RSCPublishing ChemComm

D-π-A-π-D type benzothiadiazole-triphenylamine based small molecules containing cyano on π-bridge for solution-processed organic solar cells with high open-circuit voltage

Journal:	*ChemComm*
Manuscript ID:	CC-COM-08-2012-035754.R1
Article Type:	Communication
Date Submitted by the Author:	07-Sep-2012
Complete List of Authors:	Zeng, Shaohang; Dalian Universtiy of Technology, School of Chemistry Yin, Lunxiang; Dalian University of Technology, School of Chemistry Ji, Changyan; Dalian Universtiy of Technology, School of Chemistry Jiang, Xueying; Jilin University, li, kechang; jilin university, chemistry Li, Yanqin; Dalian University of Technology, School of Chemistry Wang, Yue; Jilin University, State Key Baboratory of Supramolecular Structure and Materails, College of Chemistry

Journal Name

ChemComm

Dynamic Article Links ► View Online

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

D-π-A-π-D type benzothiadiazole-triphenylamine based small molecules containing cyano on π-bridge for solution-processed organic solar cells with high open-circuit voltage†

Shaohang Zeng,[a] Lunxiang Yin,[a] Changyan Ji,[a,b] Xueying Jiang,[b] Kechang Li,[b] Yanqin Li*[a] and Yue Wang*[b]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Two novel D-π-A-π-D structured small molecules composed of benzothiadiazole and triphenylamine were designed and synthesized. BDCTBT with cyano on π-bridge exhibited a deep HOMO energy level, resulting an impressive V_{OC} up to 1.04 V with a PCE of 3.85%, while non-cyano substituted BDETBT yielded the V_{OC} of 0.94 V and the PCE of 1.99%.

Organic solar cells, as a promising alternative to traditional inorganic photovoltaic devices, have attracted extensive investigation in last two decades, due to their low-cost, light-weight and flexible characteristics.[1] Solution processed bulk-heterojunction organic solar cells (BHJ OSCs) possess potential for commercialization because of their high internal quantum efficiency and large-scale printing technique.[2] Although polymers have been widely applied to BHJ OSCs[3] and achieved impressive progress of power conversion efficiencies (PCEs) over 8%,[4] the interests of solution-processable small molecular π-conjugated organic donors have been accelerating for BHJ photovoltaic applications in recent years, owing to the advantages of definite structure, facile purification, high purity and well photovoltaic performance reproduction.[5] Despite Heeger and Bazan et al. reported a competitive PCE of at around 7% for small molecular OSCs,[6] in general, the application efficiencies obtained from these small molecules are relatively lower than the PCEs of polymeric counterpart. Thus, in order to introduce small molecular semiconductors into commercial solar cells, their efficiencies need to be improved.

To meet this need, two straightforward strategies have been considered: 1) reducing the band-gap of molecular donors to broaden the absorption range, which results higher short-circuit current density (J_{SC}) of devices, and 2) lowering the highest occupied molecular orbit (HOMO) of molecular donors so as to increase the open-circuit voltage (V_{OC}) of applications.[7] Obviously, developing new D-A organic small molecules is an efficient way to maximize the photovoltaics parameters, because this structure can not only narrow the band-gap by utilizing intramolecular charge transfer (ICT) transition between electron donating and withdrawing units inside molecules, but also control the energy levels through employing different donor or acceptor moieties into the molecules. So far, with the increased interests in exploring low band-gap small molecules to absorb sunlight at longer wavelength, small molecular BHJ solar cells have reached considerable J_{SC} up to 14 mA·cm^{-2}.[6, 8] On the other hand, the BHJ devices with high V_{OC} over 1 V have scarcely been realized using a p-type small molecule as a donor,[9] on account of the barrier of narrowing the band-gap of small molecules without sacrificing lowest unoccupied molecular orbit (LUMO) for effective charge separation as well as large V_{OC} values depending on the low-lying HOMO. Therefore, careful modification of energy levels from functional groups selection is of the utmost importance in improvement of device properties, especially achieving reduced HOMO without enhancing molecular band-gap. Among conjugated polymer donors, fluorine-containing polymers exhibit lower HOMO and LUMO levels as a result of the high electron affinity nature of fluorine atom, suggesting that the addition of electron-acceptor groups is effective in further stabilizing energy levels.[10] Moreover, cyano is a well electron-withdrawing group which has been extensively used in organic dyes for dye-sensitized solar cells.[11] Noticeably, lower energy levels were observed for dyes containing one more cyano group on their π-bridge.[12] In addition, some conjugated polymers substituted with cyano-groups at their vinylic linkage have been reported as photovoltaic materials.[13] Consequently, we envisioned that incorporating an cyano unit into the D-A conjugated small molecules could decrease the HOMO value to obtain high V_{OC} for photovoltaic application.

