Organic Electronics 52 (2018) 342–349

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Fluorination effects of A-D-A-type small molecules on physical property and the performance of organic solar cell

Ko-Wei Chen[a], Li-Yen Lin[a], Yi-Hua Li[b], Ya-Ze Li[b], Thanh Phuc Nguyen[b], Sajal Biring[b], Shun-Wei Liu[b],**, Ken-Tsung Wong[a,c,*]

[a] *Department of Chemistry, National Taiwan University, Taipei, 106, Taiwan*
[b] *Department of Electronic Engineering and Organic Electronics Research Center, Ming Chi University of Technology, New Taipei City, 243, Taiwan*
[c] *Institute of Atomic and Molecular Science, Academia Sinica, Taipei, 10617, Taiwan*

ARTICLE INFO

Keywords:
Organic photovoltaics
Small-molecule organic solar cell
A-D-A donor
Fluorination effect
2,1,3-Benzothiaidiazole

ABSTRACT

Four new molecules with acceptor-donor-acceptor (A-D-A) configuration where cyclopenta[2,1-b:3,4-b′]dithiophene (CPDT) as the electron-donating core connecting to cyano(CN)-substituted 2,1,3-benzothiaidiazole (BT) as electron-withdrawing end groups are reported. With the same acceptor CN-BT, we found that CPDT can serve as a better donor as compared to that of dithieno[3, 2-b: 2′, 3′-d]silole (DTS) to give stronger intramolecular charge transfer (ICT) character and therefore better light harvesting ability. The number and orientation of F-substitution on the BT ring, giving a clear structure-property relationship, can subtly manipulate the physical characteristics. These A-D-A type molecules were employed as electron donor in conjunction with C_{70} as the electron acceptor in vacuum-deposited bulk heterojunction (BHJ) small-molecule organic solar cells (SMOSCs). Among them, the device based on **CBCIF** containing BT ring with one F group directing toward the CPDT core gave the best device performance with a power conversion efficiency of 4.94% with J_{sc} of 10.16 mAcm^{-2}, V_{oc} of 0.98 V, fill factor (FF) of 0.50. The superior device characteristics were attributed to the suitable morphology of the donor/C_{70} film.

1. Introduction

Organic photovoltaics (OPVs) have attracted substantial attention due to the advantages such as lightweight, mechanical flexibility, material diversity, green and cost-effective manufacturing as compared to those of Si-based photovoltaics. In the last two decades, many research endeavors have been made to improve the OPV device performance, which included the developments of new conjugated polymers and small molecules with diverse light-harvesting regions and the exploitation of novel device architectures. These interdisciplinary efforts have made significant improvements on the device performance and durability [1–9]. The power conversion efficiencies (PCEs) of solution-processed bulk heterojunction (BHJ) solar cells employing polymers as the donor in conjunction with fullerene derivatives as acceptor have achieved great accomplishments [10,11]. To date, PCE better than 11% has been reported with a single-junction BHJ solar cell using polymer as donor [12–16]. Furthermore, solution-processed polymeric donor-based OPVs with multiple-junction tandem structures have also been reported to achieve PCE up to 11.60% [17]. Polymeric donors could be roughly divided into two broad types such as homopolymers or push-pull copolymer (Donor-Acceptor polymers). In spite of synthetic simplicity on homopolymer systems using single monomers, there were limited cases of homopolymeric donors reported to give PCE higher than 6% [18], mainly owing to the unsatisfactory light absorption region, which might restrict the short circuit current (J_{sc}) values of the device [19–22]. In contrast, copolymers composed of electron-donating (D) and electron-accepting (A) blocks are more successful both for the modulation of physical characteristics and the control of film morphologies, leading to better device performance [23–27]. In addition to the various structural features (D or A, twisted or coplanar) imposing on the molecular backbone, the introduction of fluorine atoms onto the conjugated backbone has also attracted attention recently. For example, polymer employing 3-fluorothieno [3,4-b]thiophene [26,28,29], difluorinated benzo[d] [1-3]triazoles (FTAZ) [30], mono- or difluorinated- 2, 1, 3-benzothiaidiazole (BT) [31–34], and mono-fluorinated isoindigo [35,36] exhibited superior device performance than those of non-fluorinated counterparts. These results can be partially attributed to the benefit of lowering down the frontier energy

