Solar Cells

Subnaphthalocyanines as Electron Acceptors in Polymer Solar Cells: Improving Device Performance by Modifying Peripheral and Axial Substituents

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Abstract: A new class of subnaphthalocyanines bearing various peripheral and axial substituents have been synthesized for use as electron acceptors in solution-processed bulk-heterojunction polymer solar cells. The resulting solar cells exhibit modest photovoltaic performance with contributions from both the polymer donor and subnaphthalocyanine acceptor to the photocurrent.

Bulk-heterojunction (BHJ) polymer solar cells (PSCs) hold great promise as the next-generation photovoltaic technology due to their advantages, such as low-cost, flexibility, and compatibility with roll-to-roll processing and inkjet printing. Recently, tremendous progress has been achieved in this field with power conversion efficiencies (PCEs) in excess of 12%. In a BHJ-PSC, the core component is the active layer, in which the blend of an electron–donor and an electron–acceptor forms a phase separated morphology with a bicontinuous interpenetrating network. Although numerous electron donors including both conjugated polymers and small molecules have been extensively invented by chemists, the electron acceptors were dominated by fullerene derivatives in the past two decades. However, fullerene-based acceptors possess a few limitations, such as difficulty in synthesis and purification, low absorption coefficients, limited variability in the energy levels, and poor morphological stability in BHJ films. Encouragingly, efficient non-fullerene acceptors have been developed in recent years that can overcome the shortcomings associated with fullerene-based acceptors. The state-of-the-art PSCs built on non-fullerene acceptors produced remarkable PCEs over 13% in both single- and multi-junction devices, outperforming fullerene-based acceptors.

Despite many different n-type materials that were developed and assessed as acceptors in PSCs, two families of small molecular non-fullerene acceptors presently reach PCEs over 10% when blended with conjugated polymers. These are derivatives of aromatic diimides and donor–acceptor–donor (A–D–A) type molecules with large central fused rings. Nevertheless, the development of new non-fullerene acceptors beyond aromatic diimides and A–D–A molecules are also highly desired and may offer new properties. Recently, we and other groups demonstrated that subphthalocyanines (SubPcs) are promising non-fullerene acceptors for PSCs. SubPcs are aromatic chromophoric molecules with a boron at their inner cavity, a cone-shaped structure, and electron-transporting characteristics. These characteristics render SubPcs good electron acceptor property and solution processability. By using PTB7-Th as the electron donor, solar cells with a PCE up to 4% and an external quantum efficiency (EQE) approaching 60% have been achieved by a SubPc derivative with chlorine atom as both peripheral and axial substituent (SubPc-Cl₂).

Subnaphthalocyanines (SubNcs) are similar to SubPcs, but offer extended conjugation in the peripheral cone of the molecule, becoming an important family of chromophores that exhibit outstanding photophysical properties showing strong electronic absorption and high fluorescence quantum yields. Historically, SubNcs have been used as electron acceptors in vacuum-evaporated solar cells, reaching an impressive PCE of 8.4%. However, SubNcs have never been tested as either
donors or acceptors in solution-processed BHJ solar cells. Herein, we report five SubNcs bearing different peripheral and axial substituents as electron acceptors in BHJ solar cells for the first time. Through the modification of the peripheral and axial substituents, the energy levels and the aggregation and crystallization behavior, and consequently, the photovoltaic device performance of the molecule can be tuned. A maximum PCE of 1.09% has been achieved for SubNc-F$_{12}$-OPhBu demonstrating the ability of SubNcs to act as electron acceptor in BHJ PSC. This work paves the way to a new family of non-fullerene acceptors for BHJ PSCs through rational molecular modification.

The structure of the new SubNcs is shown in Scheme 1. The motivation for the design of these molecules starts from SubPc-Cl$_{12}$-Cl, which is our previously developed successful SubPc-based acceptor.$^{[9a]}$ The related SubNc is SubNc-Cl$_{12}$-Cl, which has the same peripheral and axial substituents. More peripheral chlorine atoms were introduced onto SubNc-Cl$_{12}$-Cl to downshift the lowest unoccupied molecular orbital (LUMO) level and to obtain acceptor character.

