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FEATURE ARTICLE

Thiophene-based conjugated oligomers for organic solar cells

Fan Zhang,^{*a} Dongqing Wu,^a Youyong Xu^a and Xinliang Feng^{*ab}

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Owing to their efficient light harvesting, structural versatility and intrinsic charge transport behavior, thiophene-based π -conjugated systems have attracted much attention in developing high performance organic solar cells. In comparison to the relevant conjugated polymers that are used as active materials in photovoltaic devices, conjugated oligomers possess some critical advantages: (1) well-defined molecular structures lead to their synthetic reproducibility with high purity which is vital to obtain repeatable device performance; (2) crystalline features of oligomers favor the long range order in the solid state and benefit the charge carrier transport; (3) the devices can be readily fabricated by both solution-processable and vacuum-deposited techniques. In this feature article, thiophene-based conjugated oligomers with molecular architectures from 1D to 3D, which play an essential role in the device performance of organic solar cells, will be summarized. We aim to address the influence of the thiophene motifs on the electronic, optical and self-assembly properties of the materials, and eventually conclude the relationship between the molecular structures and photovoltaic properties.

1. Introduction

Exploration and development of clean, inexpensive and renewable energy have received significant progress in harvesting sun

energy. Organic solar cells (OSCs) represent a promising candidate because of their potential to be fabricated on large-area flexible substrates by simple processing techniques to make low-cost and lightweight products. Over the last two decades, the power conversion efficiency of OSCs has been dramatically improved from 1 to 8%.¹

Tang reported the first efficient organic solar cell device, comprising copper phthalocyanine as a hole transporting material (p-type) and perylene as an electron transporting material (n-type), respectively, in a heterojunction structure, which was fabricated by the vacuum-deposition method.² This work, for the first time, combined the key steps of a typical efficient photovoltaic device: generation of excitons in the donor layer upon the absorption of light energy; the diffusion and dissociation of excitons at the donor–acceptor interface; transport of the separated charge carriers to the opposite electrodes, which in turn produce the photocurrent and photovoltage. However, in such a planar heterojunction (PHJ) device, the short exciton diffusion length (less than 10 nm) limits effective charge separation, and only provides a small area of charge-generating interface between bilayers. Therefore, the power conversion efficiency (PCE) of PHJ device is normally very low. A significant achievement of PCE ($\sim 4.2\%$) was obtained later by the use of C₆₀ as the acceptor component in the above PHJ cell.³ Furthermore, Forrest *et al.* developed a hybrid molecular heterojunction structure by sandwiching a mixed layer of donor and acceptor materials between homogeneous donor and acceptor layers to offer a considerably improved PCE of ca. 5.0%.⁴

In order to achieve a large donor–acceptor interfacial area, the bulk heterojunction (BHJ) structure was proposed by blending the mixtures of donor and acceptor materials to create an

^aSchool of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai, 200240, P.R. China. E-mail: fan-zhang@sjtu.edu.cn; Fax: +86-21-5474753510

^bMax-Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany. E-mail: feng@mpip-mainz.mpg.de



Xinliang Feng

Dr Xinliang Feng, after obtaining his Master's degree of organic chemistry from Shanghai Jiao Tong University in March 2004, he joined the group of Prof. K. Müllen at the Max Planck Institute for Polymer Research (MPIP) and obtained his PhD degree in April 2008. Since December 2007, he became a project leader in MPIP. Since June 2010, he has been a professor of Shanghai Jiao Tong University and was appointed as director for establishing the Institute of Advanced

Organic Materials. His current scientific interests include the graphene, two-dimensional nanomaterials, organic conjugated materials, carbon-rich molecules and materials, for electronic and energy-related applications.

interpenetrating network through controlling the phase separation between the donor and acceptor parts in bulk (Fig. 1). Accordingly, the photoexcitons within these nanometre-scale regions of the resultant large donor–acceptor interfaces can favor the charge separation, giving rise to increased internal quantum efficiencies. The enhanced charge transport properties from the interpenetrating network lead to an efficient charge collection along two channels of holes in the donor domain and electrons in the acceptor domain, respectively. For both small molecule and polymer based BHJ solar cells, control of microscopic morphology plays a key role in achieving high PCE.^{4,5} The blend morphology can be tailored by various fabrication methods, including the choice of appropriate solvent, control of solvent evaporation rate, thermal annealing treatment and so on. By adopting these processing protocols, crystalline phase-separated domains (~20 nm) tend to be formed.⁵

The exploration of donor materials has been centered on p-type conjugated small molecules and polymers that own strong absorption of sunlight spectra covering an extensively broad range, ease of film formation, good charge mobility and suitable frontier orbital energy levels. From the view of these points, thiophene-based π -conjugated oligomers are among the most promising materials for OSCs.⁶ The structural versatility of thiophene motifs provides tailor-made materials for tuning the device performances. In the late 1980s and early 1990s, Fichou started to systematically explore α -sexithiophene (α -6T) for charge carrier transport in organic field-effect transistors.⁷ The first thiophene-based photovoltaic device on the basis of α -8T as the p-type donor material associated with perylene as the n-type acceptor material was fabricated by using vacuum deposition techniques, which only exhibited an efficiency of 0.6%, but matched copper- and titanyl-phthalocyanine-based devices at that time.^{6a} Currently, organic solar cells with excellent PCEs of over 8% by using oligothiophene-based donor materials have been achieved.⁸ Thiophene-based conjugated oligomers with well-defined molecular architectures ranging from 1D to 3D represent an abundant source of materials for OSCs, and possess competitive advantages over polymeric materials: at first, their synthetic reproducibility can guarantee a stable device performance; second, they can form long range crystalline ordering in the solid state which is beneficial for the charge carrier transport; moreover, considering their good thermal stabilities and low molecular weights, they offer vacuum-deposited or solution-processable (or both) methods for device fabrications (PHJ or BHJ cells).

Fullerene (C_{60}) derivatives have proven to be good acceptors and have shown high efficiency in organic solar cell devices. These compounds possess a low-lying lowest unoccupied molecular orbital (LUMO) energy level, which favorably accept

electrons transferred from the donor material in a range of femto-second time scale, which is faster than the radiative decay of photoexcitation or electron recombination by several orders of magnitude. On the other hand, the reduced fullerene derivatives enable stabilization of up to six negative charges through effectively delocalizing over their large conjugated molecular systems. These features are favorable for electron hopping from donor molecules to fullerene derivatives, leading to efficient charge separation and collection. The low solubility and the tendency to crystallize of unsubstituted fullerene in organic solvents make it inapplicable in solution-processable OSCs, but highly useful by vacuum-deposited techniques. In order to overcome the drawback of bare C_{60} in BHJ solar cells, [6,6]-phenyl- C_{61} -butyric acid methyl ester (PC₆₁BM) was proposed and synthesized by Wudl *et al.* (Fig. 2).⁹ A blend of regular poly(3-hexylthiophene) (P3HT) and PC₆₁BM led to a high PCE (~5%) that offers a textbook example.¹⁰ Another acceptor molecule, PC₇₁BM on the basis of the higher fullerene analogue C_{70} was later developed, which displays much more sufficient light harvesting in the visible region than PC₆₁BM. In this way, remarkably improved efficiencies of BHJ devices have been achieved by employing PC₇₁BM as the acceptor (Fig. 2).¹¹ Other fullerene derivatives have also been explored in the last decade, and one of the newest examples is PC₆₁BM-CN (Fig. 2).¹²

