Structural engineering of porphyrin-based small molecules as donors for efficient organic solar cells†

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Porphyrin-based small molecules as donors have long been ignored in bulky heterojunction organic solar cells due to their unfavorable aggregation and the low charge mobility. With the aim of striking a delicate balance between molecular design, morphology, interfacial layer and device fabrication to maximize the power conversion efficiency (PCE) of organic solar cells, three comparable porphyrin-based small molecules with an acceptor–donor–acceptor configuration have been developed for use as donor materials in solution processed small molecule bulk heterojunction organic solar cells. In these molecules, electron-deficient 3-ethylrhodanine is introduced into the electron-rich porphyrin core through 5,15-bis(phenylethynyl) linkers. Structural engineering with 10,20-bis[3,5-di(dodecyloxyl)phenyl], and 10,20-bis[4-dodecyloxylphenyl], can simultaneously facilitate stronger intermolecular π–π stacking and higher charge transfer mobility in the film, leading to a maximum PCE of 7.70% in a conventional device. The inverted devices have also been demonstrated to have long-term ambient stability and a comparable PCE of 7.55%.

1. Introduction

Solution processed small molecule (SM) bulk heterojunction organic solar cells (BHJ OSCs) have shown great prospect in the realization of low-cost and large-scale devices due to their characteristics of well-defined structure and molecular weight, and easy synthesis and purification of small molecules.1,2 Generally, a small molecule as a donor in a solution processed BHJ OSC needs to possess the following features: (i) strong photo-absorption in the visible and near-infrared (NIR) region; (ii) sufficient solubility in solvents; (iii) strong intermolecular interaction in the solid state for efficient charge transfer; and (iv) excellent film formation ability. In the search for appropriate small molecule donors, various frameworks have been examined, including benzene[1,2-b:4,5-b′]dithiophene (BDT),3,4 boron dipyrromethene,5,6 diketopyrrolopyrrole,7,8 phthalocyanine,9 merocyanine,10 and squarine.11,12 Over the past decade, the power conversion efficiencies (PCEs) of the solution processed SM BHJ OSCs have steadily improved. Since Bazan and Heeger et al. first reported a PCE of 6.7% based on a small molecule donor with 3,3′-di-2-ethylhexylsilylene as the central building block,13 the PCE was steadily enhanced to 9.02% by the structural optimization of both small molecules and devices in BHJ OSCs.14,15 Chen et al. also reported a series of small molecules with an oligothiophene unit as the core unit, and the efficiency was also over 9% after the optimization of the molecular structure.16,17 On the other hand, porphyrins and their analogues exhibit some intrinsic features that are attractive for their application in photovoltaics.18 They have strong absorption with high extinction coefficients (ε) in both the blue (Soret band) and red (Q-band) regions, and their photo- and electrochemistry can readily be adjusted through peripheral functionalization and by varying of the metal center. It is known that “push–pull” porphyrin derivatives have been successfully applied in dye-sensitized solar cells.21-23 However, discouraging PCEs were obtained when employing porphyrins and their analogues as donor materials in BHJ devices. Very recently, Peng and co-workers used [5,15-bis[3,5-di(dodecyloxyl)phenyl] porphyrinato]zinc(u) and 2,1,3-benzothiadiazole (BTU) to
construct donor–acceptor–donor (A–D–A) small molecules as donors in BHJ OSCs. Since the two bulky 3,5-di(dodecylxoyl) phenyl substituents that are almost perpendicular to the porphyrin core suppress the intermolecular \( \pi-\pi \) stacking, a relatively poor photovoltaic performance was achieved.

Subsequently, they employed less bulky meso-substituents such as 4-octyloxy-phenyl and 5-(2-ethylhexyl)-thienyl in the new A–D–A porphyrin-cored molecules, which can exhibit stronger intermolecular \( \pi-\pi \) stacking in the solid state, leading to a higher hole mobility and better photovoltaic performance. It is obvious that the meso-phenyl substituents with an almost orthogonal orientation relative to the porphyrin plane significantly prevent the intermolecular \( \pi-\pi \) stacking, as well as intermolecular charge transport.

Our recent work further demonstrated that the direct peripheral meso-alkyl substituents on the porphyrin ring could not only improve the solubility of small molecules in most organic solvents, but also control the film morphology and crystallinity, leading to an enhancement of charge transport.

