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A theorectical design of performant chlorinated benzothiadiazole-based polymers as donor for organic photovoltaic devices

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ABSTRACT

Chlorination is often adopted in the synthesis of donor materials considering the obvious improvement on efficiency of organic photovoltaic (OPV) device. Thus the chlorination effect was firstly probed based on density functional theory (DFT) calculation, which shows that the chlorinated benzothiadiazole connected with two thiophene rings (**BTClTT**) fragment although has larger optical bandgap and relatively blue-shifted spectrum, its deeper frontier molecular orbital (FMO) energy level, larger charge transfer distance (D_{CT}) and much more transferred charges (C_T), obvious negative natural population analysis (NPA) charges, larger twisted dihedral angles and smaller value of BLA indicate its favorable properties for the application in OPVs. Then, we designed a series of donor materials **2**–**7** adopting two strategies based on the experimental polymer **1** which contains **BTClTT** fragment. The calculated physical parameters characterizing OPV performance such as open-circuit voltage (V_{OC}) and absorption-properties manifest that the design through side chains modifications for **2**–**5** may have slight influence on their cell performance while the backbone replacements for **6** and **7** exhibit prominent enhancement whether on V_{OC} and photon-absorption property or on the charge separation ability. Therefore, our calculations suggest feasible strategies of designing donor materials for the chlorinated BT-based donor materials in OPVs. We hope our work can provide some guidelines for the future study on chlorinated donor materials.

1. Introduction

Organic photovoltaic voltages (OPVs) constructed with polymer as donor (D) and **$PC_{71}BM$** as acceptor (A) with a number of merits including low cost, transparency, flexibility, light-weight and large-area have attracted mounting interests, as power conversion efficiency (PCE) of OPVs has made some improvements in recent years [1–7]. And considerable efforts have been put on enhancing the PCE of OPVs [8–13]. Importantly, molecular design and optimization of both D and A are widely adopted in recent advances [14,15], among which introducing substituent in donor polymers has aroused much attention [16,17]. Particularly, fluorinations have been intensively used in donor materials to improve performance of OPVs and made a bit of achievements in PCE [18–21], yet fluorinated molecules with higher prices but lower yields in the reactions limit their commercial manufacture in a degree. Recently, some scientists have turned their eyes to chlorinated molecules. Early in 2009, Bao et al. pointed out that chlorinated semiconductors have similar or superior properties in electron mobility and ambient stability than fluorinated ones. Confirmed by their calculations and measurements, chlorinated molecules tend to have lower lowest unoccupied molecular orbital (LUMO) energy level than fluorinated molecules [22]. From then on, chlorinated molecules have been gradually investigated on OPVs. Jian Pei et al. synthesized molecules **Cl-IIDT** and **F-IIDT** as D to construct **$PC_{71}BM$**–based OPVs, which present the PCE of 4.60% and 1.19%, respectively. They reported that chlorinated molecules with better performance than fluorinated molecules is ascribed to their larger torsional angles which could reduce the crystallization tendency [23]. In 2015, Hao-Li Zhang and coworkers demonstrated that the fluorinated and chlorinated donors present similar frontier orbital energy levels and optical absorption [24]. Recently, Feng He and coworkers reported a PCE of 9.11% for OPVs constructed with chlorinated polymers and **$PC_{71}BM$** [25]. And then they designed and synthesized another chlorinated benzothiadiazole-based polymer reaching a PCE of 8.21%. They pointed out that chlorination could lower the highest occupied molecular orbital (HOMO) energy level and subtly tuned the optical bandgap, which meant the

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potential application of chlorinated polymers in OPVs [26]. In these excellent chlorinated polymers mentioned above, the chlorinated benzothiadiazole was always adopted, indicating that it may be an essential building block in this kind of donor materials.

Since chlorinated polymers exhibit advanced performance in OPVs and the chlorinated benzothiadiazole is one essential unit in these donors, what are the advantages of the chlorinated benzothiadiazole compared to benzothiadiazole, and how can we improve the capability of this kind of donors containing chlorinated benzothiadiazole unit in OPVs? These questions arouse our interest in exploring their performance in OPV. A systemic theoretical investigation is necessary, since numerous theoretical works focusing on OPVs have been carried out and already demonstrated to be helpful to understanding the mechanism and improving efficiency in recent years [27–30]. For instance, recent studies have explored interfacial mechanism [31–33], charge transport process [34,35] and donor/acceptor (D/A) arrangement [36,37]. Also, other works have concentrated on designing donor and acceptor materials [38–40], investigating on electron interfacial process and so forth [41,42]. Therefore, it is meaningful to find the advantage of chlorinated benzothiadiazole in OPVs and design more efficient donors based on this special unit from theoretical perspective.

