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REVIEW ARTICLE

Conjugated dendritic oligothiophenes for solution-processed bulk heterojunction solar cells

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Abstract This mini-review summarizes the recent achievements of developing conjugated dendritic oligothiophenes (DOT) for use in solution-processed bulk heterojunction (BHJ) solar cells. These DOTs are structurally defined molecules with relatively high molecular weight. Therefore, this novel class of thiophene based material possesses not only some advantages of oligomers, such as defined and monodispersed molecular structure, high chemical purity, but also some characteristics of polymers, for example, good solution-processability. In addition, the step-by-step approach of its synthesis allows precise functionalization of dendritic backbones with desired moieties, which is helpful to finely tune the optical and electronic properties of materials. Power conversion efficiencies (PCE) of BHJ solar cells were achieved up to 2.5% when functionalized thiophene dendrimers were used as electron donor and electron acceptor was a fullerene derivative. These results indicated that dendritic oligothiophenes are a novel class of the materials of electron donor for solution-processed organic solar cells.

Keywords conjugated dendrimers, dendritic oligothiophenes (DOT), organic semiconductors, bulk heterojunction (BHJ) solar cells

1 Introduction

The issues of climate control and the world's future energy demands are powerful drivers for the development of alternative sustainable energy sources. Solution-processed polymer solar cell or bulk heterojunction (BHJ) solar cell has been considered as one of the most promising renewable energy technologies due to its light-weight, flexible shape, versatile materials synthesis and device fabrication schemes, and potential of large-scale industrial production [1]. The key component of a BHJ solar cell is the photoactive layer comprised of a p-type conjugated polymer as electron donor and an n-type semi-conductor (usually is a fullerene derivative) as electron acceptor. Within this photoactive layer, nano-scale phase separation occurs between donor and acceptor materials, providing a donor/acceptor (D/A) heterojunction structure, whereby photo-induced charge separation occurs [2,3]. The realization of high efficiency of polymer solar cells depends on the light harvesting ability and charge carrier mobility of the materials [4], as well as the nano-scale morphology of the blended thin film [5].

In respect of p-type semiconducting polymers for use in BHJ solar cells, poly(3-hexylthiophene) (P3HT) has been the most prominent materials for its favorable crystalline property and high charge carrier mobility [6]. However, P3HT has a mismatched absorption band to solar emission spectrum. P3HT absorbs photons with energy higher than 1.9 eV, which limits the efficiency of 6% for P3HT: $PC_{61}BM$ based devices [6,7]. Thus, new polymers with improved light harvesting ability, i.e., with reduced optical band gap E_g, emerged in the last few years. One of the strategies to red-shift the absorption spectrum is to introduce electron donating (D) and electron accepting (A) units into the conjugated backbone [4,8]. Novel low band gap polymers have been successfully developed, and efficiencies of 5.5%–7.4% have been reported very recently (see Fig. 1 for the chemical structure of these polymers) [9–13].

In parallel to π-conjugated polymers, development of structure-defined small molecules or oligomers for use in BHJ solar cells has also attracted much attention recently [14–23]. In comparison with polymers, oligomers have certain advantages, such as defined chemcial structure, high purity, and consequent better reproducibility in device application. Nguyen et al. recently reported a diketopyrrolopyrrole (DPP) derivative DPP(TBFu)2 (Fig. 1), which shows narrow bandgap of ca. 1.8 eV and a broad visible

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absorption spectrum. High power conversion efficiency of 4.4% was achieved for a BHJ device using DPP(TBFu)2 as electron donor and $PC_{71}BM$ as acceptor [23].

Dendrimer belongs to a class of macromolecules combining both advantages of polymers and oligomers [24–26]. In respect of dendrimers for organic electronic applications, all-thiophene dendrimers (DOT) developed recently is the most representative examples [27–30]. Unlike conventional dendrimers with flexible backbones, these thiophene dendrimers are structurally rigid and shape-persistent, therefore they are materials with potential isotropic properties [31]. In addition, these structurally defined molecules can be further functionalized with various functional groups at different positions to tune optical and electronic properties [32]. They can serve as excellent building blocks for constructing novel thiophene based materials for organic electronic applications. In this mini-review, the recent progress in synthesis and functionalization of dendritic oligothiophene based molecules will be summarized. Optical properties and applications of these materials in solution-processed BHJ solar cells will be also discussed. Results indicated that dendritic oligothiophenes are a novel class of electron donor materials for use in solution-processed organic solar cells.

2 Original all-thiophene dendrimers

Advincula and coworkers reported the first synthesis of all-thiophene dendrons and dendrimers up to a 30-mer (Fig. 2) [27,28]. In this pioneering work, n-hexyl groups were used as periphery protecting groups, and generation thiophene dendrons (3T, 7T, and 15T in Fig. 2) were built up by palladium-catalyzed Stille coupling reactions in a convergent approach. The corresponding dendrimers were synthesized by oxidative homocoupling reaction (for 14T) or coupling of the stannylated dendrons with a bithiophene core (for 14T-2 and 30T). These thiophene dendrons and dendrimers show broadband absorption over 300–550 nm owing to the existence of multiple π-conjugation units [28]. However, no application of these materials in BHJ solar cells was reported.

Recently, our research group developed a new synthetic strategy to higher generation thiophene dendrimers [29]. By using trimethylsilyl (TMS) as protecting groups, all-thiophene dendrons and dendrimers up to a fourth generation (a 90-mer) have been successfully synthesized (Fig. 3). Unlike Advincula's dendrimer, the TMS protecting groups in these novel all-thiophene dendrimers can be easily removed with tetrabutylammonium fluoride