To rigorously evaluate the effect of peripheral aromatic or aliphatic meso-substituents of the porphyrin ring on the light harvesting, solubility, morphology, exciton diffusion and dissociation, charge transport and collection, and ultimate PCE, three A–D–A structural type porphyrin-based small molecules were carefully designed and prepared. Typically, 3-ethylrhodanine as the terminal unit bridged by a phenylethynyl moiety with porphyrins \( \{5,15\text{-bis}(4\text{-dodecylxoyl})\text{-phenyl}\}_x\text{porphyrinato} \) zinc(u), \( \{5,15\text{-bis}(4\text{-dodecylxoyl})\text{-phenyl}\}_x\text{porphyrinato} \) zinc(u), and \( \{5,15\text{-bis}(2\text{-hexynyl})\text{-porphyrinato} \) zinc(u), afforded 4a, 4b and 4c, respectively (Scheme 1). Subsequently, their photovoltaic performances as donors were investigated systematically in conventional devices with a configuration of ITO/PEDOT:PSS/SM:PC71BM/PFN/Al (where PFN is poly[\( \{9,9\text{-bis}(3\text{-N,N-dimethylanilino})\text{-propyl}\}_2,7\text{-fluorene}\]-alt-2,7-[9,9-dioctylfluorene]]). Inverted devices of ITO/Ca/SM:PC71BM/MoO3/Ag were also fabricated and tested in the following studies.

2. Results and discussion

2.1 Synthesis and characterization

The synthetic route for 4a–c is shown in Scheme 1. It should be noted that the use of the zinc porphyrin complex instead of a porphyrin free base is necessary, due to the higher stability of the metal complex and it also helps to improve the photovoltaic properties of the OSC devices. The Sonogashira coupling of 2a–c with 4-ethyl-2,5-bis(hexyloxy)benzaldehyde produced the porphyrin intermediates 3a–c in good yields. The target compounds 4a–c were prepared by the Knoevenagel condensation of 3-ethylrhodanine with 3a–c, respectively. Although the solubility of 4a and 4b is not as good as 4c in organic solvents such as chloroform, THF, and toluene, all three \( \pi \)-conjugated small molecules could be readily processed in solution to form smooth and pinhole-free films using spin-coating technology.

2.2 Optical and electrochemical properties

The normalized UV-vis absorption spectra of 4a–c in \( \text{CH}_2\text{Cl}_2 \) solutions and spin-casted thin films are depicted in Fig. 1, and the relevant optical data including the wavelengths of the absorption maxima \( (\lambda_{\text{max}}) \), molar extinction coefficients \( (\epsilon) \), absorption edge wavelengths \( (\lambda_{\text{onset}}) \), and optical band gaps \( (E_g) \) are summarized in Table 1. As shown in Fig. 1, 4a in dilute \( \text{CH}_2\text{Cl}_2 \) solution shows a Soret band at 504 nm with a molar extinction coefficient \( \epsilon \) of \( 1.55 \times 10^5 \text{M}^{-1} \text{cm}^{-1} \) and a Q band at 682 nm with a molar extinction of \( 1.39 \times 10^5 \text{M}^{-1} \text{cm}^{-1} \). Additionally, 4b in \( \text{CH}_2\text{Cl}_2 \) solution presents a similar Soret band at 505 nm with a \( \epsilon \) of \( 1.61 \times 10^5 \text{M}^{-1} \text{cm}^{-1} \) and a bathochromically shifted Q band at 720 nm with a \( \epsilon \) of \( 1.53 \times 10^5 \text{M}^{-1} \text{cm}^{-1} \). As for meso-2-hexynonyl substituted 4c, a Soret band at 502 nm with a \( \epsilon \) of \( 1.95 \times 10^5 \text{M}^{-1} \text{cm}^{-1} \) and a Q band at 696 nm with a \( \epsilon \) of \( 1.87 \times 10^5 \text{M}^{-1} \text{cm}^{-1} \) were observed. Apparently, 4c exhibits much stronger absorption at both Soret and Q bands than 4a and 4b.

