APPENDIX B

Oral Presentation and Poster Contributions to Conferences

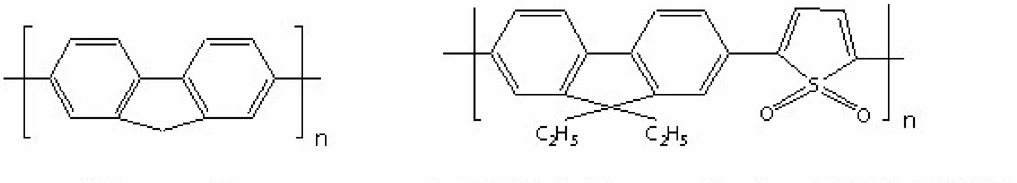
Oral Presentation I

Potjaman Poolmee, Songwut Suramitr, Rungtiwa Chidthong, Supa Hannongbua, Theoretical investigation on electronic property of blue-light emitting conducting polymers. 11th Asian Chemical Congress, August, 24-26, 2005, Korea University, Seoul, Republic of Korea.

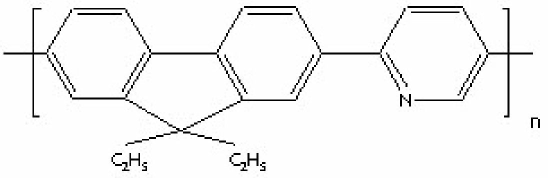
Theoretical Investigation on Electronic Property of Blue-Light Emitting Conducting Polymers

Potjaman Poolmee, Songwut Suramitr, Rungtiwa Chidthong and Supa Hannongbua
Department of Chemistry, Faculty of Science, Kasetsart University, Bangkok, Thailand, 10900
E-mail address: fscisph@ku.ac.th

Recently, conjugated polymers have attracted intense interest over the last two decades, owing to their unique combination of characteristics: electronic, optical, magnetic properties of semiconductors and processing advantages of polymers [1]. Polydiakylfluorene derivatives are one of the most widely investigated PLEDs due to their high efficient blue emission in both photoluminescence (PL) and electroluminescence (EL) [2]. In this work, the energy gaps of fluorene derivatives, as shown in Fig. 1, were investigated. HOMO-LUMO differents of these polymers were calculated by using density functional theory. Time-dependent density functional theory was performed to calculate excitation energy at the optimized geometries of the ground states using density functional theory. Energy gaps of polymers were obtained by plotting the energy of monomer through pentamers against reciprocal chain lengths and extrapolating to infinite chain length. This electronic property of polymers are obtained by employing the oligomer extrapolation technique, which has been successfully employed in investigating several series of polymers [3-4]. It was found that the energy gap of I calculated from B3LYP/6-31G* is 3.26 eV which is consistent with experiment (3.20 eV) [5]. In case of II, the predicted HOMO-LUMO energy gaps can also be useful to estimate the energy gap. The HOMO-LUMO energy gap calculated by B3LYP/6-31G* level are 2.20 eV. It shows the excellent agreement with experimental data (2.19 eV) [6]. However, the orbital energy difference between the HOMO and LUMO is still an approximate estimate to the transition energy because the transition energy also contains significant contributions from some two-electron integrals. TD-DFT(B3LYP/6-31G*)//B3LYP/6-31G*, therefore, was performed on oligomers III. It was observed that the energy gap is 2.75 eV which is good agreement with experiment (2.87 eV) [7]. It can be concluded that the good agreement between the theoretical results and experiment can bring to a rotational design of the tunable-light emitting fluorene derivatives.



polyfluorene (I) poly(9,9′-diethylfluorene-thiophene-S,S-dioxide) (II)



poly(9,9′-diethylfluorene-2,5-pyridine) (III)

Figure 1. Blue-light emitting conducting polymer

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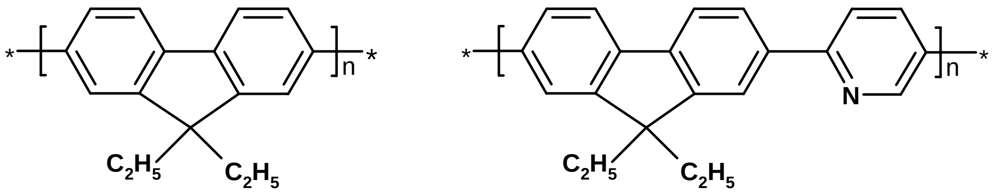
Oral Presentation II

Rungtiwa Chidthong, Potjaman Poolmee, Songwut Suramitr and Supa Hannongbua, Study of the electronic and absorption properties of the fluorene-pyridine conjugated polymers by theoretical investigation. Modeling Interactions in Biomolecules II, September, 5-9, 2005, Prague, Czech Republic.