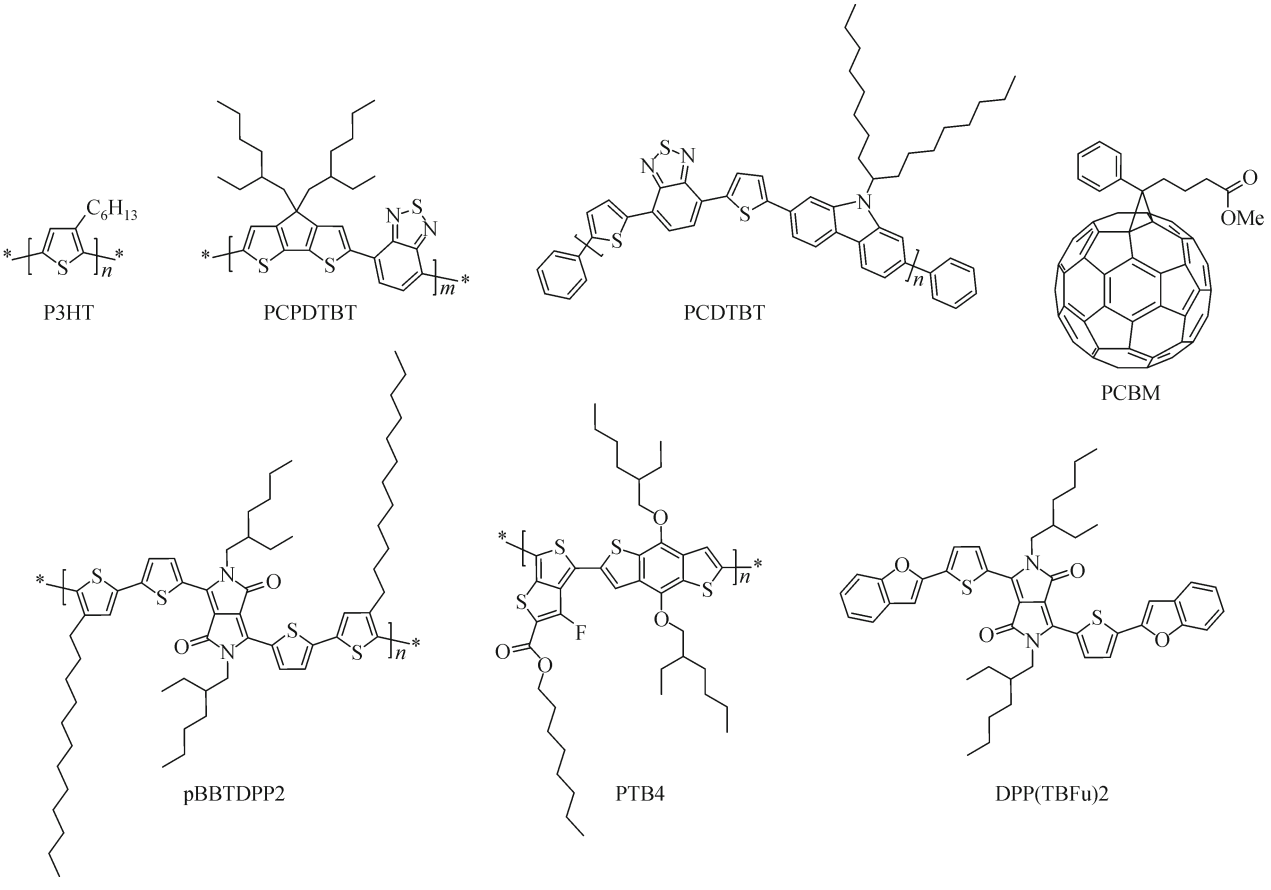

Fig. 1 Examples of thiophene based polymers and oligomers for use in solution-processed bulk heterojunction solar cells

(TBAF), yielding "pure" all-thiophene dendimers (Fig. 3, R = H) [29]. Surprisingly, these "pure" thiophene dendrimers are highly soluble in organic solvents, although there is no solublilizing group. Similar to Advincula-type thiophene dendrimers, these all thiophene dendrons and dendrimers show broad and featureless absorption spectra over 300–550 nm. Optical band gaps (E_g) of 2.5–2.2 eV were determined for these materials depending on the size of the molecule [29,33].

Solution-processed bulk heterojunction solar cells with a standard device structure of ITO/PEDOT:PSS/DOT:PCBM/LiF/Al were fabricated and tested, where thiophene dendrimer serves as electron donor and fullerene derivative PCBM serve as electron acceptor [33]. For all devices a gratifying high open circuit voltage V_{OC} of around 1.0 V has been found, as well as appreciable short-circuit currents J_{SC}, fill factors *FF*, external quantum (EQE) and power conversion efficiencies η up to 1.72% (Table 1) [33]. In comparison with that of well established P3HT:$PC_{61}BM$ solar cell, the DOT based devices are superior with respect to V_{OC}, but give lower J_{SC} and *FF*. The lower J_{SC} can be explained, at least partially by the modest match of the absorption of DOTs with the solar spectrum, which is evidenced by the photocurrent response (EQE) that maximizes for blue light (Fig. 4).

Close analysis of the device performance revealed general trends with respect to device performance related to molecular architecture (dendrons versus dendrimers), generation, and periphery group (with or without TMS-protecting groups). In general, the higher generation compounds show better device performance; dendrimers give superior results compared to dendrons as well as non-protected compared to protected derivatives. Experimentally, the hort-circuit current J_{SC} correlates linearly with the estimated number of absorbed solar photons (Fig. 5). In polymer solar cells, the weight ratio is usually used to describe the proportion between donor and acceptor materials. Since the molecular structures of dendrimers

