CONCLUSIONS

1. The torsional potential by using bicarbazole and bifluorene at high-level ab initio and DFT results

We investigated the torsional potential energy curves for bicarbazole and bifluorene using HF, B3LYP BH&HLYP and MP2 level of theory, and bigger basis sets than those reported in previous studies. The torsional potentials were fitted to a six-term truncated Fourier expansion. The B3LYP and BH&HLYP energy profiles agree quite reasonably indicating that convergence has virtually been achieved, where compared with MP2 by high basis set. The bond angles do not suffer appreciable variation with the B3LYP and BH&HLYP methods in the bicarbazole molecule, as well as bifluorene molecule. But the bond lengths from B3LYP calculations are longer than the distance from BH&HLYP calculations. For the TD-B3LYP/6-311++G(2d,2p) excitation energies calculations from B3LYP and BH&HLYP geometries give excellent prediction of the excitation energies with experimental data in the range of 0.1-0.2 eV. The ground state geometry from BH&HLYP calculations can provide relatively accurate predictions of vertical excitation energies more than B3LYP geometry. Therefore, we can conclude that the BH&HLYP optimize geometry method is considered to be the most suitable approach to calculate the ground state geometry. It can be conclude that the Fourier least-squares-fitted method is appropriate for validate methods. This procedure is important methods for using to understand and design the structure and electronic property of novel conducting polymers.

2. Theoretical Investigation of Structural and Electronic Properties of Conjugated Polymers Based on Fluorene, Carbazole, Dibenzofuran and Dibenzothiophene Oligomers

The performance of TD-B3LYP/6-311G(2d,2p) method, for accurate prediction of the lowest vertical excitations of the $(FL)_N$, $(Cz)_N$, $(DBZF)_N$ and $(DBZTh)_N$ oligomers, compared to the results obtained by ZINDO method and available experimental data. Comparing to experimental excitation energies available for $(FL)_N$ and $(Cz)_N$ (2.88-2.97 and 3.83 eV, respectively), it can be seen that TD-B3LYP/6-311G(2d,2p) calculation give excellent prediction of the excitation energies for the S_1 transition (2.90 and 3.07 eV, respectively). Whereas the ZINDO method provide similar results with TD-B3LYP/6-311G(2d,2p) calculation of about 0.2 eV and gave difference of about 0.2 eV compared to experimental data. However, the TD-B3LYP/6-311G(2d,2p) calculation can provide relatively accurate predictions of vertical excitation energies for all oligomers. Compared with the available experimental excitation energies for Cz-dimer, Cz-co-Fl and Cz-co-Th, the average deviation of the calculated excitation energies is only 0.1 eV. Therefore, the TD-PBE1PBE method is considered to be the most suitable approach to estimate the absorption energy, and it was employed to investigate the details of the different states of electronic transitions.

3. Theoretical Investigation on Electronic Transition of Carbazole-Based Molecules by TD-DFT Methods

In the present study, the performance of current TD-DFT methods for the accurate prediction of excitation energies and transitions for carbazole-based molecules in comparison with recent *ab initio* methods and experimental data was discussed. TD-DFT in combination with exchange-correlation potentials, some of which have been especially designed for the calculation of electronic properties, can successfully be used to calculate the electronic excitation energy of carbazole-based molecules. The TD-DFT method with the hybrid (PBE1PBE) density function is a feasible way to estimate excitation properties of carbazole-based dimers. The excitation energies calculated by TD-B3LYP are comparable with those of TD-PBE1PBE with the same basis set (6-311++G(2d,2p)), and agree with experimental data to within 0.10 eV. However, other TD-DFT, ZINDO and SAC-CI methods give differences in the range of 0.3-0.5 eV.

For carbazole-copolymerized with six-membered aromatic rings, Cz-dimer and Cz-co-Fl, it was found that the vertical excitation with the S_1 state plays a major role, but in the case of Cz-co-P, the S_2 transition was important. The behavior of these molecules depends on the rotation of the inter-ring of the monomer units, and this can be explained by the HOMO-LUMO energy diagrams which clearly show the different shapes of HOMO and HOMO-1 delocalized orbitals of the molecules.

The same characteristics were found in the carbazole-copolymerized with a five-membered aromatic ring, Cz-co-Th, which also had the S_2 transition as the main contribution. In addition, based on the method used, TD-PBE1PBE/6-311++G(2d,2p)//B3LYP/6-311G(d,p) calculations lead to a better understanding of some optical properties that might not be observable by experimental methods due to unstable transitions as in the case of Cz-co-P and Cz-co-F molecules.

4. Understanding on Absorption and Fluorescence Electronic Transitions of Carbazole-Based Conducting Polymers

Absorption and Emission properties of Cz-dimer, Cz-co-Fl and Cz-co-Th, are presented. The optimization (relaxation) of ground state (GS) and the first singlet excited electronic state (ES) have been done by using the density functional theory (DFT), the *ab initio* approximate coupled cluster singles and doubles (CC2) methods. The structural geometry of ground and excited state were performed by the B3LYP and TD-B3LYP, respectively, using several density functional theories with the SVP and TZVP basis sets. Geometry optimizations have been performed for the ground state and for the first electronically excited state. The excitation to the S_1 state cause important changes in the geometrical parameters of the compounds, as is experimentally corroborated by the small Stokes shifts. The geometry of excited state is more planar than ground state. Absorption and emission energies from the relaxed excited states have been obtained from TDDFT calculations performed on the S_1 optimized geometries and have been excellent agree well with experimental data. As predicted from theoretical calculations, all compounds exhibit small Stokes shift, which testify the rigidity of carbazole-based oligomer. Moreover, this theoretical approach provides a good evaluation of the bathochromic shifts caused by the type of monomer in the carbazole-based oligomer. Comparing to experimental fluorescence excitation energies available for Cz-dimer, Cz-co-Fl and Cz-co-Th (3.20, 3.20 and 3.21 eV, respectively), it can be seen that TD-B3LYP/SVP calculation give agree prediction of the excitation energies for the S_1 transition (3.24, 3.20 and 3.35 eV, respectively). Therefore, the B3LYP/SVP calculation is considered to be the most suitable approach to estimate the absorption energy and fluorescence energy, and it was employed to investigate the details of the different states of electronic transitions.