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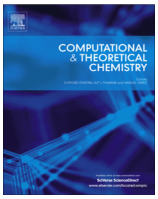

Influence of push–pull group substitution patterns on excited state properties of donor–acceptor co-monomers and their trimers

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ABSTRACT

Organic electronics form a very promising new generation of cheap, lightweight and flexible devices. Of special interest is the ability to engineer photo-physical properties of organic molecules by chemical modification. In this regard, the purpose of this research is to understand the influence of push–pull group substitution patterns on excited state properties of several donor–acceptor co-monomers an their trimers. Part of this work focuses on organic photovoltaic applications to demonstrate the practical use of the structure–property relations. In this context, the strong exciton binding energy determined by the electron–hole interaction is an important property. (Time-dependent) Density Functional Theory calculations showed a significant difference between linear- and cross-conjugated push–pull group pathways for the electron–hole interaction and the vertical exciton binding energy, which can be understood from simple Hückel theory. A linear relation between the dipole moment change upon excitation and the vertical exciton binding energy hints to a possible correlation, although this relation is less pronounced for the trimers. The overlap density between the frontier molecular orbitals alone already reveals valuable information about the relative size of the electron–hole interaction and the vertical exciton binding energy. Application of our findings in the context of organic photovoltaics results in significant support for cross-conjugated mesomeric push–pull group pathways in order to spatially separate the HOMO and LUMO.

1. Introduction

Nowadays organic molecules find their way in all kinds of applications, like thin-film transistors (TFT), light emitting diodes (OLED) and thin-film photovoltaic cells (OPV). In comparison to conventional silicon-based electronics, organic electronics have the advantage of low-cost fabrication processes using for example roll-to-roll methods. A new generation of cheap, lightweight and flexible organic electronic devices is entering the commercial world [1]. In order to make significant progress in this field, insight in the relation between chemical structure and excited state properties is one of the key issues. Of special interest is the ability to engineer photo-physical properties by chemical modification through adding particular functional groups at different positions.

Further accelerated progress is expected by application of this knowledge in the development of new organic materials for OPV. Currently the efficiency of organic solar cells is only about 10% [2], which is limited by several factors [3]. The best-performing organic solar cell consists of a three-dimensional (bulk) heterojunction composed of a hole-conducting donor (typically a conjugated polymer) and an electron-conducting acceptor (fullerene derivative) [4]. An electronic state diagram illustrating the solar energy conversion to free charges is shown in Fig. 1 [5]. After light absorption by mainly the donor material, excitons are formed. These excitons are electron–hole pairs, bound by the Coulomb force, with an exciton binding energy (E_b^{exc}) of 0.3–0.5 eV [3]. They diffuse towards the donor–acceptor interface, where electrons transfer from donor to acceptor molecules. Typically, the electron–hole pair remains bound, leading to the formation of an intermolecular charge-transfer (CT) state [3,6]. To prevent recombination, the charge-transfer state binding energy (E_b^{CT}) has to be overcome, *e.g.*, with the involvement of hot CT states [5,7]. Finally, collection of free charges takes place at different electrodes of the solar cell. If the exciton binding energy can be lowered, more efficient and cost effective solar cells are within reach [3].

Several experimental and theoretical studies have shown that not only Frenkel excitons, but also more separated excitons are formed by primary photo-excitations in donor polymers. These less bound excitons are believed to play a significant role in the

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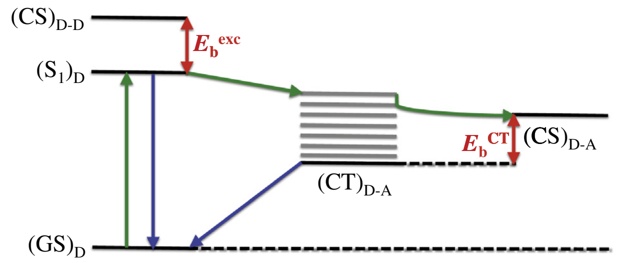

Fig. 1. Electronic state diagram describing the mechanism of converting solar energy to electric energy in organic solar cells. The green arrows show the basic steps after light absorption to create free charges when hot CT states are involved. The blue arrows show recombination pathways. The red arrows show the energy differences E_b^{exc} and E_b^{CT}, as introduced previously. $(CS)_{D\text{–}D}$ is defined as the energy difference between the ionization potential (IP) of D and electron affinity (EA) of D, and $(CS)_{D\text{–}A}$ as the energy difference between IP of D and EA of A (GS = ground state, S_1 = first excited state, CS = charge-separated state, CT = charge-transfer state, *D* = donor, *A* = acceptor). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

photovoltaic process because they would increase the probability of electron transfer from donor to acceptor, decrease the energy needed for charge separation and reduce geminate recombination [8,9]. In order to distinguish between the two types of excitons, an observable can be used that correlates with their internal degree of charge separation: the change in dipole moment between the ground and excited state of the donor molecule, $\Delta\mu_{ge}$ [8–10]. It was explained by Carsten et al. [9] that a larger $\Delta\mu_{ge}$ correlates with a lower exciton binding energy. A relation was found between the device efficiency and the change in dipole moment upon excitation of several donor–acceptor co-monomers: when $\Delta\mu_{ge}$ is larger, the efficiency increases [8]. Still, this and other correlations between solar cell performance and intrinsic properties of the donor polymers, like chemical structure, and their possible relation to the exciton binding energy of the primary photo-excitation, are not completely understood [10,11].

