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MOLECULAR GEOMETRY AND ELECTRONIC EXCITATIONS. QUANTUM CHEMICAL SIMULATIONS OF ORGANIC SEMICONDUCTORS

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Abstract

Simulation of the probable molecular geometry and corresponding electronic excitation properties for organic hole-transporting materials (HTMs) spiro-indane based enamines (as *p*-type semiconductors) were provided using density functional theory (DFT) Cam-B3LYP method and 6-31G(d) basis set (Gaussian16 package). Character of orientation of the substituents was estimated as chaotic. Absence of the significant rotational barriers for substituents creates the possibility of quite effective partially allowed intramolecular charge redistribution.

Keywords: organic photovoltaics, OPV, organic hole-transporting materials, HTMs, quantum chemistry simulation.

1 Introduction

Modern innovative industry requires organic photo-voltaic (OPV) sensors due to several properties: cheap chemical synthesis and purification, efficient energy conversion for weak signal detection [1], the possibility of applying the sensors *in vivo* systems as an implant, etc. [2]. As OPV, organic hole-transporting materials (HTMs) are important as effective energy converters, for example, perovskite solar cells [3]. In many cases, layered HTMs devices could be constructed using *p*-type semiconductors [4] where partially broken π-conjugated system of the core is related to the rotation motion of substituents which effectively modified the π-conjugated properties of core.

This work represents the quantum chemistry simulation of molecular geometry and energetical properties of the HTM enamine units (central core) related to the spiro-bis-indane-based compounds by combining different aniline substituents [5], see Fig. 1. Due to well-expressed hole-drift mobility properties, constructed novel spiro-indane based enamines are important as *p*-type semiconductors.

2 Simulation

Gaussian16 [6] package was used for simulation of the geometry at the ground electronic state. According to the standard spectrometric approach, the electronic excitations of the most probable structures were obtained using density functional theory (DFT) Cam-B3LYP method and 6-31G(d) basis set (supplemented with polarization functions (d)). Due to the large volume of molecular structures, solvation effects were not considered in all cases. Semiempirical TD method (for singlets only) was used for estimation of parameters of Frank-Condon type transition and corresponding charge redistribution. Fig. 1 represents several molecular realizations of the most probable conformers V1476 (a) and V1481 (b). Substituents are oriented in a chaotic manner resulting in a vast array of different conformers. All structures were derived using the *grad-optimization* technique, ensuring convergence of all parameters such as Maximum Force, RMS Force, Maximum Displacement and RMS Displacement. Both HTMs exhibit high thermal stability and relatively high hole-drift mobility, making them viable candidates for application as HTMs.

Fig. 2 represents molecular orbitals of V1476 and V1481 involved into spectroscopic transitions. In all cases, the predominant and most significant electron jump of the CT transition (π–π*) type occurs between the HOMO and LUMO.

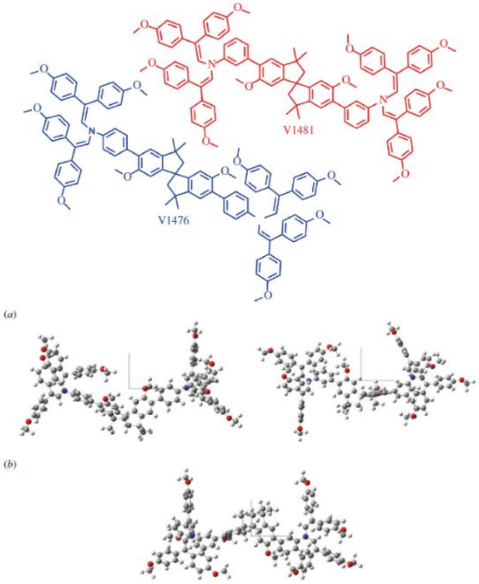

Figure 1 Structures of HTMs V1476 and V1481 (top).
Most probable conformers of V1476 (a) and V1481 (b).

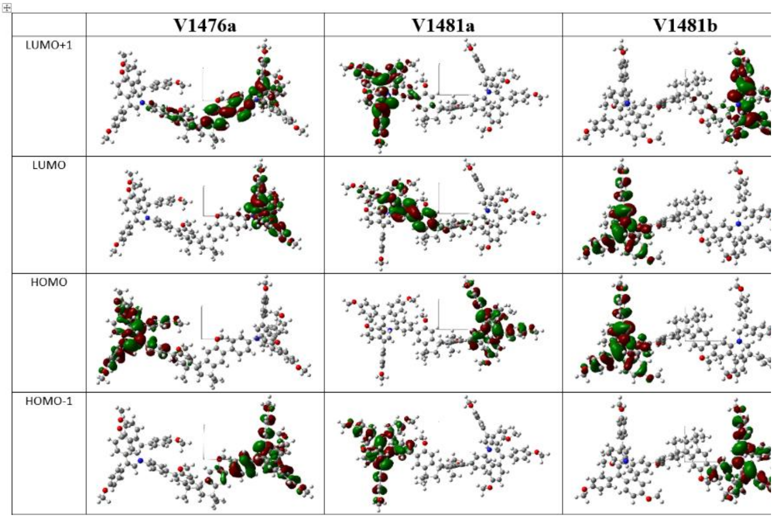

Figure 2. Molecular orbitals of V1476 and V1481 involved into spectroscopic transitions.
Method TD(singlets, nstate=6) B3LYP/6-31G(d) fchk=all sp

Conclusion

Molecular charge redistribution is provided between substituents only, and central core fragment (two pentarings oriented at an angle of about 80° instead of perpendicular) does not participate in CT excitations.

For all simulated conformers, the orientation of the substituents (relative to each other) is chaotic, but the presence of many phenyl moieties associated with the single bond (each with no significant rotational barrier) creates the possibility of quite effective partially allowed charge redistribution.

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