There is no significant changes in Soret bands due to minor electronic perturbations between the porphyrin ring and either meso-aliphatic or aromatic substituents. In comparison with
**Table 1** Optical and electrochemical data for 4a–c

| Comp. | $\lambda_{\text{max}}$/nm (CH$_2$Cl$_2$) (ε/10$^3$ M$^{-1}$ cm$^{-1}$) | $\lambda_{\text{max}}$/nm (film) | $\lambda_{\text{onset}}$/nm (film) | $E_{\text{on}}$ [V] | $E_{\text{HOMO}}$ [eV] | $E_{\text{LUMO}}$ [eV] | $E_{\text{opt}}$ [eV] |
|-------|---------------------------------|---------------------------------|---------------------------------|----------------|----------------|----------------|----------------|
| 4a    | 475 (1.55), 504 (1.73), 683 (1.39) | 537, 733                        | 779                             | 0.49           | −5.19          | −3.59          | 1.60           |
| 4b    | 484 (1.61), 505 (1.61), 720 (1.53) | 526, 726                        | 790                             | 0.45           | −5.15          | −3.60          | 1.55           |
| 4c    | 472 (1.64), 502 (1.95), 696 (1.81) | 520, 735                        | 780                             | 0.42           | −5.12          | −3.52          | 1.60           |

$^a$ HOMO levels were measured in DCM with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF) calibrated with ferrocene/ferrocinium (Fe/Fe$^+$) as an external reference. $^b$ The HOMO and LUMO levels were estimated by the following equation: $E_{\text{HOMO}} = -(4.70 + E_{\text{on}})$, $E_{\text{LUMO}} = E_{\text{HOMO}} - E_{\text{opt}}$. Optical band gap estimated from the formula of 1240/$\lambda_{\text{onset}}$, $\lambda_{\text{onset}}$ is the absorption onset of the film spectrum.

4a, the absorption maxima of the Q bands in 4b and 4c exhibit a significant red-shift of 38 and 14 nm, respectively, which indicates a stronger intramolecular charge transfer (ICT) between the donor and acceptor units in 4b and 4c. On the other side, their absorption maxima for both the Soret and Q bands in the thin films were significantly red-shifted, which indicates that a strong π–π intermolecular interaction exists in the solid state due to the optically active J-aggregation.

Cyclic voltammetry (CV) was performed to investigate the electrochemical properties of 4a-c and the electrochemical data are shown in Table 1. The HOMO energy levels of 4a-c were calculated to be −5.19, −5.15 and −5.12 eV, respectively. Furthermore, the optical band gaps ($E_{\text{g}}$) for 4a-c were estimated from the absorption spectra in the films with values of 1.60, 1.55 and 1.60 eV, respectively. Therefore the potential levels of the LUMO for 4a-c were obtained from $E_{\text{LUMO}} = E_{\text{HOMO}} - E_{\text{g}}$, with values of −3.59, −3.60 and −3.52 eV, respectively. The HOMO levels of 4a are located within the band gap of PC$_{61}$BM, while the LUMO levels are sufficiently high (around −3.5 eV) than that of PC$_{61}$BM (−4.0 eV). The results indicate that 4a-c are compatible with the commonly used acceptor material PC$_{61}$BM or PC$_{71}$BM in BHJ OSCs.

### 2.3 Photovoltaic properties

Subsequently, BHJ OSCs using 4a-c as donor materials were fabricated and tested under AM1.5 illumination, 100 mW cm$^{-2}$ in a device structure of ITO/PEDOT:PSS/SM:PC$_{61}$BM (or PC$_{71}$BM)/PFN/Al. Following the conventional practice for fabricating solution processed SM BHJ OSCs, the active layers were spin-coated from their chlorobenzene solutions with 1 vol% pyridine as an additive and a film thickness of approximately 80 nm was obtained. The optimized $J$–$V$ curves are reported in Fig. 2a, and the photovoltaic performances are summarized in Table 2. With the optimized weight ratio of 4a to PC$_{61}$BM at 1 : 1, the best but low PCE of 1.42% was obtained, together with a short circuit current ($J_{\text{SC}}$) of 6.44 mA cm$^{-2}$, an open-circuit voltage ($V_{\text{OC}}$) of 0.76 V, and a fill factor (FF) of 28.9%. The optimized weight ratio of 4b to PC$_{61}$BM was also found to be 1 : 1, yielding a moderate PCE of 4.55% with $V_{\text{OC}}$ of 0.80 V, $J_{\text{SC}}$ of 10.09 mA cm$^{-2}$ and FF of 56.3%. In contrast, the device based on 4c/PC$_{61}$BM (1 : 1, w/w) received an impressive PCE of 4.98%, with a $V_{\text{OC}}$ of 0.89 V, a FF of 52.1%, and a significantly higher $J_{\text{SC}}$ of 10.72 mA cm$^{-2}$ due to its good solubility, high light harvesting properties and strong π–π stacking intermolecular interaction.