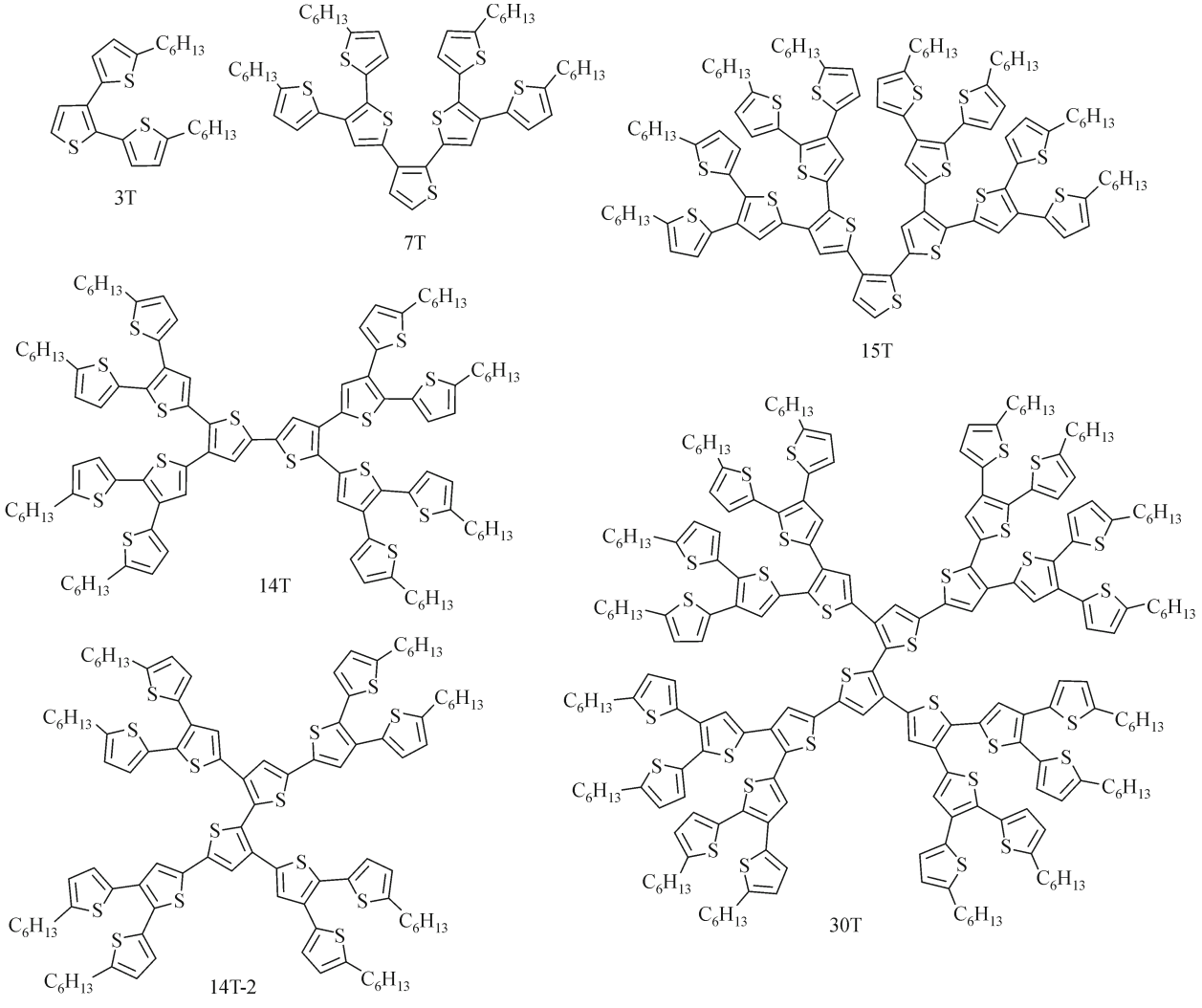

Fig. 2 Chemical structure of Advincula-type all-thiophene dendrons and dendrimers

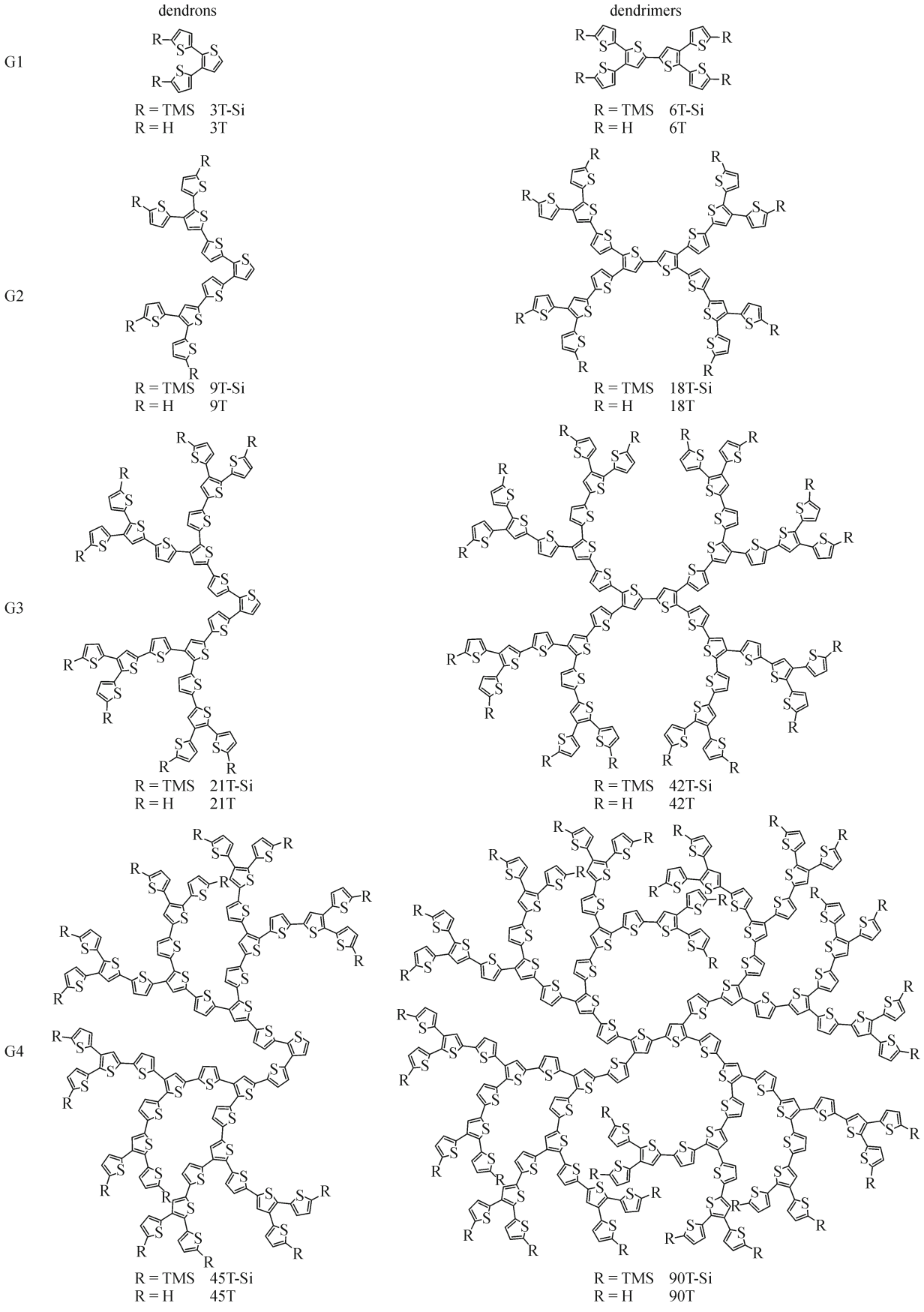

Fig. 3 Chemical structure of generation all-thiophene dendrons and dendrimers

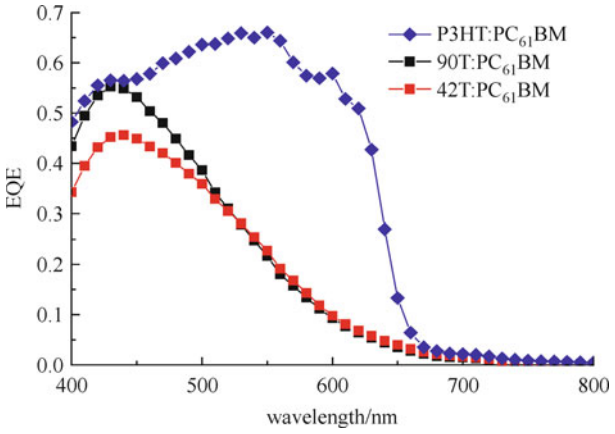

Fig. 4 EQE spectrum comparison of P3HT:$PC_{61}BM$ (1:1, *w*/*w*), 42T:$PC_{61}BM$ (1:2, *w*/*w*), and 90T:$PC_{61}BM$ (1:2, *w*/*w*) based devices

