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Theoretical design of new small molecules with a low band-gap for organic solar cell applications: DFT and TD-DFT study

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ABSTRACT

In search of novel high-performance materials for use in organic solar cells, we used density-functional theory and time-dependent density functional theory to design a series of organic small molecules derived from the recently synthesized BT(-2T-DCV-Hex)$_2$ donor molecule. In this work, we replaced the BT unit by different acceptors in order to improve their electronic properties, optical absorption and performance in organic solar cell applications. We found that the hybrid functional B3PW91 with the 6-31G(d) basis set gave highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the BT(-2T-DCV-Hex)$_2$ in better agreement with the experimental oxidation and reduction potentials. However, the range-separated hybrid functional WB97XD was the most appropriate functional for describing the maximum absorption wavelength. Our calculation indicate that the designed small molecules donor proposed here are expected to offer better performances compared to the BT(-2T-DCV-Hex)$_2$, such as a lower HOMO energy, a narrower HOMO-LUMO energy gap, a larger absorption range and may lead to power conversion efficiencies reaching the (7–9)% range.

1. Introduction

Recent years have witnessed intensive research in developing high-efficiency bulk heterojunction (BHJ) solar cells with small conjugated molecules donors [1,2]. In fact, their power conversion efficiency (PCE) is better than those of polymer BHJ solar cells. Indeed, they have reached record efficiencies in the range of 8–10% in single junction devices [3–8] and 10.1% for a tandem cell device [9]. In comparison to polymer donor materials, small molecule materials have advantages in terms of well-defined molecular structure, including a precise molecular weight, high purity, easier energy level control and less batch-to-batch variation [10,11]. The objective of this article is to design novel promising small molecule (SM) donor materials with varying optoelectronic properties and so as to improve the performance of organic photovoltaic properties.

On the one hand, the combination of electron-rich (donor) and electron-deficient (acceptor) units in the main chain structure used to construct π-conjugated polymer donors can also be used to construct π-conjugated small molecule donors. It is worth to mention that using a donor–acceptor (D-A) structure is identified as one of the most efficient strategies for modulating their electronic properties [12–15] and obtaining optimally low observed band gap of small molecules between 1.6 and 1.8 eV [16,17]. On the other hand, it is widely known that the efficiency, which is the most used parameters to compare the performance of one solar cell to another, is related to several parameters such as the open circuit voltage (V_{oc}), the short circuit current density (J_{sc}) and the fill factor (FF). So, to improve SM solar cell efficiency, one needs to optimize the intrinsic properties of donor materials such as highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital LUMO and the HOMO-LUMO energy band gap $E_{H\text{-}L}$ by virtue of Koopmans theorem [18] which approximates the first ionization potential (IP) and electron affinity (EA). A low energy band gap material is favorable for light absorption and for generating large photocurrent J_{sc} [19].

Consequently, using density functional theory (DFT) and time-dependent density functional theory (TD-DFT), we have firstly studied a A-D-A-D-A structure denoted BT(-2T-DCV-Hex)2 [20], which is a small molecule synthesized with the benzothiadiazole (BT) as the core, bithienyl (2T) as the donor unit and dicyanovinyl (DCV) as the terminal acceptor groups to understand structure–property relationships. SM0 showed several interesting properties: a maximal absorption peak at 546 nm, a low HOMO energy level of -5.53 eV and LUMO energy level

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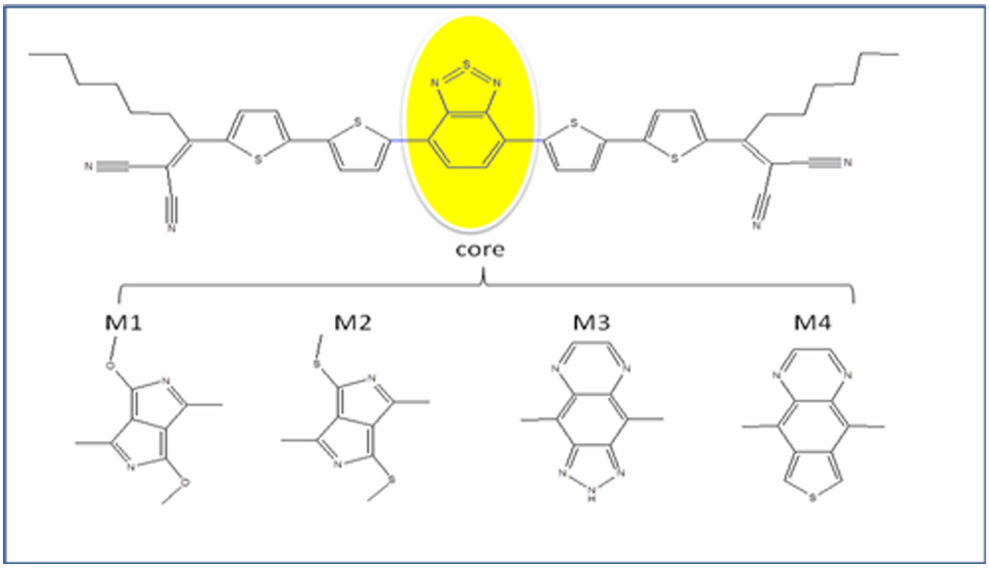

