

Previews

The rise of polythiophene photovoltaics

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Compared with prevailing photovoltaic polymers with complex structures and tedious synthesis, polythiophenes possess a greater commercial promise. However, their photovoltaic performances are rather poor due to mismatched energy levels and unfavorable mixing with state-of-the-art non-fullerene acceptors. In a recent *Joule* article, Duan and colleagues developed a new series of polythiophene-based donors (P5TCN-Fx) via just four steps and achieved a record-high efficiency that surpasses 17%. Furthermore, both polymer solubility and molecular miscibility were found to play crucial roles in achieving this unprecedented performance. The future perspectives are discussed.

Benefitting from the innovation of non-fullerene acceptors and the development of novel polymer donors, the power conversion efficiency (PCE) of organic photovoltaic (OPV) cells continues to realize new heights, rapidly approaching the requirements for commercial application. However, the synthetic complexity and poor scalability of high-efficiency photovoltaic polymers with the donor-acceptor alternating structure result in considerably high production costs, which put great constraints on the commercial development of OPVs. In this context, high-performance but low-cost materials are urgently needed. Due to the simple chemical structures and facile synthetic routes, polythiophenes are considered the most promising polymer donor candidates for large-scale industrial production.

In the past 5 years, the development of non-fullerene acceptors has revolutionized OPVs based on polythiophenes such as poly(3-hexylthiophene) (P3HT) and ester-substituted polythiophenes. For instance, the combined use of two indacenodithiophene-benzothiadiazole-rhodanine-based non-fullerene acceptors pioneered by the McCulloch group¹ afforded a respectable PCE of 7.7%, which set a milestone for P3HT cells.

The continued developments of various electron acceptors resulted in steady progress in device efficiency; also noteworthy is that the employment of a Y-series acceptor (i.e., ZY-4Cl²) have broken the 10% efficiency benchmark for P3HT-based OPVs. Limited by the intrinsically high-lying highest occupied molecular orbital (HOMO) level and complicated phase behavior, P3HT still lags far behind those of predominantly used donor-acceptor alternating conjugated polymers, in terms of device efficiency. Though over 12% efficiency can be realized in ester-substituted polythiophenes with downshifted HOMO levels, the excessively high miscibility between these polythiophenes and Y-series acceptors significantly limits the efficiency improvement.³ Therefore, designing new polythiophenes to match well with the current high-performance Y-series acceptors is a grand challenge in the OPV field.

To address the miscibility limitations, structural optimizations of polythiophenes have come to the fore (see Figure 1). In 2021, Yip and Duan et al. achieved a high PCE of ~13.6%⁴ by blending a Y-series acceptor (Y6-BO) with a fluorinated polythiophene (P4T2F-HD).⁵ Compared with P3HT, P4T2F-HD can not only downshift the energy levels

significantly but also improve the crystallinity. A desired nanoscale phase-separated morphology was formed due to the moderate miscibility. However, P4T2F-HD still suffers from a relatively high-lying HOMO level, which resulted in a low open-circuit voltage (V_{OC}) of 0.72 V and restricted the PCE. Shortly afterward, Duan et al.⁶ pointed out that the cyano-substituted version of P4T2F-HD (i.e., P5TCN-2F) exhibits a much deeper-lying HOMO level than that of P4T2F-HD, which can contribute to a higher V_{OC} and lower energy loss. Accordingly, P5TCN-2F performs efficiently when blended with four different Y-series acceptors, and the device based on P5TCN-2F:Y6 yielded a remarkable PCE of 16.1% in binary OPVs.

In recent work published in *Joule*, Duan and co-workers⁷ have designed and synthesized a set of new polythiophenes (P5TCN-Fx) by incorporating cyano-group substitution and varying the content of backbone fluorination to delicately control the polymer crystallinity and molecular miscibility with Y6. As a result, multiple new polythiophenes realized over 16% efficiencies in binary devices. Furthermore, the ternary blend comprising P5TCN-F25, Y6, and fullerene gave rise to a much higher efficiency of 17.2%, which sets a new efficiency record and milestone for polythiophene-based OPVs. Furthermore, this group demonstrated that the film morphology and performance of P5TCN-Fx:Y6 blends vary heavily with the extent of fluorination. Compared with the non-fluorinated polymer P5TCN-F0, P5TCN-F25 shows much

