

# 유기태양전지의 전자 받개 물질들

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## Electron Acceptors in Organic Solar Cells

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### 초 록

최근 유기태양전지의 효율이 18%를 넘어섰다. 이러한 급속한 효율의 증가는 전자 주개 고분자와 짝을 이루는 전자 받개 물질의 개발과 깊은 연관성을 가지고 있다. 이 미니 리뷰에서는 전자 받개 물질의 개발 과정을 통해 유기태양전지의 발전 양상을 살펴본다. 본 리뷰의 첫 번째 파트에서는 유기태양전지 발전의 전반부를 이끌었던 풀러렌 기반 전자 받개 물질에 대해 살펴본다. 그리고 두 번째 파트에서는 풀러렌 기반 전자 받개 물질의 단점들을 극복할 잠재력을 가지고 있으며, 유기태양전지에 새로운 전기를 가져다 준 비(非)풀러렌 기반 전자 받개 물질에 대해서 소개한다. 마지막 파트에서는 리뷰의 전체적인 요약과 더불어 20% 효율을 넘어설 전략에 대해 간단히 논의하며 본 리뷰를 마무리한다.

### Abstract

The power conversion efficiency of organic solar cells has reached over 18%. The rapid increase in the efficiency is largely associated with the development of electron acceptors paired with proper electron donor polymers. In this mini review, the progress of organic solar cells is reviewed in terms of the development of electron acceptors. In the first part of the review, fullerene-based electron acceptors that have led the first half of organic solar cell development were dealt with. In the second part of it, nonfullerene-based electron acceptors, which have potentials to overcome the demerits of fullerene-based electron acceptors and opened a new era of organic solar cells, were introduced. Lastly, some suggestions to tackle the efficiency barrier of 20% are given with the summary of the review in the closing section.

**Keywords:** Organic solar cells, Electron acceptor, Fullerene, Nonfullerene

## 1. Introduction

Organic solar cells are photovoltaic devices based on organic photoactive semiconductors such as conjugated small molecules and/or conjugated polymers that convert incident light to electricity. Since the first report of photoconductivity of anthracene by Pochettino in 1906 [1,2], there have been great progress in device structure and materials (Figure 1). The 1<sup>st</sup> generation organic solar cells had a single layer of

an organic photoactive material sandwiched by two metal electrodes, where very low power conversion efficiencies (PCEs) of ~0.1% or lower than that were obtained[2,3]. Since organic semiconductors generate excitons (bound electron-hole pairs) rather than free charge carriers when photoexcited, some driving force or energy greater than exciton binding energy (a few hundreds meV) is needed to split up excitons into free electrons and holes[4].

In 1986, Tang[5], for the first time, introduced an exciton splitting layer in a heterojunction structure (2<sup>nd</sup> generation) comprising two layers of organic semiconductors, where excitons generated in a layer split into free electrons and holes at the interface of two organic layers, donating electrons to the other organic layer which acts as electron acceptor. Based on the heterostructure, Tang achieved 10 times higher PCE (~1%) than that from a single layer of an organic semiconductor

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2021: Li reported the world record efficiency of 18.32% in nonfullerene-based organic solar cells.
2016: Zhao hurdled the 11% efficiency barrier in nonfullerene-based organic solar cells using the combination of PBDB-T and ITIC.
2015: Lin synthesized nonfullerene-based electron acceptor, ITIC, demonstrating nonfullerene-based organic solar cells with high efficiency of 7%.
2015: Zhang hurdled the 10% efficiency barrier in organic solar cells.
1995: Yu fabricated the first polymer:PCBM bulk heterojunction solar cell.
1995: Hummelen synthesized C60 fullerene derivative, PCBM.
1993: Sarificiftci reported the first polymer/C60 fullerene heterojunction solar cell.
1991: Hiramoto announced the first bulk heterojunction (BHJ) organic solar cell.
1986: Tang reported a two-layer organic photovoltaic cell which is the first heterojunction solar cell.
1964: Delacote observed a rectification from a device comprising copper phthalocyanine (CuPC) sandwiched by gold electrodes.
1906: Pochettino reported the first photoconductivity study of anthracene.

Figure 1. Progress of organic solar cells from the first study of photoconductivity of an organic pigment to the current state of the art[2].

[5]. The Tang's report influenced every aspect of organic solar cell research with the emphasis on a necessity of electron acceptor as well as a rethink of device structure. In 1991, Hiramoto announced the first bulk heterojunction (BHJ) organic solar cells (3<sup>rd</sup> generation) by co-depositing two organic pigments[6]. In the BHJ, electron donating and accepting organic semiconductors are mixed and interpenetrating each other. Since exciton diffusion length is as short as ~10 nm[7-9], the interpenetrating network in the BHJ structure help compensate for the short diffusion length. Despite having an efficient structure for charge transfer, exciton splitting efficiency was still low. Around the same time, Sarificiftci *et al.* found that C60 fullerene (buckminsterfullerene) facilitates efficient exciton splitting, demonstrating a large photo-response as a result of photoinduced electron transfer across the heterojunction interface from the semiconducting polymer to C60 fullerene [10].