Searching for relatively less-abundant n-type (electron-transporting) π -conjugated systems as low-cost high-performance acceptor alternatives of OSCs is directed to maximizing absorption across the solar spectrum in combination with p-type donor materials. In addition, the LUMO energy level of acceptors should not only preserve sufficient energy offsets (>0.3 eV) (between the LUMO energies of the donor and acceptor species) but also not result in the loss of the open-circuit photovoltage (V_{oc}) (between LUMO of the acceptors and HOMO of the donors). This means a comprehensive balance for an optimized state. Moreover, acceptor materials should be able to create effective phase separation from donor species upon blending which allows for charge separation and facilitates charge transport. Currently, some non-fullerene acceptors have been developed which show significant improvements in spectral absorption, photostability and electron transport.¹³ Nevertheless, these acceptors still cannot compete with fullerene derivatives in terms of morphology control upon mixing with donor moieties. The advantage of thiophene units for the construction of new n-type electron-transport materials consists of the readily available chemical modification protocols that allows for tuning the HOMO and LUMO energy levels. The thiophene-*S,S*-dioxide derivatives are among the most promising n-type motifs due to their favorable LUMO energy, good optical properties and facile chemical functionalization.¹³

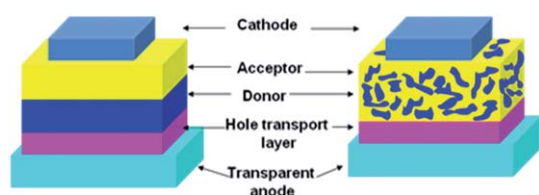


Fig. 1 Diagrams of PHJ (left) and BHJ (right) OSCs.

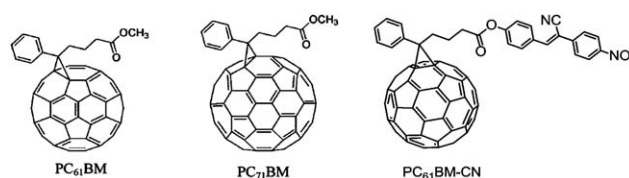


Fig. 2 Molecular structures of representative fullerene derivatives.

In this feature article, we will give an overview of the recent progress in thiophene-based oligomer solar cells, and discuss the relationship between the molecular architectures and photovoltaic properties.

2. Thiophene-based linear oligomers

Thiophenes are promising building blocks for the design and synthesis of conjugated materials because they possess remarkable optic, electronic and redox properties as well as prominent supramolecular behavior on the solid surface or in the bulk. In addition, thiophenes can be selectively modified at the α -, β -positions or even sulfur atoms of heterocycle rings to establish versatile structures. For instance, the incorporation of the α -linked thiophene units into oligomers renders an efficient conjugation along the main chain backbone, while attaching long alkyl side-chains at the α - or β -position guarantees solution processibility and self-assembly capability. The soft sulfur atoms in thiophene rings have high polarizability that makes a prominent contribution to the electron-donating and charge-transport properties of thiophene derivatives. Previously, OSCs based on oligothiophenes as donor materials have been widely investigated. They show low PCEs mainly caused by the narrow absorption of sunlight spectra.^{6a}

The introduction of electron-withdrawing or electron-donating building blocks into thiophenes or oligothiophenes has been later revealed to be the most straightforward way to construct new oligomers with well-defined structures and tunable HOMO and LUMO energy levels. The donor-acceptor (D-A) conjugated oligomeric systems can serve as excellent donor components in organic photovoltaics due to their unique features: (1) the well-defined structures make them synthetically reproducible; (2) the light-absorbing regions can be enlarged to cover low-energy long-wavelength spectra; (3) the strong intermolecular interactions arising from the D-A moieties can favor the self-organization of the oligomers into ordered structures and close packing with increasing π - π orbital overlap; (4) both vacuum-deposited and solution-processable methods can be applicable to fabricate devices. In the last few years, several new families of D-A oligomers consisting of electron-donating thiophenes/oligothiophenes (D) have been developed as donor materials in high-performance OSCs. According to each electron-withdrawing building block (A) utilized, functionalized thiophene-based oligomers can be classified and outlined in the following sections.

2.1. Dicyanovinylene (DCV)-containing oligomers

DCV (dicyanovinylene) is considered as a strong electron-withdrawing group, which can be readily coupled with oligothiophene backbones in high yields by simple formylation conversion to the dialdehyde, and then transformed into oligothiophenes end-capped with DCV groups. Bäuerle and his colleagues have designed and synthesized several series of DCV-containing oligothiophenes (Fig. 3), which exhibit strong bathochromic shifts in their absorption spectra and low band gap properties, as well as high thermal stabilities. Under vacuum-deposited processing, these DCV-based oligothiophenes as donor materials blended with C_{60} lead to a series of high-performance solar cell devices. In

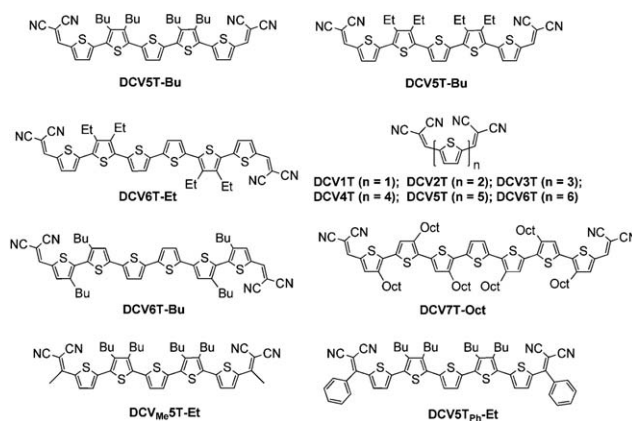


Fig. 3 Molecular structures of DCV-containing oligomers.

2006, in collaboration with Leo and Pfeiffer, they utilized α,α' -bis (2,2-dicyanovinyl)-quintathiophene (DCV5T-Bu) as the donor and achieved single cell with high EQE value (48% at 570 nm) and a power conversion efficiency of 3.4% under 118 mW cm⁻² simulated sunlight.¹⁴ An optical band gap of 1.77 eV in thin films was observed for DCV5T-Bu, much lower than that of 2.5 eV for unsubstituted quinquethiophene (5T). The coplanarization of the thiophene units and the intermolecular CN...H bonds between the terminal nitrile groups and the thiophene cores in this molecule might be the main reasons for the remarkable red-shift (about 60 nm) of absorption from solution to thin film. A suitable ionization energy of 5.6 ± 0.1 eV for DCV5T-Bu results in efficient exciton separation and high photovoltage up to 1.0 V. Furthermore, the photovoltaic properties of two derivatives of dicyanovinyl-quintathiophenes (DCV5T-Bu and DCV5T-Et) carrying a butyl and ethyl side chain, respectively, were investigated. The DCV5T-Et based device afforded a lower PCE of 2.5%, while comparable V_{oc} values were observed for both derivatives due to the same HOMO energy levels. Compared with DCV5T-Bu, the lower PCE for DCV5T-Et could be ascribed to its lower hole transport mobility.¹⁵ Very recently, a series of DCVnTs without solubilising alkyl side chains were synthesized in high yields by a convergent synthetic approach.¹⁶ For vacuum-deposited solar cells with the use of C_{60} as the acceptor, DCV5T gave a PCE up to 2.8% for planar heterojunction and 5.2% for co-evaporated bulk heterojunction solar cell under simulated AM 1.5G sunlight. The PCE of 5.2% is also one of the highest values for organic vacuum-deposited single BHJ solar cells reported so far.