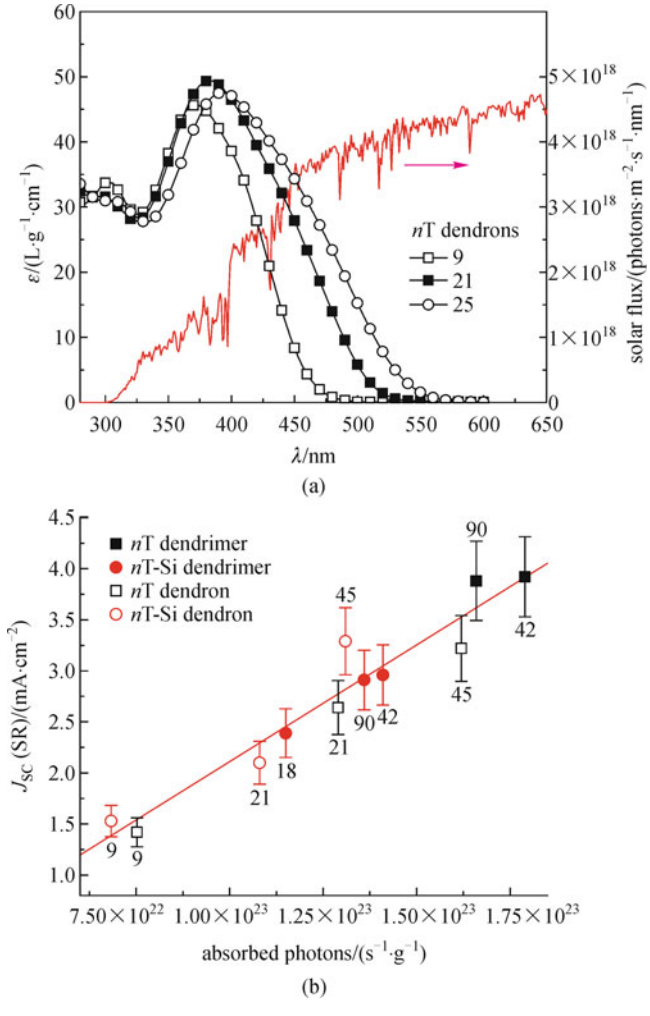

Fig. 5 (a) Weight-averaged absorption coefficient of *n*T dendrons and solar flux (AM1.5G); (b) correlation between J_{SC} and number of absorbed solar photons ($s^{-1}\cdot g^{-1}$) for DOTs. (Reproduced with permission from Ref. [33], Copyright 2008 Wiley-VCH)

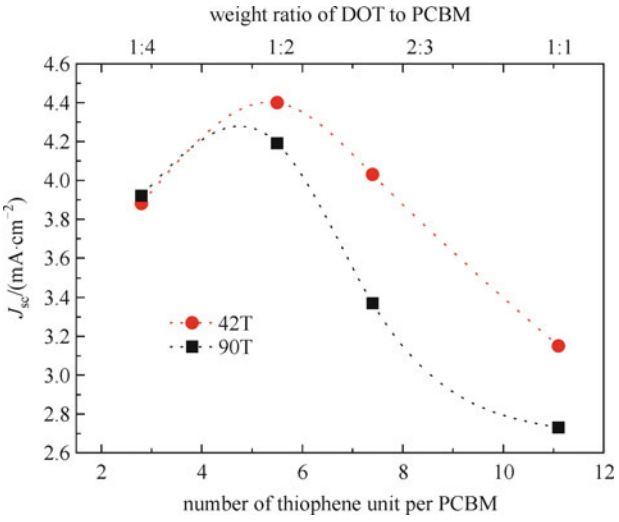

Fig. 6 Correlation between short-circuit current density J_{SC} and ratio of DOT:PCBM as well as number of thiophene units per PCBM molecule (reproduced with permission from Ref. [33], Copyright 2008 Wiley-VCH)

are defined, the weight ratio between donor and acceptor can be transfer to molecular molar ratio, and it turned out that the optimal value corresponded to 5–6 thiophene units per PCBM unit (Fig. 6) [33].

Charge carrier mobilities of four model compounds (18T-Si, 42T-Si, 42T and 21T) were studied using the charge extraction by linearly increasing voltage technique (CELIV) [34]. CELIV technique has been considered as the most realistic method to measure the charge carrier mobility of a solar cell. Because this method uses the same device structure as a real working solar cell, values from CELIV measurement are inherently close to the actual value in the device [35,36]. Hole mobility of these four thiophene dendrimers were measured to be around 10^{-6} $cm\cdot V^{-1}\cdot S^{-1}$, which is in the same magnitude as that of P3HT and PPV polymers measured by the same method [36,37]. Close comparison on the structure-dependent mobility values revealed important structure-property correlations: hole mobility of 21T-Si (dendron) and 42T-Si (dendrimer) were found to be similar to each other (around 1.5×10^{-6} $cm\cdot V^{-1}\cdot S^{-1}$), indicating that shape of the studied dendrimers have little effect on their charge transport properties. Hole mobility of compounds having TMS protecting groups is decreased by a factor of 10 to 30 in comparison with that of compounds without TMS protecting groups. This can be attributed to the intrinsically slower electron transfer rates between the TMS-protected dendrimer molecules (Table 1) [34]. New design strategies to enhance hole mobility of all-thiophene dendrimers by increasing the interdigitation between dendrimers as well as improving molecular packing by introducing asymmetric dendrimers are then proposed.