In this communication, we reported the syntheses, theoretical calculation, photophysical and electrochemical properties, and photovoltaic performances of two novel D-π-A-π-D type low band-gap benzothiadiazole-triphenylamine based small molecular donor materials, **BDCTBT** and **BDETBT**, one of which contained cyano groups anchoring on π-bridge (see Fig. 1(a) for

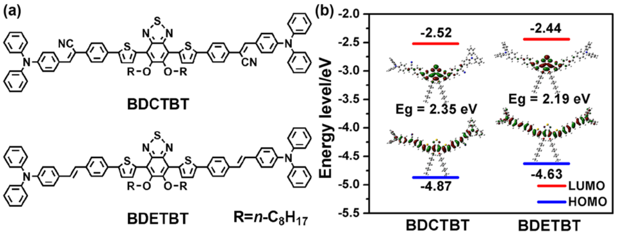
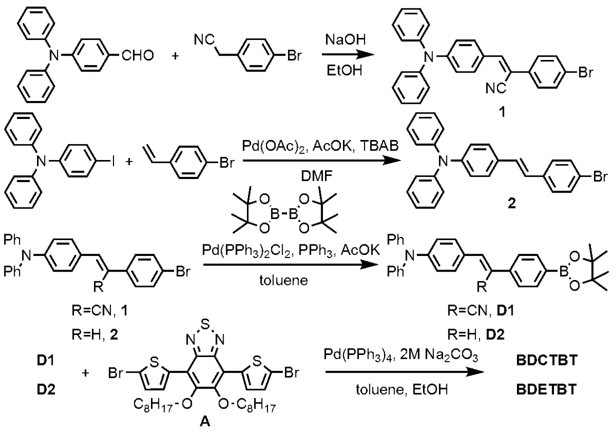


Fig. 1 The structure (a), ground-state geometry and electronic-density distribution (b) of small molecules

structure). Benzothiadiazole was selected as central acceptor since it has been well-known as one excellent acceptor utilized in low band-gap polymers for OSCs.[2b, 10d, 14] Motivation for choosing triphenylamines as capped donors was attributed to its good electron-donating properties caused by easy oxidation of nitrogen center and good charge transportation as its propeller starburst molecular structure.[15] Significantly, linear or star-shape small molecules composed of benzothiadiazole and triphenylamine have shown high V_{OC} over 0.9 V for BHJ OSCs.[16] It is rational to add cyano groups in D-A-D type benzothiadiazole-trphenylamine molecules to get deep-lying HOMO and high *Voc*. The design of **BDETBT** was for the purpose of exploring the effect of cyano on photovoltaic properties of molecules. In addition, Fig. 1(b) presented the density functional theory (DFT) calculated geometry and electronic properties for two molecules (calculation method supported in ESI†). In both molecules, the electron density of the HOMO delocalized over the whole molecules, while that of the LUMO concentrated on the central benzothiadiazole groups, demonstrating that an electron transfer from the triphenylamines groups to the central acceptors during the process of being excited from HOMO to LUMO. From the calculated energy levels, the HOMO and LUMO values of **BDCTBT** were lower than those of **BDETBT** for 0.24 eV and 0.18 eV, respectively. These results explained that, in theoretical calculation, cyano groups can lower the HOMO level without significantly costing narrow band-gap.



Scheme 1 Synthetic route for the small molecules

Synthetic route for the small molecules are shown in Scheme 1. The benzothiadiazole-based acceptor moiety (compound **A**) was synthesized in six steps starting from commercial available catechol following the procedures reported in the literature.[17] Knoevenagel condensation reaction of 4-(N,N-diphenylamine)-benzaldehyde and 4-bromobenzyl acetonitrile were carried out using NaOH as base in EtOH resulting compound **1** with a yield of 89%. Compound **2** was obtained in a yield of 47% by $Pd(OAc)_2$ catalyzed Heck coupling reaction between N,N-diphenyl-4-iodoaniline and 4-bromostyrene. The donor units (compound **D1** and **D2**) were both synthesized by Miyaura borylation in high yields. Finally, **BDCTBT** and **BDETBT** were prepared by $Pd(PPh_3)_4$-assisted Suzuki coupling reaction in high yields of 87% and 88%, respectively. Detailed synthetic procedures and characterization are supported by ESI.†