After the first report of the C60 fullerene utilization in organic solar cells, in 1995, Hummelen *et al.* synthesized C60 fullerene derivative, [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM)[11], which can be dissolved in common organic solvents such as toluene, chlorobenzene, dichlorobenzene and chloroform. In the same year, Yu *et al.* fabricated organic solar cells based on BHJs comprising a semiconducting polymer and PCBM, achieving a surprisingly high PCE of 2.9%[12]. Over the past 20 years since 1995, PCBM and other fullerene derivatives have led the development of organic solar cells, and finally a psychological barrier of PCE of 10% was overcome in 2015[13].

After breaking the 10% barrier, there was another long stagnant period prolonged until small molecules that are not based on fullerenes were rediscovered and used as electron acceptors in 2017. The small molecule electron acceptors have a push-pull molecular structure where electron accepting moieties are connected to electron donating moieties in a backbone of a molecule[14]. Since these electron acceptors have no fullerene moieties, they are called nonfullerene acceptor. With the nonfullerene acceptors, PCEs of organic solar cells have dramatically increased and finally reached up to ~18% in 2021[15], which is only ~2% left to overcome another barrier for commercialization.

In this mini review, two categories of electron acceptors, fullerene-based and nonfullerene-based electron acceptors, will be dealt with in terms of organic solar cell developments; for example, what electron acceptors led the developments of organic solar cells and how they did it. At the end of the review, we also suggest the strategy to overcome another hurdle of 20% based on the analysis from the review.

## 2. Fullerene-based electron acceptors

C60 fullerene has ball-like structure where constituent carbon atoms are in the conjugated system (Figure 2)[16]. This conjugated framework promotes delocalization of electrons, and induces strong electron affinity and unipolar electron transport[17]. Despite these advantages, C60 fullerene has been limitedly used in a narrow research area of or-

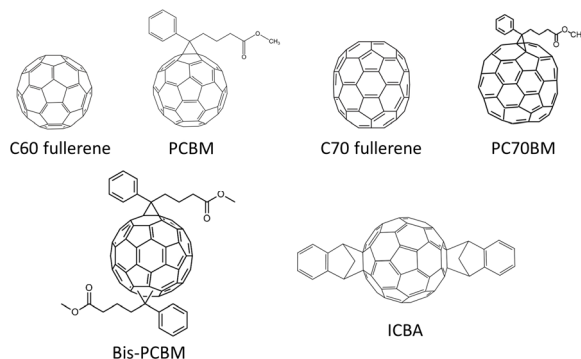


Figure 2. C60 fullerene, C70 fullerene, and their derivatives with different functional groups.

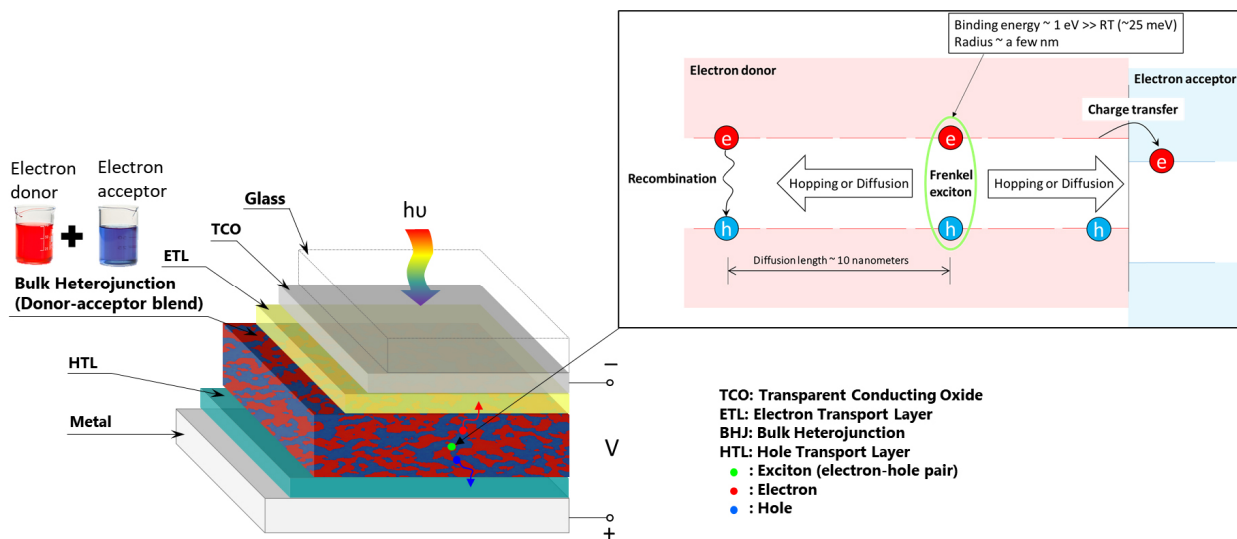


Figure 3. A schematic illustration of exciton generation and separation at the interface of donor and acceptor in the bulk heterojunction of organic solar cells under illumination.

