Basically, it is not easy from the light $J-V_{APP}$ curves to find big difference between as-fabricated cells (A0) and stored cells (A1).

However, a careful inspection can lead that the stored cells provided very slightly reduced current density at round ca. 0.75 V (a rounded part). How this change affects the solar cell performance is explained by the marginally decreased fill factor (FF) as summarized in Table 1. Further evidences are supported

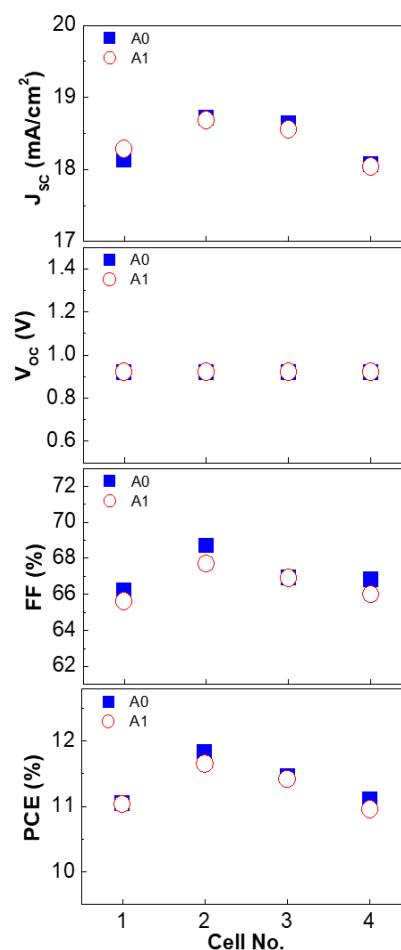
Table 1. Summary of solar cell parameters according to the cell position (number) for the PBDB-T:IT-M solar cells. A0 and A1 denote as-fabricated cells and stored cells (for 24 h), respectively

Parameters	1		2		3		4	
	A0	A1	A0	A1	A0	A1	A0	A1
VOC (V)	0.92	0.92	0.92	0.92	0.92	0.92	0.92	0.92
J _{SC} (mA/cm ²)	18.13	18.27	18.70	18.68	18.63	18.55	18.06	18.03
FF (%)	66.2	65.6	68.7	67.7	66.9	66.9	66.8	66.0
PCE (%)	11.04	11.03	11.81	11.64	11.46	11.41	11.10	10.95
R _S (kΩ·cm ²)	0.07	0.06	0.06	0.06	0.07	0.06	0.07	0.07
R _{SH} (kΩ·cm ²)	17.8	4.3	3.3	11.0	2.4	6.0	11.5	19.7

**Fig. 3.** Light (a) and dark (b) J - V_{APP} curves between as-fabricated cells (A0) and stored cells (A1) for the PBDB-T:IT-M solar cells

by the dark J - V_{APP} curves which show the similar current density difference between A0 and A1 cells (see Fig. 3b).

The detailed solar cell parameters are compared with respect to the cell position (number) in Fig. 4. As discussed, the J_{SC} value was higher for cell 2 and cell 3 than cell 1 and cell 4. Interestingly, this trend was not changed even after storage for 24 h. The V_{OC} value was almost unchanged after storage, while it was independent upon the cell position on the substrate. However, the FF value was varied depending on the cell position and slightly reduced after storage. Here it is worthy to note that the FF value of cell 2 and cell 3 was also higher than that of cell 1 and 4, which is similar to the J_{SC} trend. As a consequence, the PCE of devices was higher for cell 2 and cell

**Fig. 4.** V_{OC} , J_{SC} , FF, and PCE as a function of cell number for the PBDB-T:IT-M solar cells. A0 and A1 denote as-fabricated cells and stored cells, respectively

3 than cell 1 and cell 4. This trend was not changed after storage for 24 h even though the PCE of stored cells was marginally decreased from that of as-fabricated cells.

4. Conclusions

The polymer:nonfullerene (PBDB-T:IT-M) solar cells with high PCEs (ca. 11%), which are based on an inverted-type

device structure, were fabricated using a patterned ITO-glass substrate. The performance of each cell made on the ITO-glass substrate seemed to be apparently similar, but further detailed investigation revealed that the device performance was considerably dependent on the cell position on the ITO-glass substrates. The current density-voltage curves under one sun condition showed that the performance of devices was relatively lower for the cells far from the center of substrate resulted in lower J_{SC} than those close to the center. In addition, it was disclosed that the J_{SC} value was similar for the cells with the same distance from the center of substrate. In particular, this trend was almost well kept even after storage for 24 h in a glovebox filled with an inert gas. The $J-V_{APP}$ curves of stored cells (devices) was almost similar to those of as-fabricated cells, but a slightly reduced current density was measured at round ca. 0.75 V (a rounded part) for the stored cells. Although very small variations were measured for J_{SC} , the FF value was relatively largely reduced for the stored cells. As a result, the PCE of devices was slightly decreased after storage for 24 h. However, the PCE trend was unchanged with respect to the cell position after storage.

