The influence of molecular geometry on photophysical properties and self-assembly of phthalimide end-capped thiophene-based organic molecules

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ABSTRACT

The synthesis of π-conjugated organic small molecules with n-octyl substituted thiophene phthalimide end-capping units have been reported. A combination of absorption and emission spectroscopy, cyclic voltammetry, ultraviolet photoelectron spectroscopy, density functional theory calculations and atomic force spectroscopy were used to elucidate the impact of molecular dimensionality on photophysical properties and self-assembly.

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1. Introduction

Organic π-conjugated materials offer a platform for a broad range of optical and electronic applications such as light-emitting diodes, organic photovoltaics, and organic field-effect transistors [1–6]. This is mainly attributed to their optoelectronic characteristics, low fabrication costs and ease of processing [7–9].

Key geometries of organic semiconductors realized by researchers are propeller or pin-wheel architectures (often referred as star-shaped) [10–14] and non-planar, dimeric scaffolds [15–17]. These architectures showed superior solar cell performance over planar structures due to their tendency to suppress molecular aggregation which result in formation of small domains on the order of exciton diffusion length [14,16]. Zhan and co-workers reported a star-shaped perylene diimide (PDI) electron acceptor with triphenylamine core for solution processed organic solar cells. The achieved high power conversion efficiency (PCE, ~3.3%) in bulk hetero-junction (BHJ) solar cells was explained by the quasi-three-dimensional structure that facilitate miscibility with the donor [14]. Non-planar PDI dimer showed promising performance in BHJ solar cell as electron acceptor with ~4% PCE [16]. Very recently, a three dimensional molecular structure based on tetraphenylethylene core with four PDI units was exploited as an electron acceptor to construct a non-fullerene organic solar cell with a high PCE of 5.53% [18].

Recently, our group has reported the optimized synthesis and opto-electronic characteristics of phthalimide end-capped oligothiophene small molecules that bear terminal alkyl chains [19,20]. When combined with poly(3-hexylthiophene) (P3HT) in BHJ solar cell, bithiophene core molecule (PthTh2Pth (1), Fig. 1A) exhibited a high open circuit voltage (VOC ~0.94 V) and low PCE (~0.2%). The low efficiency was attributed to the tendency of PthTh2Pth to undergo crystallization from donor–acceptor blends, which result in formation of micron-size domains compared to exciton diffusion length [21]. So, improvement the molecular design of PthTh2Pth still needed toward respectable PCE values [22]. In this study, we have investigated the influence of molecular geometry of small molecules based on phthalimide thiophene building block on the photophysical properties and molecular self-assembly which are limiting factor in achieving high efficiency organic solar cells.

2. Results and discussion

Similar to PthTh2Pth [19,20], (PthTh)3BZ (2) and (PthTh)3TPA (3) (Fig. 1B and C, respectively) were synthesized using a
combination of Stille and direct hetero-arylation C–C bond forming reactions. Full synthetic and characterization data of compounds 2 and 3 are provided in the electronic supplementary information.

The photophysical properties of compounds 1, 2 and 3 were measured by UV–vis and fluorescence spectroscopy. Fig. 1 shows the normalized absorption and emission spectra of the three compounds in chloroform solution and their optical absorption in thin films. In solution, PthTh₂Pth exhibits absorption and emission maxima at 420 and 510 nm, respectively. The absorption maximum is blue-shifted to 385 nm after transitioning from solution into thin-film, due to the tendency of PthTh₂Pth to self-assemble in an ordered face to face orientation (H-aggregates) [19,20]. The absorption maxima of (PthTh)₃BZ and (PthTh)₃TPA in thin films are red-shifted compared with those obtained in solution (390 versus 380 nm and 445 versus 433 nm, respectively). This can be explained by the improved molecular aggregation in solid state.

In comparison to PthTh₂Pth, the absorption maximum of (PthTh)₃BZ in solution is shifted hypsochromically (380 versus 420 nm). This is attributed to the meta-substituents at the benzene ring which result in reducing the π-conjugation length [23,24]. On the other hand, the increased conjugation length along the TPA core molecule compared to PthTh₂Pth and (PthTh)₃BZ led to a bathochromic shift in its absorption maximum in solution. Interestingly, the progressive increase in Stokes shift of compounds 1, 2 and 3 (90, 94, and 160 nm, respectively) suggests a less energetic structural reorganization upon photoexcitation in solution.

The electrochemical properties of PthTh₂Pth, (PthTh)₃BZ and (PthTh)₃TPA were investigated using voltammetry (CV), ultraviolet photoelectron spectroscopy (UPS) and density functional theory (DFT). The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the three compounds are presented in Table 1. CV measurements indicated that the three compounds exhibit similar LUMO levels, which means equal electron injection ability. The higher HOMO level of (PthTh)₃TPA compared to the other two compounds is explained by the improved molecular aggregation in solid state.

