Star-shaped organic semiconductors with planar triazine core and diketopyrrolopyrrole branches for solution-processed small-molecule organic solar cells

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ABSTRACT

A series of novel triazine-cored, star-shaped, conjugated molecules have been synthesized as donor materials for small molecule based organic solar cells. The structural features of these star-shaped molecules include a planarized triazine as the central core, 2,5-thienyl diketopyrrolopyrrole and 1,4-phenylene diketopyrrolopyrrole as the π-conjugated bridge, and *tert*-butyl-substituted triphenylamine and *tert*-butyl-substituted carbazole as the role of end groups and donor units. Photovoltaic properties of the solar cells based on the star-shaped molecule with 2,5-thienyl diketopyrrolopyrrole branches were much better than those of the solar cells based on the one with 1,4-phenylene diketopyrrolopyrrole branches. A power conversion efficiency of 1.57%, a short-circuit current density of 6.34 mA/cm^2, an open-circuit voltage of 0.73 V, and a fill factor of 0.34 were observed for the organic solar cell based on the star-shaped molecule with 2,5-thienyl diketopyrrolopyrrole branches.

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1. Introduction

Bulk heterojunction (BHJ) type organic solar cells (OSCs) based on the conjugated small molecules as the electron donor materials, with the fullerene derivatives (PC$_{61}$BM or PC$_{71}$BM) as the electron-acceptor, have attracted much attention in recent years, because of their unique advantages of well-defined structure, easy purification, definite molecular weight, easy large scale production and good batch to batch reproducibility [1—4]. In particular, star-shaped molecules (SSMs) have been developed as a photoactive materials for solar cells due to a number of advantages, including good solution processability, high mobility, and a low band gap and broad absorption in the visible region [5—10]. By tailoring the core, peripheral groups, and conjugated bridges with various donor and acceptor units, SSMs based solar cells with high photo-energy conversion efficiency (PCE) could be achieved [11—15].

Electron donor—π conjugated—acceptor (D—π—A), electron donor—acceptor—donor (D—A—D), and donor—donor—acceptor (D—D—A) structured SSMs with different electron donating cores, conjugated bridges, and electron-acceptor groups have been investigated [16—20]. A strong electron-donating triphenylamine (TPA) unit cored SSM with three dimensional structure shows high hole-transporting ability and good solution processability. The conjugated branches with peripheral strong electron-acceptor for the TPA cored molecule would enhance the light absorption and intramolecular charge transfer (ICT), and reduce the band gap energy, resulting in an improved photovoltaic properties (PV) of the SSMs [21—25]. The photo-physical properties of such SSM with strong peripheral electron-acceptors were closely related to the branching numbers. The TPA cored molecule with a higher degree of branches showed a broad absorption band and low band gap energy [26]. In addition, the TPA cored SSM with an unsymmetrical structure (i.e., two conjugated branches) led to a broad absorption, high absorption coefficient, and a low lying HOMO level, resulting in a high V_{OC} of such molecule based solar cell [8]. It is noteworthy that the TPA cored SSMs with longer conjugated branches induced a shift of the absorption onset toward longer wavelength and higher PCE than the cell based on the SSM with shorter conjugated branches [27—29]. Apart from that, planarized SSMs with trithienobenzene, triindole, isotruxene or triazatruxene as the cores for

the photoactive layers of solar cells have been studied [23,30—33]. The incorporation of the planar core could reduce the dihedral angle between the core and the arms of SSM. The combined effects of planarization and rigidification of the trithienobenzene core led to a significant enhancement of π-electron delocalization associated with a decrease of the energy gap for SSMs [34,35]. Despite the fact that the highest PCEs (4—5%) of the solution processable SSM based BHJ type solar cells has been reported, PV performance of the molecules with different cores, conjugated bridges, and peripheral groups have not been thoroughly investigated.

Accordingly, SSMs with electron-donating cores have been extensively studied [6—41]. For these D—π—A, D—A—D, or D—D—A structured SSMs, the direction of the dipole moments is divergent from the core to the peripheral groups along the conjugated branches (Fig. 1(a)—(c)). One might wonder what would happen if the direction of the dipole moments is convergent from peripheral groups to the core along the conjugated branches (Fig. 1(d)). The triazine group exhibits high thermal stability, molecular symmetry, spatial coplanarity, and great potential for structural modification [42]. Moreover, the incorporation of an electron deficient triazine group as core would decrease the LUMO level and energy gap of the molecule. This is favorable for the harvesting of large amounts of solar radiation. Furthermore, the convergence of dipole moments from peripheral groups to the core along the conjugated branches could avoid the formation of a long range and coplanar π—π stacking, which is beneficial to the charge transport across the thin film based solar cell [43]. The molecules with planar core seem to adopt a preferential horizontal orientation on the surface of substrate, leading to more efficient absorption of incident light [23]. In this study, a novel series of solution processable A—A—D structured SSMs with a triazine as the core and acceptor unit, 2,5-thienyl diketopyrrolopyrrole (TDPP) and 1,4-phenylene diketopyrrolopyrrole (PDPP) as π-conjugated

Fig. 1. Illustrations of (a) D—π—A, (b) D—A—D, (c) D—D—A, and (d) A—A—D structured SSMs.

bridge and acceptor, and *tert*-butyl-substituted triphenylamine (tTPA) and *tert*-butyl-substituted carbazole (tCz) as end groups and donor units. TDPP-TPA, PDPP-TPA, and PDPP-Cz were synthesized for the application as donor materials in BHJ type solar cells. The incorporation of low band gap moieties (TDPP and PDPP) in branches as electron-acceptors favors for the enhancement of ICT and solar light absorption of molecules [36—39]. Strong electron-donating peripheral groups (tTPA and tCz) are expected to enhance the charge transfer ability and red-shift the absorption band in the visible region. The BHJ type OSCs based on these SSMs as the electron donor materials, with the fullerene derivatives (PC$_{61}$BM or PC$_{71}$BM) as the acceptor moiety were fabricated. The influence of the molecular-structural features of the A—A—D structured SSMs on solar cell performance was also discussed.