On the other hand, control of morphology is one of the important strategies to improve the performance of solar cell devices. For (DCV6T-Et): C_{60} heterojunction layer, Wynands *et al.* demonstrated that controlling the deposition temperature of the substrate at 90 °C led to an increased and red shifted absorption bands compared to other deposition conditions,¹⁷ implying an improved molecular ordering. The enhanced luminescence of composite film indicated an extended phase separation between DCV6T-Et and C_{60} . AFM images further revealed that the 90 °C deposited sample showed larger domain size and high surface roughness in comparison to an amorphous mixed phase fabricated at 30 °C (Fig. 4). Hence, the former favored the charge carrier transport, and a significantly improved PCE of

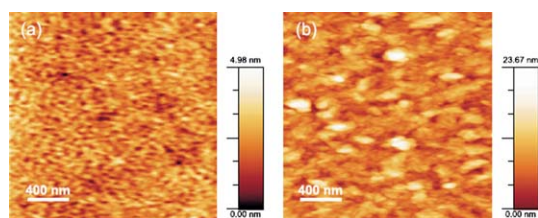


Fig. 4 AFM images of DCV6T-Et:C₆₀ mixed layers in a ratio of 2 : 1, 20 nm deposited at substrate temperatures of 30 °C (a) and 90 °C (b) on top of 15 nm C₆₀/ITO. Reproduced with permission from ref. 17. Copyright 2010 American Institute of Physics.

3.8% was obtained (vs. PCE of 1.6% for the 30 °C deposited sample). Subsequently, they reported a much improved PCE value of 4.9% for DCV6T-Bu-based solar cell under similar processing conditions.¹⁸

Bäuerle and his coworkers further revealed the influence of the modification of dicyanovinylene (DCV) groups on the photovoltaic properties of the resulting oligothiophene materials. They replaced the vinylic proton in DCV5T backbone by methyl or phenyl substituents to construct two new dicyanovinyl-substituted quinquethiophenes (DCV_{Me}5T-Et and DCV_{Ph}5T-Et, Fig. 3).¹⁹ Both of them showed slightly increased thermal stability compared with DCV5T-Et. As expected, these molecules exhibited low band gaps (around 1.9 eV) with deep lying HOMO energy levels (~5.6 eV). PHJ solar cells using these molecules as donor blended with C₆₀ afforded moderate PCE values of 2.60 and 1.46%, for DCV_{Me}5T-Et and DCV_{Ph}5T-Et, respectively. It is likely that introduction of larger substitutes into the terminal dicyanovinyl groups leads to the non-planarity structure of DCV_{Me}5T-Et and DCV_{Ph}5T-Et, and thus decreases intermolecular π - π interactions and results in the lower FF and J_{SC} .

DCV-based oligothiophenes have also been demonstrated for solution-processable BHJ solar cells. For instance, DCV7T-Oct (Oct: *n*-octyl) as donor was blended with PC₆₁BM as acceptor for a solution processed BHJ device, affording a PCE of 2.45% by using a simple spin-coating method without any special treatment.²⁰

The vacuum-processed method is much more suitable for manufacturing tandem cells than solution-processed means.^{14,21} By using DCV-based oligothiophene, a vacuum-deposited tandem solar cell with an excellent PCE value of 8.3% on 1.1 cm² was achieved recently by Heliatek GmbH.⁸

2.2. Benzo[c][1,2,5]thiadiazole (BTDA)-containing oligomers

Benzo[c][1,2,5]thiadiazole (BTDA) is one of the most popular acceptor moieties for the construction of low-band gap semiconductors because of its good optical properties, high thermal stability and suitable frontier orbital energy levels, as well as strong intermolecular interactions. Bäuerle *et al.* developed a series of A–D–A–D–A-type oligothiophene-based pentamers (A: acceptor; D: donor), in which the central A is BTDA, and the terminal A is electron-withdrawing trifluoroacetyl group (Fig. 5).²² The high molar extinction coefficients of these oligomers could be attributed to the increased quinoidal character from BTDA unit and the terminal trifluoroacetyl groups, leading to

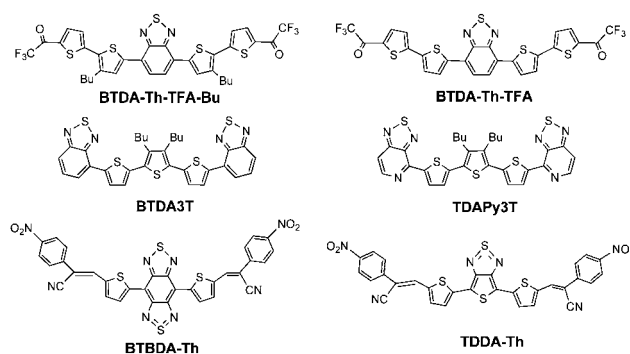


Fig. 5 Molecular structures of BTDA-containing oligomers.

the extended conjugated systems. Compared to its absorption maximum at 518 nm in solution, the film of oligomer BTDA-Th-TFA-Bu shows a broad absorption band and a red shift of 15 nm, possibly due to the strong intermolecular π -stacking effect in the solid state. Differently, the film of BTDA-Th-TFA displays a broad absorption at 466 nm, which is significantly blue shifted by 43 nm compared to the absorption in solution, indicating the formation of H-aggregates in the solid state. Vacuum-deposited PHJ OSCs on the basis of these oligomers as donor and C₆₀ as acceptor afforded a PCE of 1.56 and 1.45% for BTDA-Th-TFA-Bu and BTDA-Th-TFA, respectively, under AM 1.5G simulated sunlight. The open circuit voltages up to 1.17 and 1.10 V for BTDA-Th-TFA-Bu and BTDA-Th-TFA based cells are among the highest values for organic solar cells, attributable to their low-lying HOMO energy levels.

In a very recent report, the same group used terthiophene as core cap-ended with BTDA and structural analogue thiadiazolopyridine (TDApy) groups to respectively construct two A–D–A-type molecules (Fig. 5).²³ With the vacuum-deposited technique, the m-i-p-type PHJ and BHJ cell devices were fabricated by using these two oligomers as donors and C₆₀ as acceptor. The PCEs (PHJ: η = 3.15%; BHJ: η = 1.94%) for TDPAPy3T were remarkably higher than those (PHJ: η = 1.73; BHJ: η = 1.50%) for BTDA3T. The improved efficiencies for TDPAPy-containing oligomer could be attributed to the increased intra-/inter-molecular interactions through the additional nitrogen atom at the pyridine of the TDPAPy unit.

The thiadiazole moiety critically decides the properties of the BTDA building block in electron affinity, planarity and intermolecular interactions. Some BTDA analogues comprising thiadiazole group were synthesized by Mikroyannidis *et al.* and used to build up two low band gap small molecules of benzo-bisthiadiazole- and thienothiadiazole-core oligothiophenes with end-capped cyanovinylene 4-nitrophenyl units (BTBDA-Th and TDDA-Th) (Fig. 5).²⁴ By using PC₆₁BM as acceptor, solution-processable BHJ devices based on these two molecules gave PCEs of 1.05 and 1.23%, respectively. With PC₆₁BM-CN as acceptor material, the PCEs of the devices could be improved up to 2.02 and 2.72% for BTBDA-Th and TDDA-Th, respectively. The higher performance of TDDA-Th than that of BTBDA-Th could be ascribed to the good charge carrier transport property of the former. The influence of morphology on efficiency was further investigated for the TDDA-Th:PC₆₁BM-CN device. The sample cast from mixed solvents of chlorobenzene/THF, yielded the PCE of up to 3.65%. Absorption spectra, XRD (X-ray

diffraction) patterns and AFM (atomic force microscopy) images of the cast films disclosed the improved crystallinity by using a suitable solvent system (Fig. 6). Therefore, the best performance of the corresponding device (Fig. 6c) was originated from the improved ordering upon thermal treatment and thus enhanced the charge carrier transport property.