Following up on SubNc-Cl$_{12}$-Cl, another two SubNcs were synthesized by cyclotrimerization reaction of appropriate naphthalene-2,3-dicarbonitrile precursors, namely, SubNc-(SO$_2$Pent)$_{12}$-Cl and SubNc-F$_{12}$-Cl. Axial substitution of the corresponding SubNc-triflate derivative by reaction with tert-butylphenol afforded SubNc-Cl$_{12}$-OPhBu and SubNc-F$_{12}$-OPhBu, respectively. The synthetic procedures are shown in the Supporting Information. The solubility of the parent SubNc-Cl$_{12}$-Cl derivative is extremely poor in organic solvents, and hence, further characterizations were performed only on the other four SubNcs. X-ray diffraction analysis unequivocally determined the structure of SubNc-F$_{12}$-Cl, confirming the cone-shape structure characteristic of the subporphyrinoid family, as well as its tendency to build a columnar stacking organization (Figure 1, see the Supporting Information, selected crystallographic data).

The optical absorption spectra of the SubNcs in films and in solutions are shown in Figure 2a and Figure S4 (see the Supporting Information), respectively. SubNc-F$_{12}$-Cl and SubNc-F$_{12}$-OPhBu exhibit very similar absorption profiles, indicating a small influence of the axial substituent. More pronounced fluctuations in absorption spectra were observed when the peripheral substituents were changed, as was evidenced by the differences between SubNc-F$_{12}$-Cl and SubNc-(SO$_2$Pent)$_{12}$-Cl, and between SubNc-F$_{12}$-OPhBu and SubNc-Cl$_{12}$-OPhBu. In particular, SubNc-(SO$_2$Pent)$_{12}$-Cl shows the most redshifted absorption among all SubNcs. This indicates that the electronic coupling of the peripheral substituent to the SubNc framework is stronger than that of the axial substituent. Overall, SubNcs have redshifted and broader absorption compared to SubPcs, which can contribute to more efficient light absorption in solar cells.$^{[9c]}$ The fluorescence quantum yields ($\Phi_f$) were also measured in toluene,$^{[12c]}$ being around 0.20–0.30. The similarity of these values with the reported by Bender et al. suggest a same photoelectronic behavior of SubNcs.$^{[12c]}$ Notably, SubNcs exhibit a lower $\Phi_f$ than SubPcs, suggesting shorter exciton lifetimes for SubNcs.$^{[9c]}$ Electrochemical properties and frontier orbital levels of the SubNcs were studied by cyclic voltammetry (CV) in tetrahydrofuran (THF). The CV data are presented in Figure S6 (see the Supporting Information) and the relevant frontier orbital energy levels are collected in Figure 2b and summarized in Table 1. The LUMO and highest occupied molecular orbital (HOMO) energy levels were estimated from the reduction potentials obtained by CV measurements and optical band gap ($E_g$) values. Interestingly, the axial substituent has important influence on both the LUMO and HOMO levels of the SubNcs, whereas the peripheral substituents exert only significant influence on the LUMO levels but not on the HOMO levels of the SubNcs. For example, changing the axial substituent from SubNc-F$_{12}$-Cl to SubNc-F$_{12}$-OPhBu results in a consid-

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**Figure 1.** X-ray crystal structure of SubNc-F$_{12}$-Cl (CCDC 1583669 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre). (a) Molecular structure showing thermal ellipsoids at the 50% probability level. (b) Column packing along the $b$ axis.

**Figure 2.** SubNcs: (a) optical absorption spectra of their films. (b) Their energy levels.
able up-shifting (\(>\) 0.1 eV) of both LUMO and HOMO levels. On the contrary, the change of peripheral substituent (SubNc-\(\text{F}_{12}\)-Cl versus SubNc-(SO\(_2\)Pent)\(_{12}\)-Cl, and SubNc-\(\text{F}_{12}\)-OPh\(_{Bu}\) versus SubNc-Cl\(_2\)-OPh\(_{Bu}\)) cause about 0.1 eV fluctuation of LUMO levels but a much smaller fluctuation of HOMO levels. Nevertheless, all SubNcs possess deep-lying LUMO levels (below \(\approx\) 3.76 eV), endowing them with electron-accepting character.