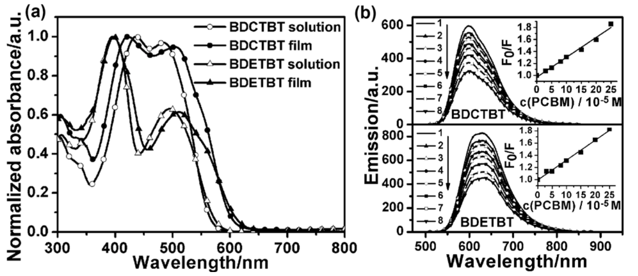


Fig. 2 Photophysical properties of **BDCTBT** and **BDETBT**. (a) UV-vis absorption spectra of small molecules in chloroform and in spin-coated thin film. (b) Fluorescence emission spectra of both materials in $CHCl_3$ (1.0×10^{-5} M) with increasing concentration of $PC_{61}BM$ ($\times10^{-5}$ M): 0.0(1), 3.0(2), 5.0(3), 8.0(4), 10.0(5), 15.0(6), 20.0(7), 25.0(8); the insets are Stern-Volmer quenching plots for two compounds respectively.

The UV-vis absorption spectra of the synthesized molecules in chloroform and in films were shown in Fig. 2(a) and the corresponding optical data were collected in Table 1. Both of molecules exhibited a broad absorption range covering the 300-600 nm wavelength in solution and in film. In solution, the maximum absorption peak (λ_{max}^{sol}) of **BDCTBT** was 484 nm, which was blue-shifted compared with that of **BDETBT** (496 nm), because the cyano groups hindered the ICT transition for their electron-withdrawing effect. In comparison with their absorption spectra in solution, the absorption band for **BDCTBT** and **BDETBT** in films were red-shifted, extending absorption onset to 604 nm and 619 nm, respectively, and thus showing a strong intermolecular π-π interaction in solid state.

In order to investigate the electrochemical energy levels ($HOMO^{CV}$, $LUMO^{CV}$ and E_g^{CV}) of two compounds, the cyclic voltammetry (CV) was employed to drop-casted film (Fig. S1, ESI†) and related electrochemical data were summarized in Table 1. Encouragingly, **BDCTBT** and **BDETBT** presented a fairly low-lying $HOMO^{CV}$ levels of -5.32 eV and -5.25 eV, respectively, which guaranteed the high V_{OC} of the organic photovoltaic devices blending with small molecules and $PC_{61}BM$. As speculation above, comparing energy levels between two materials, cyanos successfully deepened the HOMO level without greatly reducing the band-gap.

To investigate the charge separation process between small molecules and $PC_{61}BM$, the fluorescence quenching experiments were taken place and the fluorescence emission spectra were shown in Fig. 2(b). When the concentration of $PC_{61}BM$ increased, fluorescence intensity of small molecules gradually decreased, indicating that photoinduced exciton transfer from the LUMO of small molecular donors to that of $PC_{61}BM$ to form charge separation.[18] Furthermore, at low concentration of quencher, the relationship between the fluorescence intensity and the concentration of $PC_{61}BM$ was related to Stern-Volmer equation: $F_0/F = 1 + K_{SV}\cdot[C]$, in which F_0 and F represented the fluorescence intensity in the absence and present of $PC_{61}BM$, respectively, K_{SV} was the quenching constant, and [C] was concentration of $PC_{61}BM$. The K_{SV} of **BDCTBT** and **BDETBT** were 3320 M^{-1} and 3260 M^{-1}, respectively.

Photovoltaic performances of two synthesized molecules were preliminary investigated by fabricating solution-processsable BHJ devices in a conventional device structure of ITO/PEDOT:PSS/Donor:$PC_{61}BM$(1:2,w/w)/Al. The detailed device fabrication process was described in the ESI† and the

Table 1 The photophysical, electrochemical and photovoltaic properties of **BDCTBT** and **BDETBT**

Compound	λ_{max}^{sol}/nm	λ_{max}^{film}/nm	E_g^{optc}/eV	$HOMO^{CV}$/eV	$LUMO^{CV}$/eV	E_g^{CV}/eV	K_{SV}/M^{-1}	J_{SC}/mAcm^{-2}	V_{OC}/V	FF	PCE/%
BDCTBT	484	504	2.05	-5.32	-3.33	1.99	3320	11.2	1.04	0.33	3.85
BDETBT	496	511	2.00	-5.25	-3.30	1.95	3260	6.33	0.94	0.33	1.99