---

[*] Corresponding author. Department of Chemistry, National Taiwan University, Taipei, 106, Taiwan.
[**] Corresponding author. Department of Electronic Engineering and Organic Electronics Research Center, Ming Chi University of Technology, New Taipei City, 243, Taiwan.
E-mail addresses: swliu@mail.mcut.edu.tw (S.-W. Liu), kenwong@ntu.edu.tw (K.-T. Wong).

https://doi.org/10.1016/j.orgel.2017.11.021
Received 3 October 2017; Received in revised form 16 November 2017; Accepted 18 November 2017

levels but remain optical energy gap of fluorinated polymers, which could evidently increase the open circuit voltage (V_{oc}) of the device [31,33,37,38]. In addition, the molecular dipole along the C—F bond and the small size as well as the high electronegativity of fluorine atom are believed to be highly beneficial for reinforcing the intermolecular interactions for better exciton diffusion and charge extraction [30,39,40].

Compared with the thoroughly explored polymeric donors, small molecule-based donors have also received great concern over the past few years. Small molecules exhibit advantages like well-defined structure and molecular weight, higher purity given by simpler purification without batch-to-batch variation, more flexibility for device fabrication (solution-processed and/or vacuum-deposited). Up to date, solution-processed small molecule organic solar cells (SMOSCs) with PCE better than 9% have been reported [41,42]. Besides, vacuum-processed single junction cell with PCE better than 8% [43] and multi-junction tandem cell with PCE better than 10% [44] have also been successfully achieved. The comparable high performance achieved in SMOSCs opens a new space for innovative ideas of designing novel small molecules with tailor-made structures and designated physical characteristics. Among various structures, central symmetric small molecules configuring as acceptor-donor-acceptor (A-D-A) or donor-acceptor-donor (D-A-D) exhibit low molecular dipole moment, which could reduce the energetic disorders and facilitate charge transport in bulk state [45], giving better device performance as they were utilized as donors. Various electron-withdrawing groups such as dicyanovinylene, cyanoacetate, rhodamine, BT, diketopyrrolopryrole and isoindigo have been introduced as A, whereas oligothiophene, coplanar arene/heteroarenes and arylamines were selected as D [46–55]. Similar to the F-introduced polymeric donors, the introduction of fluorinated electron-withdrawing groups for making small molecule-based donors has resulted in improved PCEs [56–66].

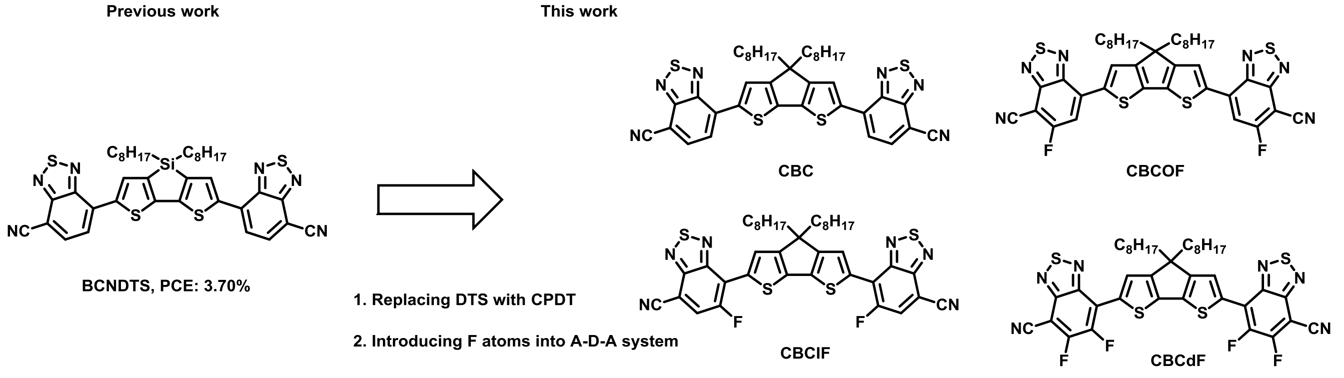
Previously, we reported an A-D-A small-molecule donor (**BCNDTS**, Scheme 1) consisting of dithieno [3, 2-b: 2′, 3′-d]silole (DTS) as the donor core and cyano-substituted BT as the terminal acceptor [67]. The SMOSC employing **BCNDTS**/C_{70} (1:1.5) as active layer showed a PCE of 3.7%, which is better than the device using C_{60} as the electronic acceptor. We found that DTS and its C-bridged analogue cyclopenta [2,1-b:3,4-b′]dithiophene (CPDT) have been widely exploited as the electron-donating moiety in D-A copolymers for OPVs and other applications [68–71]. In addition, the absorption region of a CPDT-containing polymer exhibits better light-harvesting ability for long wavelength photons as compared to that of its DTS-containing counterpart. Therefore, we envisioned that the replacement of central electron-donating DTS moiety in **BCNDTS** with CPDT would lead the new A-D-A donor to have different optical and/or electronic features and hence improve the device performance. In this work, we made a new CPDT-centered A-D-A donor (**CBC**) for exploring the bridge atom effects on the physical characters as well as device performance. In addition, we introduced different number and position of F-substitution onto the BT ring to probe the fluorination effects on the physical properties of the resulting A-D-A molecules (**CBCOF**, **CBCIF**, and **CBCdF**, Scheme 1) and the device characteristics of vacuum-processed SMOSCs. This systematic study has concluded a clear structure-property-performance relationship. The fluorination subtly modulates the energy levels (gaps), molecular dipoles of donors, and the D/A-blended films morphologies to strongly govern the device characteristics. Among these four new A-D-A-type donors, device based on **CBCIF**/C_{70} (1:3) as the active layer gave the best device performance with a J_{sc} of 10.16 $mAcm^{-2}$, V_{oc} of 0.98 V, fill factor (FF) of 0.50 and PCE up to 4.94% (maximum), which outperforms the difluorinated donor **CBCdF**-based device.