2.3. Diketopyrrolopyrrole (DPP)-containing oligomers

Diketopyrrolopyrrole (DPP) has been widely used as a key component in building up D–A conjugated systems,²⁵ because of: (i) its high optical density; (ii) attaching alkyl chains to the aryl groups bound to the DPP core for increasing solubility and adjusting self-assembly behavior; (iii) its electron affinity properly lowering frontier orbitals for creating low-band gap molecules; (iv) formation of the hydrogen bonds between DPP cores for creation of interpenetrating network. Nguyen and co-workers reported a series of thiophene-based oligomers incorporating DPP chromophores.²⁶ These materials exhibit strong absorption at low energy regions and good charge carrier mobilities. The nanoscale ordering of materials on films can be effectively adjusted through the tailoring of the alkyl substituent bonded to the DPP core at nitrogen atom and the number of thiophene units attached to the backbone. Using 2,5-di-(*tert*-butoxycarbonyl)-3,6-bis-(5-*n*-hexyl [2,2,5,2]terthiophen-5-yl)-pyrrolo[3,4-*c*]pyrrole-1,4-dione (α,α -DH6TDPP) as donor and PC₆₁BM as acceptor, a PCE of 2.3% was achieved for BHJ solar cells.²⁷ However, the low thermal stability of α,α -DH6TDPP due to thermolytic loss of the *t*-Boc group at high temperature precluded further device optimization. To replace the *t*-Boc group, an ethylhexyl substituent was introduced into DPP. Therefore, the corresponding oligothiophene–DPP molecule, 2,5-di-(2-ethylhexyl)-3,6-bis-(5-*n*-hexyl[2,2,5,2]terthiophen-5-yl)-pyrrolo[3,4-*c*]pyrrole-1,4-dione (SMDPPEH) shows remarkable improvements in thermal stability, solubility, and film-forming properties. Solution-processed BHJ solar cells incorporating SMDPPEH as a donor with PC₇₁BM as an acceptor in a 1 : 1 blend ratio yielded PCE up to 3%.²⁸ Accordingly, the hole and electron mobilities (1.0×10^{-4} vs. 4.8×10^{-4} cm² V⁻¹ s⁻¹) are in good balance, which are comparable to those of polymer BHJ solar cells (such as P3HT:PCBM blends). Fused benzofuran motifs were employed to synthesize benzofuran-substituted-DPP-oligothiophene, 3,6-bis(5-(benzofuran-2-yl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-*c*]pyrrole-1,4-dione (DPP(TBFu)₂) by the same group (Fig. 7).²⁹ DPP(TBFu)₂ exhibits a broad spectral coverage and a low-band gap of 1.7 eV estimated from the onset of the absorption spectrum. A deeper HOMO level of 5.2 eV for DPP(TBFu)₂ was calculated according to the electrochemical results. A

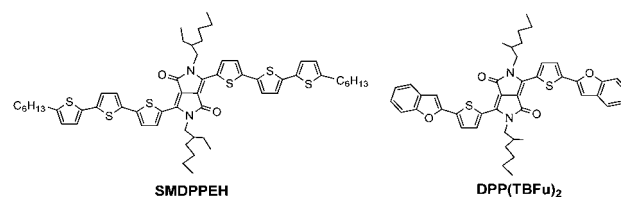


Fig. 7 Molecular structure of representative DPP-containing oligomers.

solution processed BHJ solar cell made of DPP(TBFu)₂ and PC₇₁BM gave PCE up to 4.4% with a high V_{oc} of 0.9 V under AM 1.5G illumination (100 mW cm⁻²). Obviously, introduction of benzofuran units can increase the planar conjugated effect, and effectively stabilize the HOMO energy level through the electronegative oxygen atom of benzofuran, and thus leads to a high device performance. The morphology of DPP(TBFu)₂:PC₇₁BM (70 : 30) blend film at different annealing temperatures were examined by AFM (Fig. 8). The topographic image of the sample annealed at 90 °C reveals small domains (10–50 nm) with a surface roughness of 1.1 nm. In contrast, the average size of the domains increases to 100 nm with a surface roughness of 2.3 nm for the sample treated at 100 °C. Similar changes in morphology were also observed for the DPP(TBFu)₂:PC₇₁BM blends of other ratios. The devices on the basis of DPP(TBFu)₂:PC₇₁BM (703 : 30) blends annealed at 100 °C and DPP(TBFu)₂:PC₇₁BM (60 : 40) blends annealed at 110 °C gave efficiencies of 4.2 and 4.4%, respectively, significantly higher than those of the devices treated under low temperatures. These results are also in agreement with the formation of high quality films and increased crystallinity upon high temperature treatment. As discussed above, nanometre-scale phase separation has proved to be a crucial morphology feature for developing.

2.4. D–A block co-oligomers

High-performance OSC devices comprising donor and acceptor blends, which can overcome the short exciton diffusion distance (approximately 10 nm), improve the charge separation and transport. However, it remains challenging to realize such

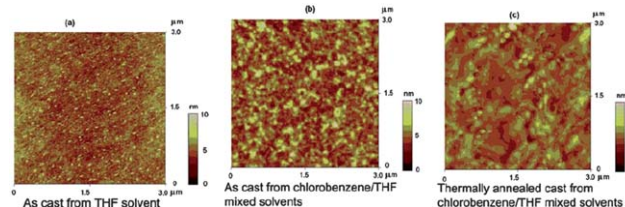


Fig. 6 AFM images of TDDA-Th:PC₆₁BM-CN device blends cast from different solvent systems. Reproduced with permission from ref. 24. Copyright 2011 The Royal Chemical Society.

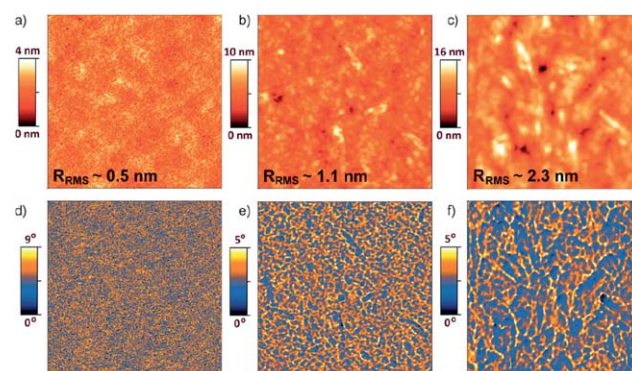


Fig. 8 AFM images of 70 : 30 DPP(TBFu)₂:PC₇₁BM films spin-coated on ITO/PEDOT:PSS substrates and annealed at various temperatures. Height images of as-cast film (a), annealed at 90 °C (b), and at 100 °C (c). Phase images of films as-cast (d), annealed at 90 °C (e), and at 100 °C (f). The scan size for all images is 2 μ m \times 2 μ m. Reproduced with permission from ref. 29. Copyright 2009 Wiley-VCH Verlag GmbH & Co. KGaA.