organic solar cells since non-soluble C60 fullerene was only deposited using physical vapor deposition (PVD). Therefore, only way to have a BHJ structure with C60 fullerene is to co-evaporate electron donating small molecules using PVDs. This limited applications and developments of electron donor materials; there were many conjugated polymers considered promising candidates as electron donors in organic solar cells, but the polymers with high molecular weights were not be able to be co-evaporated via PVDs.

Explosion of BHJ studies was initiated by the functionalization of C60 fullerenes, which allows for solution processing. One of the representative functionalized C60 fullerene derivatives is phenyl-C61-butyric acid methyl ester (PCBM)[11]. PCBM can be synthesized by mixing C60 fullerene with the side chain moiety containing a diazomethane group, e.g., 1-phenyl-1-(3-(methoxycarbonyl)propyl)diazomethane since the addition of unsymmetrically substituted diazoalkanes is the only way to produce a fulleroid and carbene additions produce only methanofullerenes[18-20]. Having side chains or functional groups enables the electron accepting C60 fullerene to dissolve in organic solvents together with electron donating polymer counterpart, allowing for solution processing and constructing BHJ structures using solution proc-

essing techniques. Since organic molecules that have a dimension of 0-D (e.g., C60 fullerene and its derivatives) or 1-D (e.g., polymers or oligomers) generate excitons rather than polarons or free charge carriers when photoexcited, and the exciton lifetime is as short as a-few-hundred picoseconds[21], BHJ structure has benefits to compensate for short exciton lifetime and diffusion length (Figure 3). Well-mixed phase in the BHJ structure might promise to compensate for the shortcomings in the lifetime and diffusion length, but the BHJ structure should also have to satisfy the requirement for efficient charge transport through the component molecules that convey respective charge carriers to each electrode[22]. Thus, BHJ structures should have a proper thickness of each domain normally in the range of a few tens of nanometers to fulfill the both requirements of charge transfer and transport[22]. The most standard BHJs are the composites consisting of conjugated polymers as electron donors and PCBM as electron acceptors. With these polymer-PCBM composites, critical techniques to control the phase separation and thickness have been established, such as thermal annealing, solvent annealing, and solvent additives[23-25]. These techniques, in principle, control the phase separation and interpenetrating network, which eventually promote better

charge transfer/transport.

Along with the inventions of phase-control techniques, on the other side, chemists synthesized new fullerene derivatives based on C60 fullerene. Bis(1-[3-(methoxycarbonyl)propyl]-1-phenyl)-[6,6]C62 (bis-PCBM) [26], which has two functional groups on both sides of C60 buckyball is the by-product occurring during preparation of PCBM. Lenes *et al.* separated the bis-PCBM fraction from the product mixture using standard column chromatography (silicagel, eluent:chloroform/toluene 1:1). The fraction was collected after removal of the monoadduct fraction, i.e., PCBM, and collection of the bisadduct mixture was continued until liquid chromatography mass spectrometry (LC-MS) analysis showed the appearance of the trisadducts. The bis-PCBM has a substantially high-lying lowest unoccupied molecular orbital (LUMO) level ( $\sim 3.7$  eV) compared to the LUMO level ( $\sim 3.8$  eV) of PCBM. The high-lying LUMO level correspondingly raises the open-circuit voltage ( $V_{OC}$ ) of organic solar cells by approximately 100 meV, so that the resulting PCE was enhanced by more than 10%. This research triggered a new way of modification of C60 fullerenes with the adoption of different functional groups such as indene[27]. He *et al.* employed indene groups into C60 fullerenes, synthesizing a new fullerene derivative, indene-C60 bisadduct (ICBA)[27]. The ICBA has an even higher LUMO level of  $\sim 3.9$  eV than that of bis-PCBM. ICBA-based organic solar cells exhibited higher  $V_{OC}$  of  $\sim 0.84$  V, leading to almost 40% enhancement in PCE[27]. Device optimizations using solvent and thermal annealing techniques resulted in 6.5% in PCE[28].