2. Experimental section

2.1. Synthesis

Synthesis of 7-bromo-6-fluorobenzo[c] [1,2,5]thiadiazole-4-carbonitrile (**4**). A mixture of **3** (6.24 g, 20 mmol) [32,58], $Zn(CN)_2$ (1.41 g, 12 mmol), and $Pd(PPh_3)_4$ (2.31 g, 2 mmol) in *N*-methyl-2-pyrrolidone (NMP) (60 mL) was stirred and heated at 120 °C under argon for 2 h. After the reaction mixture was cooled to room temperature, 100 mL water (H_2O) was added to the mixture, the solution was poured to celite with water to remove NMP, and then used the dichloromethane (DCM) as eluent, followed by extraction with DCM/H_2O. The organic layer was separated, dried over $MgSO_4$ and then the solvent was removed by the rotary evaporation. The crude mixture was purified by column chromatography with DCM/hexane (1:1) as eluent to afford **2** as a yellow solid (2.17 g, 42%), mp: 143–144 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, $J = 8.0$ Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.42, 157.89, 153.47, 153.41, 149.37, 126.72, 126.40, 113.64, 113.61, 106.02, 105.77, 105.13, 105.03, 77.32, 77.00, 76.68. ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.29 (d, $J = 8.0$ Hz, 1F); IR (KBr) υ 3448, 2236, 1636, 1593, 1484, 1394, 1326, 1318, 1298, 1191, 899, 876, 845 cm^{-1}. HRMS-FAB$^+$(m/z): Calcd for $C7H^{79}BrFN_3S$ 256.9059; found, 256.9055. $C7H^{81}BrFN_3S$ 258.9038; found, 256.9037.

Synthesis of 7,7′-(4,4-dioctyl-4*H*-cyclopenta[2,1-b:3,4-b′]dithiophene-2,6-diyl)bis(benzo[c] [1,2,5]thiadiazole-4-carbonitrile) (**CBC**). A mixture of **1** (0.981 g, 1.0 mmol) [71,72], **2** (0.480 g, 2.0 mmol) [66], and $PdCl_2(PPh_3)_2$ (0.007 g, 0.01 mmol) in anhydrous *N*,*N*-Dimethylmethanamide (DMF) (10 mL) was stirred and heated at 100 °C under argon for 4 h. After the reaction mixture was cooled to room temperature, the crude was reprecipitated with DCM and methanol (MeOH) for removing DMF and some impurities. Then, the suspension was filtered and washed with MeOH. The resulting mixture was purified by column chromatography with DCM/hexane (1.5:1). After removal all of the solvent, the solid was reprecipitated with DCM and pentane to afford **CBC** as a brown solid (0.490 g, 0.68 mmol, 68% yield). mp: 235 °C (DSC). ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 2H), 8.03 (d, $J = 7.6$ Hz, 2H), 7.91 (d, $J = 7.6$ Hz, 2H), 2.07–1.96 (m, 4H), 1.15 (s, 20H), 1.10–1.02 (m, 4H), 0.78 (t, $J = 6.6$ Hz, 6H). ^{13}C NMR (101 MHz,



Scheme 1. Molecular structures of **BCNDTS** and new CPDT-based molecules.