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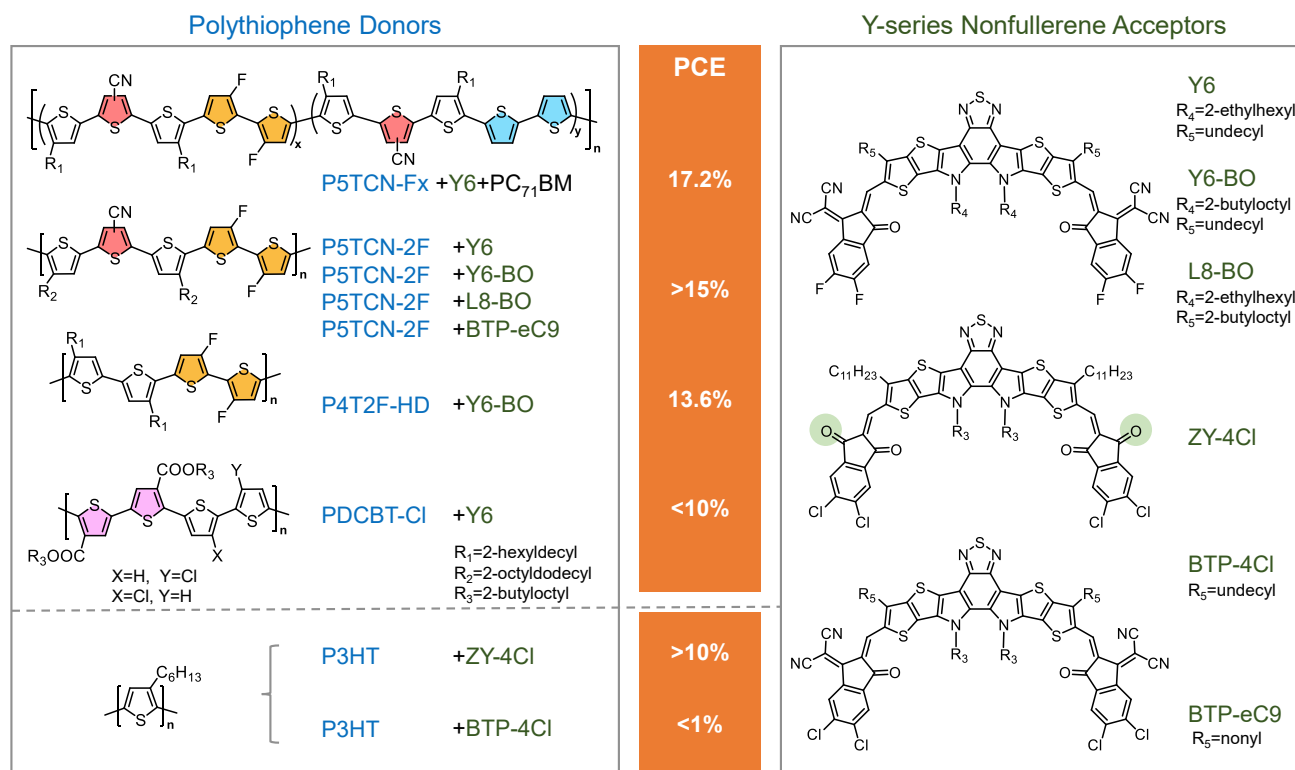


Figure 1. The recent development of highly efficient OPVs based on polythiophene and Y-series acceptor blends

better mixing with Y6 in blend films. To reveal the performance and morphology difference, the solubilities of P5TCN-Fx and Flory-Huggins interaction parameters (χ_{aa}) between P5TCN-Fx and Y6 were thoroughly determined. As χ_{aa} gets higher with increasing fluorination degree, P5TCN-Fx with higher fluorination degree exhibits decreased miscibility with Y6. However, the surface and bulk morphology data showed that the P5TCN-F0:Y6 blend exhibits the largest surface roughness and excessive phase separation. Together, the largest phase separation and low χ_{aa} of P5TCN-F0:Y6 blend imply that the phase evolution of this blend is not simply governed by thermodynamics but by film casting kinetics. The hypersolubility of P5TCN-F0 in chloroform results in liquid-liquid phase separation during the spin-coating process of the blend solution. By comparison, strong phase separation can be avoided due to the considerably decreased polymer solubility of other P5TCN-Fx polymers. In particular, the blends based on

P5TCN-F25 exhibited the most optimal morphology with a properly well-dispersed fibrillar structure and bi-continuous interpenetrating networks, which gave the best performance.

