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A recent overview on the porphyrin-based π -extended small molecules as donors and acceptors for high-performance organic solar cells

Venkatesh Piradi,^{a,b} Feng Yan,^{*b} Xunjin Zhu,^{a*} and Wai-Yeung Wong^{c*}

Organic solar cells (OSCs) have been considered as a promising cost-effective alternative to silicon-based solar cell counterparts due to their lightweight, mechanical flexibility, and easy fabrication features. Over the past few years, organic semiconducting materials have been developed rapidly in bulk heterojunction (BHJ) OSCs. Among them, porphyrin-based small molecules have been widely applied as electron donors and electron acceptors in BHJ OSCs due to their large conjugated plane and strong absorption. In this short review article, we mainly focus on summarizing the recent progress of the rational design of push-pull porphyrin-based small molecules for OSC application. After the various structural developments, the power conversion efficiencies (PCEs) of porphyrin-based small molecules as donors in OSCs have exceeded 12%. Apart from that, a PCE of 9.6% has been recorded for the device based on a porphyrin acceptor. This paper would provide a good insight into the structure-performance correlation and molecular engineering strategies of porphyrin-based small molecules in a stepwise manner.

1. Introduction

Energy shortage has become an essential problem in the modern world due to the combustion of excessive fossil fuels. Therefore, it is urgent to develop renewable energy power sources. Though there are several renewable energy sources, solar energy stands out as inexhaustible clean energy and has become an environmental-friendly one. Among those various technologies that have been developed so far to harness this energy source, photovoltaic (PV) technology has shown an extensively attractive route to the global industry. Organic solar cells (OSCs) are regarded as a rising star in the field of PV technology for the last two decades due to their significant features such as low cost, lightweight, mechanical flexibility, and ease of fabrication. Most importantly, they have been considered as a promising cost-effective alternative to the inorganic (silicon-based) solar cell counterparts.¹⁻⁴

A typical OSC mainly has a composition of electron donor (D) and electron acceptor (A), which constitutes to the active layer and is sandwiched between two electrodes of anode and cathode. The bilayer OSC (**Figure 1 (a)**) is an example of a typical OSC and called organic Schottky cell, which has been used widely in the early days. The power conversion efficiencies (PCEs) were relatively lower than 2% in this kind of cell due to the short exciton diffusion length in the D-A interfaces.⁵ Later on, Yu et al.⁶ and Halls et al.⁷ fabricated the first bulk heterojunction (BHJ) OSC device, in which they proposed the concept of bicontinuous and interpenetrating D-A composites as a blend film, as shown in **Figure 1 (b)**. Since then, the architecture of BHJ solar cells has been considered the standard

device in the OSC industry with significantly good performances.

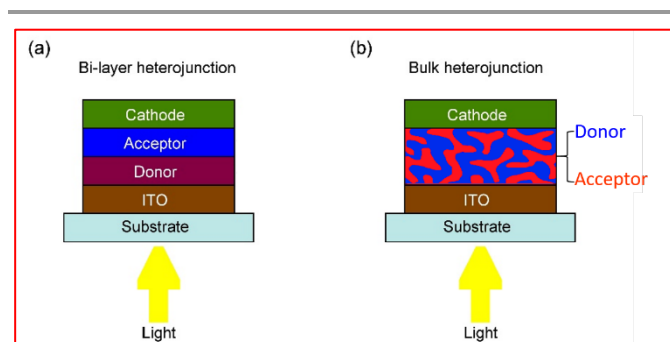


Figure 1. Schematic structures of (a) bi-layer and (b) bulk-heterojunction solar cells.⁸

During the past several years, there has been a growing research progress on developing new organic semiconducting materials, including polymers and small molecules as donors and acceptors in BHJ OSCs. Small-molecule donors have grabbed the attention of the polymer donor counterparts due to their attractive features such as easily modified structural layouts, definite molecular weight, easy purifications, and minimum batch-to-batch variations.⁹⁻¹² Porphyrin, a familiar photosensitizer, and its derivatives play a vital role in many biological processes, catalysis, and artificial photosynthesis, which are like chlorophylls as natural light harvesters in photosynthesis. The word porphyrin is originated from Greek 'porphura' ($\pi \circ \rho \phi \acute{\upsilon} \rho \alpha$) which means purple and it is a tetrapyrrolic 18 π -electron aromatic macrocycle. Recently, porphyrin analogs have found growing attention as electron donors and acceptors in BHJ OSCs, due to a number of intrinsic features associated with them: 1) wide absorption regions (Soret and Q bands in ultraviolet-visible range) with high molar extinction coefficients (ϵ), 2) easily tunable electronic properties by changing the different substituents at the peripheral positions (*meso*- and β -) and various metal insertions at the central core of the porphyrin (**Figure 2**), 3) good thermal stabilities, and 4) efficient material for electron transfer reactions.

^a Department of Chemistry, Hong Kong Baptist University, Waterloo Road, Kowloon Tong, Hong Kong, P. R. China.

^b Department of Applied Physics, The Hong Kong Polytechnic University Hung Hom, Kowloon, Hong Kong, P. R. China.

^c Department of Applied Biology & Chemical Technology and Research Institute for Smart Energy, The Hong Kong Polytechnic University, Hong Kong, P. R. China and The Hong Kong Polytechnic University Shenzhen Research Institute, Shenzhen 518057, P. R. China.

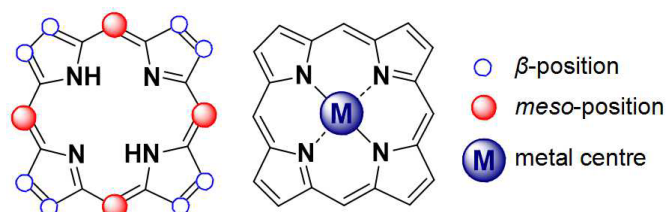


Figure 2. Typical structure of a porphyrin featuring four *meso*- and eight β -positions to be functionalized for tunable electronic and photophysical properties.

It is known that many porphyrin derivatives are found enormously in dye-sensitized solar cells (DSSCs) as photosensitizers and perovskite solar cells (PSCs) as interlayers.¹³⁻¹⁶ By tuning the structures of porphyrins, the PCEs have surpassed 13% in DSSCs.^{17, 18} On the other hand, porphyrins are eventually studied as electron donors in solution processed BHJ solar cells, however, their inferior performances in early years are discouraging when simple porphyrin chromophores like tetraphenylporphyrin (TPP) are employed as a donor in BHJ device. Later, the rapid development of modified porphyrin-based π -conjugated systems are substantially employed as electron donors and acceptors in BHJ OSCs, and their performances have been improved significantly in the last few years.¹⁸⁻²¹ To the best of our knowledge, very few reviews have been reported on porphyrin-based photovoltaic materials for BHJ OSCs from various points of view. In this mini-review, we will briefly outline the rational design of π -extended porphyrin-based small molecules as electron donors and acceptors and their performances in BHJ OSCs.

