

Elucidating the photophysics of organic photovoltaic systems

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INTRODUCTION

Understanding the fundamental photophysics of organic photovoltaics is a challenge for theoretical chemistry. Their basic process after solar incidence is the production of excitons, bound electron-hole pairs that must be split via a charge transfer (CT) state to produce an electric current. In organic solar cells, exciton dissociation mostly happens at the interface between electron donor and electron acceptor distinct materials as in the bulk heterojunction (BHJ).

In this work, we used the ab initio wave function-based polarization propagator method algebraic diagrammatic construction to second order, ADC(2), to investigate and characterize the excited electronic states of different systems of practical interest including the recently synthesized poly(thieno[3,4-b]-thiophene benzodithiophene) donor polymer, PTB1, and two substituted derivatives either alone or combined with a C₆₀. PTB polymers display remarkable properties as electron donors in BHJs solar cells by combining the electron deficient thienothiophene (TT) and benzodithiophene (BDT) moieties in each oligomer unit.

METHODS

The ADC(2)/SV(P) and time dependent density function theory (TDDFT)/SV(P) methods were used to study the first 4 excited states of PTB1 and two substituted derivatives, PTB6 and PTB7, and PTB1/C₆₀. For TDDFT, five correlation exchange-potential with different degrees of Hartree-Fock exchange were used. The Turbomole Program version 6.6 was employed.

RESULTS AND DISCUSSION

For the PTB1, PTB6 and PTB7 copolymers, excitons can be trapped in the middle of the chain thereby degrading their performance in a BHJ (Figure 1a). Side chains in PTB6 and especially in PTB7 has a crucial role in the electronic spectra,

and not only on the easiness of synthesis of these polymers. Only the PBE functional, which does not include any amount of Hartree-Fock exchange, did not display trapping effects.

For the PTB1/C₆₀ model system, we showed that:¹ (1) CT states are localized below the bright interchain excitonic state and are directly accessible via internal conversion processes; (2) discrete bands of CT states originated by a lateral C₆₀ are also formed and; (3) interchain charge delocalization is important for the stability of the CT states (Figure 1b). In this case, a simple model for the charge separation step showed the energetic feasibility of the overall photovoltaic process in this BHJ.

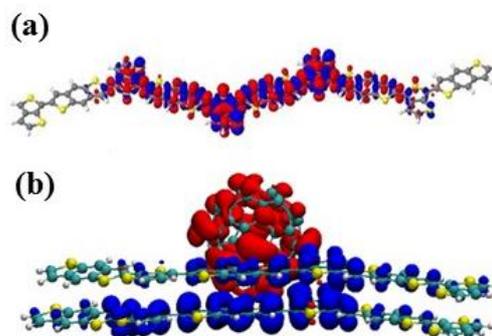


Figure 1. Isodensity plot of the density difference showing the $S_0 \rightarrow S_1$ charge transfer transition. (a) PTB1; (b) PTB1/C₆₀. Red: Charge accumulation. Blue: Charge depletion.

CONCLUSIONS

A comprehensive study of donor polymers and a BHJ that lead to several new physical insights was done using an ab initio method and TDDFT. New results are going to be presented in SBQT.

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