This achievement of polythiophene-based OPVs with efficiencies over 17% can be ascribed to the following three points. First, the incorporation of the simple building block 3-cyanothiophene⁸ with strong electron-withdrawing effect and fluorination can downshift the energy levels significantly, which gives a higher V_{OC} . Second, the non-covalent interactions induced by a small extent of fluorination result in stronger aggregation of polythiophene in solution, which improves the stacking order and crystallinity. Thus, the high molecular order of P5TCN-F25 endows high hole mobility up to $\sim 4 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is beneficial to realize high short-circuit current density (J_{SC}) and fill factor. Third and most importantly, delicate control of the fluorination degree can finely tune the molecular

interaction and polymer solubility, thereby affording appropriate miscibility with Y6 and offering a proper phase separation. Such a favorable morphology correlates well with the high J_{SC} and fill factor. Based upon the study, they further highlighted that the concurrent control of polymer solubility and molecular miscibility is the key to achieving such unprecedented performance in both binary and ternary solar cells. Importantly, the record-high efficiency reported by Duan et al. shows for the first time that polythiophenes with much simpler structures are on par with the prevailing donor polymers in device performance. This study presents a stimulating insight into the design and optimization of cost-effective polymer donors and their implications in non-fullerene solar cells.

Though the best efficiency has surpassed 17%, some issues still need to be addressed for advancing polythiophene-based OPVs (Figure 2). Polythiophenes are often semi-crystalline, and

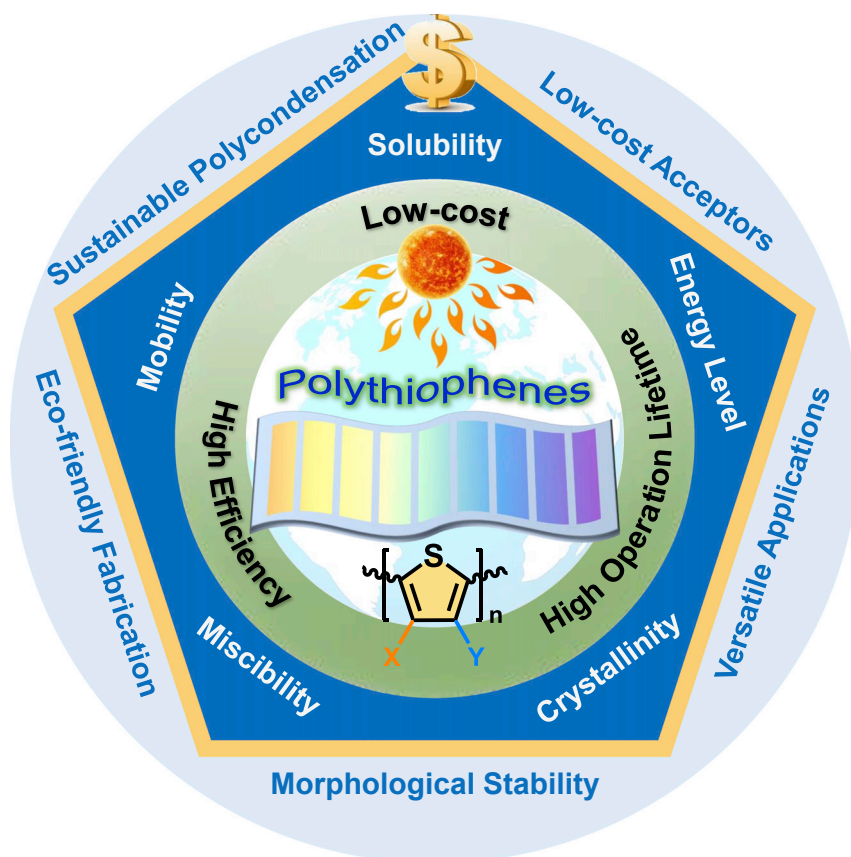


Figure 2. The commercialization requirements of polythiophene-based OPVs.