2. Porphyrin small molecules as electron donors

2.1 Influence of porphyrin molecular design for efficient organic solar cells

Porphyrins can be synthesized easily by different methods, and a simple method to prepare tetrasubstituted porphyrin, for example, TPP, involves the condensation of pyrrole and aldehyde precursor in the presence of acid catalysts (**Figure 3**). However, the performances of simple porphyrin donors in OSCs were discouraging in early 2012 with PCEs <1%²² due to the poor crystallinity and low charge mobility with fullerene acceptors. Furthermore, porphyrins were flanked by ethynylene substituted electron-donor or acceptor building blocks, which enabled the D-A conjugated configuration. This molecular design has shown great interest in solution processed OSCs to study the intramolecular charge and electron transfer within the conjugated molecule, and to stabilize the highest occupied molecular orbital (HOMO) and lowest unoccupied

molecular orbital (LUMO) energy levels of the D-A structure. Consequently, the *trans*-A₂B₂ porphyrin molecule performed better with fullerene acceptor because the *trans* pattern enables the push-pull electronic interactions and favors the desirable surface morphology over the *cis*-A₂B₂ porphyrin. (**Figure 3**).^{23, 24}

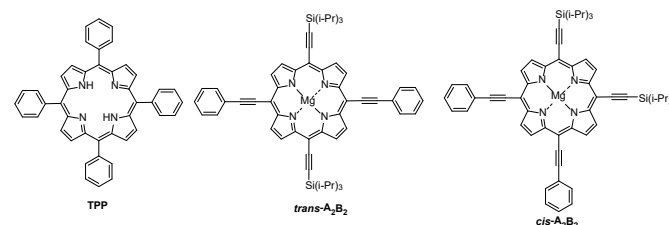
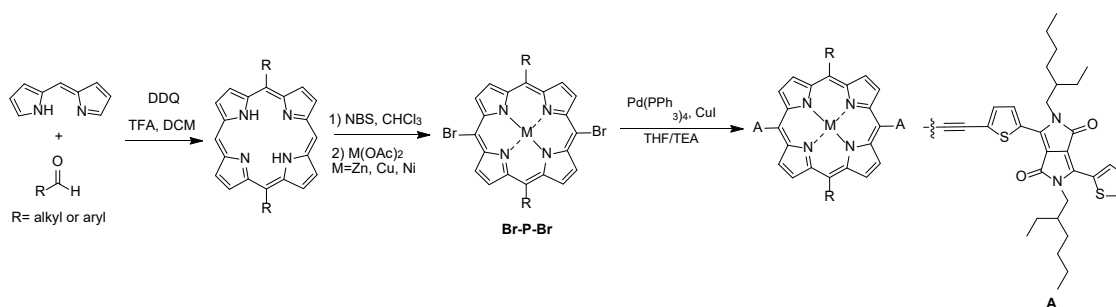


Figure 3. The chemical structures of porphyrin-based donors.

2.2 A-D-A based porphyrin small molecule donors for fullerene based devices

To further improve the intramolecular charge transfer (ICT) of D-A porphyrin and extend the absorption into the near-infrared (NIR) region for the better use of photocurrent, a typical A-D-A based molecular design of porphyrins has been introduced. The use of a strongly electron deficient diketopyrrolopyrrole (DPP) unit to the porphyrin core via ethynylene bridges is effective in red-shifting the absorption and thus elevates the photovoltaic performance. The DPP moiety has been widely used in OSCs as an electron withdrawing chromophore due to its rigidity and planarity of the building block, which facilitates the intermolecular packing in the solid state.²⁵⁻²⁷ The porphyrin core for this kind of small molecules can be synthesized in good yield by using dipyrromethane and alkyl or aryl substituted aldehyde in the presence of an acid catalyst trifluoroacetic acid (TFA), dichloromethane (DCM) as a solvent, followed by oxidation of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (**Scheme 1**). Furthermore, the bromination with N-bromosuccinimide (NBS) and next, the metalation would give the key precursor of Br-P-Br, which can be finally coupled with mono-ethynylene substituted DPP by Sonogashira reaction to obtain an A-D-A porphyrin-DPP-based small molecules in good yields.

Peng et al. for the first time in 2013 reported the porphyrin-DPP based small molecular donor in a A-D-A configuration (**P1**, **Figure 4**), in which the bis(dodecyloxy)phenyl *meso*-substituents on the porphyrin core ensure high solubility for solution processing. The extended π -conjugation of **P1** spanned the absorption from visible to NIR region and a PCE of 3.71% (**Table 1**) was achieved for the BHJ device based on **P1**:[6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM). Furthermore, the PCE was improved to 4.78% using pyridine as a solvent additive.²⁵



Scheme 1. Synthetic route for the A-D-A porphyrin-DPP based small molecules.

To study the impacts of different lengths of alkyl side chains on the thiophene units on the crystallinity of the active layer and the cell performance, Peng's group continued to report a series of porphyrin-DPP based small molecular donors by varying the vertical *meso*-substituents on the porphyrin core with 2-ethylhexylthienyl, 2-butyloctylthienyl and 2-hexyldecylthienyl groups, respectively (**P2–P4**, **Figure 4**). The molecules **P2–P4** with different alkyl chains showed similarly strong absorption profiles in the NIR region and energy levels due to the similar π -conjugation of the backbone. Under the optimization condition of pyridine and 1,8-dioctane (DIO) mixture, the champion device **P3**: [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) performed an outstanding PCE of 9.06% with a short circuit current density (J_{SC}) of 19.58 mA cm⁻². The devices **P2**:PC₇₁BM and **P4**:PC₇₁BM also exhibited decent PCEs of 8.08% and 8.24%, respectively.^{26,28} The best performance of the device **P3**:PC₇₁BM was mainly due to the well-ordered surface morphology of D-A domains that led to increased crystallinity, and thus gave rise to high J_{SC} and FF values. Therefore, the compound **P3** with 2-butyloctylthienyl side chain can be a model molecule for further optimizing the device performance. Subsequently, by the same group, the device **P3**:PC₇₁BM was employed as the rear subcell to fabricate tandem OSC, while the DR3TSBDT small molecule was used as a front subcell, and thus, the tandem device afforded an excellent PCE of 12.5% under 1 sun condition.²⁹

To improve the open circuit voltage (V_{oc}) of the cells, Peng et al. further reported a small molecular donor **P5** (**Figure 4**) with the same porphyrin-DPP backbone, by introducing the benzothiophene groups to the *meso*-porphyrin core. Under pyridine addition, thermal annealing (TA) and solvent vapor annealing (SVA) treatments, the optimal device **P5**:PC₆₁BM exhibited a PCE of 9.08% (**Table 1**) with a V_{oc} of 0.80 V.³⁰

2.3 3-Ethylrhodanine (RH) capped A- π -D- π -A porphyrin small molecules

The concept of push-pull structure was of great interest and has been demonstrated as a successful strategy in the field of porphyrin-based OSCs. Another state-of-the-art design of A- π -D- π -A porphyrin based donors can be realized by symmetrically

introducing a phenylene ethynylene or thienyl ethynyl π -linker to *meso*-substituted porphyrin core and then end-capping with 3-ethylrhodanine (RH) as a typical electron withdrawing unit. It was believed that introducing π -linkers to the porphyrin chromophores could further extend the conjugation as well as control the film morphology and crystallinity, and the strong acceptor RH could enhance the ICT and improve the light absorption capability. In 2014, Palomares et al. reported a conjugated A- π -D- π -A porphyrin donor **P6** (**Figure 5**), in which the ethylenemalononitrile units end-capped symmetrically to the porphyrin core via thiophene ethynyl π -bridges. The donor **P6** showed a strong absorption profile due to the strong ICT of the electron withdrawing ethylenemalononitrile group. Based on the films **P6**:PC₇₁BM processed from THF only and pyridine-THF, respectively, the cell performance was enhanced from 3.65% to 5.24% (**Table 2**).³¹ In 2015, Palomares et al. further synthesized a porphyrin small molecule **P7** (**Figure 5**), which has a longer π -linker terthiophene-ethynylene unit symmetrically conjugated to the porphyrin core and is terminated with RH unit symmetrically. The blend film **P7**:PC₇₁BM gave a moderate PCE of 5.5% after the addition of pyridine and TA treatment. It was found that the impurity of **P7** might affect its photovoltaic performance although the device gave a good V_{oc} of 0.82 V.³² Therefore, it is suggested that those porphyrin based small molecules should be purified as much as possible.³³ By using gel permeation chromatography (GPC) and high performance liquid chromatography (HPLC) techniques, these could help ensure the purity in HPLC grade rather than nuclear magnetic resonance (NMR) grade.³⁴