The photovoltaic properties of the SubNcs acceptors were evaluated in solar cells in combination with PTB7-Th as a low-band-gap donor polymer in an ITO/ZnO/PTB7-Th:SubNc-X/MoO\(_3\)/Ag device structure. The charge transport and recombination of charge carriers in the blend films of PTB7-Th:SubNc were investigated. Hole mobilities \((\mu_h)\) and electron mobilities \((\mu_e)\). Table S3 in the Supporting Information were estimated from single-carrier PTB7-Th:SubNc devices by fitting the \(J-V\) data (Figure S7 in the Supporting Information) to a space-charge-limited current model, resulting in a \(\mu_h \approx 10^{-4}\) and a \(\mu_e \approx 10^{-6}\) \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\) for all four acceptors. Bearing in mind that both the \(\mu_h\) and \(\mu_e\) of PTB7-Th-fullerene blends are usually \(\approx 10^{-5}\) \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\), the greatly reduced electron-transport capability of the PTB7-Th:SubNc films is likely causing the low \(J_{sc}\) and low FF. Moreover, the transport of hole and electron in these films is highly imbalanced as suggested by the high \(\mu_h/\mu_e\) value of >100 for all SubNc-based acceptors.

Table 1. Optical properties and energy levels of the SubNcs.

<table>
<thead>
<tr>
<th>SubNc-X</th>
<th>(\lambda_{\text{max}}) [nm]</th>
<th>(E_{\text{opt}}^{\text{AM1.5G}}) [eV]</th>
<th>HOMO [eV]</th>
<th>LUMO [eV]</th>
<th>(\psi_j)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{SO}<em>2\text{Pent}</em>{12})-Cl</td>
<td>677</td>
<td>682</td>
<td>1.80</td>
<td>-5.79</td>
<td>-3.99</td>
</tr>
<tr>
<td>(\text{F}_{12})-Cl</td>
<td>646</td>
<td>662</td>
<td>1.89</td>
<td>-5.78</td>
<td>-3.89</td>
</tr>
<tr>
<td>(\text{Cl}<em>{12})-OPh(</em>{Bu})</td>
<td>644</td>
<td>666</td>
<td>1.88</td>
<td>-5.72</td>
<td>-3.84</td>
</tr>
<tr>
<td>(\text{F}<em>{12})-OPh(</em>{Bu})</td>
<td>640</td>
<td>650</td>
<td>1.91</td>
<td>-5.67</td>
<td>-3.76</td>
</tr>
</tbody>
</table>

(b) Corresponding EQE spectra.

Table 2. Solar cell characteristics and charge carrier mobilities of PTB7-Th:SubNc devices.

<table>
<thead>
<tr>
<th>SubNc-X</th>
<th>(J_{sc}) [mA cm(^{-2})]</th>
<th>(V_{oc}) [V]</th>
<th>FF</th>
<th>PCE [%]</th>
<th>EQE(_{max})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{SO}<em>2\text{Pent}</em>{12})-Cl</td>
<td>2.9</td>
<td>0.58</td>
<td>0.42</td>
<td>0.71</td>
<td>0.18</td>
</tr>
<tr>
<td>(\text{F}_{12})-Cl</td>
<td>3.4</td>
<td>0.52</td>
<td>0.46</td>
<td>0.82</td>
<td>0.20</td>
</tr>
<tr>
<td>(\text{Cl}<em>{12})-OPh(</em>{Bu})</td>
<td>3.2</td>
<td>0.62</td>
<td>0.44</td>
<td>0.86</td>
<td>0.21</td>
</tr>
<tr>
<td>(\text{F}<em>{12})-OPh(</em>{Bu})</td>
<td>3.9</td>
<td>0.73</td>
<td>0.38</td>
<td>1.09</td>
<td>0.25</td>
</tr>
</tbody>
</table>

(a) Determined by integrating the EQE spectrum with the AM1.5G spectrum.

Figure 3. (a) \(J-V\) curves of the PTB7-Th:SubNc solar cells in dark (dashed lines) and under illumination (solid lines). (b) Corresponding EQE spectra.