morphology control due to the incompatible nature between the donor and acceptor components. The incorporation of donor and acceptor moieties into one molecular or polymeric structure may provide a means to adjust the phase separation at the nanometre scale by tailor-made synthesis. Several copolymers consisting of (oligo)thiophene and fullerene or perylene diimide as donor and acceptor building blocks, respectively, have been reported.³⁰ Nevertheless, OSC devices using these polymers as single active component only afforded very poor efficiency, mostly due to their polydispersity and rigid nature. In a different approach, Geng *et al.* reported a series of D–A type co-oligomers comprising oligo(fluorine-*alt*-bithiophene)s as D and perylene diimide as A segment respectively (Fig. 9).³¹ The film-forming properties of these co-oligomers were profoundly investigated. Among them, F5T8-hP co-oligomer showed high ordering in thin films with tunable lamellar nanostructures, likely due to the feature of D–A segregation and long molecular length. The device consisting of a solvent-vapor annealed film of F5T8-hP provided a high PCE of up to 1.5%, which is among the highest device efficiencies of single-molecular OSCs. Both D and A segments of the co-oligomer contributed photocurrents according to the absorption spectrum analysis. Therefore, the nanostructured films could simultaneously transport electrons and holes.

3. Thiophene-based dendrimers/dendrons

Conjugated dendrimers/dendrons consisting of regular or irregular repeating units are well-defined structures with different branching degrees. They feature mono-dispersion, synthetic reproducibility and highly processable purity. In addition, similar to the polymeric materials, they also show good solubility in common organic solvents, good film-forming properties and broad sunlight absorption. Dendrimers/dendrons normally possess the characteristics of both small molecules and polymers, and thus hold promise in organic electronics, such as thin-film organic field transistors (OTFT), organic light emitting devices (OLEDs) and organic solar cells.³² Thiophene-based dendrimers/dendrons have been revealed as good p-type semiconductors. A series of simple branched oligothiophenes have been synthesized using thiophene as cores (DT-Th, DT-2Th and DT-Th-Et, Fig. 10).³³ The different conjugation pathways in the molecular backbones lead to broad absorption spectra. The bulk heterojunction photovoltaic cells employing these branched oligomers as donors and PC₆₁BM as acceptor yielded PCEs from 0.04 to 0.8%, depending on the oligothiophene chain length. Kopidakis *et al.* reported a family of dendrimers consisting of phenyl cores and thiophene arms 3G1-S and 4G1-nS (Fig. 10).³⁴ Photovoltaic properties arising from the blends of these dendrimers and PC₆₁BM were investigated. The highest efficiency of 1.3% was

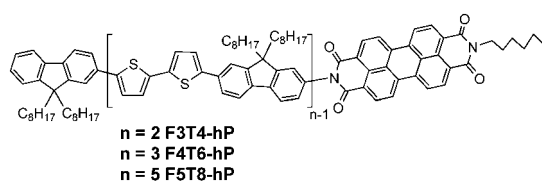


Fig. 9 Molecular structure of a representative D–A block co-oligomer.

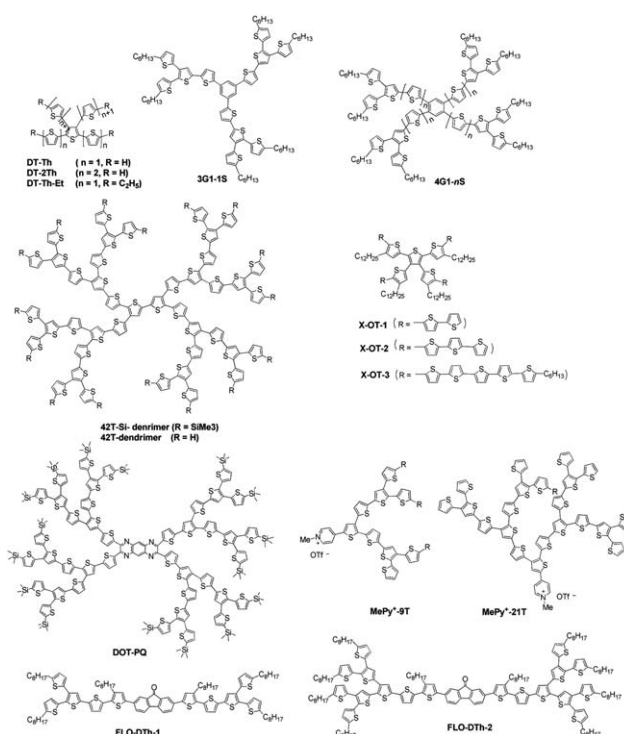


Fig. 10 Molecular structures of representative thiophene-based dendrimers/dendrons.

achieved by using 4G1-3S as donor material. An increase in the length of the thiophene branch in the four-arm dendrimer led to the improvement of device performance, which could be attributed to the increased charge transport property.

Divergent and convergent synthetic strategies are two typical protocols towards the synthesis of extended dendritic molecules. By combining these two strategies, Bäuerle *et al.* efficiently built up a new family of structurally well-defined dendritic oligothiophenes, and two of the representative species 42T-Si-dendrimer and 42T-dendrimer are depicted in Fig. 10.^{35a} The 3D branched structures of these dendritic oligothiophenes helpfully improve the solubility in common organic solvents. Therefore, the good solution-processability of these conjugated dendrimers/dendrons of different generations is convenient for the investigation of optoelectronic properties and device performances, making them promising alternatives to polythiophenes. The absorption spectra are contributed from multiple chromophores which mainly correlate with α -linked subunits. A representative compound 42T-dendrimer, blended with PC₆₁BM in a solution-processed BHJ device provides the highest PCE value of 1.7% (V_{oc} of 0.97 V, FF of 42%), under AM 1.5G simulated sunlight among this family of dendritic oligothiophenes.^{35b} A series of X-shaped oligothiophenes (X-OT-1, X-OT-2 and X-OT-3) were reported recently by Zhan *et al.* Solution-processed organic solar cells based on the blends of these oligothiophenes and PC₆₁BM or PC₇₁BM gave PCE values of 1.02 and 1.54%, respectively, under AM 1.5, 100 mW cm⁻².³⁶

Electron-deficient pyrazino[2,3-*g*]quinoxaline unit can also be employed as a central building block attached with oligothiophene dendron branches for the construction of dendritic oligothiophenes (*e.g.* DOT-PQ in Fig. 10).³⁷ In comparison with the

all thiophene-based dendrimers, the optoelectronic properties of the pyrazino[2,3-*g*]quinoxaline-core dendrimers show reduced band gaps owing to the donor–acceptor character. Blends of DOT-PQ and PC₆₁BM in a BHJ device gave a PCE of 1.3% with an excellent V_{oc} of 1.00 V. In addition, a series of core-functionalized dendritic oligothiophenes containing pyridine or methylpyridinium unit (MePy⁺-9T and MePy⁺-21T) have been synthesized (Fig. 10). An intramolecular charge transfer process can be concluded based on the bathochromically shifted absorption of the functionalized dendritic oligothiophenes arising from the donor–acceptor feature of MePy⁺-9T or MePy⁺-21T. These dendritic compounds were applied in bulk heterojunction solar cells with fullerene PC₆₁BM as acceptor, affording an efficiency up to 0.45%.³⁸