There is another ball-shape fullerene which is C70 fullerene[29]. C70 fullerene looks like a bit compressed shape of C60 since with 70 carbons a perfect sphere cannot be made. Like PCBM, C70 fullerene can be functionalized by mixing C70 fullerene with a side chain moiety containing a diazomethane group, e.g., 1-phenyl-1-(3-(methoxycarbonyl)propyl)diazomethane, and the reaction produces methano[70]fullerene (PC70BM)[30]. Lower symmetry of C70 relaxes forbiddenness of absorption, strengthening light absorption of PC70BM in the visible region (400–650 nm)[31], which in turn improves external quantum efficiency (EQE) of the corresponding absorption range of wavelength and enhances short-circuit current ( $J_{SC}$ ) of the PC70BM-based organic solar cells.[30]. Since the absorption coefficient of PC70BM in the visible range is greater than that of PCBM (for example, at 500 nm, more than 3 times higher), photocurrent gains in the visible range are significant. With PC70BM, the first 10% in PCE has been achieved with the combination of a narrow bandgap polymer donor (main absorption peak at 750 nm), benzo[1,2-b:4,5-b']dithiophene (BDT)-based polymer (PBDT-TS1)[13, 32, 33].

To date, PCBM, PC70BM, and other fullerene derivatives have been widely used in organic solar cells and they are considered the most reliable electron acceptors especially when it comes to performance testing of new donor polymers. Despite the superior reliability, the fullerene derivatives have some critical shortcomings. Most fullerene derivatives have very weak absorption in visible range of solar spectrum[29]. Although PC70BM absorbs light in the visible range from 400 to 650 nm, absorption coefficient in the range is quite low,  $\sim 10^4$  cm<sup>-1</sup> at best[29, 31], which is less than 1/2 of that of donor counterpart.

Moreover, charge transfer exciton binding energies between donor polymers and fullerene derivatives are as high as  $\sim 0.8$  eV[34], which leads to loss in  $V_{OC}$  in fullerene-based organic solar cells[35]. Therefore, electron acceptors that overcome these issues have been sought.

### 3. Nonfullerene-based electron acceptors

Nonfullerene-based electron acceptors are usually referred to as small molecules that have no fullerene moieties in their molecular structures[14]. More specifically, small molecules called nonfullerene-based electron acceptors in organic solar cells have structures enabling intramolecular charge transfer[36]. For intramolecular charge transfer, there should be moieties giving electrons as well as taking the charge carriers in a molecular structure. This alternating sequence in a molecule induces charge transfer states that account for strong oscillator strengths in visible range[14,36]. Letting alone the superior light absorption of nonfullerene acceptors in visible range, nonfullerene acceptors have lower charge transfer energy loss of 0.1–0.2 eV, which leads to better charge transfer/transport and higher  $V_{OC}$ . Since excitons in organic semiconductors are tightly bound electron-hole pairs with quite large binding energies of 0.2–1.5 eV[4,37–39], a large driving force is required to separate the bound pairs. This driving force is normally given by the offset of the LUMO level of electron donors and HOMO level of electron acceptors in BHJ[40,41]. The dissociation process occurring at the interface of donor and acceptor molecules incurs an energy loss during charge transfer (CT)[35]. Ball-shape symmetric fullerene derivatives tend to more closely packed each other and have large energy loss during charge transfer as large as  $\sim 0.6$  eV[35]. In contrast, the large conjugated volumes of push-pull nonfullerene acceptors decrease their exciton binding energy and intra- and intermolecular electron-phonon couplings, reducing CT state energy loss of only 0.22–0.35 eV[35]. Thus, the nonfullerene-based electron acceptors have promising potentials to achieve high photocurrent and photovoltage as well as enhanced fill factor from higher absorption coefficient in visible range and lower CT state energy loss.

The best seller in nonfullerene-based electron acceptors is 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d':3'-d'']-s-indaceno[1,2-b:5,6-b']dithiophene (ITIC) (Figure 4)[42]. This molecule is based on a bulky seven-ring fused core (indacenodithieno[3,2-b]thiophene, IT), end-capped with 2-(3-oxo-2,3-dihydroinden-1-ylidene)malononitrile (INCN) groups, and with four 4-hexylphenyl groups substituted on it. The push-pull molecule can be constructed by modular synthesis with two major elements: aromatic core in the center (donor unit, IT) and end-capping groups at both ends (acceptor unit, INCN). The push-pull structure in ITIC can induce intramolecular charge transfer, extending absorption up to 800 nm, where main peak is found at 700 nm with the absorption coefficient of  $\sim 10^5$  cm<sup>-1</sup>[42], which is greater than that of fullerene derivatives. Furthermore, the four rigid 4-hexylphenyl substituents out of the IT main plane regulate solubility in organic solvents and can restrict too much molecular stacking, aggregation, and large phase separation in BHJ blend films. This nonfullerene molecule, ITIC, was synthesized in