The transport and recombination of charge carriers in the blend films of PTB7-Th:SubNc were investigated. Hole mobilities \((\mu_h)\) and electron mobilities \((\mu_e)\). Table S3 in the Supporting Information were estimated from single-carrier PTB7-Th:SubNc devices by fitting the \(J-V\) data (Figure S7 in the Supporting Information) to a space-charge-limited current model, resulting in a \(\mu_h \approx 10^{-4}\) and a \(\mu_e \approx 10^{-6}\) \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\) for all four acceptors. Bearing in mind that both the \(\mu_h\) and \(\mu_e\) of PTB7-Th-fullerene blends are usually \(\approx 10^{-5}\) \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\), the greatly reduced electron-transport capability of the PTB7-Th:SubNc films is likely causing the low \(J_{sc}\) and low FF. Moreover, the transport of hole and electron in these films is highly imbalanced as suggested by the high \(\mu_h/\mu_e\) value of >100 for all SubNc-based acceptors. The build-up of space charge due to the imbalanced hole/electron transport further increased the possibility of bimolecular charge recombination, an important factor resulting in photocurrent loss and poor FF. The strong bimolecular recombination was further evidenced by the large difference between the EQE measured with light bias (EQE\(_{bias}\)) and without light bias (EQE\(_{nobias}\); Figure S8 in the Supporting Information). The average values for \(\rho = \text{EQE}_{bias}/\text{EQE}_{nobias}\) (Figure 4) can be used to evaluate the bimolecular recombination efficiency through \(\eta_{BR} = 1 - \rho\). Clearly, the low \(\rho\) values indicate substantial bimolecular recombination. State-of-the-art PSCs often show a \(\rho\) value approaching unity. The \(\rho\) values of these PTB7-Th:SubNc solar cells are all lower than 0.85, suggesting significant bimolecular recombination losses, even at short circuit. The extensive bimolecular recombination in the maximum power point and at short circuit was also evidenced by the steady increase of current density of illuminated solar cells under reverse bias (Figure 3a), in which the enhanced electric field promotes transport of the slower carriers. The fact that the dark current does not increase to the same extent under reverse bias excludes the possibility that the increased current density under illumination is due to a low shunt resistance. Such behavior is
often found in bulk-heterojunction blends with an intimately mixed morphology and one slow carrier.\textsuperscript{[16]}

The morphology of PTB7-Th:SubNc blend films was studied by transmission electron microscopy (TEM). In TEM data, all PTB7-Th:SubNc blends exhibit rather homogeneous films without noteworthy phase separation (Figure 5). In such intimately mixed blends, charge separation is impeded because of the lack of pure domains. It is well recognized that pure domains promote charge dissociation from the donor/acceptor interface, whereas impure domain often results in serious geminate recombination.\textsuperscript{[17]} Moreover, charge transport is blocked in such intimately mixed blends due to lack of continuous pathways for the transport of the photogenerated charge carriers, causing accumulation of space charge and recombination losses. Collectively, the low-charge mobility, imbalanced hole/electron transport, and the suboptimal BHJ morphology are factors that contribute to recombination losses and that limit the $J_{sc}$ and FF of PTB7-Th:SubNc solar cells.

Notably, the highest PCE of SubNcs is much lower than that of our previously reported successful acceptor SubPc-CI$_6$-Cl (1.09\% versus 4.0\%).\textsuperscript{[9a]} This can be rationalized considering the following aspects. First, SubPc-CI$_6$-Cl has a small chlorine atom in the axial position, whereas SubNc-F$_{12}$-OPh$^t$Bu, which provided the best solar cells, has a bulky OPh$^t$Bu group in the axial position. The small axial chlorine atom favors the formation of head-to-tail columnar stacks and thus prompts charge transport, whereas the bulky OPh$^t$Bu group precludes this behavior and thus deteriorates charge transport.\textsuperscript{[9a]} Second, the shorter exciton lifetimes of SubNcs compared to SubPc-CI$_6$-Cl as suggested by the lower fluorescence quantum yields is limiting the fraction of excitons that reach the donor/acceptor interface, in which the exciton dissociates, reducing the EQEs of the SubNcs-based solar cells. Third, the SubNcs show redshifted absorption spectra with respect to SubPcs,\textsuperscript{[9a]} which have a considerable spectral overlap between SubNcs and the polymer donor PTB7-Th.

In conclusion, boron subnaphthalocyanines bearing different peripheral and axial substituents have been synthesized and utilized as electron acceptors in BHJ polymer solar cells for the first time. Due to their acceptor character, their blends with PTB7-Th, a narrow band gap conjugated polymer, exhibit photovoltaic performance with contributions from both the polymer donor and the SubNc acceptor to the photocurrent. Nevertheless, the highest PCE of the SubNc-based solar cells is only 1.09\%. The main limitations of these SubNc-based solar cells is their low $J_{sc}$ and FF, which is a combined result of low charge mobility, imbalanced hole/electron transport, and a suboptimal BHJ morphology contributing to recombination losses. Therefore, the future research involving subnaphthalocyanines should focus on improving electron mobility, and controlling morphology of the blends to avoid geminate recombination and reduce bimolecular recombination losses.

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Conflict of interest

The authors declare no conflict of interest.