Fig. 1. Chemical structure of all studied small molecules donors.

of −3.44 eV. These results agree reasonably well with the experimental results [20].

Our design strategy consist of replacing the core BT of the prototype molecule BT(-2T-DCV-Hex)$_2$ with different acceptor fragment as shown in Fig. 1, in order to improve the electrical properties, optical absorption and performance in organic solar cell applications. Theses fragments were chosen for the central building block due to their planarity and extendable conjugation and the ability to form a D-A-D structure with two tiophene units on both sides. Indeed, they were widely used as “pull” building block in the donor molecules for high efficiency BHJ photovoltaic devices [21–23].

2. Methods of computation

All molecular calculations were performed using the polarizable continuum model using (CPCM) [24] and the solvent dielectric constant of o-dichlorobenzene using the GAUSSIAN 09 program [25]. Simulated spectra were plotted using the associated GAUSSVIEW program [26]. The ground-state geometries of molecules were optimized using DFT. In order to find the functional needed to obtain a satisfactory agreement between experimental and theory for BT(-2T-DCV-Hex)$_2$ and to apply this functional to proposed small molecules, the geometrical structure of the synthesized small molecule SM0 has been firstly optimized. We tested three widely-used functionals for computing the ground states geometries; the Becke three-parameter exchange functional with nonlocal correlation provided by the Lee-Yang-Parr method, denoted B3LYP [27,28]; the Becke’s three parameter hybrid functional [29] combined with the non local correlation provided by Perdew and Wang’s (PW91) [30], denoted B3PW91 and the Perdew, Burke and Ernzerhof exchange-correlation functional denoted PBE0 [31]. In each case the same 6-31G(d) basis set [32] was used. After structural minimization, the calculation of vibrational frequencies was evaluated to check that no imaginary frequency is present, showing that the optimized geometry is located at a minimum point of the potential surface.

In a second step, two different functional were used for TD-DFT calculations of the absorption spectra namely CAM-B3LYP [33] and WB97XD [34] with the same basis set 6-31G(d). This allowed us to determine the best agreement between theory and experimental for the maximum absorption λ_{max} of SM0.

Finally, the functional giving the closest results to the experimental ones were used to optimize the ground-state geometries of all the investigated small molecules and to calculate for absorption spectra the first singlet excitation energy corresponding to the maximum absorption wavelength. The SWIZARD program was used to evaluate the singlet excited state configuration to each electronic transition [35]. Meanwhile, the electron-hole coherence of charge transfer upon electronic transitions was investigated by means of the transition density matrix (TDM) and charge density difference (CDD) implanted in Multiwfn 3.1 [36].

3. Results and discussion

3.1. The choice of method describing opto-elctronic properties of BT (-2T-DCV-Hex)$_2$

In order to elucidate the effect of conjugation lengths, we carried our calculation on planar BT(-2T-DCV-Hex)$_2$ like a planar structure. This small molecule present three conformations differed by the relative positions of DCV. These optimized geometric structures are shown in Fig. 2. As a first step, we have tried to determine the most stable conformation by computing the energies of each conformation; which allowed us to estimate their relative stabilities. The more stable structure is deeply related to the lower molecular energy [37]. The calculated total energy differences are summarized in Table 1. The values appear to be too small ($< 0.5\,\text{kcal mol}^{-1}$) to distinguish between the isomers. Nevertheless, the calculations performed using different functionals, showed that the relative energies are only weakly dependent upon the choice of functional which increases the plausibility of stability. For each functional, conformation 3 was found like the most stable structure than the others.

As a second step, we investigated the HOMO and LUMO energy levels of the studied molecule. The corresponding experimental values have been measured electrochemically using cyclic voltammetry (CV) [20]. Our calculated HOMO and LUMO energy levels are shown in Table 2. The B3PW91 functional gave a value in better agreement with experiment than did the other two functional (0.20–0.17 eV) but this is probably fortuitous.

Finally, given the influence of functional selection on the vertical transition energy, the absorption spectrum of BT(-2T-DCV-Hex)$_2$ was computed with two classical range-separated hybrid functional (CAM-