Table 1 Optical and physical data as well as device performance of selected thiophene dendrimers

DOT	λ_{abs}^{max}/nm[a)]	E_g/eV[a)]	V_{OC}/V[b)]	J_{SC}/(mA·cm^{-2})[b)]	FF[b)]/%	PCE/%[b)]	μ_h/(cm·V^{-1}·S^{-1})[c)]
18T-Si	392	2.35	0.94	2.39	0.35	0.79	1.5×10^{-6}
21T	383	2.43	0.99	2.64	0.37	0.96	1.5×10^{-5}
42T-Si	395	2.29	0.94	2.96	0.37	1.03	3.6×10^{-6}
42T	3.93	2.28	0.98 0.97[d)]	3.92 4.19[d)]	0.43 0.42[d)]	1.65 1.72[d)]	1.2×10^{-5}
90T	3.87[e)]	2.24[e)]	0.94[d)]	4.40[d)]	0.40[d)]	1.65[d)]	-

Notes: a) measured in DCM at 1×10^{-6} mol·L^{-1}; b) device structure: ITO/PEDOT:PSS/DOT:PC$_{61}$BM (1:4 *w*/*w*)/LiF/Al; c) measured by photo-CELIV; d) the ratio of DOT:PC$_{61}$BM (1:2 *w*/*w*); e) measured in THF at 6×10^{-8} mol·L^{-1}

3 Functionalization of all-thiophene dendrons with different core units

Although the pristine all-thiophene dendrimers show reasonable power conversion efficiencies in BHJ solar cells, the rather poor light harvesting ability limits the overall device performance (Fig. 4 and Table 1). To get high performance materials, red-shift of the absorption spectrum is urgently needed. Generally, there are three different ways to red-shift the absorption spectrum of a conjugated molecule: a) by increasing the π-conjugation chain; b) by introducing alternative donor-acceptor unit into the conjugated backbone; c) by corporation of dye chromophore to the molecules. All three ways have been tested in the last

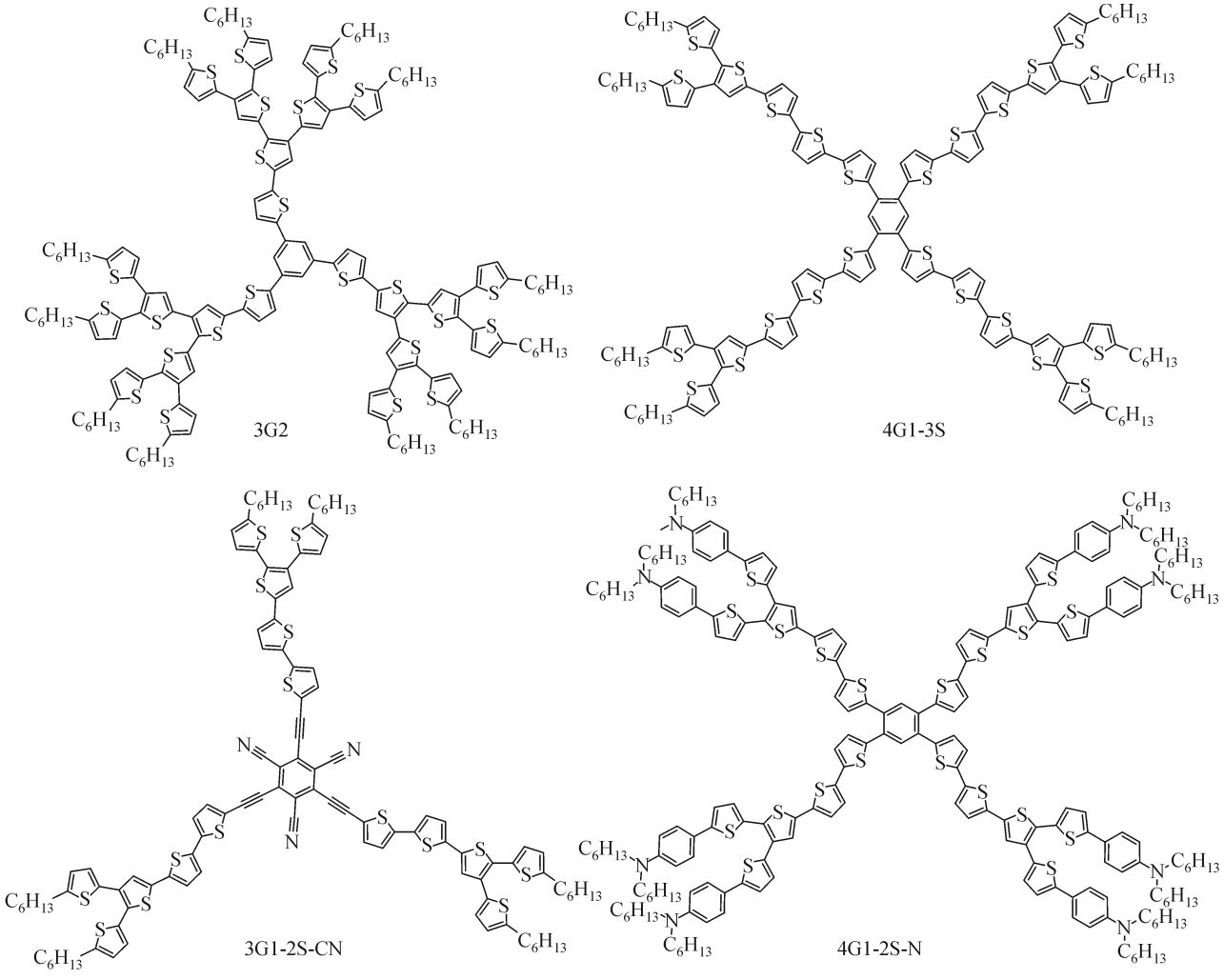

Fig. 7 Chemical structures of benzene ring cored-thiophene dendrimers

two years, and the results are described as following.

Following the pioneering work of Advincula, Mitchell et al. synthesized benzene-cored thiophene dendrimers with three or four Advincula-type thiophene dendron branches (3G2 in Fig. 7) [38,39]. In addition, compounds with oligothiophene bridges in between benzene ring and thiophene dendron branches were also synthesized by the same research group (e.g., 4G1-3S in Fig. 7). Spectroscopic results revealed that compounds with four branches have broader absorption band than that of three-branch ones. This is not very surprising, because π-conjugation is usually blocked for a *meta*-connection in a benzene ring, whereas conjugation chain is extended via para- or ortho-connections. Similar to their parent thiophene dendrimers, these compounds showed broad and featureless absorption bands. The optical band gaps of these materials were determined to be 2.7–2.3 eV. Solution-processed BHJ solar cells using these dendrimes as electron donor showed power conversion efficiencies of 0.2%–1.3%. The best device performance was achieved from a device with blended film of 4G1-3S:$PC_{61}BM$ (1:4, *w*/*w*) [40]. To further improve the light harvesting ability of the materials, the same research group synthesized benzene-cored thiophene dendrimers with electron acceptor unit at the core or electron donating unit at periphery positions (3G1-2S-CN and 4G1-2S-N in Fig. 7) [41,42]. These compounds showed reduced optical band gaps owing to the formation of D-A structure. However, no PV result was reported yet.