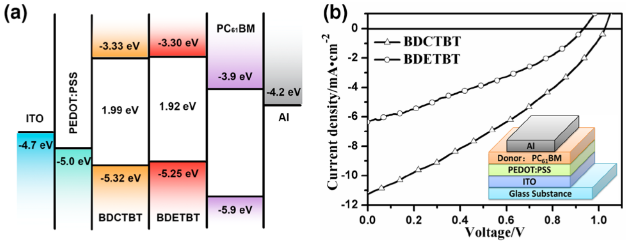


Fig. 3 Schematic energy-level diagram for BHJ solar cells (a) and J-V curves (b) of photovoltaic applications based on donor:PC$_{61}$BM at 1:2 ratio (w/w) under an illumination of AM 1.5G (100 mW·cm^{-2}).

corresponding parameters of photovoltaic devices were listed in Table 1. The device with blended **BDCTBT** and PC$_{61}$BM as active layer provided a V_{OC} of 1.04 V, a J_{SC} of 11.2 mA/cm^2, a fill factor (FF) of 0.33, resulting a PCE of 3.85%. In contrast, the device based on **BDETBT** with the same fabrication process delivered an inferior photovoltaic properties with a V_{OC} of 0.94 V, a J_{SC} of 6.33 mA/cm^2, a FF of 0.33, yielding a PCE of 1.99%. The higher V_{OC} value of **BDCTBT** was consistent with its deeper low-lying HOMO level caused by the cyano groups on π-bridge.

In summary, we have explored that the utilization of cyano groups on π-bridge can be a promising way to reduce HOMO value for conjugated D-A type small molecular photovoltaic materials. A **BDCTBT**-based BHJ device shows a preliminary PCE of 3.85% with a high V_{OC} up to 1.04 V. We envisage that further optimization of morphology on active layer and modification of electrode will highly improve the performance of devices.

The authors would like to thank the NSFC (21102013, 20803030), the Dalian Committee of Science and Technology (2011J21DW001), the SRF for ROCS-SEM (No. 201001438, No. 201001439), the Fundamental Funds for the Central Universities (DUT11LK20), and the RFDP (No.20090041120017) for financial support.