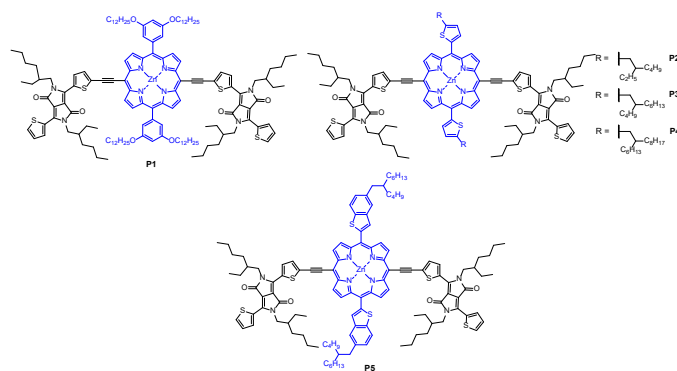


Figure 4. The chemical structures of A-D-A porphyrin-DPP based small molecules.

Table 1. Photovoltaic performances of porphyrin based A-D-A small molecular donors.

Active layer	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)	μ_h cm ² V ⁻¹ s ⁻¹	μ_e cm ² V ⁻¹ s ⁻¹	Ref
P1 :PC ₆₁ BM (1:1)	11.88	0.80	50.2	4.78	4.6×10 ⁻⁵	1.9×10 ⁻⁴	25
P2 :PC ₆₁ BM (1:1.2)	16.76	0.78	61.80	8.08	4.85×10 ⁻⁴	-	26
P3 :PC ₇₁ BM (1:1)	19.58	0.73	63.38	9.06	2.75×10 ⁻⁴	1.55×10 ⁻⁵	28
P4 :PC ₇₁ BM (1:1)	17.23	0.73	65.54	8.24	3.23×10 ⁻⁴	1.05×10 ⁻⁵	28
P5 :PC ₆₁ BM (1:1)	16.82	0.80	67.54	9.08	3.03×10 ⁻⁴	1.70×10 ⁻⁴	30

In early 2015, Zhu et al. investigated the role of alkyl chains on the vertical *meso*-porphyrin core and introduced phenylene ethylene as the π -linker between the porphyrin and RH units to afford A- π -D- π -A architecture. The three porphyrin donors have different alkyl groups of 5,15-bis(2-octylundecyl) (**P8**), 5,15-bis(3-octyl-1-tridecyl) (**P9**), and 5,15-bis(4-octyl-1-tetra-decyl) (**P10**) (**Figure 5**). The PCEs were recorded under optimized conditions for **P8** (6.49%), **P9** (2.53%), and **P10** (5.12%) with PC₇₁BM as electron acceptor. Unexpectedly, the device **P9** showed comparatively lower PCE than the devices **P8** and **P10** due to inefficient phase separation and insufficient exciton separation.³⁵ To further increase the cell performance while maintaining the same backbone of porphyrin-based small molecules, a series of porphyrins were developed by introducing the long alkyl aromatic and aliphatic peripheral substituents at the *meso*-porphyrin core. They are (5,15-bis[3,5-di(dodecyloxy)phenyl]-porphyrin (**P11**), [5,15-bis(4-dodecyloxyphenyl)-porphyrin (**P12**) and [5,15-bis(2-hexylonyl)-porphyrin (**P13**), (**Figure 5**).³⁶ The conventional device based on **P13**:PC₇₁BM showed a higher PCE of 7.7% with a V_{oc} of 0.91 V. It was found that the inverted device based on **P13**:PC₇₁BM showed a comparable performance with the PCE of 7.55%, and remained 83% of the original value even after storage in air for 30 days. On the other hand, the devices based on **P11**:PC₇₁BM and **P12**:PC₇₁BM exhibited PCEs of 3.21% and 5.07% (**Table 2**), respectively. The highest PCE for **P13** with the aliphatic substituted porphyrin, was mainly attributed to the well-ordered surface morphology and stronger intermolecular π - π stacking, which led to higher J_{sc} and FF values.

However, it is still a bottleneck to enhance the intermolecular interactions between porphyrin molecules and to expand the backbone conjugation for the optimal energy levels to ensure descent charge carrier mobility. Therefore, Zhu et al. replaced the phenylene ethynylene with 3,3''-dihexylterthiophene (TT) ethynylene as the linker and end capped it with electron-withdrawing RH for **P14** and 2-(1,1-dicyanomethylene)-3-ethylrhodanine (CNR) for **P15** (**Figure 5**).³⁷ Interestingly, both **P14** and **P15** compounds showed stronger absorptions in solution and solid state, and the optimized device based on **P15**:PC₇₁BM exhibited a higher PCE of 8.21%, while the device **P14**:PC₇₁BM obtained a PCE of 7.66% (**Table 2**).

Supramolecular self-assembly of molecules is indeed useful for nano-scale interpenetrated morphologies to further improve the photovoltaic performance of OSCs.³⁸ Some reports highlighted that the organic polymers with alkylthio groups can enhance the supramolecular self-assemblies via sulfur-sulfur intermolecular interactions, that could be beneficial for the high performance in OSCs.^{39,40} In order to study the self-assembly of porphyrins, Zhu et al. further modified the peripheral substitutions on the porphyrin core by replacing alkoxy phenylene ethynylene linkers with alkyl and alkylthio phenylene groups to afford **P16** and **P17** (**Figure 5**). After the addition of pyridine and SVA treatments, the blend film **P17**:PC₇₁BM demonstrated a higher PCE of 8.04% (**Table 2**) when compared with the device **P16**:PC₇₁BM (5.86%). The higher performance of **P17** is mainly attributed to the preferential J-aggregation self-assembly with PC₇₁BM, which could be driven by sulfur-sulfur interactions from the substituents.⁴¹

The previous structure-property correlation studies on porphyrin small molecules disclosed that the photovoltaic performance is also affected by the π -linkage. Zhu et al., therefore, designed and synthesized three porphyrin small molecules **P18**, **P19**, and **P20** (**Figure 5**) and investigated the effect of π -conjugation length by introducing oligo(phenyleneethynylene)_n (n = 1, 2, 3) linkers between the porphyrin core with 5-alkylthio-2-thienyl peripheral substituents and the ending RH units. All three molecules **P18**–**P20** possessed stronger absorption profiles from 400 nm to 750 nm. After being blended with PC₇₁BM and under optimization conditions, the device based on **P18** having a short π -linkage afforded a notable PCE of 8.66%, while the other devices demonstrated lower PCEs of 8.29% and 7.93% on **P19** and **P20**, respectively (**Table 2**). Though **P19** and **P20** films gave rise to lower PCEs than **P18**, higher FF and hole mobilities were recorded which might be attributed to the longer π -conjugation length with better morphology.⁴²