Table 1

<table>
<thead>
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<th>CV</th>
<th>UPS/Optical</th>
<th>DFT</th>
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<tbody>
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<td></td>
<td>HOMO</td>
<td>LUMO</td>
<td>$E_g$</td>
</tr>
<tr>
<td>PthTh₂Pth, (1)</td>
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<td>−3.10¹⁰</td>
<td>2.45¹⁰</td>
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<tr>
<td>(PthTh)₃BZ, (2)</td>
<td>−5.60</td>
<td>−3.03</td>
<td>2.57</td>
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<tr>
<td>(PthTh)₃TPA, (3)</td>
<td>−5.11</td>
<td>−3.05</td>
<td>2.06</td>
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</table>

Fig. 1. Chemical structures and absorption–emission spectra in solution and thin films of A: 5,5′-(2,2′-bithiophene)-5,5′-diylbis(2-octylisoindoline-1,3-dione) (PthTh₂Pth), B: 5,5′,5″-(5,5′,5″-(benzene-1,3,5-triy)tris(thiophene-5,2-diyl)tris(2-octylisoindoline-1,3-dione) ((PthTh)₃BZ) and C: 5,5′,5″-(5,5′,5″-(nitrilotris(benzene-4,1-diyl))tris(thiophene-5,2-diyl)tris(2-octylisoindoline-1,3-dione) ((PthTh)₃TPA).
by the significant contribution of the electron rich triphenyl amine (TPA) moiety to the HOMO orbital (*vide infra*), which results in a relatively low optical band gap compared to PthTh₂Pth and (PthTh)₃BZ.

The UPS measurements, which are more relevant toward the usage of organic semiconductors in optoelectronic applications, indicated that compound 2 exhibits a slightly deeper HOMO compared to compounds 1 and 3. In comparison with the data obtained by the CV measurements, the energy of the frontier molecular orbitals estimated from the UPS measurements are found to be lower in energy and following a similar trend [25]. This difference in energy is justified by the different procedures followed to evaluate the orbitals energy, which influence significantly the obtained results [26,27]. DFT calculations showed a similar trend to the experimental data. The differences between the two sets of data is mainly attributed to the lower accuracy of DFT in predicting the HOMO–LUMO energies [28].

Depictions of the HOMO and LUMO frontier molecular orbitals obtained from DFT calculations (Fig. 2) show fully delocalized orbitals over the entire framework of PthTh₂Pth. The orbital localization throughout the backbone of (PthTh)₃BZ and (PthTh)₃TPA are highly dependent on the identity of the central core unit.

The LUMO and HOMO orbitals of (PthTh)₃BZ are centered at the phenyl core unit, but they are not fully delocalized over the three substituted phthalimide terminals. On the other hand, (PthTh)₃TPA possess a highly localized LUMO and HOMO orbitals centered on the substituted phthalimide terminals and the TPA core, respectively. In this regard, the nitrogen lone pair act in a “donating fashion” and result in a less low lying HOMO.

Atomic force microscopy (AFM) is a useful technique for investigating the morphology of solid-supported films at the nanometer scale. Fig. 3 shows AFM images of neat films comprised of PthTh₂Pth, (PthTh)₃BZ and (PthTh)₃TPA and their blends with P3HT. As shown in Fig. 3A, PthTh₂Pth tend to form stick-like shape domains that had lengths ranging from ~3 to 5 μm. Film of (PthTh)₃BZ (Fig. 3B) consists of semi-circular domains of ~0.5–1 μm in diameter. Images of neat films comprised of (PthTh)₃TPA (Fig. 3C) indicate the formation of micron size, flower-shaped domains. The correlation of the obtained domain shapes with the molecular dimensionality of the investigated compounds is intuitive, where the stick-like shape, the semi-circular and the flower-shaped domains represent the one, two and three dimensional analogous of compounds 1, 2 and 3 respectively. So, the huge morphological differences displayed by the neat films of the
three compounds emphasize how structural differences in molecular shape impact the self-assembly of small organic molecules in solution processed thin films. Blending P3HT with PthTh2Pth or (PthTh)5BZ (Fig. 3D and E, respectively) diminish the aggregation tendency of the two molecules. The interfacial organization of P3HT-(PthTh)5TPA composite (Fig. 3F) indicates the formation of micron-size interconnected stands of either component or their mixture. Further studies still needed to examine the impact of films processing strategies on the microstructure of donor–acceptor composites with an ultimate goal of obtaining an interpenetrating phase separated donor–acceptor domains toward high device performance.

3. Conclusions

We have reported on the design and synthesis of three π-conjugated small molecules based upon n-octyl substituted thiophene phthalimide end-capping terminals. The topology of the bithiophene core molecule had an influence on the optical properties through the localization/delocalization of frontier molecular orbitals over the molecular backbone. Atomic force microscopy measurements indicated the profound effect of molecular dimensionality on aggregation properties in thin films, which can be exploited to optimize films morphology for optical or electronic applications.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2015.05.136.

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