The core affecting factors and optimization requirements are outlined to advance these OPVs.

their crystallization and phase behaviors can be easily modulated through processing conditions. From the device manufacturing viewpoint, the control of microstructures should be explored to further improve the efficiencies of polythiophenes to reach or even surpass those of prevailing donor-acceptor alternating polymers when blended with many other acceptors. As the molecular weights of polythiophenes⁹ strongly affect their aggregation behaviors in solution and crystallinity in film, their molecular weight dependences need to be elucidated. For stretchable electronics, it is necessary to employ scalable and reproducible polythiophene batches with molecular weights that are above the entanglement molecular weight.

It is still imperative to further reduce the production cost and batch-to-batch

variation of present low-cost materials through improved chemical synthesis routes and polymerization methods. Presently, the nearly defect-free sustainable synthesis of polythiophenes is still a grand challenge for materials chemists. As an environmentally benign method, direct (hetero)arylation polymerization¹⁰ has been successfully applied to synthesize a series of simple polythiophenes¹¹ via cost-effective raw materials and eco-friendly solvents; this method might aid in preparing low-defect and regioregular polythiophenes, exhibiting comparable characteristics with their counterparts derived from classical cross-coupling methods. Additionally, the Y-series non-fullerene acceptors used in these top-performance polythiophene OPVs are much more expensive than polythiophenes. Thus, developing non-fullerene acceptors with a simpler structure and lower

cost compared with the present Y-series acceptors is eagerly needed.

As the thin-film morphology directly affects the operation lifetime of solar cells, future research needs to focus more on stabilizing the morphology of high-performance polythiophene:non-fullerene blend films under elevated temperatures¹² from the viewpoint of polymer physics and continuous exposure to light. Given the low cost of polythiophene materials, the potential of these systems in a variety of light-harvesting applications, such as powering simple devices that are part of the growing “internet of things” is worthy of evaluation. To speed up the commercialization of OPV technology, the field should pay more attention to simultaneously realizing high efficiency and excellent stability, as well as low cost in one material system featuring both cost-effective polythiophenes and easily accessible non-fullerene acceptors.

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DECLARATION OF INTERESTS

The authors declare no competing interests.

1. Baran, D., Ashraf, R.S., Hanifi, D.A., Abdelsamie, M., Gasparini, N., Rohr, J.A., Holliday, S., Wadsworth, A., Lockett, S., Neophytou, M., et al. (2017). Reducing the efficiency-stability-cost gap of organic photovoltaics with highly efficient and stable small molecule acceptor ternary solar cells. *Nat. Mater.* 16, 363–369.
2. Yang, C., Zhang, S., Ren, J., Gao, M., Bi, P., Ye, L., and Hou, J. (2020). Molecular design of a non-fullerene acceptor enables a P3HT-based organic solar cell with 9.46% efficiency. *Energy Environ. Sci.* 13, 2864–2869. <https://doi.org/10.1039/d0ee01763a>.
3. Liang, Z., Li, M., Wang, Q., Qin, Y., Stuard, S.J., Peng, Z., Deng, Y., Ade, H., Ye, L., and Geng, Y. (2020). Optimization requirements of efficient polythiophene:nonfullerene