To further optimize their photovoltaic performance in BHJ OSCs, PC$_{71}$BM was used as the electron acceptor for its higher absorption coefficient in the visible range. As expected, the active layers based on 4a-c/PC$_{71}$BM (1 : 1, w/w) yielded improved device performances with PCEs of 3.21%, 5.07% and 5.20%, and $J_{\text{SC}}$ of 7.2, 10.14, and 12.14 mA cm$^{-2}$ for 4a, 4b and 4c (Table 2), respectively. Specifically, the devices with PC$_{71}$BM as the acceptor exhibit an exceptionally higher $V_{\text{OC}}$ of 0.90 V, 0.90 V and 0.89 V for 4a, 4b and 4c, respectively. It’s not surprising that the morphologies and thus performance of state-of-the-art donor small molecules are sensitive to the choice of fullerene. Peng and co-workers reported that devices based on DPP-porphyrin small molecules performed better with PC$_{61}$BM as the acceptor rather than PC$_{71}$BM. During the device optimization, it was found that the performance of the cells based on 4c could be further improved by reducing the annealing time. When the annealing time is 5 min, the device yielded an impressive PCE of 6.11%, with a $J_{\text{SC}}$ of...
12.28 mA cm\(^{-2}\), a \(V_{OC}\) of 0.91 V, and a FF of 54.6%. Since 4c shows a much better solubility than 4a or 4b in organic solvent, the weight ratio of 4c to PC\(_{61}\)BM was further optimized to be 1 : 1.2, yielding the highest PCE of 7.70% with a \(V_{OC}\) of 0.91 V, a \(J_{SC}\) of 13.32 mA cm\(^{-2}\) and a FF of 63.6%. In general, the energy loss (\(E_{loss}\)), which connects \(E_g\) and \(V_{OC}\) together and is defined as \(E_{loss} = E_g - eV_{OC}\), is one of the most important parameters to evaluate solar cells. In this study, an exceptionally high \(V_{OC}\) of 0.91 V was obtained for the optimized cell based on 4c, in spite of a high energy loss of 0.69 eV. By comparison, Peng and his co-workers reported a DPP-porphyrin small molecule with a very low energy band gap of 1.37 eV and an open circuit voltage of 0.78 V obtained in BHJ OSCs, corresponding to a very low energy loss of 0.59 eV.\(^{26}\)

The external quantum efficiency (EQE) spectra of the optimized devices based on 4a–c are shown in Fig. 2b. The EQE curve of 4c/PC\(_{71}\)BM (w/w, 1 : 1.2) with 1% pyridine exhibits efficient photo-electron conversion efficiency from 400 to 800 nm, with the highest EQE value reaching 73% at 735 nm. The calculated \(J_{SC}\) integrated from the EQE for 4c is 13.32 mA cm\(^{-2}\). shows a mismatch of about 5% compared to the \(J_{SC}\) from the \(J-V\) measurement. In comparison, the EQE values of the devices based on 4a or 4b are below 50% in the range of 620–800 nm, resulting in lower \(J_{SC}\) values. This is also consistent with the weaker absorptions of 4a and 4b in solution, as compared to 4c. Definitely, the incorporation of the alkyl side chains could indeed improve significantly the photo-electron conversion efficiency.

To circumvent the degradation problem in the conventional structure, the inverted structure has been intensively investigated in polymer-based BHJ solar cells.\(^{33–37}\) Very recently, some SMs have also been explored and have performed well in inverted device architectures.\(^{38–41}\) Hence, an inverted architecture of ITO/Ca/SM:PC\(_{71}\)BM/MoO\(_3\)/Ag has been applied to 4c, which yielded a PCE of 7.55%, corresponding to a \(J_{SC}\) of 12.89 mA cm\(^{-2}\), a \(V_{OC}\) of 0.91 V, and a FF of 65.1% under the optimized conditions (Fig. 3 and Table 2). It should be noted that the inverted photovoltaic devices were processed and characterized under ambient atmosphere (see ESI†). Although the inverted structure shows a comparable performance to that of the conventional one, the former exhibits impressive stability with the same PCE of 7.53% measured after 3 days of storage in air and retains 83% of the original value even after storage in air for 30 days.