2.4 Porphyrin-based dimers for near-infrared absorption

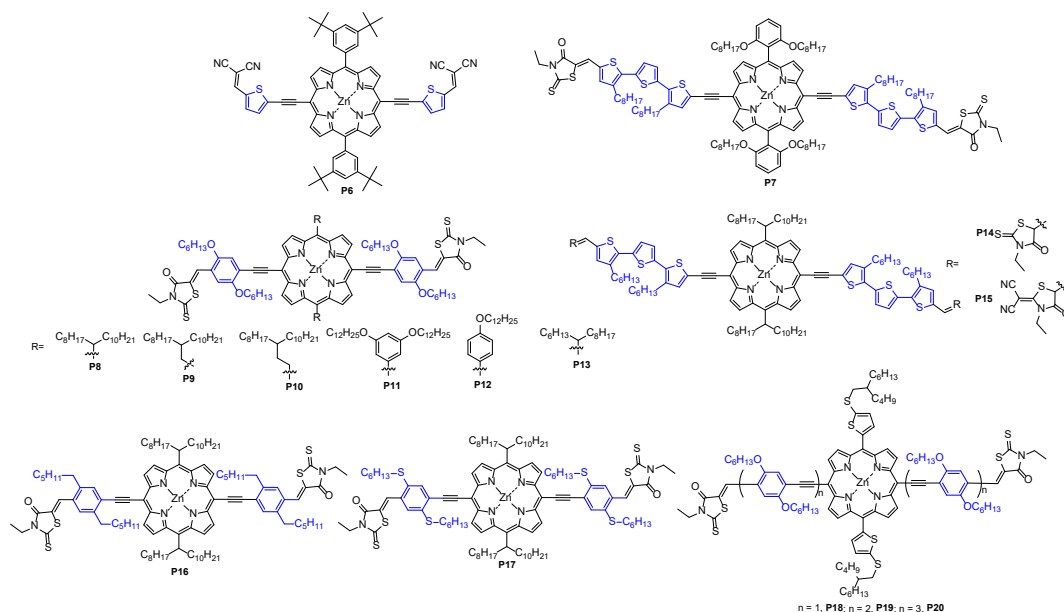


Figure 5. The chemical structures of A- π -D- π -A RH-capped porphyrin donors.

As we discussed early, those A-D-A and A- π -D- π -A based porphyrin donors have greatly shown their impressive photovoltaic performances in OSCs. However, most of these porphyrin-based small molecular donors showed limited absorption less than 850 nm. To further extend absorption into the near-infrared region, Langa et al. designed and synthesized a conjugated D-A-D based porphyrin dimer **P21** (Figure 6) bridged with DPP-ethynylene and terminated with thiophene groups. The cell based on the dimer **P21** with PC₇₁BM exhibited a high PCE of 8.03% (Table 3) with low energy loss and strong external quantum efficiency (EQE) over 900 nm.⁴³ Peng et al. also developed a series of largely conjugated porphyrin donors based on A- π -D₁-D₂-D₁- π -A architecture, by flanking three different electron rich units (diethynylene, diethynylene-dithiophene, and diethynylene-phenylene) between the two porphyrin cores and replacing RH with DPP as terminal units via an ethynylene linkage to afford **P22**, **P23**, and **P24** (Figure 6), respectively.⁴⁴ Due to the elongated π -conjugation, the three compounds showed improved ICT which lowered their bandgaps. The optimized device based on **P22**:PC₆₁BM accumulated the highest PCE of 6.42% than the other devices **P23**:PC₆₁BM (4.5%) and **P24**:PC₆₁BM (5.5%). This could be attributed to suitable energy levels and better film morphology of the donor-acceptor interfaces. The same group further modified the former structure of porphyrin dimers and synthesized a new dimeric porphyrin **P25** (Figure 6) using an ethynylene linker. Impressively, the optimized device **P25**:PC₆₁BM showed a broad photoresponse up to 1000 nm and the blend film recorded a remarkable PCE of 8.45% (Table 3) with an impressive J_{SC} of 19.65 mA·cm⁻².⁴⁵

Except for those porphyrin dimers with DPP terminating units, Zhu et al. synthesized A- π ₂-D- π ₁-D- π ₂-A configured porphyrin dimer **P26** (Figure 6) by employing electron withdrawing RH as ending units via phenylene ethynyl linker.⁴⁶ As expected, the targeting molecule further extended the absorption edge over 1100 nm, after being blended with PC₇₁BM and after TA+SVA treatments the device furnished a respectable PCE of 8.29% (Table 3) with a high FF of 70%. Apart from the efficiency, the device showed an energy loss (E_{loss}) of 0.43 eV, which is the lowest value among those reported in porphyrin-based BHJ OSCs.

Recently, Peng et al. incorporated an electron deficient benzothiadiazole (BT) as the bridge to dimeric porphyrin and RH as terminals through thiophene linkers to afford **P27** (Figure 6) with an A₁- π -D-A₂-D- π -A₁ configuration. The compound **P27** with enhanced ICT showed an elongated π -conjugation, and a strong absorption in the NIR region, and deeper HOMO energy levels. The device based on **P27**:PC₆₁BM processed with pyridine additive and SVA treatments led to a promising PCE of 10.02% (Table 3) with increasing values of J_{SC} and V_{oc} .⁴⁷

Very recently, Langa et al. synthesized two D-A-D porphyrin dimers by introducing DPP as the central unit, differentiating by two electron-donating bis(dodecyloxy)phenyl (**P28**), 5-hexylthieno[3,2-b]thiophen-2-yl (**P29**) substituents at the *meso*-porphyrin cores (Figure 6).⁴⁸ The dimer **P29** possessed a higher charge carrier mobility and more balanced charge transport properties compared to **P28** due to the strong electron donating property of the thieno-thiophene unit. The optimized blend films with PC₇₁BM exhibited the overall PCEs of 8.05% for **P28** and 8.89% (Table 3) for **P29** with stronger absorption profiles up to 900 nm.

Table 2. Photovoltaic properties of porphyrin-based A- π -D- π -A donors.

Active layer	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)	μ_h cm ² V ⁻¹ s ⁻¹	μ_e cm ² V ⁻¹ s ⁻¹	Ref
P6 :PC ₇₁ BM (1:1)	10.64	0.88	56.0	5.24	8.34×10 ⁻⁵	2.32×10 ⁻⁴	31
P7 :PC ₇₁ BM (1:1)	11.67	0.76	62.0	5.50	8.45×10 ⁻⁵	-	32
P8 :PC ₇₁ BM (1:1)	13.72	0.90	52.12	6.49	4.59×10 ⁻⁴	-	35
P9 :PC ₇₁ BM (1:1)	6.29	0.85	47.88	2.53	-	-	35
P10 :PC ₇₁ BM (1:1)	10.50	0.87	56.87	5.12	6×10 ⁻⁵	-	35
P11 :PC ₇₁ BM (1:1)	7.20	0.90	48.12	3.21	1.57×10 ⁻⁵	-	36
P12 :PC ₇₁ BM (1:1)	10.14	0.90	55.60	5.07	8.48×10 ⁻⁵	-	36
P13 : PC ₇₁ BM (1:1.2)	13.32	0.91	63.60	7.70	2.18×10 ⁻⁵	-	36
P14 :PC ₇₁ BM (1:1)	14.93	0.80	64.18	7.66	1.67×10 ⁻⁴	-	37
P15 :PC ₇₁ BM (1:1)	14.30	0.82	70.01	8.21	4.14×10 ⁻⁴	-	37
P16 :PC ₇₁ BM (1:1.2)	11.53	0.87	58.50	5.86	2.44×10 ⁻⁵	1.62×10 ⁻³	41
P17 :PC ₇₁ BM (1:1.2)	13.19	0.91	66.70	8.04	2.31×10 ⁻⁴	2.26×10 ⁻³	41
P18 :PC ₇₁ BM (1:1.2)	14.84	0.91	64.11	8.66	1.3×10 ⁻⁵	-	42
P19 :PC ₇₁ BM (1:1.2)	14.44	0.90	63.21	8.29	1.6×10 ⁻⁵	-	42
P20 :PC ₇₁ BM (1:1.2)	13.56	0.89	65.12	7.93	3.8×10 ⁻⁴	-	42