We recently reported a series of fluorenyl hexa-peri-hexabenzocoronene (FHBC) cored-thiophene dendrimers (see Fig. 8 for the chemical structure of the 2nd generation compound pFHBC-9T) [43]. Hexa-peri-hexabenzocoronene (HBC) is a planar aromatic molecule consisting of 13 fused six-membered rings, and can be considered as a "super benzene ring" [44]. HBC and its derivatives show intensive absorption over 300–450 nm, and have been shown to self-assemble into column structures giving rise to ordered morphology in solid state [45,46]. Charge carrier mobility of $5 \times 10^{-3}\,cm \cdot V^{-1} \cdot S^{-1}$ was reported in organic field effect transistors (OFET) using dodecyl substituted HBC molecule [46]. The corporation of thiophene dendron to FHBC core yields broader and more intensive absorption spectrum (Fig. 8). In comparison with that of 18T (2.35 eV), compound pFHBC-9T has a larger E_g (2.51 eV), indicating a lack of conjugation through the entire structure of pFHBC-9T [43]. The break in conjugation is probably due to the relative conformation of the 9,9-dioctylfluorene units in relation to the HBC core.

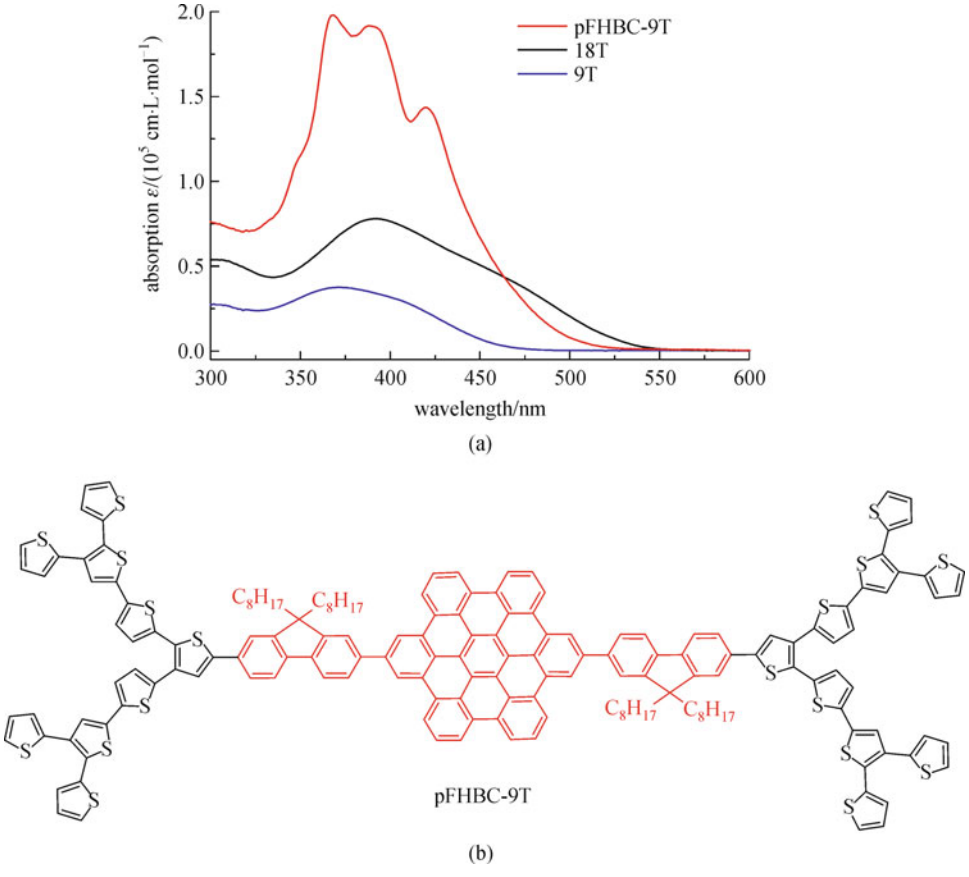

Fig. 8 (a) Absorption comparison between pFHBC-9T, 9T, and 18T; (b) chemical structure of pFHBC-9T

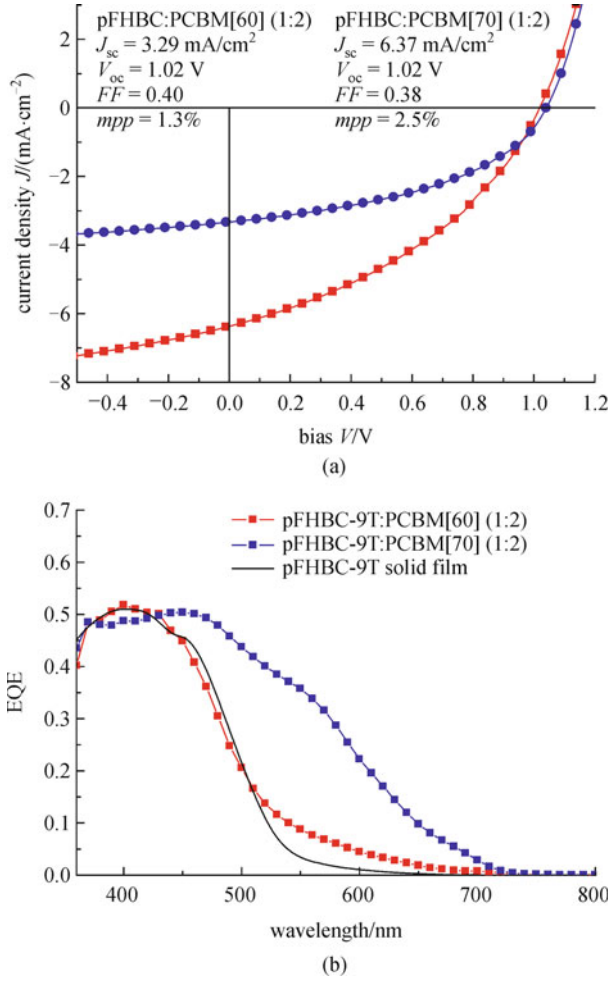

Fig. 9 *J-V* curve (a) and EQE spectra (b) of pFHBC-9T:PCBM based devices

Despite this observation, pFHBC-9T has significantly higher extinction coefficient than either 9T or 18T, which will prove advantageous in solar cell applications. Similar to their parent FHBC cores, these FHBC-DOT hybrids showed intensive intermolecular interactions in solution and ordered structure in thin solid film [43]. Bulk heterojunction solar cell using FHBC-DOT hybrids showed high V_{OC} of 1.0 V and reasonable J_{SC}. Power conversion efficiency of 2.5% was achieved for pFHBC-9T:$PC_{71}BM$ based device (Fig. 9) [43].