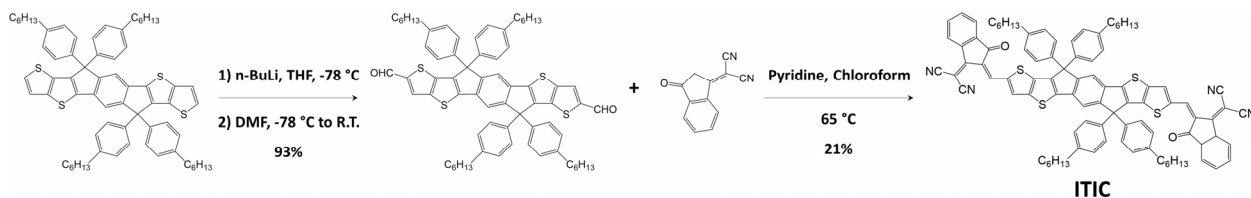


Figure 4. Synthetic route to nonfullerene electron acceptor, ITIC and its chemical structure.

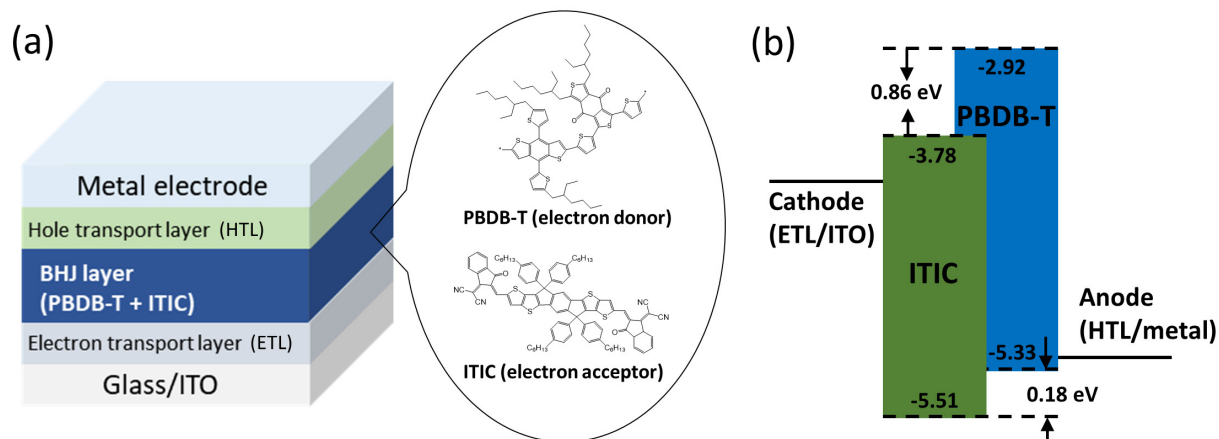


Figure 5. (a) Device architecture and chemical structures of electron donor (PBDB-T) and electron acceptor (ITIC). (b) Energy band diagrams of a device based on PBDB-T:ITIC.

2015, but didn't draw attention because the device performance (~7%) was way below that from fullerene-based solar cells (~10%) at the time.

1 year later after the Lin's report, Zhao *et al.* demonstrated nonfullerene-based organic solar cells with over 11% in PCE by combining ITIC and a conjugated donor polymer which was already reported in 2012, 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) (Figure 5)[43,44]. They focused on interactions of donor polymers and acceptor small molecules and their molecular orientations which are determining factors for charge transfer and transport. Compared with the isotropic ball-like conjugated systems in fullerene derivatives, nonfullerene-based acceptors have anisotropic conjugated structures which make  $\pi-\pi$  interactions between donor and acceptor molecules in BHJ harder. Therefore, pairing with the right donor polymers that fit push-pull molecular moieties of the nonfullerene acceptors is critically important, which results in optimal molecular interfacing as well as fine-tuned phase separation. PBDB-T that has a push-pull framework and a very rigid backbone in the polymer chain may help ITIC interface the donor polymer backbone, which finally went beyond fullerene-based organic solar cells. After Zhao's report, various push-pull-type donors and acceptors were synthesized[14,36,45-47], and finally in 2021, the world record efficiency of 18.32% with unprecedentedly high fill factor of 81.5% was achieved using poly[(2,6-(4,8-bis(5-(2-ethylhexyl)-3-fluoro)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-F, or simply abbreviated to PM6) and nonfullerene acceptor,

L8-BO which is based on 2,2'-((2Z,2'Z)-((12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (simply abbreviated to Y6) with 2-butyloctyl substitution[15].