Acknowledgements

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References

- Lee, T. D., Ebong, A. U., "A review of thin film solar cell technology and challenges," *Renewable Sustainable Energy Rev.*, Vol. 70, pp. 1286-1297, 2017.
- Husain, A. A. F., Hasan, W. Z. W., Shafie, S., Hamidon, M. N., Pandey, S. S., "A review of transparent solar photovoltaic technologies," *Renewable Sustainable Energy Rev.*, Vol. 94, pp. 779-791, 2018.
- Kim, K., Nam, S., Jeong, J., Lee, S., Seo, J., Han, H., Kim, Y., "Organic solar cells based on conjugated polymers: history and recent advances," *Korean J. Chem. Eng.*, Vol. 31, No. 7, pp. 1095-1104, 2014.
- Kim, B.-J., Park, E.-H., Kang, K.-S., "Optical properties of soluble polythiophene for flexible solar cells," *Curr. Photovoltaic Res.*, Vol. 6, No. 4, pp. 91-93, 2018.
- Lee, S., Seo, J., Kim, H., Kim, Y., "Investigation of short-term stability in high efficiency polymer: nonfullerene solar cells via quick current-voltage cycling method," *Korean J. Chem. Eng.*, Vol. 35, No. 12, pp. 2496-2503, 2018.
- Lee, S., Park, J., Kim, Y., Kim, S., Iftiqar, S., M., Yi, J., "New generation multijunction solar cells for achieving high efficiency." *Curr. Photovoltaic Res.*, Vol. 6, No. 2, pp. 31-38, 2018.
- Zafar, M., Yun, J.-Y., Kim, D.-H., "Performance of inverted organic photovoltaic cells with nitrogen doped TiO₂ films by atomic layer deposition," *Korean J. Chem. Eng.*, Vol. 35, No. 2, pp. 567-573, 2018.
- Zheng, Z., Awartani, O. M., Gautam, B., Liu, D., Qin, Y., Li, W., Bataller, A., Gundogdu, K., Ade, H., Hou, J., "Efficient Charge Transfer and Fine-Tuned Energy Level Alignment in a THF-Processed Fullerene-Free Organic Solar Cell with 11.3% Efficiency," *Adv. Mater.*, Vol. 29, No. 5, p. 1604241, 2017.
- Kim, J.-Y., Shin, K.-Y., Raza, M. H., Pinna, N., Sung, Y.-E., "Vertically aligned TiO₂/ZnO nanotube arrays prepared by atomic layer deposition for photovoltaic applications," *Korean J. Chem. Eng.*, Vol. 36, No. 7, pp. 1157-1163, 2019.
- Zhao, W., Li, S., Yao, H., Zhang, S., Zhang, Y., Yang, B., Hou, J., "Molecular optimization enables over 13% efficiency in organic solar cells," *J. Am. Chem. Soc.*, Vol. 139, No. 21, pp. 7148-7151, 2017.
- Yang, L., Zhang, S., He, C., Zhang, J., Yao, H., Yang, Y., Zhang, Y., Zhao, W., Hou, J., "New wide band gap donor for efficient fullerene-free all-small-molecule organic solar cells," *J. Am. Chem. Soc.*, Vol. 139, No. 5, pp. 1958-1966, 2017.
- Jeong, J., Seo, J., Nam, S., Han, H., Kim, H., Anthopoulos, T. D., Bradley, D. D. C., Kim, Y., "Significant stability enhancement in high- efficiency polymer:fullerene bulk heterojunction solar cells by blocking ultraviolet photons from solar light," *Adv. Sci.*, Vol. 3, No. 4, p. 1500269, 2016.
- Sun, Y., Welch, G. C., Leong, W. L., Takacs, C. J., Bazan, G., C., Heeger, A. J., "Solution -processed small-molecule solar cells with 6.7% efficiency". *Nat. Mater.*, Vol. 11, pp. 44-48, 2012.
- Nielsen, C. B., Ashraf, R. S., Treat, N. D., Schroeder, B. C., Donaghey, J. E., White, A. J. P., Stingelin, N., McCulloch, I., "2,1,3-benzo thiadiazole-5,6-dicarboxylic imide -a versatile building block for additive-and annealing-free processing of organic solar cells with efficiencies exceeding 8%," *Adv. Mater.*, Vol. 27, No. 5, pp. 948-953, 2015.
- Seo, J., Nam, S., Kim, H., Bradley, D. D. C., Kim, Y., "Nanocrater morphology in hybrid electron-collecting buffer layers for high efficiency polymer:nonfullerene solar cells with enhanced stability," *Nanoscale Horiz.*, Vol. 4, pp. 464-471, 2019.
- Zhang, Q., Kan, B., Liu, F., Long, G., Wan, X., Chen, X., Zuo, Y., Ni, W., Zhang, H., Li, M., Hu, Z., Huang, F., Cao, Y., Liang, Z., Zhang, M., Russell, T. P., Chen, Y., "Small-molecule solar cells with efficiency over 9%," *Nat. Photonics*, Vol. 9, pp. 35-41, 2015.
- Park, E., Seo, J., Han, H., Kim, H., Kim, Y., "High-efficiency polymer:nonfullerene solar cells with quaterthiophene-containing polyimide interlayers," *Adv. Sci.*, Vol. 5, No. 8, p. 1800331, 2018.
- Hou, J., Inganäs, O., Friend, R. H., Gao, F., "Organic solar