Evidently, the absorption of FHBC-DOTs is still not ideal for BHJ solar cell application. In another attempt, we introduced an electron accepting unit, pyrazino[2,3-g] quinoxaline (PQ) as the core to construct new thiophene dendrimers [47]. Unlike many PQ based polymers [48–50], where the conjugation chain was connected via 9,10-position of PQ unit, these conjugated thiophene dendrimers were built up by connecting thiophene dendron branches to the PQ unit via 2,3,7,8-positions (Fig. 10). As can be seen from Fig. 11, both PQ-cored thiophene dendrimers (PQ-3T-Si and PQ-9T-Si) showed two absorption bands with λ_{abs}^{max} around 400 and 580 nm, respectively. The former absorption band can be attributed to the absorption of thiophene dendron moieties, whereas the later one is attributed to the formation of D-A structure between PQ core and thiophene branches. Small band gaps of 1.9 and 1.7 eV were determined for PQ-3T-Si and PQ-9T-Si, respectively. Additionally, such a D-A structure changes the HOMO/LUMO energy levels of these dendrimers as well. In comparison with corresponding thiophene dendrons, both HOMO and LUMO energy of PQ-cored dendrimers are decreased (Fig. 11(b)). Application of these compounds in BHJ solar cells showed

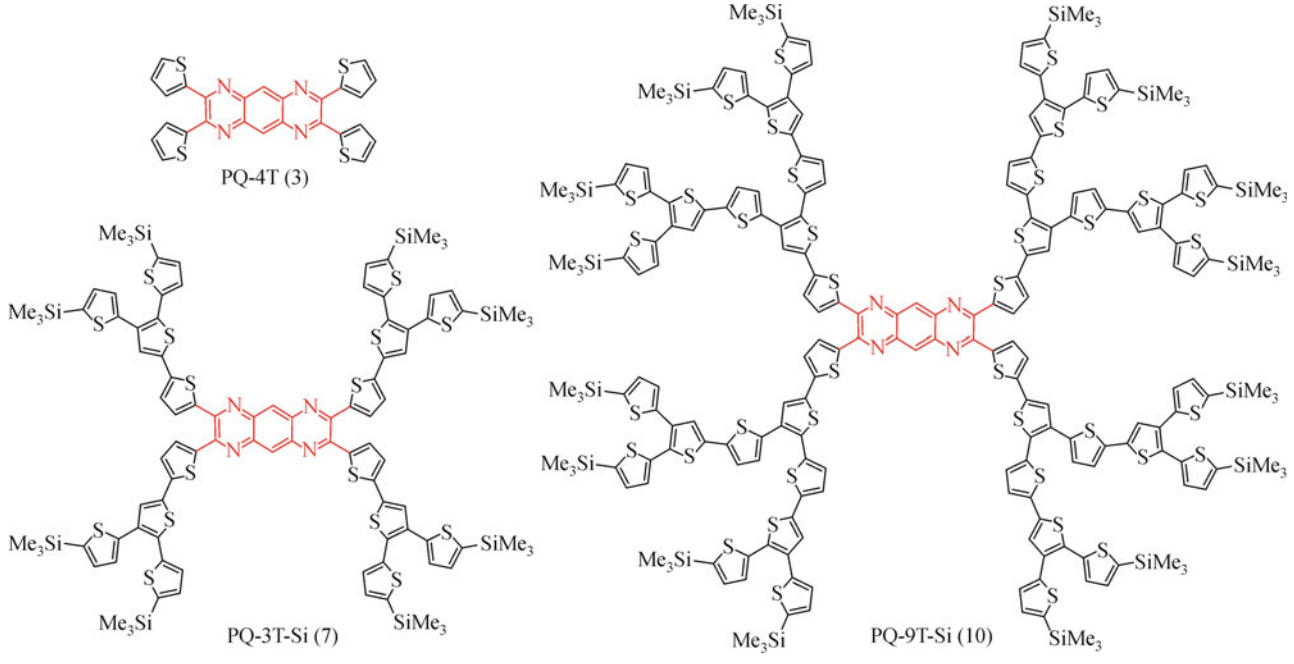

Fig. 10 Chemical structure of pyrazino[2,3-g]quinoxaline (PQ)-cored thiophene dendrimers

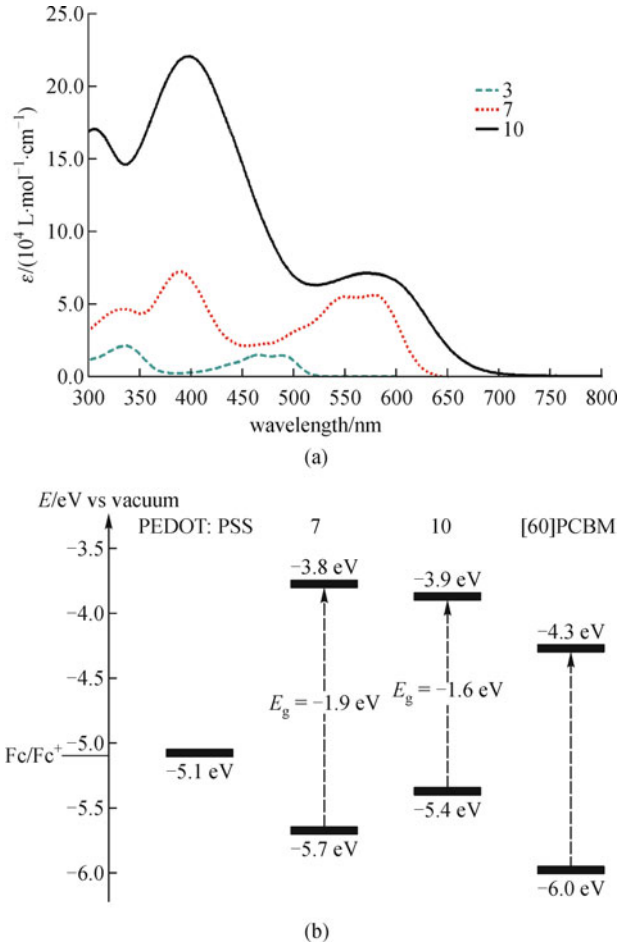

Fig. 11 Absorption spectra (a) and electronic energy levels of PQ-cored thiophene dendrimers (b) (reproduced with permission from Ref. [47], Copyright 2009 American Chemical Society)

improved J_{SC} for its broader absorption spectrum in comparison with corresponding all-thiophene dendrimers, and power conversion efficiencies of 0.7% and 1.3% were achieved for PQ-3T-Si and PQ-9T-Si based devices, respectively [47].

