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New acceptor–donor–acceptor (A–D–A) type copolymers for efficient organic photovoltaic devices

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ABSTRACT

Three new conjugated systems alternating acceptor–donor–acceptor (A–D–A) type copolymers have been investigated by means of Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT) at the 6-31g (d) level of theory. 4,4′-Dimethoxy-chalcone, also called the 1,3-bis(4-methoxyphenyl)prop-2-en-1-one (BMP), has been used as a common acceptor moiety. It forced intra-molecular S⋯O interactions through alternating oligo-thiophene derivatives: 4-AlkylThiophenes (4-ATP), 4-AlkylBithiophenes (4-ABTP) and 4-Thienylene Vinylene (4-TEV) as donor moieties. The band gap, HOMO and LUMO electron distributions as well as optical properties were analyzed for each molecule. The fully optimized resulting copolymers showed low band gaps (2.2–2.8 eV) and deep HOMO energy levels ranging from −4.66 to −4.86 eV. A broad absorption [300–900 nm] covering the solar spectrum and absorption maxima ranges from 486 to 604 nm. In addition, organic photovoltaic cells (OPCs) based on alternating copolymers in bulk heterojunction (BHJ) composites with the 1-(3-methoxycarbonyl) propyl-1-phenyl-[6,6]–C_{61} (PCBM), as an acceptor, have been optimized. Thus, the band gap decreased to 1.62 eV, the power conversion efficiencies (PCEs) were about 3–5% and the open circuit voltage V_{oc} of the resulting molecules decreased from 1.50 to 1.27 eV.

1. Introduction

The challenge of using polymers is to obtain flexible electronic devices with the highest efficiency. Organic polymers, in particular π-conjugated oligomers, continue to attract great interest for their use as an active layer in organic light emitting diodes (OLEDs) [1] and organic photovoltaic cells (OPCs) [2]. In fact, a wide variety of structure architectures has been deeply investigated theoretically and experimentally [3]. Thus, we have recently reported the design of two new copolymers involving poly(N-vinylcarbazole) PVK blended with poly(p-phenylenevinylene) (PPV) [4] and poly (3-methylthiophene) (P3MeT) [5,6]. Such copolymers present interesting photo-physical properties.

In parallel, conjugated small molecules still attract much attention due, in particular, to their electronic and optical properties. Furthermore, OPCs consisting of donor (D) and acceptor (A) molecules together as an active layer seem to improve the photoconversion [7]. Likewise, symmetrical A–D–A, D–A–D or simply D–A represents the most successful molecular architecture [8,9]. These systems allow intra-molecular charge transfer (ICT) process that leads to a broad absorption spectrum and a small energy band gap. In other words, the matching of the energy level of the donor material to that of the acceptor compound is one of the key steps to improve the total efficiency of the cell [10,11]. However, the charged defects could act as dopants and affect the exciton dissociation and charge transport in the active layer of OPCs [12].

In order to design new organic materials with lower band gaps, quantum-chemical methods have been applied to investigate a variety of polymers as well as to optimize their optoelectronic properties. This paper aimed at theoretically designing and modeling of three new conjugated π-copolymers with A–D–A architecture. For that, 4,4′-dimethoxy-chalcone (BMP) as a common acceptor unit linked to three different appropriate donors such as 4-ATP, 4-ABTP and 4-TEV were chosen (henceforth they are abbreviated as P_1, P_2 and P_3, respectively). Their corresponding chemical structures are depicted in Fig. 1. The band gap, Highest Occupied Molecular Orbital (HOMO), Lowest Unoccupied Molecular Orbital (LUMO) electron distributions, electronic structure as well as the optical properties were theoretically analyzed for each molecule by using Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT) at the 6-31g (d) level of theory. Likewise, the donor-pended effects on the optoelectronic parameters were discussed.

Besides, for a better understanding of the optoelectronic parameters that affect OPCs efficiencies, we have elucidated the structure–property relationship of the studied compounds. Accordingly,