2.5 Ternary organic solar cells based on porphyrin small molecules

Indeed, porphyrin derivatives have been successfully explored in BHJ OSCs due to their excellent light-harvesting properties in the visible and NIR regions. However, there is still a weak absorption between Soret and Q bands.⁴⁹ On the other side, the absorption towards the NIR region is still a bottleneck for binary layer OSCs based on wide bandgap electron donors. Thanks to the new concept of ternary organic solar cells, the light harvesting capability can be improved by employing one donor and two acceptors or two donors and one acceptor with complementary absorption profiles in the active layer.⁵⁰ It has been revealed that the addition of a third component can enable manipulating the film morphology and charge transport properties and thus leading to enhanced photovoltaic performance of a solar cell. Without any doubt, porphyrins are excellent light absorbing materials and can be fabricated for ternary devices to strengthen UV-visible-NIR light harvesting and achieve high efficiency in BHJ OSCs.

In 2016, Peng et al. constructed a ternary solar cell by the introduction of low bandgap porphyrin (**P30**, **Figure 6**) into PTB7 (poly-thieno[3,4-b]thiophene):PC₇₁BM blend film.⁵¹ The ternary device exhibited an improved PCE of 8.39% (**Table 4**), which is 12% higher than that of the binary layer of PTB7:PC₇₁BM (7.23%). The better performance of the ternary one than the binary one is mainly attributed to the full photoresponse over 900 nm. Inspired by the previous results of **P30** in the ternary OSC, the same group fabricated a ternary device based on the addition of 30% **P2**, (**Figure 4**) into PTB7:PC₇₁BM. Impressively, the blend film exhibited an expanded full photoresponse and enhanced the device performance. It resulted in a promising PCE of 11.03% (**Table 4**) with a J_{sc} of 18.94 mA cm⁻², an FF of 75.63%, and a V_{oc} of 0.77

V.⁵² The high performance of the device could be attributed to the complementary absorption in the NIR region and well balanced charge extraction and recombination dynamics.

Recently, Langa et al. constructed a ternary device by the addition of two porphyrins **P31** and **P32** (**Figure 6**) as donors and PC₇₁BM as acceptor.⁵³ The ternary device based on **P31**:**P32**:PC₇₁BM (0.2:0.8:2) showed a PCE of 6.72%, and the PCE was further improved to 9.44% (**Table 4**) after SVA treatment together with a J_{sc} of 15.98 mA cm⁻² and a V_{oc} of 0.85 V. The binary layers hold a comparatively lower PCE of 3.11% for **P31**: PC₇₁BM and 4.03% for **P32**: PC₇₁BM. The enhanced efficiency of the ternary solar cell could be ascribed to the well-ordered nano-scale morphology of the active layer, which is beneficial for enhancing the charge transport properties and thus, device performance.

Subsequently, Zhu et al. designed and synthesized an A₂- π -D-A₁-D- π -A₂ porphyrin dimer **P33** (**Figure 6**) as the donor for ternary solar cells.⁵⁴ The **P33** has two porphyrin units flanked by an electron deficient DPP units as the core, endcapped with RH unit via a phenylene ethynylene linker. The compound **P33** exhibited stronger absorption ranges from 400 to 900 nm with a small valley at 550-650 nm in both liquid and solid states. To compensate for the absorption gap between Soret and Q bands, a wide bandgap small molecule donor DR3TBDTTF⁵⁵ with a complementary absorption (**Figure 7a**) was used as the second donor for ternary solar cells. Using PC₇₁BM as an acceptor, the device based on the ternary layer of **P33**:20% DR3TBDTTF:PC₇₁BM provided a remarkable PCE of 11.15% (**Table 4**) with a panchromatic photoresponse. The PCE of the binary device based **P33**:PC₇₁BM was accumulated as 9.30% (**Figure 7b**). It is obvious that such a ternary combination with porphyrin-based small molecules as one component in the ternary active layer can significantly improve the device performance through enhancing the light-harvesting capability over 1000 nm. These results demonstrate that the choice of the

third component is quite crucial for highly efficient ternary solar cells.

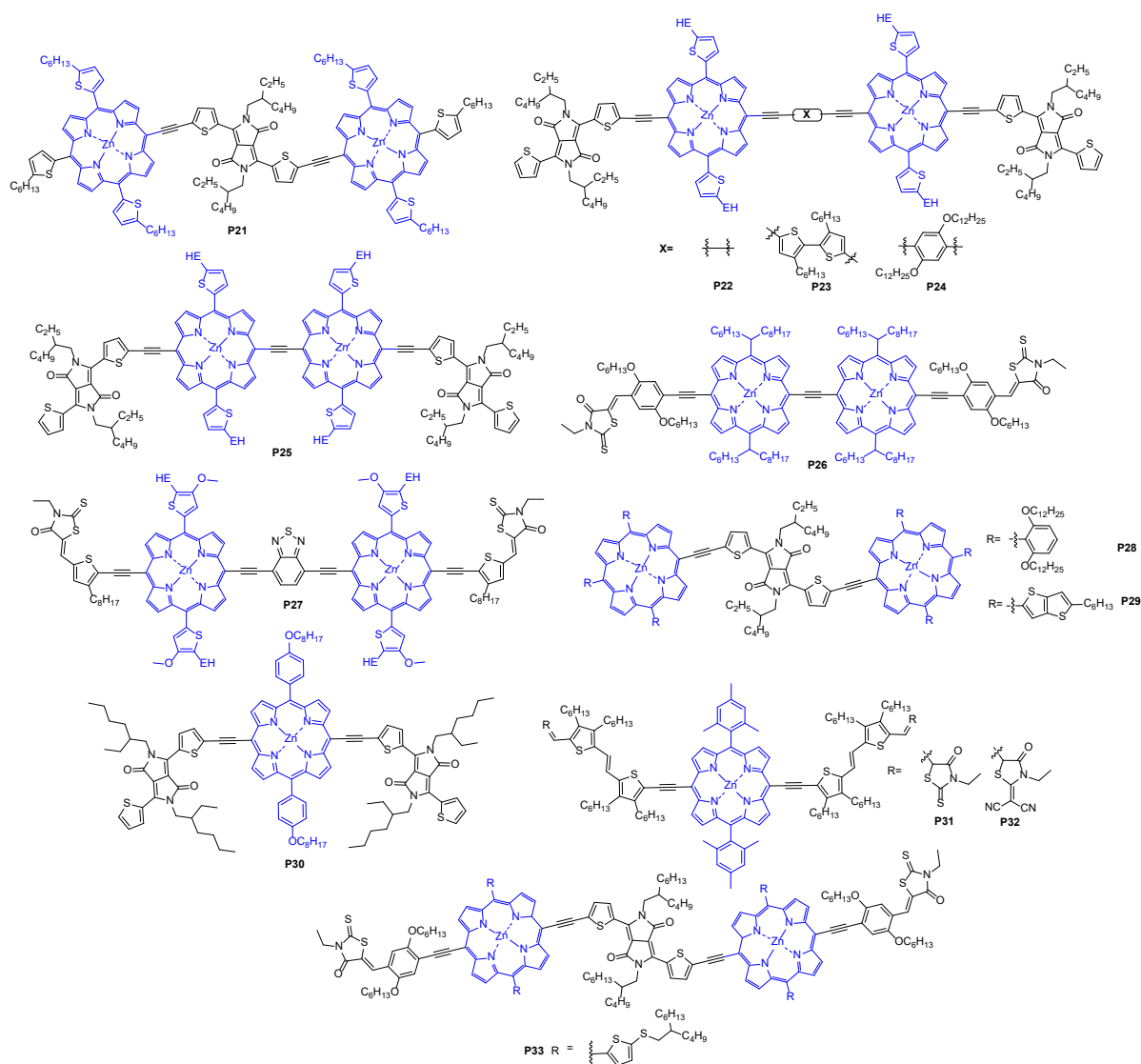


Figure 6. The chemical structures of conjugated porphyrin dimers.