Donor–acceptor type conjugated molecules of fluorenone-core dendritic oligo(thiophene)s (FLO-DTh-1 and FLO-DTh-2) were also reported recently (Fig. 10). Typically, a FLO-DTh-1-based heterojunction solar cell device with PC₇₁BM as acceptor provided a moderate PCE of *ca.* 0.8% with an active area of 0.28 cm².³⁹

Planar disk-shaped conjugated molecules generally show prominent supramolecular behavior on the surface and in bulk. Columnar superstructures and stable liquid crystalline phase are featured for extended disk-shaped polyaromatic systems, which lead to high one-dimensional charge carrier mobility due to the large π -orbital overlap.⁴⁰ By taking these advantages, Wong *et al.* used fluorenyl hexa-*peri*-hexabenzocoronene (FHBC) as the scaffold, which was coupled with a series of thiophene dendrons for obtaining broad UV-vis absorption and tailorable thin film morphology (HBC-*p*-F8-*n*T) (Fig. 11).⁴¹ The BHJ solar cell devices fabricated using these FHBC compounds as donor materials blended with PC₆₁BM showed high open-circuit voltages (V_{oc}) of 0.9–1.0 V, comparable to those of pure thiophene-dendrimer analogues. The short circuit currents (J_{sc}) and fill factors of FHBC-based devices were remarkably higher than those of corresponding thiophene dendrons, which could be ascribed to the better charge transport in the active layer induced by the pronounced supramolecular organization of the FHBC moiety. With the PC₇₁BM as the acceptor material, a HBC-*p*-F8-9T based device provided a high power conversion efficiency of 2.5%.

In another case involving planar disk molecule, trithieno-benzene-core branched oligothiophenes (TTB-D*n*T) have been reported (Fig. 11).⁴² The branched oligomers exhibited lower oxidation potentials and red-shifted absorption spectrum in

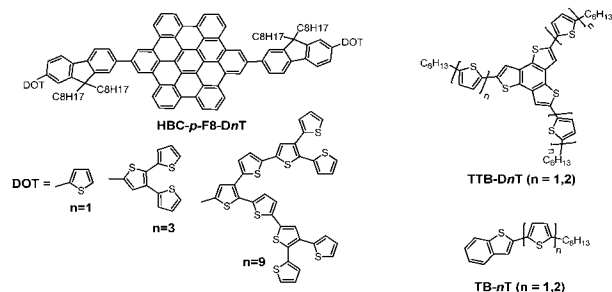


Fig. 11 Molecular structures of representative core-functionalized dendritic oligothiophenes.

comparison to the linear analogues (TB-*n*T), owing to an increased π -conjugated delocalization. TTB-D2T also showed a much higher thermal stability ($T_d > 400$ °C) than the linear compounds TB-2T ($T_d > 200$ °C). Using TTB-D2T as the donor and *N,N'*-bis(tridecyl)perylene-3,4,9,10-tetracarboxylic diimide as the acceptor, a moderate performance of BHJ solar cell with PCE of *ca.* 0.8% was obtained. Triphenylamine (TPA) is well known for its hole transporting properties and has been incorporated into dendritic oligothiophenes. Typically, star-shaped TPA-D3T and TPA-D3T-EDOT (Fig. 12) could be synthesized by using Stille and Suzuki cross-coupling reactions.^{32c} Bilayer solar cells fabricated with these two compounds as donors and C₆₀ as acceptor offered low PCE values from 0.14 to 0.32% with a poor fill factor of around 0.3. By applying Suzuki cross-coupling, the benzothiadiazole core was coupled with triphenylamine through oligothiophenes to form A–D type branched conjugated molecules (BDTA-2T-TPA and BDTA-2T-TPA-Hex, Fig. 12).⁴³ Blended with PC₇₁BM as electron acceptor, PCEs of 1.4% ($V_{oc} = 0.84$ V) and 1.6% ($V_{oc} = 0.89$ V) were achieved for the devices using BDTA-2T-TPA and BDTA-2T-TPA-Hex, respectively. Bäuerle and his colleagues developed D–A type star-shaped conjugated molecules of triphenylamine-core oligothiophenes end capped with *N*-(2,4-diisopropylphenyl)perylene-3,4,9,10-tetracarboxylic diimide units (TPA-*n*T-PRL).⁴⁴ A BHJ solar cell device on the basis of TPA-2T-PRL and PC₆₁BM gave a PCE of 0.25%. One of the substantial limits is a low fill factor (around 0.29).

The sequence of the donor (D) and acceptor (A) segments in a molecular structure also exerts a strong influence on the frontier orbital levels, light absorption and film-forming characteristics of the materials. Towards this end, a new star-shaped small molecule containing triphenylamine-core benzothiadiazole-bridged oligothiophenes with a D–A–D structure (S(TPA-BT-HTT), Fig. 12) was reported by Zhan *et al.* After blending with PC₇₁BM as acceptor, PCE as high as 4.3% was achieved for the devices fabricated by feasible solution-processing without any post-treatment.⁴⁵ The high J_{sc} observed was attributed to the strong and broad absorption as well as high mobility of

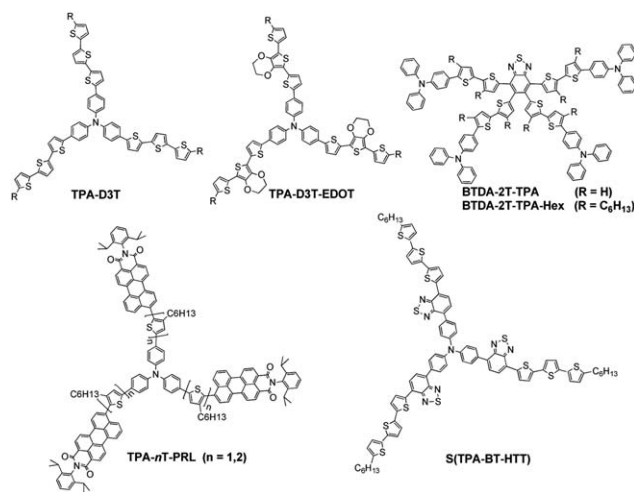


Fig. 12 Molecular structures of TPA-containing dendritic oligothiophenes.

S(TPA-BT-HTT). On the other hand, the lower HOMO of S (TPA-BT-HTT) is beneficial for improving V_{oc} value (0.87 V).

Dendritic silicon-core oligothiophenes (DSi-3T-Hex and DSi-3T-SHex) have been readily synthesized by the reaction of oligothiophenelithium with tetrachlorosilane (Fig. 13).⁴⁶ The bilayer solar cells using *N,N*-bis-tridecylperylene-dicarboximide as the acceptor gave a PCE value of 0.20% for DSi-3T-Hex as donor and 0.17% for DSi-3T-SHex, which are four–five times higher than that of 0.04% for a dihexylterthienyl-based reference system with a comparable effective conjugation length. Such significant improvements can be ascribed to the 3D molecular structures of the dendritic silicon-core oligothiophenes that allow for better absorption of the incident light and higher hole transport properties. Additionally, in a blend containing DSi-3T-SHex and PC₆₁BM, a BHJ solar cell gave an efficiency of 0.29%.