In this work, we firstly probe the chlorination effect in benzothiadiazole **(BTT)** fragment on the photoelectric properties in detail to explore the importance of chlorination in further donor-material design, since OPVs constructed with Benzothiadiazole (BT)-based polymers and fullerenes are widely reported. Then based on one chlorinated polymer **1** constructed with benzo [1,2-b:4,5-b]dithiophene**(BDT)** unit and chlorinated benzothiadiazole fragment **BTTCl** which was reported a PCE of 9.11% for OPVs with **$PC_{71}BM$** as acceptor, we designed four polymers depicted in Scheme 1 trying to obtain more efficient donor materials. However, the tiny improvement in cell performance indicates our design strategy only through changing side units of **BDT** is not very effective. Thus we further took the replace of the whole **BDT** unit by thiophene analogue cyanomethylene-**CPDT** for **6** and cyclopenta [2,1-b:3,4-b0]dithiophen-4-one for **7** with the aim of finding available design for donor. It is gratifying that the designed molecules **6** and **7** presented in Scheme 1 realize a better balance between the open-circuit voltage (V_{OC}) and short circuit density (J_{SC}) and thus improve the ability of charge separation significantly. Therefore, our calculations indicate that the strategy of designing donor materials is feasible and chlorinated BT-based donor materials could be optimized or designed to improve performance of OPVs. We hope our work can provide some guidelines for the future study on chlorinated donor materials.

2. Computational methods

For chlorinated polymers **1–7**, all of the branched chains were replaced by alkyl to save computational cost [43,44]. Besides, frontier molecular orbital (FMO) energy levels were calculated as our previous work [45]. All of the ground-state structures of building blocks and investigated polymers were optimized under PBE0 functional and 6-311G (d,p) basis set with no imaginary frequencies allowing for that PBE0 functional is proper to thiophene derivatives in some researches [45,46]. For an accurate description of optical properties, functionals B3LYP, PBE0, CAM-B3LYP, BHandHLYP and M06-2X were employed and the result computed at TD-PBE0/6-311G (d,p) level is closer to the experimental data [25], which are listed in the supporting information. Thus, all of the optical properties were calculated at this level and absorption spectra were simulated by GaussSum 3.0 software [47]. As for interface models, fifteen starting structures, in which the top panel of donor was plotted with three selected positions (above D unit, DA unit or A unit) for acceptor, and there are five D/A stacking patterns for each position as shown in Fig. 1 (taking the position above DA unit as example) and Fig. S1 in supporting information, were chosen with initial distance between donor and **$PC_{71}BM$** as 3.5 Å and further optimized at B3LYP/6-311G (d,p) level. While for more information about initial models and the optimized interface models would be detailed in section 3.2.3. Based on the optimized structures, we calculated the counterpoise-corrected total interaction energies, which demonstrate that the Face-onD-Conf-3D configuration is favored as it shows strongest interaction energy among these fifteen configurations. Thus, the following investigated systems adopted this configuration for further calculations. Moreover, the excited-state properties of the interface model were calculated at TD-CAM-B3LYP/6-311G (d,p) level, in view of its better description on the charge transfer states verified by many theoretical works [48,49]. All of the calculations mentioned above were performed in the Gaussian 09 program [50]. Beisdes, We identified charge transfer (CT) states by Multiwfn software [51] based on TD-DFT calculations for interface model. Meanwhile, the charge transfer rate $k_{inter\text{-}CT}$ and charge recombination rate $k_{inter\text{-}CR}$ were assessed by Marcus charge transfer theory [52], which is detailed in supporting information.

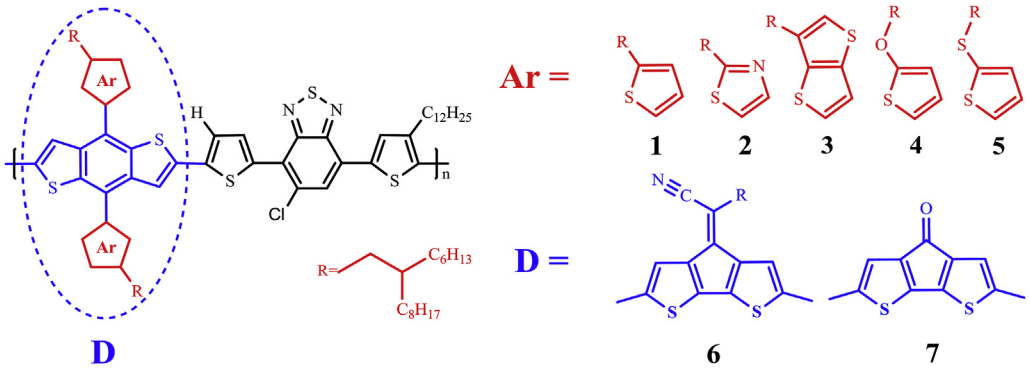
3. Results and discussions

3.1. A systemic theoretical investigation on the effect of chlorination in BTTT unit

As mentioned above, the chlorinated benzothiadiazole is an essential building block in these excellent chlorinated polymers. A detailed investigation about it will favor our understanding of the chlorination and further effective design of this kind of materials. Therefore, we firstly analyzed the fragment **BTClTT** contained in chlorinated polymer **1** and compared it with non-chlorinated fragment **BTTT** to gain insight into the chlorinated effect in this kind of donor materials.

3.1.1. Geometric and electronic properties

DFT and TD-DFT methods were applied to analyze structure-property relationship to gain insight into photoelectric properties of benzothiadiazole building blocks presented in Scheme 2. The dihedral



Scheme 1. Chemical structures of investigated polymers **1–7**.