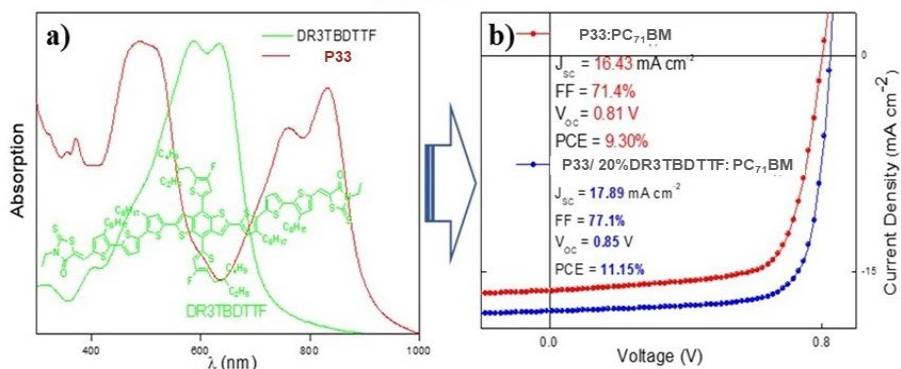


Figure 7a) Absorption spectra of P33 (red) and DR3TBDTF (green) (insert: molecular structure of DR3TBDTF) b) Current density-voltage (J - V) curves of P33:PC₇₁BM (red) and P33:20% DR3TBDTF:PC₇₁BM (blue).⁵⁴

Table 3. Photovoltaic performances of conjugated porphyrin dimers.

Active layer	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)	μ_h cm ² V ⁻¹ s ⁻¹	μ_e cm ² V ⁻¹ s ⁻¹	Ref
P21 :PC ₇₁ BM	14.19	0.82	69.0	8.03	5.64×10 ⁻⁵	-	43
P22 :PC ₆₁ BM (1:1)	14.37	0.68	46.04	4.50	1.46×10 ⁻⁴	-	44
P23 :PC ₆₁ BM (1:1)	13.36	0.79	51.77	5.50	3.35×10 ⁻⁴	-	44
P24 :PC ₆₁ BM (1:1)	16.34	0.68	57.77	6.42	4.74×10 ⁻⁴	-	44
P25 :PC ₆₁ BM	19.65	0.65	66.15	8.45	1.44×10 ⁻⁴	-	45
P26 :PC ₇₁ BM (1:1.2)	15.19	0.79	69.82	8.29	1.40×10 ⁻⁴	-	46
P27 :PC ₇₁ BM	17.66	0.84	67.15	10.02	4.94×10 ⁻⁴	-	47
P28 :PC ₇₁ BM	13.83	0.91	64.15	8.05	1.29×10 ⁻⁴	2.53×10 ⁻⁴	48
P29 :PC ₇₁ BM	16.98	0.79	66.31	8.89	1.67×10 ⁻⁴	2.62×10 ⁻⁴	48

Table 4. Photovoltaic parameters of porphyrin-based donors for ternary OSCs.

Active layer	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)	μ_h cm ² V ⁻¹ s ⁻¹	μ_e cm ² V ⁻¹ s ⁻¹	Ref
P30 :PTB7:PC ₇₁ BM (1:0.2:1)	17.22	0.72	67.65	8.39	3.91×10 ⁻⁴	-	51
P2 :PTB7:PC ₇₁ BM (0.7:0.3:1.5)	18.86	0.77	75.5	11.03	3.41×10 ⁻³	-	52
P31 : P32 :PC ₇₁ BM (0.2:0.8:2)	16.24	0.87	69.5	9.44	7.76×10 ⁻⁵	2.48×10 ⁻⁴	53
P33 :D*:PC ₇₁ BM (1:0.2:1)	17.98	0.85	77.10	11.15	3.21×10 ⁻⁴	2.84×10 ⁻⁴	54

D*=DR3TBDTTF

2.6 Porphyrin-based donors for nonfullerene organic solar cells

Though the fullerene derivatives PC₆₁BM and PC₇₁BM are employed as efficient electron acceptors in BHJ solar cells, they still suffer from intrinsic shortcomings such as limited absorption and poor mechanical properties.⁵⁶⁻⁵⁸ At the same time, nonfullerene acceptors (NFAs) have been developed rapidly to overcome the above issues for the fullerene counterparts. Apart from that, they possess some extensive properties like easy synthesis, tunable electronic properties, and more balanced charge mobilities for the future commercialization of OSCs. The PCEs of OSCs based on polymer donors and NFAs have reached recently from 9 to 18%⁵⁹⁻⁶²

Recently, Peng et al. used porphyrin small molecule **P3** (Figure 4) as the donor and one terthieno[3,2-*b*]thiophene (6TIC) based acceptor to construct nonfullerene OSCs.⁶³ Usually, it is very rare to show high efficiency based on the device of all small-molecule OSCs rather than using polymer counterparts. Surprisingly, upon the DIO additive and SVA treatment, the optimized device **P3**:6TIC gave an outstanding PCE of 12.08% with a remarkable J_{sc} of 20.44 mA cm⁻². The better efficiency of the device is mainly attributed to the increasing crystallinity after SVA treatment and the formation of multi length scale morphology.

Wan et al. synthesized a porphyrin donor **P34** (Figure 8) by introducing thieno[3,2-*b*]thiophene (TT) unit at the vertical meso-porphyrin core and fabricated all small-molecule OSCs with NFA IDT-C8 as acceptor. At the optimized condition, the device **P34**:IDT-C8 showed a moderate PCE of 5.14%. Though both molecules exhibited complementary absorption to each other, they formed unfavorable phase morphology that could be the reason for the low J_{sc} .⁶⁴

Very recently, Zhu et al. synthesized two A- π -D₂-D₁-D₂- π -A dimeric porphyrin small-molecule donors **P35** and **P36** (Figure 8) bridged by 2-ethylhexylthienyl and 2-ethylhexylthiothienyl substituted benzodithiophene (BDT), respectively.⁶⁵ Both compounds have a similar strong photoresponse range from 400 nm to 900 nm with a small valley at 600 nm. Under optimal processing conditions with 6TIC as acceptor, the donor **P36** with sulfur linkages on BDT exhibited a high PCE of 10.39% and a high J_{sc} of 19.53 mA cm⁻², while the device **P35**:6TIC showed slightly lower PCE of 8.73% with a lower J_{sc} of 17.75 mA cm⁻². The results indicated that side chain engineering could influence the device performance by changing the surface morphology and enhancing the charge mobility and charge extraction.