In this regard, the objective of this work is to study the influence of push–pull group substitution patterns on excited state properties, in particular the exciton binding energy, of several donor–acceptor co-monomers and their trimers. In this way we are able to understand and engineer the photo-physical properties of new molecular structures. Part of this work focuses on OPV applications to demonstrate practical use of the structure–property relations. This knowledge may be used to formulate design guides for developing new organic materials with lower exciton binding energies.

We concentrated on understanding the photo-physical properties of a donor–acceptor co-monomer (**1** in Fig. 2). Monomer **1** is 4,4′-bis-(2-methyl)-4H-cyclopenta[2,1-b;3,4-b′]-dithiophene-4-(2-thienyl)-2,1,3-benzothiadiazole (CPDTTBT), which consists of the donating fragment CPDT and the accepting fragment BT, linked via one thiophene spacer T. The main reason for applying donor–acceptor co-polymers in organic solar cells is their low band gap enabling the absorption of more of the incoming light [12].

We studied the effect of adding NH_2 as electron donating group (EDG) and NO_2 as electron withdrawing group (EWG) to respectively the donor and acceptor side of this co-monomer. These groups exert mesomeric (by resonance, *i.e.*, through π-bonds) effects. Linear- and cross-conjugated substitution patterns were compared to study their effect on excited state properties (**2** and **3** linear- and **4** and **5** cross-conjugated, Fig. 2). It is known that cross-conjugated groups show weaker electronic communication than linear-conjugated ones [13].

We investigated one conformation with CH_3 as EDG and F as EWG added to respectively the donor and acceptor side of the co-monomer (**6**, Fig. 2) to get insight in the influence of inductive (*i.e.*, through the σ-framework) effects on excited state properties. NH_2 is inductively electron withdrawing and by resonance electron donating, however resonance dominates induction. NO_2 is electron withdrawing both by induction and resonance, so here resonance reinforces induction. CH_3 is inductively electron donating, while F is inductively electron withdrawing and by resonance electron donating. Here induction outcompetes resonance, so F is a weak electron acceptor [14].

For all monomers, the effect of trimerization on their excited state properties was studied to see if the trends valid for the monomers still apply. Trimerization of the reference monomer **1** and the 5 substituted monomers led to the molecules **7**–**12** (reference trimer **7** and **8**–**12**, Fig. 3).

We focused on the following excited state properties: first excited state energy, oscillator strength, HOMO energy, LUMO energy, orbital energy difference between HOMO and LUMO, vertical ionization potential, and vertical electron affinity. Properties relevant for OPV applications were: change in dipole moment between the ground and excited state of the donor molecule $\Delta\mu_{ge}$, vertical exciton binding energy, the electron–hole interaction as defined in the Hartree–Fock method, and the degree of spatial overlap between occupied and virtual orbitals involved in the excitation.

This paper is organized as follows: the computational methods used in this work are described in the next section; Section 3

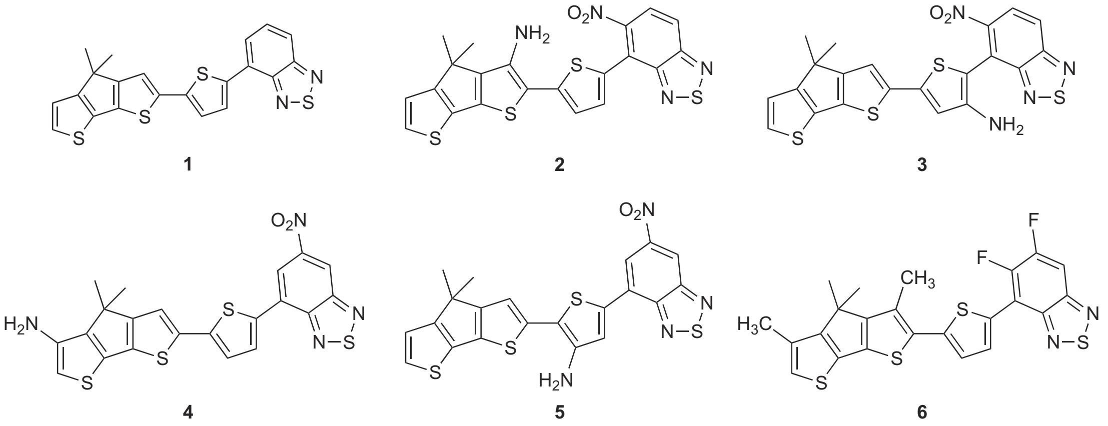

Fig. 2. Chemical structures of monomers **1**–**6**. Molecule **1** is the reference monomer CPDTTBT. Conformations **2** and **3** are linear-conjugated and **4** and **5** are cross-conjugated. Monomers **2**–**5** contain mesomeric groups and monomer **6** contains inductive groups.

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