Table 2  Solar cell characteristics of the optimized solar cells based on 4a–c/PC\(_{71}\)BM (or PC\(_{61}\)BM)

| Device   | Additive     | Annealing time at 90 °C (min) | \(J_{SC}\) (mA cm\(^{-2}\)) | \(V_{OC}\) (V) | FF (%) | PCE (%) |
|----------|--------------|-----------------------------|----------------------------|---------------|--------|---------|
| 4a/PC\(_{61}\)BM\(^a\) | 1% pyridine  | 10                          | 6.44                       | 0.76          | 28.98  | 1.42    |
| 4a/PC\(_{71}\)BM\(^a\) | 1% pyridine  | 10                          | 7.20                       | 0.90          | 48.12  | 3.21    |
| 4b/PC\(_{61}\)BM\(^a\) | 1% pyridine  | 10                          | 10.09                      | 0.80          | 56.33  | 4.55    |
| 4b/PC\(_{71}\)BM\(^a\) | 1% pyridine  | 10                          | 10.14                      | 0.90          | 55.60  | 5.07    |
| 4c/PC\(_{61}\)BM\(^a\) | 1% pyridine  | 10                          | 10.72                      | 0.89          | 52.12  | 4.98    |
| 4c/PC\(_{71}\)BM\(^a\) | 1% pyridine  | 10                          | 12.14                      | 0.89          | 48.07  | 5.20    |
| 4c/PC\(_{71}\)BM\(^a\) | 1% pyridine  | 5                           | 4.84                       | 0.92          | 29.18  | 1.30    |
| 4c/PC\(_{71}\)BM\(^a\) | 1% pyridine  | 5                           | 12.28                      | 0.91          | 54.67  | 6.11    |
| 4c/PC\(_{71}\)BM\(^a\) | 1% pyridine  | 20                          | 12.22                      | 0.90          | 50.35  | 5.54    |
| 4c/PC\(_{71}\)BM\(^a\) | 1% pyridine  | 5                           | 13.32                      | 0.91          | 63.60  | 7.70    |
| 4c/PC\(_{71}\)BM\(^a\) | 1% pyridine  | 5                           | 6.26                       | 0.892         | 38.1   | 2.12    |
| 4c/PC\(_{71}\)BM\(^a\) | 1% pyridine  | 5                           | 12.89                      | 0.901         | 65.1   | 7.55    |
| 4c/PC\(_{71}\)BM\(^a\) | 1% pyridine  | 5                           | 12.87                      | 0.910         | 64.5   | 7.55    |
| 4c/PC\(_{71}\)BM\(^a\) | 1% pyridine  | 5                           | 12.87                      | 0.882         | 39.2   | 6.65    |
| 4c/PC\(_{71}\)BM\(^a\) | 1% pyridine  | 5                           | 12.53                      | 0.876         | 57.0   | 6.26    |

\(^{a}\) 4a–c/PC\(_{61}\)BM or 4a–c/PC\(_{71}\)BM with a 1 : 1 weight ratio in solar cells with conventional structures based on fresh cells. \(^{b}\) 4c/PC\(_{61}\)BM with a 1 : 1.2 weight ratio in solar cells with conventional structures based on fresh cells. \(^{c}\) 4c/PC\(_{71}\)BM with a 1 : 1.2 weight ratio in solar cells with inverted structures based on fresh cells. \(^{d}\) 4c/PC\(_{71}\)BM with a 1 : 1.2 weight ratio in solar cells with inverted structures with encapsulation based on aging for 3 days. \(^{e}\) 4c/PC\(_{71}\)BM with a 1 : 1.2 weight ratio in solar cells with inverted structures with encapsulation based on aging for 10 days. \(^{f}\) 4c/PC\(_{71}\)BM with a 1 : 1.2 weight ratio in solar cells with inverted structures with encapsulation based on aging for 30 days.
2.4 Morphology and mobility

