

Computational Modeling of the Electronic Structure of Organic Semiconductors for Solid-State Lighting and Solar Cells

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Introduction

Increasing energy cost and fears of global warming continue to drive alternative energy source development. Solar cells have gained a firm place in the energy market as a clean, renewable energy source well suited for many applications. Organic photovoltaics (OPVs) have been emerging recently as an increasingly viable technology to lower solar cell energy costs and drastically improve novel applications of solar energy harvesting. Power conversion efficiency of OPVs currently prevents their widespread use. Improving the understanding of the charge transfer (CT) process and energy paths lie at the heart of optimizing OPV technology.

Procedure

Ab initio quantum-chemical techniques were used at the Density Functional Theory (DFT) level of theory to investigate two model donor-acceptor systems, tetraminoethylene/tetracyanoethylene (TAE/TCNE) and pentacene/ C_{60} . Charge transfer (CT) and binding energies were calculated as a function of intermolecular distance and dielectric constant of surrounding medium for the two systems. Realistic intermolecular distances included ranged from 4Å to 9Å for the TAE/TCNE system and 4Å to 6Å for the pentacene/ C_{60} system. Solvent calculations were done to simulate the effect of polarizable surrounding medium around the molecules in real devices. Dielectric constants used included $\epsilon = 1$, $\epsilon = 2.02$, $\epsilon = 4.81$ for both systems and the TAE/TCNE system additionally included $\epsilon = 2.38$, $\epsilon = 7.83$, and $\epsilon = 8.93$.

The standard DFT method was used to determine ground state energies. The recently developed constrained DFT (CDFT) method was employed to compute accurate values of the CT energies. Excited state energies were computed using time-dependent DFT (TD-DFT) methods. The 6-31G* basis set was used for all calculations of the TAE/TCNE system and the 3-21G basis set was used for the calculations of the pentacene/ C_{60} system. All calculations were performed with the B3LYP exchange functional. The COSMO model was used to simulate the medium effect on energetics. Calculations were carried out with the NW Chem software package.

Results and Discussion

In TAE/TCNE complex, CT energy had negative values, as expected for a charge transfer salt (in which the ground state is a CT state). The binding energy for the complex is destabilized with increasing dielectric constant and increasing separation distance. In contrast to binding energy, the vertical CT energy is destabilized as separation distance increases and is stabilized as dielectric constant

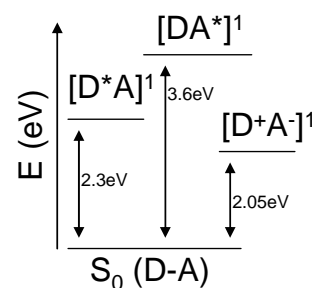
increases. The adiabatic CT energy shows the same trend as the vertical CT energy, only shifted to lower energy. Geometric conformations do not demonstrate a significant effect on the qualitative trend.

The vertical CT energies calculated for pentacene/ C_{60} complex have small positive values ranging from 1.5 to 2.4 eV. The CT energy increases as intermolecular distance increases and decreases as dielectric constant of surrounding medium increases. Adiabatic CT energies are some extent smaller, ranging from 1 to 2.1 eV. Relaxation energy did not show a strong dependence on intermolecular distance (nearly constant 0.3 eV for $\epsilon = 1$, 0.4 eV for $\epsilon = 2.02$, and 0.5 eV for $\epsilon = 4.81$). Relaxation energy was increasingly stabilized with increasing dielectric constant. Binding energies for pentacene/ C_{60} were stabilized with decreased intermolecular distance and with decreased dielectric constant.

In the pentacene/ C_{60} complex, the localized excitation on the pentacene molecule was determined to be the HOMO to LUMO+3 transition in the complex (2.3 eV [using 3-21G basis set]), which corresponds to the HOMO to LUMO excitation on isolated pentacene.

Assuming that D^*A excited state energy of pentacene/ C_{60} remains essentially constant, varying external parameters such as dielectric medium and separation distance from C_{60} is shown to tune the energy difference between D^*A excited state and D^+A^- CT state from +0.2 to -0.8 eV.

Pentacene/ C_{60} Dimer 4Å Intermolecular Dist



Summary and Outlook

Our preliminary calculations show that increasing the dielectric constant of the medium surrounding OPV material stabilizes the charge transfer process and binds the charged molecules less strongly. CDFT calculations allow accurate determination of the energy of the CT state.

Future work will include the investigation of the electronic coupling as a function of molecular orientation. More detailed study of the geometric relaxation processes should also be performed. Finally, this information should be used for the calculation of the rates of the charge separation and charge recombination processes.