Improved results of BHJ solar cells using dendritic silicon-core oligothiophenes as electron donors were reported by the synthesis of tetrasubstituted quarter- and quinquethiophenesilanes end-capped with alkyl chains. The maximum PCE of 1.0% and 1.4% for quater- and quinquethiophenesilane (DSi-4T-Hex and DSi-5T-Iso-Hex) was obtained respectively (Fig. 13). The increased PCE values are proportional to the chain length of the oligothiophene units.⁴⁷

4. Thiophene-based macrocycles

Cyclic conjugated molecules such as porphyrins and phthalocyanines featuring a 2D structure are well-known light harvesting materials, and have been intensively investigated as donor materials in OSC devices.⁴⁸ Similar to their conjugated linear and dendritic analogues, cyclic oligothiophenes are also promising materials for organic electronics due to their unique electro-optical and self-assembly properties.⁴⁹ Zhu and his colleagues reported the first organic solar cell by using thiophene-based cyclic oligomer tetrathia[22]annulene[2,1,2,1] (TTA) as active layer (Fig. 14).⁵⁰ An OFET mobility of 0.05 cm² V⁻¹ s⁻¹ was obtained for TTA, suggesting its good p-type semiconducting property. The optimized TTA-based PHJ device gave a PCE of 0.23% with PC₆₁BM as acceptor. The low PCE value is probably related to a low V_{oc} of 0.16 V. Despite the success of TTA for application in organic electronics, the expanded thiophene-based macrocycles have been rarely studied so far. The reason can be mainly attributed to the lack of efficient synthetic strategy towards such kinds of molecules with tunable properties. Very recently, Bäuerle and his coworkers presented an elegant

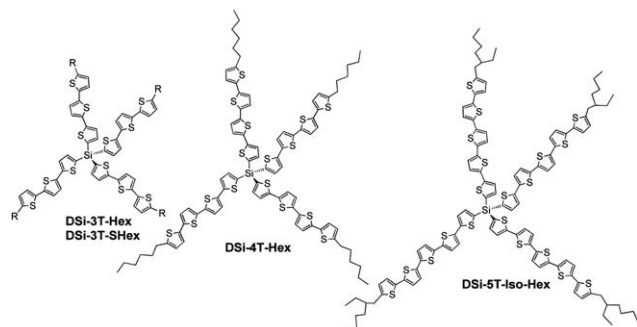


Fig. 13 Molecular structures of dendritic silicon-core oligothiophenes.

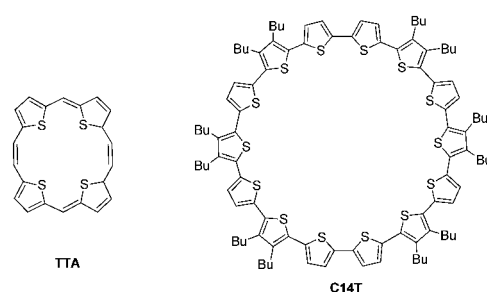


Fig. 14 Molecular structures of thiophene-based cyclic oligomers.

synthesis of cyclic oligothiophenes by Pt-mediated cyclization strategy, which made it possible to construct cyclic oligothiophenes on the basis of different oligothiophene building blocks on preparative scales.⁵¹ Preliminary results of solution-processed BHJ OCS fabricated with cyclo[14]thiophene (C14T, Fig. 14) as donor and PC₆₁BM as acceptor displayed a non-optimized PCE of 0.59% with a V_{oc} of 0.76 V.⁵²

5. Thiophene-based acceptor molecules

As we discussed above, fullerene derivatives remain the most promising acceptor materials for OSCs. However, they generally suffer from some disadvantages, such as expensive cost, poor absorption in the visible region and limited matching donor materials. Currently, significant effort has been devoted to searching for novel nonfullerene -based acceptor materials.⁵³ Regarding the thiophene based systems, it is noteworthy that the thienyl rings can be oxidized to thienyl-S,S-dioxide rings, which exhibit strong electron affinity being suitable as acceptor materials. Barbarella *et al.* for the first time, described oligothiophene-S,S-dioxide derivatives as electron acceptors in combination with P3HT as electron donor for solar cell fabrications (Fig. 15).⁵⁴ The substituents, length of the oligomers, number and position of the S,S-dioxides in the oligothiophene-S,S-dioxide segments all exert remarkable influence on the device performance. The best PCE of 0.06% was obtained by the blends of (5T-Ox-Hex-Me) as

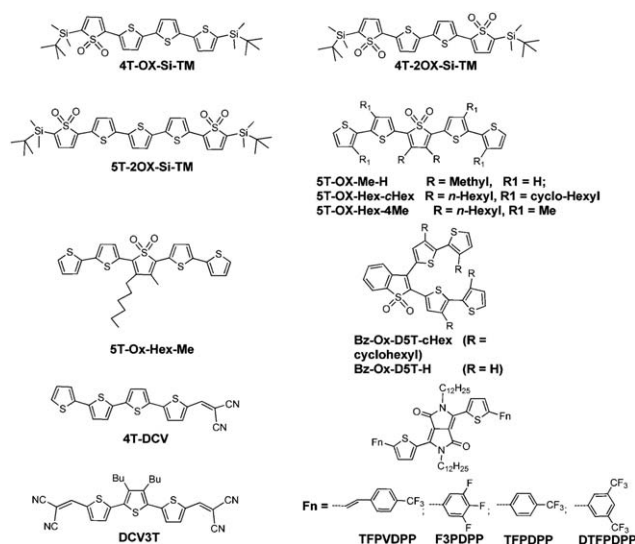


Fig. 15 Molecular structures of thiophene-based acceptors.

acceptor and P3HT as donor in a 1 : 1 ratio. Furthermore, Barbarella *et al.* synthesized quinquethiophene-*S,S*-dioxide (5T-Ox-Hex-Me).⁵⁵ The morphologies and photoresponsive properties of blends comprising (5T-Ox-Hex-Me) as acceptor (A) and regioregular poly(3-hexylthiophene) as donor (D) have been investigated in detail. The scanning force microscopy image of the samples with different ratios of D/A revealed that the 5T-Ox-Hex-Me acceptor molecule tends to form micrometre scale structures within the amorphous matrix of P3HT, and an apparent phase segregation was generated between the two components (Fig. 16). X-Ray diffraction measurement further demonstrated the high crystallinity of 5T-Ox-Hex-Me in the blended films. Therefore, an improved interaction between oligomer acceptor and polymer donor can be estimated, and as the consequence enhanced photoinduced charge separation was obtained, which directly led to increased device efficiency. Furthermore, the same group developed two branched V-shaped 2,3-bis[3,3-bis(cyclohexyl)-2,2-bithienyl]-benzo[*b*]thiophene-1,1-dioxide (Bz-Ox-D5T-cHex) and 2,3-bis(2,2-bithienyl)-benzo[*b*]thiophene-1,1-dioxide (Bz-Ox-D5T-H) molecules, and both of them displayed good solubility in common organic solvents.⁵⁶ When blending with P3HT as donor, the BHJ devices using these two branched molecules as acceptors afforded PCEs between 0.3 and 0.4%. The branched molecular structures of these V-shaped compounds significantly prevent molecular aggregation, and result in the amorphous structure upon blending with P3HT, which stands in contrast to the above linear 5T-Ox-Hex-Me.