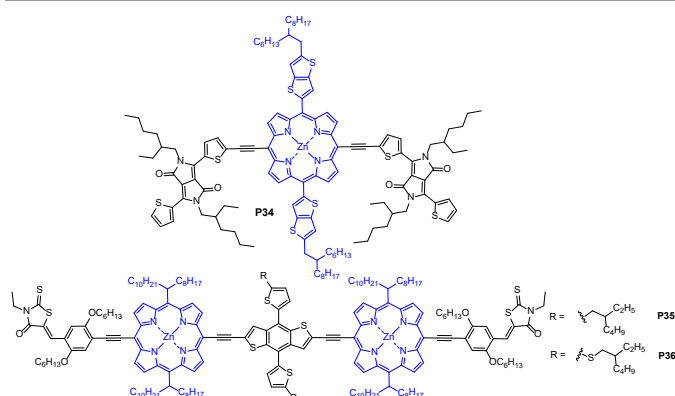


Figure 8. The chemical structures of conjugated porphyrins for nonfullerene OSCs

2.7 Porphyrin-based small molecule donors for indoor photovoltaics

As discussed above, those porphyrin-based small molecules and their device performances have shown promising results in organic photovoltaics (OPVs). However, to achieve high efficiencies, researchers have developed a new strategy for indoor photovoltaics (IPVs) by using ambient light sources like light emitting diodes (LEDs) and fluorescent tubes instead of AM1.5G 1 sun illumination. These indoor lights can easily emit light in the visible region from 400 nm to 750 nm which is beneficial for spectral overlapping with the absorption of the OPV materials.⁶⁶⁻⁶⁹ Recent literature references have reported PCEs surpassing 31% based on indoor OPV devices.⁷⁰⁻⁷⁴

For the first time, Zhu and co-workers reported porphyrin-based donor **P13** which is not only a promising material for 1 sun light but also for indoor illumination. The optimized device based on **P13**:PC₇₁BM yielded a high PCE of 19.2% with a Voc of 0.75 V, a Jsc of 29.56 $\mu\text{A cm}^{-2}$, and an FF of 66.1% under a 300 lux LED tube.⁷⁵ Next, the same group demonstrated that porphyrin donors are promising materials to construct semitransparent and high-performance indoor solar cells. Therefore, we screened out several porphyrin donors **P8**, **P19**, **P20**, and **P33** from our early reports, and fabricated the devices with PC₇₁BM under 300 lux LED illumination. Among them, the P8 based device showed a decent PCE of 11% with illuminance transparency of 68%, while the PCEs of other devices were recorded for **P19** (10.7%), **P20** (8.7%), and **P33** (8.2%).⁷⁶

3. Porphyrin-based small molecules as electron acceptors

We have discussed that the porphyrin based small molecules as donors with various structural configurations (A-D-A, A- π -D- π -A) have shown tremendous results in BHJ OSCs. On the other hand, researchers have also been intrigued to investigate porphyrin derivatives as electron acceptors in OSCs. The very early study with inferior results (PCEs < 3.3%) slowed down the development of porphyrin-based acceptors.^{77,78} In 2017, Li et al. reported a star-shaped porphyrin-based acceptor by appending four strong electron-deficient perylene diimide (PDI) units at the

meso-porphyrin core via ethynylene linkages to afford **P37** (Figure 9).⁷⁹ Interestingly, the compound **P37** showed strong absorption bands from 300 nm to 850 nm with balanced energy levels, when it was employed as an electron acceptor with PBDB-T polymer donor, the optimized device based on **P37**:PBDB-T exhibited an outstanding PCE of 7.4% with a J_{sc} of 14.5 mA cm⁻², a V_{oc} of 0.78 V, and an FF of 66% (Table 5). These results motivated the scientific community to develop more efficient porphyrin based acceptors in the field of OSCs. Jang et al. modified the structure of **P37** and synthesized an n-type porphyrin acceptor by keeping two PDI units with ethynylene groups at the *meso*-porphyrin and introducing two thiophene groups to the vertical porphyrin core to get **P38** (Figure 9).⁸⁰ The BHJ device was fabricated by using PTB7-Th as the polymer donor and **P38** as the electron acceptor to lead to the PCE of 5.25%. In addition, the blend film showed a panchromatic absorption from 350 nm to 900 nm with a remarkable E_{loss} of 0.54 eV.

In order to improve the electron mobility and light harvesting ability of porphyrin acceptors in OSCs, very recently, Zhu and his co-workers designed, and synthesized PDI-porphyrin based acceptors **P39** using *p*-phenylene instead of ethynylene as linkages (Figure 9). For comparison, **P40** (Figure 9) was synthesized with two PDI units appended to porphyrin similarly.⁸¹ The purpose of introducing *p*-phenylene bridges is to control the excessive steric interference between the PDI and porphyrin units, therefore, it can essentially disrupt the π -conjugation and maintain the electron accepting ability of PDI and donating ability of porphyrin simultaneously. The BHJ active layer was prepared by using PBT7-Th as polymer donor and porphyrin acceptors (**P39**, **P40**), and a high PCE of 9.64% was achieved for the blend film **P39**:PBT7-Th with high electron mobility, while the device based on **P40**:PBT7-Th afforded a PCE of 6.38% (Table 5).

Recently, Li et al. investigated the effect of side chains on the peripheral porphyrin core to influence the device performance. Therefore, they introduced four different side chains attached to the porphyrin core at the vertical *meso* positions differed by 2,6-di(dodecyloxy)phenyl (**P41**), (2-ethylhexyl)thiophen-2-yl (**P42**), pentadecan-7-yl (**P43**), and 3,5-di(dodecyloxy)-phenyl (**P44**) (Figure 9)⁸² and endcapped with two PDI units via ethynylene bridges to the porphyrin. These acceptors were fabricated respectively with PBDB-T polymer donor for BHJ OSCs, and the optimized blend films showed PCEs of 1.87% for **P41**, 3.79% for **P42**, 4.23% for **P43**, and 5.34% for **P44** (Table 5). These results indicated that choice of side chains is important in order to enhance the device performance of OSCs because they could affect the electronic properties, crystallinity, and microphase morphology of the active layers.

So far, porphyrin-based acceptors were reported with PDI substituents onto a porphyrin core, and they demonstrated promising performances in OSCs. Naphthalene diimide (NDI) is another efficient electron withdrawing acceptor and less bulky analogue than PDI unit, and it was employed to build up polymeric nonfullerene acceptor in OSCs. In 2018, Jang et al. developed an efficient porphyrin based acceptor, which has four NDI units incorporated at the perimeter of the porphyrin

core through ethynylene linkages to give **P45** (Figure 9).⁸³ The BHJ device based on **P45**:PBT7-Th film exhibited a notable PCE of 8.15% (Table 5) with a very low E_{loss} of 0.61eV. Apart from that, the absorption of compound **P45** was red-shifted to the NIR region over 930 nm due to the effective π -conjugation between NDI and porphyrin units.

Despite the aforementioned advantages of tetrasubstituted porphyrin acceptors based on PDI or NDI groups and their performances in OSCs, it is still challenging to obtain high Voc and balanced charge carrier mobility simultaneously. Lin et al., very recently, reported for the first time a series of n-type porphyrin derivatives endcapped with a strong electron deficient 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)-malononitrile (2FIC) acceptor via thiophene π -linkers based on a push-pull structure. The three molecules differ by

three different side chains 3,4,5-tridodecyloxyphenyl (**P46**), 2,6-didodecyloxyphenyl (**P47**), and 3,5-di-*tert*-butylphenyl (**P48**) at the vertical *meso*-porphyrin core (Figure 9).⁸⁴ Furthermore, the three porphyrin acceptors were successfully fabricated with a PTB7-Th polymer donor in OSCs. The **P47** based device showed a remarkable PCE of 7.23 % with a Voc of 0.80 V, a Jsc of 13.94 mA cm⁻², and an FF of 64.8% over the devices based on **P46** (4.10 %) and **P48** (5.48 %) (Table 5). The better performance of **P47** could be attributed to the controlled molecular aggregation of the porphyrin surrounded by the alkoxy chains which should be beneficial to form face-on orientation and thus enhance Jsc and Voc.