To understand the effect of different peripheral substitutions on the porphyrin ring, the morphology of the active layers of 4a–c/PC71BM (1 : 1, w/w%) was investigated by tapping-mode atomic force microscope (AFM). Additionally, height and phase images were taken from the blend films as shown in Fig. 4. It should be noted that the blend films of 4a–c/PC71BM were prepared with 1% pyridine as an additive, using a procedure identical to that for the active layers in the devices. The values of root-means-square (RMS) roughness are 0.852, 0.780 and 0.567 nm for the blend films 4a–c/PC71BM, respectively. The lowest RMS roughness of 4c/PC71BM indicates that 4c has the best miscibility with PC71BM and may form a finer interpenetrating network to facilitate both exciton separation and charge transport. As expected, the blend film of 4c/PC71BM exhibits a better donor/acceptor interpenetrating network with much smaller phase separation domains (Fig. 4f), which is beneficial for efficient exciton dissociation and charge transporting, and should lead to an increased $J_{SC}$ and FF in BHJ OSCs.\textsuperscript{43,44} In contrast, surface relief and a larger domain size were observed for the 4a/PC71BM and 4b/PC71BM films, which indicates the poor film-forming characteristics due to the perpendicular aromatic peripheral substitutions on the porphyrin ring. Without a doubt, the unique characteristics of 10,20-bis(5,15-aryl) substituted porphyrin are expected to form blend films possessing more efficient intermolecular $\pi-\pi$ stacking and more suitable surface morphology for BHJ OSCs.

As shown in Fig. 5, the phase and height images were taken from the blend films of 4c/PC71BM (1 : 1.2, w/w%) in inverted devices as-casted and after annealing at 90 °C for 5 minutes. The values of the root-means-square (RMS) roughness are 4.48 and 0.88 nm for the blend films 4c/PC71BM, as-cast and after annealing, respectively. Without a doubt, annealing at an appropriate temperature is necessary for the formation of high quality films with nanoscale amorphous domains that produce efficient charge separation and improved solar cell performances.

Since the values of $J_{SC}$ and FF are generally reflected by the charge transport properties of the photoactive film, the hole mobilities of the porphyrin/fullerene blend films were measured for a device configuration of ITO/PEDOT:PSS/active layer/MoO$_3$/Al, and were estimated using the space charge limited current (SCLC) model. The $J-V$ characteristics of the polymers and the porphyrin/PC71BM blend films are shown in Fig. S1.\textsuperscript{†} The hole mobilities of the 4a–c/PC71BM blend films were determined to be 1.57 $\times$ 10$^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ (4a), 8.48 $\times$ 10$^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ (4b), and 2.18 $\times$ 10$^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ (4c). Obviously, all the 4a–c/PC71BM blend films show reasonably high hole mobilities appropriate for photovoltaic devices. Notably, the device based on 4c/PC71BM exhibits the highest mobility of about one order of magnitude higher than that based on 4a/PC71BM. This is consistent with the highest $J_{SC}$ values of 13.32 mA cm$^{-2}$ and the best photovoltaic performance based on the active layer of 4c/PC71BM (1 : 1.2, w/w%). Without a doubt, the enhanced charge transport property is ascribed to the stronger intermolecular $\pi-\pi$ stacking interaction and better surface morphology of the blend film of 5,15-dialkylated porphyrin-cored small molecule. At the same time, ultraviolet photoelectron spectroscopy (Fig. S2†) shows that the work functions of the annealed layer of ITO/PEDOT:PSS/4a–c/PC71BM decrease gradually from 3.75 eV for 4a, 3.66 eV for 4b, to 3.44 eV for 4c, which also accounts for the device efficiency improvement with the increasing $J_{SC}$ from 7.20 mA cm$^{-2}$ for 4a and 10.14 mA cm$^{-2}$ for 4b, to 12.14 mA cm$^{-2}$ for 4c (Table 2).\textsuperscript{46}

3. Conclusion

In summary, three new porphyrin-based small molecules 4a–c were prepared, in which 3-ethylrhodanine as a terminal electron deficient unit was introduced into aromatic and aliphatic 10,20-meso-substituted porphyrin rings as the central building block via the 5,15-meso-phenylethynyl linker. Although the aliphatic 10,20-bis(2-hexynonyl) substitution in 4c has little influence on the optical absorption in solution, it significantly changes the optical and crystallization properties of the films. Based on 4c/PC71BM (1 : 1.2, w/w%) which has stronger intermolecular $\pi-\pi$ stacking and more suitable surface morphology, the device possesses a much higher $J_{SC}$, corresponding to the highest PCE

![Fig. 4 Tapping mode AFM height (a–c) and phase images (d–f) of 4a/PC71BM, 4b/PC71BM, and 4c/PC71BM blend films of the best devices.](image1)

![Fig. 5 Tapping mode AFM phase images (a and b) and height (c and d) of 4c/PC71BM (1 : 1.2, w/w%) in the inverted devices.](image2)
of 7.70%. Moreover, the inverted structure based on 4c/PC71BM (1 : 1.2, w/w%) shows a comparable performance to that of the conventional one, and its stability was also investigated revealing the same PCE of 7.55% measured after 3 days of storage and retaining 83% of the original value even after storage in air for 30 days. The primary results demonstrate that porphyrin derivatives can play a more important role as donors in BHJ OSCs by the judicious optimization of their molecular structures and careful device engineering.