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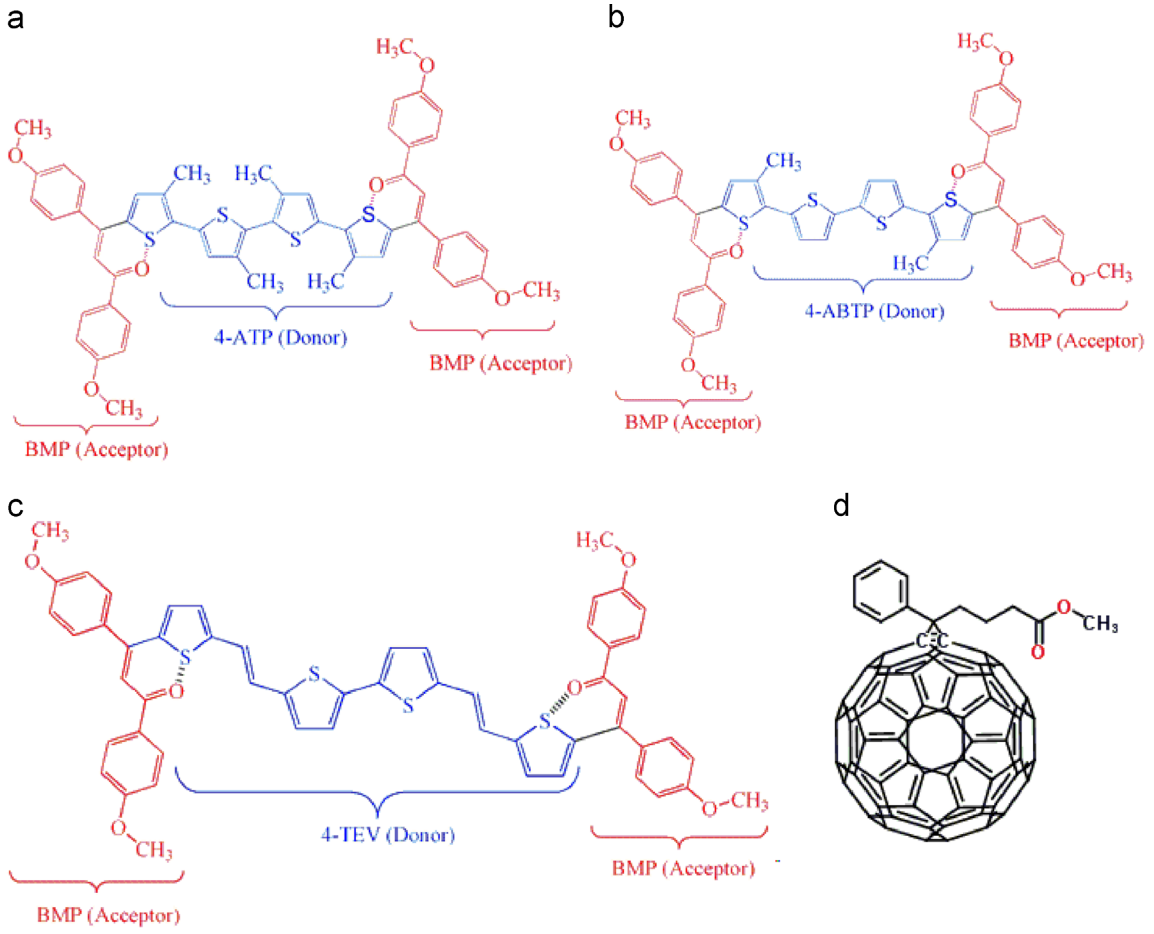

Fig. 1. Chemical structures of copolymers P_1 (a), P_2 (b), P_3 (c) and that of PCBM (d).

we have analyzed the studied copolymers for their hosting PCBM into a single layer BHJ solar cell. Then, we selected the compound having the best optoelectronic properties to be blended with PCBM in an organic bulk heterojunction (BHJ) solar cell [13].

2. Computational details

All calculations were carried out using the Density Functional Theory (DFT) implanted in the GAUSSIAN (09) program [14,15] for isolated gas-phase molecules. The geometric structure of each molecule was optimized using the most popular Becke's three parameters hybrid functional, B3 [16], with non-local correlation of Lee–Yang–Parr, LYP, abbreviated as B3LYP hybrid functional [17]. DFT calculations with B3LYP were performed with the 6-31g (d) level of theory. The electronic properties such as HOMO, LUMO energies as well as their associated gaps were also elucidated for studied copolymers. Therefore, the optimized geometries were calculated for cationic and anionic charged states. Hence, the energies for the different charged states in the relevant geometries were obtained for calculating Ionization Potential (IP) and electronic affinity (EA).

As for theoretical optical properties, the well-known Configuration Interaction Singles (CIS) method [18] with the same basis set was used to optimize the lowest singlet excited-state geometries. Besides, Time Dependent Density Functional Theory (TD-DFT) level was employed to predict the optical absorption spectra on S_0 optimized structures [19,20]. Electronic transition assignments and oscillator strengths were also calculated using the same method of calculation. The theoretical absorption spectra were simulated using the SWizard program [21]. Absorption profiles, however, were calculated using Gaussian model (1) with the half-bandwidths ($\Delta_{1/2}$) of 3000 cm^{-1}.

3. Results and discussion

3.1. Ground and excited states geometry

DFT and TD-DFT with 6-31 (d) level of theory were employed to perform the geometry on S_0 and S_1 optimized structures, respectively. For the sake of comparison, the obtained results are displayed in Table 1. In their ground states (Fig. 2) and unlike the compound P_3 which had a planar structure related to the presence of the ethylene groups in its main chain, P_1 and P_2 structures were twisted to about 22° ($\varphi_2 \approx \varphi_4 \sim 22°$). In fact, the order of coplanarity increased from P_1, P_2 to P_3 when the dihedral angle φ_3 decreased from 54.05°, 6.92° to 4.68° for the three copolymers, respectively. This effect was strictly related to the number of methyl substituted thiophene rings. It was also noted that the 4-ABTP and 4-TEV as donors improved the molecular coplanarity and were responsible for electronic delocalization along the chain backbone of P_2 and P_3 compounds. In addition, in all structures, the particularity of using BMP units resulted in intra-molecular attractive interaction forces taking place between the oxygen atoms (negatively charged) of carbonyl groups and the sulfur atoms (positively charged) of thiophene units. Consequently, non-covalent interactions lead to the molecules' conformational rigidification. In fact, the distance S—O of ~2.64 Å, which corresponded to ~79% of the sum of their Van der Waals radii, fall inside the Van der Waals contact distance