- cells based on non-fullerene acceptors," *Nat. Mater.* Vol. 17, pp. 119-128, 2018.
19. Zhao, F., Dai, S., Wu, Y., Zhang, Q., Wang, J., Jiang, L., Ling, Q., Wei, Z., Ma, W., You, W., Wang, C., Zhan, X., "Single-junction binary-blend nonfullerene polymer solar cells with 12.1% efficiency," *Adv. Mater.* Vol. 29, No. 18, p. 1700144, 2017.
 20. Holliday, S., Ashraf, R. S., Wadsworth, A., Baran, D., Yousaf, S. A., Nielsen, C. B., Tan, C.-H., Dimitrov, S. D., Shang, Z., Gasparini, N., Alamoudi, M., Laquai, F., Brabec, C. J., Salleo, A., Durrant, J. R., McCulloch, I., "High-efficiency and air-stable P3HT-base polymer solar cells with new non-fullerene acceptor," *Nat. Commun.*, Vol. 7, p. 11585, 2016.
 21. Zhang, H., Yao, H., Hou, J., Zhu, J., Zhang, J., Li, W., Yu, R., Gao, B., Zhang, S., Hou, J., "Over 14% efficiency in organic solar cells enabled by chlorinated nonfullerene small-molecule acceptors," *Adv. Mater.*, Vol. 30, No. 28, p. 1800613, 2018.
 22. Yao, H., Ye, L., Hou, J., Jang, B., Han, G., Cui, Y., Su, G. M., Wang, C., Gao, B., Yu, R., Zhang, H., Yi, Y., Woo, H. Y., Ade, H., Hou, J., "Achieving highly efficient nonfullerene organic solar cells with improved intermolecular interaction and open-circuit voltage," *Adv. Mater.*, Vol. 29, No. 21, p. 1700254, 2017.
 23. Fan, Q., Wang, Y., Zhang, M., Wu, B., Guo, X., Jiang, Y., Li, W., Guo, B., Ye, C., Su, W., Fang, J., Ou, X., Liu, F., Wei, Z., Sum, T. C., Russell, T. P., Li, Y., "High-performance as-cast non-fullerene polymer solar cells with thicker active layer and large area exceeding 11% power conversion efficiency," *Adv. Mater.*, Vol. 30, No. 6, p. 1704546, 2018.
 24. Park, G. E., Choi, S., Park, S. Y., Lee, D. H., Cho, M. J., Choi, D. H., "Eco-friendly solvent-free fullerene-free polymer solar cells with over 9.7% efficiency and long-term performance stability," *Adv. Energy Mater.*, Vol. 7, No. 19, p. 1700566, 2017.
 25. Lee, S., Kim, H., Kim, Y., "Influence of physical load on the stability of organic solar cells with polymer:fullerene bulk heterojunction nanolayers," *Curr. Photovoltaic Res.*, Vol. 4, No. 2, pp. 48-53, 2016.
 26. Xie, C., Heumüller, T., Gruber, W., Tang, X., Classen, A., Schuldes, I., Bidwell, M., Späth, A., Fink, R. H., Unruh, T., McCulloch, I., Li, N., Brabec, C. J., "Overcoming efficiency and stability limits in water-processing nanoparticulate organic photovoltaics by minimizing micro-structure defects," *Nat. Commun.*, Vol. 9, p. 5335, 2018.
 27. Doumin, N. Y., Dryzhov, M. V., Houard, F. V., Corre, V. M. L., Chatri, A. R., Christodoulis, P., Koster, L. J. A., "Photostability of fullerene and non-fullerene polymer solar cells: the role of the acceptor," *ACS Appl. Mater. Interfaces*, Vol. 11, No. 8, pp. 8310-8318, 2019.
 28. Musavi, S. H., Jilavi, M. H., May, A., Schmitt, K. P., Schäfer, B., de Oliveira, P. W., "A novel wet coating method using small amounts of solution on large flat substrates," *Appl. Surf. Sci.*, Vol. 419, pp. 753-757, 2017.
 29. Zhao, K., Hu, H., Spada, E., Jagadamma, L. K., Yan, B., Abdelsamie, M., Yang, Y., Yu, L., Munir, R., Li, R., Ndjawa, G. O. N., Amassian, A., "Highly efficient polymer solar cells with printed photoactive layer: rational process transfer from spin-coating," *J. Mater. Chem. A*, Vol. 4, pp. 16036-16046, 2016.
 30. Chen, J., Zhang, L., Jiang, X., Gao, K., Liu, F., Gong, X., Chen, J., Cao, Y., "Using *o*-chlorobenzaldehyde as a fast removable solvent additive during spin-coating PTB7-based active layers: high efficiency thick-film polymer solar cells," *Adv. Energy Mater.*, Vol. 7, No. 3, p. 1601344, 2017.
 31. Nielsen, L. D., "Distributed series resistance effects in solar cells," *IEEE Trans. Electron Devices*, Vol. 29, No. 5, pp. 821-827, 1982.