#### 4. Conclusion and outlook

Organic solar cells have been developed in line with the development of materials which were newly synthesized and/or rediscovered for some required purposes. In this mini review, we emphasized the importance of electron acceptors in the development of organic solar cells. In the first section, we introduced fullerene derivatives which led the organic solar cell boom in the initial stage of the solar cell technology and their limitations. In the second section, we dealt with how nonfullerene acceptors have been spotlighted, and what aspects of nonfullerene acceptors overcome the shortcomings of the fullerene-based acceptors. Now that promising potentials of nonfullerene acceptors have been discovered, most research are focusing on minimizing energy loss of nonfullerene-based organic solar cells, which might be largely attributed to the interactions between polymer donors and nonfullerene acceptors, and their packings in BHJs. In terms of energy loss, many strategies have been suggested; for example, functionalizing nonfullerene acceptors with halogens or bulky side chains, and introducing a third component in BHJ. The key to reduce the energy loss is to minimize the nonradiative recombination losses which are mostly

determined by the energetic disorder of component materials and the charge transfer efficiency between polymer donors and small molecule acceptors in BHJs[48,49]. A way to reduce the energetic disorder and to enhance the charge transfer is hinted by a recent report by Li *et al.*[15], where they explored alkyl chain chemistry in nonfullerene acceptors, which in turn significantly influences major intermolecular  $\pi$ - $\pi$  stacking. Attaching proper size and/or length of side chains to a right position of nonfullerene acceptor backbone, such as thiophene beta position, would reduce the intermolecular distance and induce strong electronic coupling, which give rise to multiple and long-range charge-hopping pathways, and efficient charge transfer with minimized energy loss during charge transfer. We believe that optimized nonfullerene acceptors paired with well-designed donor polymers may hurdle the efficiency barrier of 20% and more beyond that in the future.