2. Experimental details

2.1. Materials and instrumentation

Tetrakis(triphenylphosphine)palladium(0) (Pd(PPh$_3$)$_4$), potassium carbonate (K$_2$CO$_3$), n-butyllithium (2.5 M in hexane), and other reagents and chemicals were purchased from Aldrich, Alfa, Acros, and TCI Chemical Co., and used as received. Dichloromethane (DCM), tetrahydrofuran (THF), dimethylformamide (DMF), toluene, N-methyl-2-pyrrolidone (NMP), and *o*-dichlorobenzene (*o*-DCB) were freshly distilled over appropriate drying agents prior to use as solvents, and were purged with nitrogen.

^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were recorded using a Varian Unity Inova spectrometer. Fourier transform infrared (FTIR) spectrum measurement was performed on a HORIBA FT-720 FTIR spectrometer. Elemental analysis was performed using an elemental analyzer (Elementar Vario EL III). The glass transition temperature (T_g), melting temperature (T_m), and thermal decomposition temperature (T_d; temperature at which weight loss reaches 5%) of SSMs were determined by means of differential scanning calorimetry (TA Instruments, DSC-2010) and thermogravimetric analysis (TA Instruments, TGA-2050), respectively. Both analyses were performed under a N$_2$ atmosphere at a scanning (both heating and cooling) rate of 10 °C min^{-1}. The temperatures at the intercepts of the curves in the thermogram (endothermic, exothermic, or weight loss) with the leading baseline were taken as estimates of T_g and T_d. Absorption spectra were measured using a Hewlett—Packard 8453 UV—vis spectrometer. Fluorescence spectra were measured using an Acton Research Spectra Pro-150 luminescence spectro-photometer. Dilute *o*-DCB solutions of the TDPP-TPA, PDPP-TPA, and PDPP-Cz were filtered through a 0.45 μm filter to remove insoluble materials before spectral measurements. Cyclic voltammetry measurements of the TDPP-TPA, PDPP-TPA, and PDPP-Cz were determined with a CHI 611D electrochemical analyzer (CH Instruments, Inc.; scanning rate: 50 mV s^{-1}) equipped with Pt electrodes and an Ag/Ag$^+$ (0.10 M AgNO$_3$ in MeCN) reference electrode in an anhydrous, N$_2$-saturated solution of 0.1 M Bu$_4$NClO$_4$ in MeCN. A Pt plate coated with a thin polymer film was used as the working electrode; a Pt wire and an Ag/Ag$^+$ electrode were used as the counter and reference electrodes, respectively. The electrochemical potential was calibrated against ferrocene/ferrocenium. The morphology of films prepared from TDPP-TPA/PC$_{61}$BM, PDPP-TPA/PC$_{61}$BM, and PDPP-Cz/PC$_{61}$BM blends was studied using an atomic force microscope (AFM, Seiko SII SPA400), and a transmission electron microscope (TEM, JEOL JEM-1400).

2.2. Synthesis of SSMs

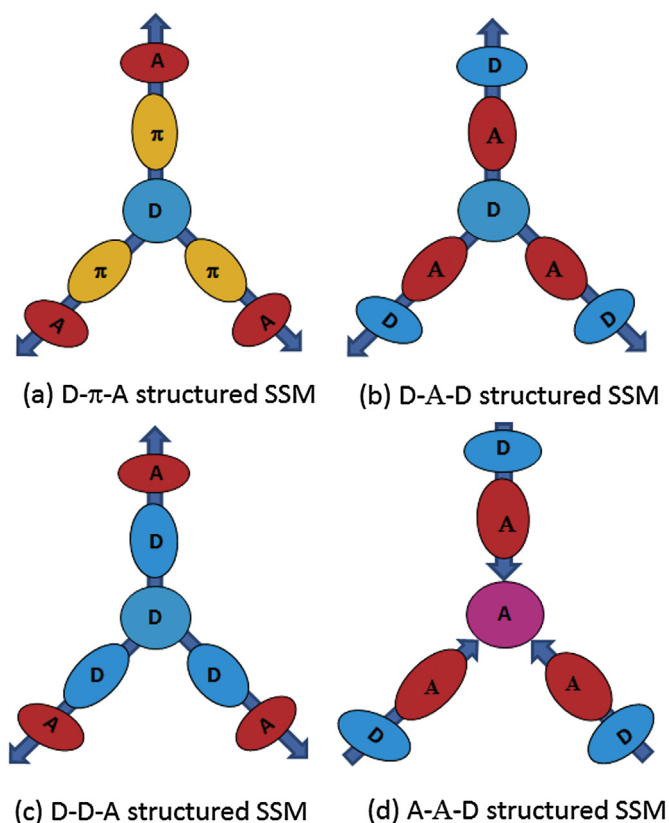Compounds 3-[4-[4-(*N,N*-Bis(4-*tert*-butyl-phenyl)amino)phenyl]thiophen-2-yl]-6-(5-bromothiophen-2-yl)-2,5-di-2-ethylhexylpyr-