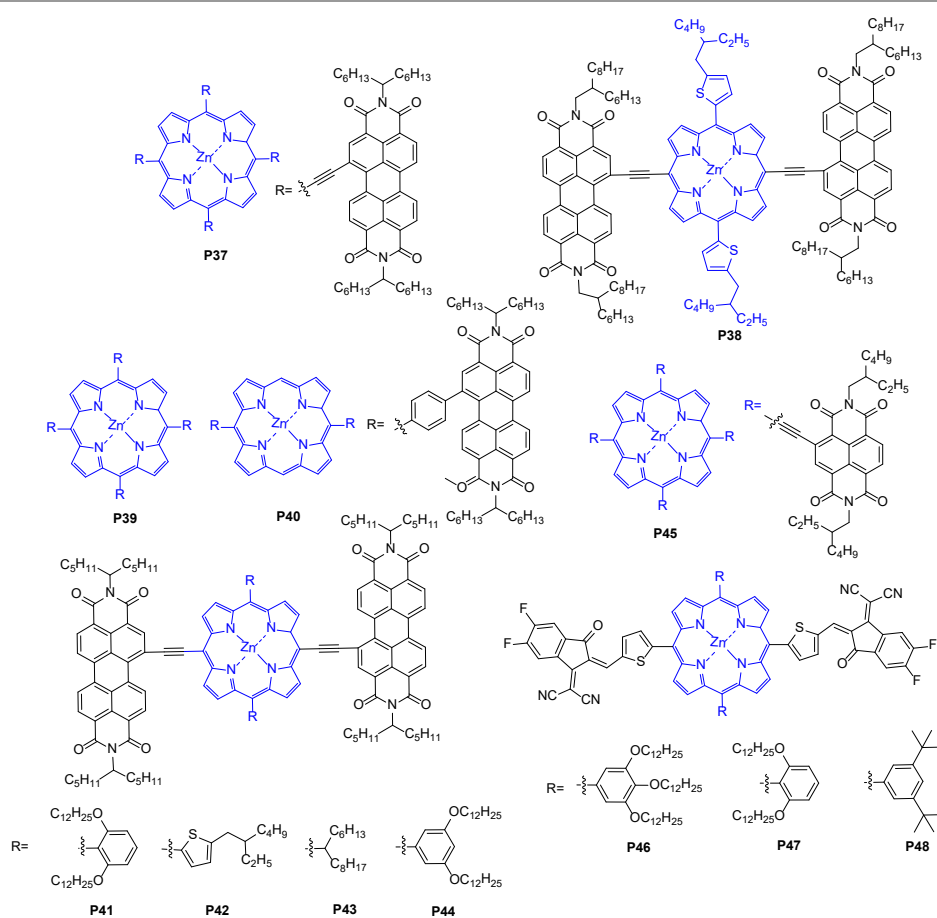


Figure 9. The chemical structures of porphyrin small molecular acceptors.

Table 5. Photovoltaic parameters of porphyrin-based donors for ternary OSCs.

Active layer	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)	μ_h cm ² V ⁻¹ s ⁻¹	μ_e cm ² V ⁻¹ s ⁻¹	Ref
PBDB-T: P37 (1:1)	14.5	0.78	66	7.4	3.1×10 ⁻⁴	1.0×10 ⁻²	79
PTB7-Th: P38	12.76	0.73	56	5.25	-	-	80
PTB7-Th: P39	15.41	0.90	70	9.64	-	-	81
PTB7-Th: P40	13.01	0.86	56	6.38	-	-	81
PBDB-T: P41 (1:1)	4.10	0.88	49	1.87	-	-	82
PBDB-T: P42 (1:1)	9.56	0.79	50	3.79	-	-	82
PBDB-T: P43 (1:1)	9.48	0.80	53	4.23	-	-	82
PBDB-T: P44 (1:1)	11.02	0.81	58	5.34	-	-	82
PTB7-Th: P45	17.34	0.72	65	8.15	3.1×10 ⁻³	4.51×10 ⁻⁵	83
PTB7-Th: P46 (1:1)	9.88	0.78	53	4.10	1.50×10 ⁻³	2.05×10 ⁻⁴	84
PTB7-Th: P47 (1:1)	13.94	0.80	64	7.23	1.86×10 ⁻³	3.97×10 ⁻⁴	84
PTB7-Th: P48 (1:1)	12.55	0.77	56	5.48	1.63×10 ⁻³	2.37×10 ⁻⁴	84

4. Conclusion and future perspectives

In summary, we have briefly discussed the recent progress in developing porphyrin-based materials as efficient donors and acceptors for BHJ OSCs by structural engineering of the π -conjugated porphyrin backbone and peripheral substitutions on the porphyrin cores and π -linkers. Among them, A-D-A porphyrin-DPP-based small molecules have been tremendously explored as electron donors and impressive PCEs up to 9% were recorded. Introducing electron-deficient units via π -linkers to the porphyrin core is another strategy to develop A- π -D- π -A porphyrin-based small molecular donors with enhanced intermolecular ICT, intramolecular π - π interaction, as well as light-harvesting capability. The state-of-the-art A- π -D- π -A porphyrin donor revealed PCEs over 8.6%. Typically, the absorption spectra of porphyrin-based small molecules have been vastly extended to the NIR region over 1100 nm by incorporating several conjugated chromophores, such as DPP, BT, as well as porphyrin unit via ethynylene linkages. Moreover, porphyrin-based ternary solar cells exhibited the PCEs of over 11% with a panchromatic absorption profile. In addition, the devices based on porphyrin donors with nonfullerene acceptors showed an outstanding PCE of 12%. Furthermore, porphyrin derivatives have been proven to be not only good materials for electron donors but also efficient candidates for electron acceptors, and the maximum PCE of 9.6% was demonstrated using the porphyrin acceptors. Last but not least, the porphyrin-based OSCs also showed high efficiency of 19.2% under indoor light illuminations.

To further improve the high efficiency of the porphyrin-based donors, researchers need to focus on developing more rationally designed porphyrin structures. For example, replacing the zinc at the porphyrin core with platinum, which would produce triplet excited states with longer lifetime, therefore, potentially leading to more efficient charge separation and transportation.⁸⁵ On the other hand, it would be very promising to develop highly efficient and stable ternary organic solar cells by using porphyrin small molecules as the third component. By a careful selection of other two or more

components for the photoactive layer, those key photovoltaic parameters would be simultaneously elevated within the ternary organic solar cells, resulting in record-high efficiency for commercial photovoltaic applications.

Morphology of the active layers affects the charge generation, dissociation and transportation process in OSCs, and therefore, is a key factor to enhance the device performance. To balance the strong π - π aggregation of porphyrin molecules, the combination of a suitable wide bandgap small molecule as the second electron donor in the ternary solar cells has been demonstrated effective and should be the focus of the future research in improving the device performance via the film morphology engineering. On the other side, the development of narrow-bandgap porphyrin-based acceptors characteristic of strong NIR absorption will be beneficial to boost the J_{sc} value for better device performances.

Conflicts of interest

There are no conflicts of interest to declare.

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