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#### References

1. A. Pochettino, Sul comportamento foto-elettrico dell'antracene, *Acad. Lincei Rend.*, **15**, 355 (1906).
2. H. Spanggaard and F. C. Krebs, A brief history of the development of organic and polymeric photovoltaics, *Sol. Energy Mater. Sol. Cells*, **83**, 125-146 (2004).
3. G. M. Delacote, J. P. Fillard, and F. J. Marco, Electron injection in thin films of copper phthalocyanine, *Solid State Commun.*, **2**, 373-376 (1964).
4. M. Knupfer, Exciton binding energies in organic semiconductors, *Appl. Phys. A-Mater.*, **77**, 623-626 (2003).
5. C. W. Tang, Two-layer organic photovoltaic cell, *Appl. Phys. Lett.*, **48**, 183-185 (1986).
6. M. Hiramoto, H. Fujiwara, and M. Yokoyama, Three-layered organic solar cell with a photoactive interlayer of codeposited pigments, *Appl. Phys. Lett.*, **58**, 1062-1064 (1991).
7. J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, and A. B. Holmes, Efficient photodiodes from interpenetrating polymer networks, *Nature*, **376**, 498-500 (1995).
8. C. Deibel, D. Mack, J. Gorenflot, A. Schöll, S. Krause, F. Reinert, D. Rauh, and V. Dyakonov, Energetics of excited states in the conjugated polymer poly(3-hexylthiophene), *Phys. Rev. B*, **81**, 085202 (2010).
9. O. V. Mikhnenko, H. Azimi, M. Scharber, M. Morana, P. W. M. Blom, and M. A. Loi, Exciton diffusion length in narrow bandgap polymers, *Energ. Environ. Sci.*, **5**, 6960-6965 (2012).
10. N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl, Photo-induced electron transfer from a conducting polymer to buckminsterfullerene, *Science*, **258**, 1474-1476 (1992).
11. J. C. Hummelen, B. W. Knight, F. LePeq, F. Wudl, J. Yao, and C. L. Wilkins, Preparation and characterization of fulleroid and methanofullerene derivatives, *J. Org. Chem.*, **60**, 532-538 (1995).
12. G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, Polymer photovoltaic cells - enhanced efficiencies via a network of internal donor-acceptor heterojunctions, *Science*, **270**, 1789-1791 (1995).
13. S. Zhang, L. Ye, W. Zhao, B. Yang, Q. Wang, and J. Hou, Realizing over 10% efficiency in polymer solar cell by device optimization, *Sci. China Chem.*, **58**, 248-256 (2015).
14. C. Yan, S. Barlow, Z. Wang, H. Yan, A. K.-Y. Jen, S. R. Marder, and X. Zhan, Non-fullerene acceptors for organic solar cells, *Nat. Rev. Mater.*, **3**, 18003 (2018).
15. C. Li, J. Zhou, J. Song, J. Xu, H. Zhang, X. Zhang, J. Guo, L. Zhu, D. Wei, G. Han, J. Min, Y. Zhang, Z. Xie, Y. Yi, H. Yan, F. Gao, F. Liu, and Y. Sun, Non-fullerene acceptors with branched side chains and improved molecular packing to exceed 18% efficiency in organic solar cells, *Nat. Energy*, **6**, 605-613 (2021).
16. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, C60: Buckminsterfullerene, *Nature*, **318**, 162-163 (1985).
17. S. Gélinas, A. Rao, A. Kumar, S. L. Smith, A. W. Chin, J. Clark, T. S. van der Poll, G. C. Bazan, and R. H. Friend, Ultrafast long-range charge separation in organic semiconductor photovoltaic diodes, *Science*, **343**, 512-516 (2014).
18. R. Taylor and D. R. M. Walton, The chemistry of fullerenes, *Nature*, **363**, 685-693 (1993).
19. M. Iyoda and M. Yoshida, Chemistry of fullerenes - the high reactivity and new developments, *J. Syn. Org. Chem. Jpn.*, **53**, 756-769 (1995).
20. A. F. Kieley, R. C. Haddon, M. S. Meier, J. P. Selegue, C. P. Brock, B. O. Patrick, G.-W. Wang, and Y. Chen, The first structurally characterized homofullerene (Fulleroid), *J. Am. Chem. Soc.*, **121**, 7971-7972 (1999).
21. N. C. Greenham, I. D. W. Samuel, G. R. Hayes, R. T. Phillips, Y. A. R. R. Kessener, S. C. Moratti, A. B. Holmes, and R. H. Friend, Measurement of absolute photoluminescence quantum efficiencies in conjugated polymers, *Chem. Phys. Lett.*, **241**, 89-96 (1995).
22. G. J. Hedley, A. J. Ward, A. Alekseev, C. T. Howells, E. R. Martins, L. A. Serrano, G. Cooke, A. Ruseckas, and I. D. W. Samuel, Determining the optimum morphology in high-performance polymer-fullerene organic photovoltaic cells, *Nat. Commun.*, **4**, 2867-2876 (2013).
23. W. L. Ma, C. Y. Yang, X. Gong, K. Lee, and A. J. Heeger, Thermally stable, efficient polymer solar cells with nanoscale control of the interpenetrating network morphology, *Adv. Funct. Mater.*, **15**, 1617-1622 (2005).
24. G. Li, Y. Yao, H. Yang, V. Shrotriya, G. Yang, and Y. Yang, "Solvent annealing" effect in polymer solar cells based on poly(3-hexylthiophene) and methanofullerenes, *Adv. Funct. Mater.*, **17**, 1636-1644 (2007).
25. J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger, and G. C. Bazan, Efficiency enhancement in low-bandgap polymer solar cells by processing with alkane dithiols, *Nat. Mater.*, **6**, 497-500 (2007).
26. M. Lenes, G.-J. A. H. Wetzelaer, F. B. Kooistra, S. C. Veenstra, J. C. Hummelen, and P. W. M. Blom, Fullerene bisadducts for enhanced open-circuit voltages and efficiencies in polymer solar cells, *Adv. Mater.*, **20**, 2116-2119 (2008).
27. Y. J. He, H. Y. Chen, J. H. Hou, and Y. F. Li, Indene-C-60 bisadduct: a new acceptor for high-performance polymer solar cells, *J. Am. Chem. Soc.*, **132**, 1377-1382 (2010).