Organic dye molecules have also been used in organic solar cells as light harvesting materials for their high light absorption coefficient [20,51,52]. We recently combined thiophene dendron to perylenebisimide dye (PDI) [53] or phthalocyanine core [54,55] via a non-conjugated connection (Fig. 12). UV-vis absorption spectra measurement showed that these compounds have both absorption features of thiophene dendron moieties (300–550 nm) and dye moiety (500–620 nm). The absorption intensity over 300–550 nm increases gradually with the increase of the size of thiophene dendron, whereas the absorption band of dye moiety are almost identical (Fig. 13). Since the thiophene dendron is not conjugated linked to dye moiety, the HOMO/LUMO energy levels were found to be independent to the size of thiophene dendrons. Therefore, device performance of these dye-functionalized dendrimers is mainly depended on the property of the dye moiety, while thiophene dendron acts as light harvesting antenna. Application of these materials in BHJ solar cells was also tested, and power conversion efficiencies of 0.6%–1.7% were achieved [54].

4 Conclusions

In summary, synthesis approach for conjugated all-thiophene dendrimers has been well established. These

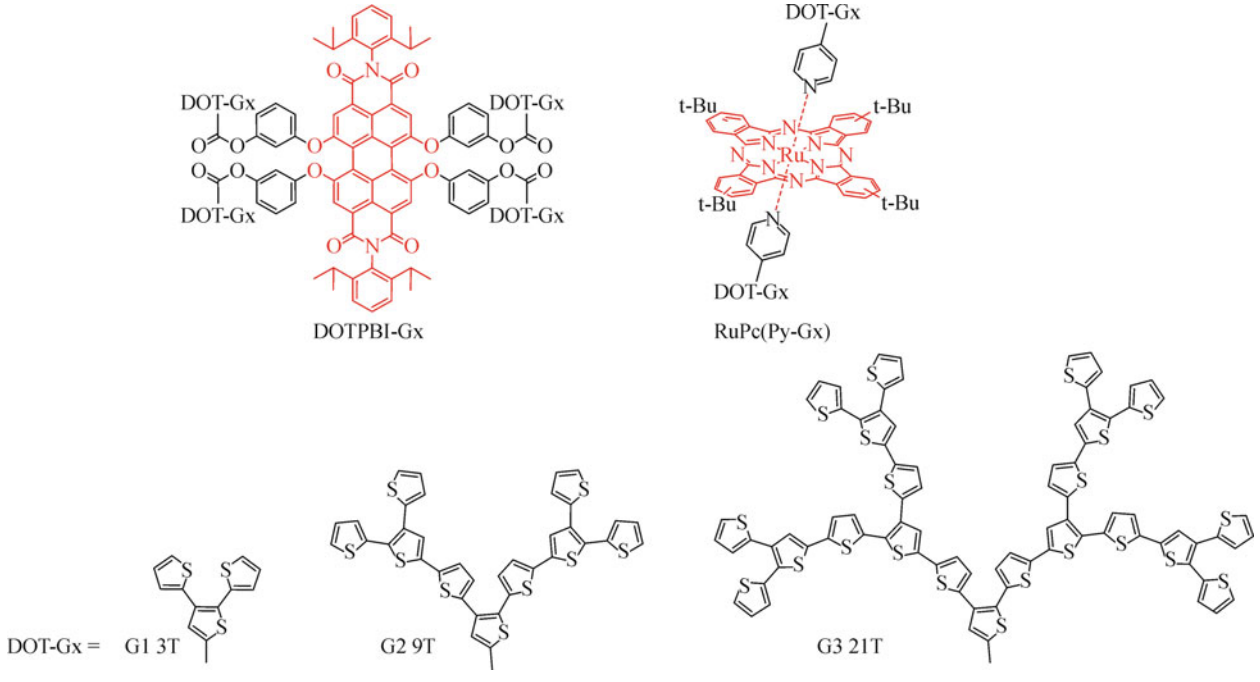

Fig. 12 Functionalization of perylenebisimide (PDI) and phthalocyanine (Pc) dyes with thiophene dendrons via non-covalent bonds

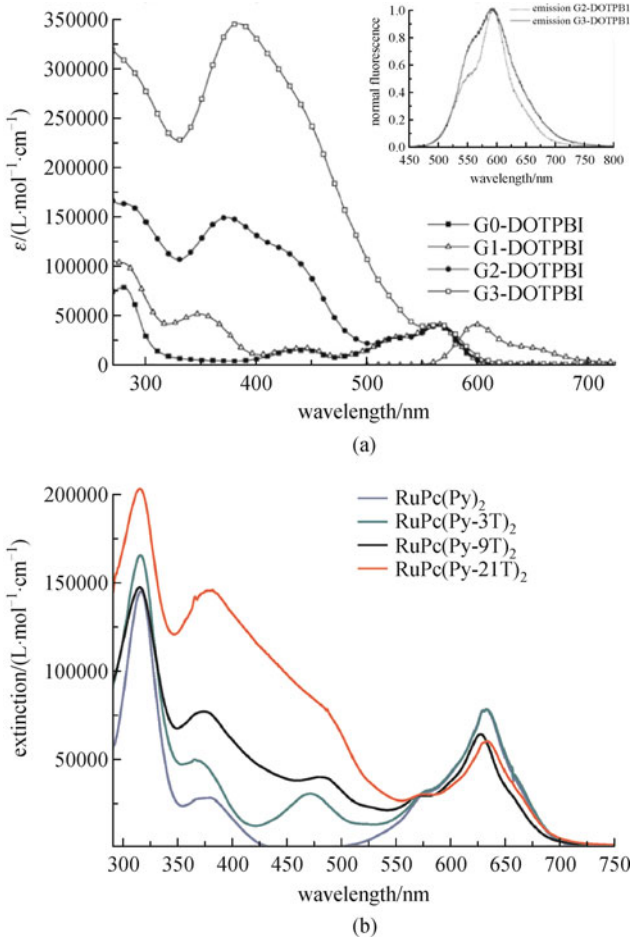

Fig. 13 (a) UV-vis absorption of PDI-DOT (reproduced with permission from Ref. [53], Copyright 2009 Royal Society of Chemistry); (b) Pc-DOT hybrids (reproduced with permission from Ref. [54], Copyright 2009 American Chemistry Society)

all-thiophene dendrimers are typical semiconducting materials with broad absorption band over 300–550 nm, and they can be used as p-type materials in solution-processed BHJ solar cells. Further functionalization of these thiophene dendrons and dendrimers with various optical and redox active moieties to tune optical and elelctronic properties was proved to be feasible. Results indicate that these all-thiophene dendrons are useful building blocks for construction novel semiconducting materials with rigid 3D geometry for BHJ solar cell application.

In spite that high power conversion efficiency of 2.5% has been achieved, the mismatched absorption spectrum of these materials to solar spectrum limits the overall device performance. Furthermore, charge carrier mobilities of these materials were found to be relative low due to unfavorable intermolecular interaction. Therefore, further functionalization on thiophene dendriemrs should be focused on improvement of light harvesting ability and intermolecular interactions of the materials.

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