- organic solar cells. *Joule* 4, 1278–1295. <https://doi.org/10.1016/j.joule.2020.04.014>.
4. Xiao, J., Jia, X., Duan, C., Huang, F., Yip, H.L., and Cao, Y. (2021). Surpassing 13% efficiency for polythiophene organic solar cells processed from nonhalogenated solvent. *Adv. Mater.* 33, 2008158. <https://doi.org/10.1002/adma.202008158>.
 5. Jia, X.e., Chen, Z., Duan, C., Wang, Z., Yin, Q., Huang, F., and Cao, Y. (2019). Polythiophene derivatives compatible with both fullerene and non-fullerene acceptors for polymer solar cells. *J. Mater. Chem. C* 7, 314–323. <https://doi.org/10.1039/c8tc04746d>.
 6. Yuan, X., Zhao, Y., Zhang, Y., Xie, D., Deng, W., Li, J., Wu, H., Duan, C., Huang, F., and Cao, Y. (2022). Achieving 16% efficiency for polythiophene organic solar cells with a cyano-substituted polythiophene. *Adv. Funct. Mater.* 32, 2201142. <https://doi.org/10.1002/adfm.202201142>.
 7. Yuan, X., Zhao, Y., Xie, D., Pan, L., Liu, X., Duan, C., Huang, F., and Cao, Y. (2022). Polythiophenes for organic solar cells with efficiency surpassing 17%. *Joule* 6, 647–661. <https://doi.org/10.1016/j.joule.2022.02.006>.
 8. Yuan, X., Zhao, Y., Zhan, T., Oh, J., Zhou, J., Li, J., Wang, X., Wang, Z., Pang, S., Cai, P., et al. (2021). A donor polymer based on 3-cyanothiophene with Superior Batch-to-batch Reproducibility for high-efficiency organic solar cells. *Energy Environ. Sci.* 14, 5530–5540. <https://doi.org/10.1039/d1ee01957k>.
 9. Wadsworth, A., Hamid, Z., Bidwell, M., Ashraf, R.S., Khan, J.I., Anjum, D.H., Cendra, C., Yan, J., Rezasoltani, E., Guilbert, A.A.Y., et al. (2018). Progress in poly (3-hexylthiophene) organic solar cells and the influence of its molecular weight on device performance. *Adv. Energy Mater.* 8, 1801001. <https://doi.org/10.1002/aenm.201801001>.
 10. Liu, Y., Xian, K., Peng, Z., Gao, M., Shi, Y., Deng, Y., Geng, Y., and Ye, L. (2021). Tuning the molar mass of P3HT via direct arylation polycondensation yields optimal interaction and high efficiency in nonfullerene organic solar cells. *J. Mater. Chem. A* 9, 19874–19885. <https://doi.org/10.1039/d1ta02253a>.
 11. Liu, Y., Xian, K., Gui, R., Zhou, K., Liu, J., Gao, M., et al. (2022). Simple Polythiophene Solar Cells Approaching 10% Efficiency via Carbon Chain Length Modulation of Poly(3-alkylthiophene). *Macromolecules* 55, 133–145.
 12. Gao, M., Liu, Y., Xian, K., Peng, Z., Zhou, K., Liu, J., Li, S., Xie, F., Zhao, W., Zhang, J., et al. Thermally stable poly(3-hexylthiophene): Nonfullerene solar cells with efficiency breaking 10%. Aggregate. Published online March 8, 2022. 10.1002/agt2.190.

Extraterrestrial artificial photosynthesis

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In this issue of *Joule*, Zou et al. studied the lunar soil sample brought back by Chang'E mission 5 for artificial photosynthesis in different approaches, which opens up new possibilities for *in situ* resource utilization on the moon.

In the movie “The Martian,” astronaut Mark Watney grew potatoes on Mars for food supply based on photosynthesis.¹ Though this is a science fiction movie, it motivates people to think about space exploration and extraterrestrial life. With the development of aerospace technology, space travel and interstellar exploration is not a dream anymore. Fulfilling the energy, food, and oxygen demand is a priority for space exploration and poses challenges for science and technology. On Earth, natural photosynthesis provides the solution. Mimicking natural photosynthesis, artificial photosynthesis can convert sunlight into chemical energy and produce oxygen with water, carbon dioxide, or wastes, which provides a promising solution for space exploration.

Indeed, this has been one of the research themes of many space exploration programs. In 2005, the National Aeronautics and Space Administration (NASA) of the USA proposed the Resource Prospector mission, which planned to use the water in lunar soil to *in situ* produce oxygen.² In 2018, NASA launched the carbon dioxide (CO₂) conversion challenge to develop novel synthesis technologies that use CO₂ as the sole carbon source to generate molecules that can be used to manufacture a variety of products.³ The current International Space Station (ISS) was installed with life support systems to provide oxygen, absorb carbon dioxide, and manage vaporous emissions from the astronauts themselves, of which the oxygen is generated

through water electrolysis.⁴ The China Academy of Space Technology also has research program to study artificial photosynthesis for recycling extraterrestrial resources and constructing life support systems to realize survival in extraterrestrial environment.^{5,6}

In 2004, China started the Lunar Exploration Program, also known as the Chang'E Project after the Chinese moon goddess Chang'E, including the orbiter, soft landers/rovers, and sample return spacecraft missions.⁷ The Chang'E Mission 5 in 2020 brought back some precious lunar soil samples, some of which were distributed for scientific research.⁸ In this work, Zou and co-workers studied the lunar soil sample brought back by Chang'E mission 5 for artificial photosynthesis in different approaches, i.e.

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