28. G. J. Zhao, Y. J. He, and Y. F. Li, 6.5% Efficiency of polymer solar cells based on poly(3-hexylthiophene) and indene-c-60 bisadduct by device optimization, *Adv. Mater.*, **22**, 4355-4358 (2010).
29. J. W. Arbogast, C. S. Foote, Photophysical properties of C70, *J. Am. Chem. Soc.*, **113**, 8886-8889 (1991).
30. M. M. Wienk, J. M. Kroon, W. J. H. Verhees, J. Knol, J. C. Hummelen, P. A. van Hal, and R. A. J. Janssen, Efficient methano [70]fullerene/MDMO-PPV bulk heterojunction photovoltaic cells, *Angew. Chem. Int. Edit.*, **42**, 3371-3375 (2003).
31. W.-y. Zhou, S.-s. Xie, S.-f. Qian, T. Zhou, R.-a. Zhao, and G. Wang, Optical absorption spectra of C-70 thin films, *J. Appl. Phys.*, **80**, 459-463 (1996).
32. L. Ye, S. Q. Zhang, W. C. Zhao, H. F. Yao, and J. H. Hou, Highly efficient 2d-conjugated benzodithiophene-based photovoltaic polymer with linear alkylthio side chain, *Chem. Mater.*, **26**, 3603-3605 (2014).
33. H. Yao, W. Zhao, Z. Zheng, Y. Cui, J. Zhang, Z. Wei, and J. Hou, PBDT-TSR: a highly efficient conjugated polymer for polymer solar cells with a regioregular structure, *J. Mater. Chem., A*, **4**, 1708-1713 (2016).
34. M. A. Izquierdo, R. Broer, and R. W. A. Havenith, Theoretical study of the charge transfer exciton binding energy in semiconductor materials for polymer: fullerene-based bulk heterojunction solar cells, *J. Phys. Chem. A*, **123**, 1233-1242 (2019).
35. X. Liu, Y. X. Li, K. Ding, and S. Forrest, Energy loss in organic photovoltaics: nonfullerene versus fullerene acceptors, *Phys. Rev. Appl.*, **11**, 024060 (2019).
36. J. H. Hou, O. Inganäs, R. H. Friend, and F. Gao, Organic solar cells based on non-fullerene acceptors, *Nat. Mater.*, **17**, 119-128 (2018).
37. S. Y. Leblebici, T. L. Chen, P. Oalde-Vecasco, W. L. Yang, and B. W. Ma, Reducing exciton binding energy by increasing thin film permittivity: an effective approach to enhance exciton separation efficiency in organic solar cells, *ACS Appl. Mater. Inter.*, **5**, 10105-10110 (2013).
38. S. Kraner, R. Scholz, C. Koerner, and K. Leo, Design proposals for organic materials exhibiting a low exciton binding energy, *J. Phys. Chem. C*, **119**, 22820-22825 (2015).
39. H.-W. Li, Z. Guan, Y. Cheng, T. Lui, Q. Yang, C.-S. Lee, S. Chen, and S.-W. Tsang, On the study of exciton binding energy with direct charge generation in photovoltaic polymers, *Adv. Electron. Mater.*, **2**, 1600200 (2016).
40. M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger, and C. J. Brabec, Design rules for donors in bulk-heterojunction solar cells - Towards 10 % energy-conversion efficiency, *Adv. Mater.*, **18**, 789 (2006).
41. G. Dennler, M. C. Scharber, T. Ameri, P. Denk, K. Forberich, C. Waldauf, and C. J. Brabec, Design rules for donors in bulk-heterojunction tandem solar cells-towards 15 % energy-conversion efficiency, *Adv. Mater.*, **20**, 579 (2008).
42. Y. Lin, J. Wang, Z.-G. Zhang, H. Bai, Y. Li, D. Zhu, and X. Zhan, An electron acceptor challenging fullerenes for efficient polymer solar cells, *Adv. Mater.*, **27**, 1170-1174 (2015).
43. W. Zhao, D. Qian, S. Zhang, S. Li, O. Inganäs, F. Gao, and J. Hou, Fullerene-free polymer solar cells with over 11% efficiency and excellent thermal stability, *Adv. Mater.*, **28**, 4734-4739 (2016).
44. D. Qian, L. Ye, M. Zhang, Y. Liang, L. Li, Y. Huang, X. Guo, S. Zhang, Z. Tan, and J. Hou, Design, application, and morphology study of a new photovoltaic polymer with strong aggregation in solution state, *Macromolecules*, **45**, 9611-9617 (2012).
45. J. Yuan, Y. Zhang, L. Zhou, G. Zhang, H.-L. Yip, T.-K. Lau, X. Lu, C. Zhu, H. Peng, P. A. Johnson, M. Leclerc, Y. Cao, J. Ulanski, Y. Li, and Y. Zou, Single-junction organic solar cell with over 15% efficiency using fused-ring acceptor with electron-deficient core, *Joule*, **3**, 1140-1151 (2019).
46. C. H. Cui and Y. F. Li, High-performance conjugated polymer donor materials for polymer solar cells with narrow-bandgap non-fullerene acceptors, *Energ. Environ. Sci.*, **12**, 3225-3246 (2019).
47. A. Armin, W. Li, O. J. Sandberg, Z. Xiao, L. Ding, J. Nelson, D. Neher, K. Vandewal, S. Shoaee, T. Wang, H. Ade, T. Heumüller, C. Brabec, and P. Meredith, A history and perspective of non-fullerene electron acceptors for organic solar cells, *Adv. Energy Mater.*, **11**, 2003570 (2021).
48. S. Hood, N. Zarrabi, P. Meredith, I. Kassal, and A. Armin, Measuring energetic disorder in organic semiconductors using the photogenerated charge-separation efficiency, *J. Phys. Chem. Lett.*, **10**, 3863-3870 (2019).
49. Y. Liu, Z. L. Zheng, V. Coropceanu, J. L. Bredas, and D. S. Ginger, Lower limits for non-radiative recombination loss in organic donor/acceptor complexes, *Mater. Horiz.*, **9**, 325-333 (2022).

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