

On the electronic origin of the high-efficiency of the PTB series donor polymers for organic photovoltaics

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Abstract: The recently synthesized poly-thienothiophene-benzodithiophene (PTB) polymer series is built from a sequence of alternating electron deficient thieno[3,4-b]thiophene (TT) and the electron rich benzodithiophene (BDT) moieties involving different substituents and side chains display remarkable properties as electron donors in organic solar cells of the bulk heterojunction type [1,2,3]. We studied the ground and the first four excited states of three different members of the PTB series, namely, PTB1 (no substituents and side chains), PTB6 (two *o*-*n*-propyl chains in BDT) and PTB7 (fluorine atom in TT and two *o*-*iso*-propyl side chain in BDT). The time-dependent density functional theory (TDDFT) with the B3LYP functional method was employed. We computed different types of bond length alternation (BLA) analysis of the ground and the first (S_1) excited states, natural population analysis (NPA) of all states, excitation energies and oscillator strengths. BLA in the ground state indicates that separation distance between oligomer units and between TT and BDT moieties in each unit are not much affected by the type of substituent. However, the same is not true in the S_1 state where the BLA showed the confinement of the exciton (electron-hole pair) in the middle of the chain and the quinoid nature of the excited state. The substituents in PTB7 decrease the difference between the C-C and C=C bond distances in the TT moiety in contrast with the corresponding negligible effect in PTB1 and PTB6. NPA charge shows a dipolar effect in the three cases, an experimental evidence of partial negative charge concentration on certain TT units and partial positive charge on the adjacent BDT that is more pronounced on the most efficient PTB7 polymer. This was also confirmed from charge difference plots of the four transitions.

Key-words: organic solar cell, pi-conjugated polymers, TDDFT

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