Very recently, a series of symmetric diketopyrrolopyrrole-core thiophenes capped with electron withdrawing trifluoromethylphenyl and trifluorophenyl groups (TFPVDPP, F3PDPP, TFPDPP and DTFPDPP) have been established to form low band gap conjugated systems (Fig. 15).⁵⁷ These compounds show intensive broad absorption bands from 300 to 700 nm. Cyclic voltammetry indicates that their frontier orbital energy levels can be effectively tuned through variation of the electron-withdrawing end-capping groups. The HOMO values of above four compounds vary from 5.18 for TFPVDPP to 5.31 eV for F3PDPP. The HOMO energy level of TFPVDPP is highest among these four molecules which can be due to an extended conjugated effect originating from a vinyl group with phenylene in the molecular backbone. The LUMO values of these compounds are in the range of 3.52 to 3.68 eV. The lowest LUMO values were found for DTFPDPP (3.57 eV) and F3PDPP (3.68 eV), due to a higher number of electron-withdrawing groups (two trifluoromethyl and three trifluoro, respectively) on

the end-capping phenyl ring. These compounds were used as acceptor materials with P3HT as donor and provided device efficiencies in the range of 0.5 to 1% under simulated AM 1.5 solar irradiation. Apart from the different molecular structures, the solvents used for the spin coating of the blends also show a significant effect on the photovoltaic properties of these materials. A TFPDPP-based device processed from toluene gave the highest PCE of 1% with $V_{oc} = 0.81$ V, $J_{sc} = 2.36$ mA cm⁻², and FF = 55%, in contrast to the performance (PCE = 0.25%, $V_{oc} = 0.9$ V, $J_{sc} = 1.04$ mA cm⁻², FF = 27%) of the device processed from chloroform.

Terthiophene was end-capped with electron-withdrawing dicyanovinylene groups to form DCV3T, of which the LUMO energy level is approximately 0.3 eV higher than that of C₆₀ (Fig. 15).⁵⁸ In this work, the authors proposed a new concept by blending of DCV3T and C₆₀ as co-acceptor materials which allowed for an increased generation of triplet excitons on the oligomer *via* a back and forth transfer of excitons. Thereby, combined with typical *N,N,N',N'*-tetrakis(4-methoxyphenyl) benzidine as donor material, two-component acceptors were used for OSCs to afford a PCE of 1.6% with a remarkably high V_{oc} up to 1.04 V. This work may pave a new path for fabricating high-performance organic solar cells because triplets have the potential for enhanced diffusion lengths due to their long life time.

6. Conclusion and outlook

Because of their excellent electro-optical properties, prominent self-assembly capabilities and versatile chemical modifications, thiophene-based conjugated oligomers have attracted tremendous attentions for developing high-performance OSCs. In this feature article, we have summarized the recent progress of OSCs involving the application of thiophene-based small molecules that feature different architectures spanning a broad range from 1D, 2D to 3D, including linear, cyclic and dendritic systems. Given the indispensable characteristics for OSCs, these materials provide not only very rich natures in electrochemistry, photo-physics and supramolecular chemistry, but also a broad tuning range in morphology and film-forming properties.

A series of linear thiophene-based small molecules have been readily synthesized and purified by presently available protocols. Their high thermal stability makes them especially suitable for vacuum-deposited device fabrications. Recently, a remarkable progress in solution-processable devices has also been achieved for small molecules, and the device efficiency of more than 4% is comparable to polymer solar cells.

D–A type molecular combinations offer a valid strategy to improve the spectral absorption, flexible tuning in frontier orbital energy levels and supramolecular behavior. In this way, various conjugated thiophene based D–A oligomers have been designed and synthesized for the new generation of photovoltaic devices. Very recently, Heliatek company reported that tandem cell using D–A oligothiophene and the vacuum-deposited method yielded a record PCE of 8.3%, which represents the highest value for such kind of devices.⁸

The 3D dendritic thiophenes possess certain mono-dispersion structures of “small molecule”, and broad spectral absorption and good film-forming properties of “polymer”. Such features

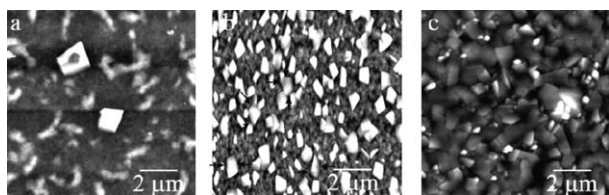


Fig. 16 Topographical SFM (scanning force microscopy) image recorded in non-contact mode of blend films with different weight ratios of P3HT:5T-Ox-Hex-Me: (a) 3 : 1; (b) 1 : 1; (c) 1 : 3. Reproduced with permission from ref. 55. Copyright 2005 The Royal Chemical Society.

for dendritic thiophenes enable the possibility to fabricate photovoltaic devices by means of solution-processable techniques. The highest efficiency for pure thiophene dendrimer-based device is however less than 2.0%. Compared to other oligothiophene-based materials, the rather poor performance can be possibly ascribed to the low crystallinity of dendritic systems in the solid state, which unavoidably leads to low charge carrier transport behavior. In order to overcome this obstacle, disk-shaped polyaromatic systems as self-organizing units have been coupled with thiophene dendrons to gain better supramolecular ordering and higher one-dimensional charge carrier mobility, which eventually lead to improved solar cell device performance. Incorporation of D–A structure into dendritic branches represents another promising approach to build up high performance OSCs because of the improvement of spectral absorption and film formation properties.

The 2D thiophene-based cyclic molecules show unique electro-optical and self-assembly properties. However, they remain a class of rarely explored thiophene systems for the OSCs. In this respect, the handicap that needs to be firstly resolved is to develop an efficient synthetic strategy that allows one to readily access these intriguing materials. Therefore, future work should be directed to establishing effective routes for the building up of expanded cyclic oligothiophenes with tunable properties. The macrocycle size and the nature of the macrocycle backbone and periphery, which play essential roles on the absorption spectra, energy levels and supramolecular behavior as well as final device performance, need to be further elucidated. We believe that there is a huge space remaining for the development of cyclic oligothiophenes with different structural complexity.

For solution-processed OSCs, polymer-based devices normally exhibit higher efficiencies than small-molecule ones, mainly attributable to the better film-forming properties of the polymeric materials. On the other hand, conjugated chain length distribution in a polymer also helps for sunlight harvesting by covering a broader region of the absorption spectrum. From the viewpoint of these, we suggest that the oligothiophene-based active materials should be designed as: (1) an extended molecular structure with a higher molecular weight for improving film-forming ability; (2) introduction of conjugated units with high coplanarity into backbone for benefiting the solid state packing and increasing charge carrier mobility; (3) incorporation of hetero-atoms and fluorine moieties for enhancing nano-scale self-assembly property by hydrogen bonding; (4) optimization of D–A type molecular combination for tuning the band gap, energy levels as well as sunlight harvesting efficiency.

In comparison to the electron donor materials, thiophene-based acceptor materials are still very rare. Introduction of electron-withdrawing group into oligothiophenes can render the transformation from p-type nature to n-type character. The photovoltaic devices using these molecules as electron acceptor showed so far only a moderate PCE value of around 1%. Therefore, exploration of small molecule-based electron acceptors in place of expensive traditional fullerene derivatives, meanwhile pairing with electron donors, remains one of the major goals to realize practical low-cost organic photovoltaic devices.

To conclude, high-performance OSCs have been constantly and rapidly emerging during the last five years, and a sunny outlook can be foreseen. During our preparation of this feature

article, a new PCE record of 9.2% for OSCs has been reported by Mitsubishi Chemical, a company in Japan.⁵⁹ The flexible, large-area applications of OSCs may open up new markets soon.

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