Notes and references

1. (a) R. F. Service, *Science*, 2011, **332**, 293; (b) J. Peet, A. J. Heeger and G. C. Bazan, *Acc. Chem. Res.*, 2009, **42**, 1700.
2. (a) G. Yu, J. Gao, J. C. Hummelen, F. Wudl and A. J. Heeger, *Science*, 1995, **270**, 1789; (b) S. H. Park, A. Roy, S. Beaupre, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee and A. J. Heeger, *Nat. Photonics*, 2009, **3**, 297.
3. (a) S. Günes, H. Neugebauer and N. S. Sariciftci, *Chem. Rev.*, 2007, **107**, 1324; (b) J. Chen and Y. Cao, *Acc. Chem. Res.*, 2009, **42**, 1709; (c) Y.-J. Cheng, S.-H. Yang and C.-S. Hsu, *Chem. Rev.*, 2009, **109**, 5868; (d) C. J. Brabec, S. Gowrisanker, J. J. M. Halls, D. Laird, S. Jia and S. P. Williams, *Adv. Mater.*, 2010, **22**, 3839; (e) G. Li, R. Zhu and Y. Yang, *Nat. Photonics*, 2012, **6**, 153.
4. (a) M. A. Green, K. Emery, Y. Hishikawa, W. Warta and E. D. Dunlop, *Progr. Photovolt.: Res. Appl.*, 2011, **19**, 565; (b) Z. He, C. Zhong, X. Huang, W.-Y. Wong, H. Wu, L. Chen, S. Su and Y. Cao, *Adv. Mater.*, 2011, **23**, 4636.
5. (a) J. Roncali, *Acc. Chem. Res.*, 2009, **42**, 1719; (b) B. Walker, C. Kim and T.-Q. Nguyen, *Chem. Mater.*, 2010, **23**, 470; (c) Y. Lin, Y. Li and X. Zhan, *Chem. Soc. Rev.*, 2012, **41**, 4245; (d) A. Mishra and P. Bäuerle, *Angew. Chem. Int. Ed.*, 2012, **51**, 2020.
6. (a) Y. Sun, G. C. Welch, W. L. Leong, C. J. Takacs, G. C. Bazan and A. J. Heeger, *Nat. Mater.*, 2011, **11**, 44; (b) T. S. Van de Poll, J. A. Love, T. Q. Nguyen, G. C. Bazan, *Adv. Mater.*, 2012, **24,** 3646.
7. C. J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromherz, M. T. Rispens, L. Sanchez and J. C. Hummelen, *Adv. Funct. Mater.*, 2001, **11**, 374.
8. Z. Li, G. He, X. Wan, Y. Liu, J. Zhou, G. Long, Y. Zuo, M. Zhang and Y. Chen, *Adv. Energy Mater.*, 2012, **2**, 74.
9. (a) H. Bürckstümmer, E. V. Tulyakova, M. Deppisch, M. R. Lenze, N. M. Kronenberg, M. Gsänger, M. Stolte, K. Meerholz and F. Würthner, *Angew. Chem. Int. Ed.*, 2011, **50**, 11628; (b) W. W. H. Wong, C.-Q. Ma, W. Pisula, C. Yan, X. Feng, D. J. Jones, K. Müllen, R. A. J. Janssen, P. Bäuerle and A. B. Holmes, *Chem. Mater.*, 2009, **22**, 457; (c) E. Ripaud, T. Rousseau, P. Leriche and J. Roncali, *Adv. Energy Mater.*, 2011, **1**, 540.
10. (a) Y. Liang, D. Feng, Y. Wu, S.-T. Tsai, G. Li, C. Ray and L. Yu, *J. Am. Chem. Soc.*, 2009, **131**, 7792; (b) H.-Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu and G. Li, *Nat. Photonics*, 2009, **3**, 649; (c) S. C. Price, A. C. Stuart, L. Yang, H. Zhou and W. You, *J. Am. Chem. Soc.*, 2011, **133**, 4625; (d) H. Zhou, L. Yang, A. C. Stuart, S. C. Price, S. Liu and W. You, *Angew. Chem. Int. Ed.*, 2011, **50**, 2995.
11. A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, *Chem. Rev.*, 2010, **110**, 6595.
12. (a) Z.-S. Wang, Y. Cui, Y. Dan-oh, C. Kasada, A. Shinpo and K. Hara, *J. Phys. Chem. C*, 2008, **112**, 17011; (b) H. Tian, X. Yang, R. Chen, R. Zhang, A. Hagfeldt and L. Sun, *J. Phys. Chem. C*, 2008, **112**, 11023.
13. (a) Q. Bricaud, A. Cravino, P. Leriche and J. Roncali, *Synth. Met.*, 2009, **159**, 2534; (b) T. Kietzke, H.-H. Hörhold, D. Neher, *Chem. Mater.*, 2005, **17**, 6532; (c) B. C. Thompson, Y,-G. Kim, J. R. Reynolds, *Macromolecules*, 2005, **38**, 5359.
14. (a) J. Hou, H.-Y. Chen, S. Zhang, G. Li and Y. Yang, *J. Am. Chem. Soc.*, 2008, **130**, 16144; (b) N. Blouin, A. Michaud and M. Leclerc, *Adv. Mater.*, 2007, **19**, 2295.
15. (a) Z. Ning and H. Tian, *Chem. Commun.*, 2009, **37**, 5483; (b) S. Roquet, A. Cravino, P. Leriche, O. Alévêque, P. Frère and J. Roncali, *J. Am. Chem. Soc.*, 2006, **128**, 3459. (c) A. Cravino, S. Roquet, O. Alévêque, P. Leriche, P. Frère and J. Roncali, *Chem. Mater.*, 2006, **18**, 2584.
16. (a) J. Zhang, Y. Yang, C. He, D. Deng, Z. Li and Y. Li, *J. Phys. D: Appl. Phys.*, 2011, **44**, 475101; (b) P. Dutta, W. Yang, S. H. Eom, W.-H. Lee, I. N. Kang and S.-H. Lee, *Chem. Commun.*, 2012, **48**, 573; (c) W. Li, C. Du, F. Li, Y. Zhou, M. Fahlman, Z. Bo and F. Zhang, *Chem. Mater.*, 2009, **21**, 5327.
17. Y. Li, Y. Chen, X. Liu, Z. Wang, X. Yang, Y. Tu and X. Zhu, *Macromolecules*, 2011, **44**, 6370.
18. (a) J. Wang, D. Wang, D. Moses and A. J. Heeger, *J. Appl. Polym. Sci.*, 2001, **82**, 2553; (b) S. H. Zeng, L. X. Yin, X. Y. Jiang, Y. Q. Li and K. C. Li, *Dyes and Pigments*, 2012, **95**, 229.

[a] *School of Chemistry, Dalian University of Technology, Dalian, China.*
[b] *State Key Baboratory of Supramolecular Structure and Materails, College of Chemistry, Jilin University, Changchun, China.*
Fax: 86-411-84986040; Tel: 86-411-84986040;
E-mail: liyanqin@dlut.edu.cn; yuewang@jlu.edu.cn

† Electronic Supplementary Information (ESI) available: Synthetic procedures, CV curves, calculation method and devices fabrication details. See DOI: 10.1039/b000000x/