4. Experimental section

4.1 Materials and methods

3,5-Di(2-dodecyl)benzaldehyde, 4-octyloxybenzaldehyde, 2-hexyldecanal and 1,4-dibromo-2,5-bis(hexyloxy)benzaldehyde were prepared according to the literature procedures, and characterized by comparing their 1H NMR and 13C NMR spectra with those found in the literature.47 [6,6]-Phenyl-C61-butyric acid methyl ester (PC71BM) was purchased from Nano-C. All other reagents were used as received without further purification, unless stated otherwise.

4.2 General procedure for the preparation of 4a-c

To a solution of 3a-c (0.137 mmol) in CHCl3 (20 mL), two drops of piperidine and 3-ethylrhodanine (228.3 mg, 1.370 mmol) under argon. The reaction was quenched with water (30 mL) and extracted with CHCl3 (3 × 20 mL). The organic layer was dried over Na2SO4 and evaporated to dryness. The solid residue was purified first on a silica gel column and second by preparative thin layer chromatography using a CHCl3 as the eluent.

4a. 170.2 mg, 56% yield. 1H NMR (400 MHz, CDCl3, δ) 0.72–0.77 (m, 18H, CH3), 0.86–0.89 (m, 6H, CH3), 1.15–1.42 (m, 9H, CH2), 1.44–1.51 (m, 4H), 1.69–1.87 (m, 16H), 2.08–2.14 (m, 4H), 4.05–4.17 (m, 20H), 6.84 (s, 2H), 6.88 (s, 2H), 7.29 (s, 4H), 7.33 (s, 2H), 8.12 (s, 2H), 8.88 (d, J = 4.4 Hz, 2H, β-pyrrolic H), 9.65 (d, J = 4.8 Hz, 4H, β-pyrrolic H).

4b. 144.5 mg, 57% yield. 1H NMR (400 MHz, CDCl3, δ) 0.86–0.95 (m, 18H, CH3), 1.20–1.24 (m, 6H, CH3), 1.31–1.46 (m, 40H, CH2), 1.48–1.52 (m, 12H), 1.65–1.67 (m, 4H), 1.76–1.78 (m, 4H), 1.85–1.89 (m, 4H), 1.99–2.02 (m, 4H), 2.24–2.26 (m, 4H), 4.14–4.16 (m, 4H), 4.20–4.26 (m, 8H), 4.33–4.36 (m, 4H), 7.16 (s, 2H), 7.46 (d, J = 8.4 Hz, 4H), 7.91 (s, 2H), 8.34 (d, J = 8.4 Hz, 4H), 8.44 (s, 2H), 9.22 (d, J = 4.4 Hz, 2H, β-pyrrolic H), 10.26 (d, J = 4.8 Hz, 4H, β-pyrrolic H). MALDI-TOF (m/z): [M + H]+ calcd for C112H182N6O10S4Zn, 2206.5417; found, 2206.5417.

4c. 154.7 mg, 65% yield. 1H NMR (400 MHz, CDCl3, δ) 0.68–0.73 (m, 12H, CH3), 0.90–1.03 (m, 46H), 1.23–1.33 (m, 12H), 1.44 (m, 12H), 1.61 (m, 8H), 1.86–1.99 (m, 8H), 2.33 (m, 4H), 2.71 (m, 4H), 2.93 (m, 4H), 4.23 (m, 8H), 4.35 (d, J = 5.6 Hz, 4H), 5.15 (m, 2H), 7.08 (d, J = 6.0 Hz, 2H), 7.44 (m, 2H), 8.28 (d, J = 4.4 Hz, 2H), 9.54 (d, 2H), 9.62 (d, 2H), 9.82 (m, 4H). MALDI-TOF (m/z): [M + H]+ calcd for C140H198N6O10S4Zn, 1837.9050; found, 1837.9050.

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