Study of the Electronic and Absorption Properties of the Fluorene-Pyridine Conjugated Polymers by Theoretical Approach

Rungtiwa Chidthong, Potjaman Poolmee, Songwut Suramitr and Supa Hannongbua
Department of Chemistry, Faculty of Science, Kasetsart University, Bangkok,
Thailand, 10900
E-mail address: g4684004@ku.ac.th, fscisph@ku.ac.th

Geometric structure, vertical excitation energies (Eg_s) and maximum absorption wavelengths (λ_{abs}) of fluorene-pyridine oligomer $(FPy)_n$ (Figure 1) were studied by various methods. The geometry optimizations of FPy were obtained using by density functional theory (DFT), B3LYP/6-31G* level of calculation. It was found that the optimized geometry show planar structure more than fluorene oligomer. The vertical excitation energies of $(FPy)_n$ were calculated using time-dependent density functional theory (TD-DFT) at the B3LYP functional with the 6-31G* basis set based on B3LYP/6-31G* optimized geometries. The electronic properties of the polymers were obtained by the extrapolating those of the oligomers to the inverse chain length equal to zero (1/n=0). The HOMO-LUMO energy differences which is employed by B3LYP/6-31G* (3.16 eV) shows the good agreement as compared with experimental data (2.87 eV). From vertical excitation energy calculations, it was found that the first electronic excitations ($S_0 \rightarrow S_1$) are much higher oscillator strength which is the promotion of HOMO to LUMO. And the vertical excitation energies of $(FPy)_n$ were also close to those determined experimentally from optical band gap. The maximum absorption wavelengths of oligomers are close to those determined experimentally from the absorption spectra records in THF and shown blue shift compared with polyfluorene. It is indicated that pyridine monomer can reduce the excitation energies of poly(fluorene). From this information is importance in a fine-tuning of the emitted color and at a significant improvement in quantum efficiency.



$(FL)_n$ $(FPy)_n$

Figure 1. Chemical structure of Fluorene $(FL)_n$ and Fluorene-Pyridine $(FPy)_n$ oligomers.

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Oral Presentation III

Apirath Phusittrakool, Sornthep Vannarat, Chanchana Thanachayanont, Songwut Suramitr and Supa Hannongbua,
The effect of aluminium atom on structure and electronic properties of MEH-PPV.
The 10th Annual National Symposium on Computational Science and Engineering Conference (ANSCSE10), March 22-24, 2006, Chiang Mai University, Thailand.

The effect of aluminium atom on structure and electronic properties of MEH-PPV

Apirath Phusittrakool[1,*], Sornthep Vannarat[1], Chanchana Thanachayanont[2],
Songwut Suramitr[3], Supa Hannongbua[3]
[1] Computing Research and Development Division, National Electronics and
Computer Technology, Pathumthani, 12120 Thailand.
[2] National Metal and Materials Technology Center, Pathumthani, 12120 Thailand.
[3] Department of Chemistry, Faculty of Science, Kasetsart University,
Bangkok 10900 Thailand.
*apirath@hpcc.nectec.or.th

Abstract

The aluminium/MEH-PPV interface is investigated theoretically, in order to understand the interactions occurring at the molecular level when the aluminium is in contact with the polymer surface. The quantum-chemical calculations based on Density-Functional Theory are performed on a molecular model system consisting of DMO-OPV$_2$ and an aluminium atom. The fully optimized of the Al/DMO-OPV$_2$ complex shows that the aluminium tends to form bonds with the carbon atoms of the vinylene linkage. The HOMO-LUMO gap is found to be narrower when the aluminium atom presents. The modification of the molecular orbitals and the charge density distribution upon Al bonding is observed.

1 Introduction

Conjugated polymers have been considered promising materials for a new class of semiconducting devices. Their organic constitution makes them soluble in common organic solvents and allows for easy processing and inexpensive mass production of thin film devices. Among the conjugated polymers, PPV (Poly[p-phenylenevinylene]) as well as its derivative MEH-PPV (poly[2-methoxy,5-(2-ethyl-hexyloxy)-p-phenylene-vinylene]) have excellent luminescent and mechanical properties, and have been used for the LED and photovoltaic applications. The simple polymer-based LEDs and photovoltaics typically consist of the MEH-PPV polymer film sandwiched between transparent indium-tin oxide (ITO) and low workfunction electrodes such as aluminium or calcium.

The contact interfaces between the electrodes and the polymer layer have strong influence to the efficiency of the devices. For the aluminium on PPV interface, XPS studies revealed the formation of a 30 Å thick insulating layer [1]. This thin layer is thought to be formed as aluminium atoms diffuse into the polymer matrix where aluminium atom chemically interact (covalent bond) and disrupt the conjugation. As a consequence, the electrons are blocked by this layer and result of poor performance.

In order to obtain more detailed information on the behavior and the exact chemical structure at the interface between aluminum and conjugated chains, and because the interaction is very localized [2], we perform quantum-mechanical calculations on a molecular model system consisting of a dimer molecule of para-methoxy-phenylenevinylene (DMO-OPV$_2$) interacting with an aluminium atom. Density-functional theory calculations are used to investigate the bonding configuration of the aluminum atom on the molecule, and the molecular orbitals, orbital energies and the charge distribution to determine the modification of the geometries and the electronic structure.

2 Computational Details

The geometries of the isolated DMO-OPV$_2$ molecule (see Fig. 1), as well as that the complex with Al, are fully optimized with the B3LYP method and the 6-31G(basis set. The energy calculations are then performed on the optimized geometries at t B3LYP/6-311+G(d) level.

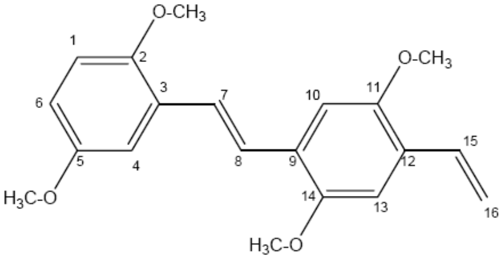


Fig .1. The chemical structure of DMO-OPV$_2$.

In the determination of the most stable configuration of the complex between and DMO-OPV$_2$, the Al atom is included in the structure with two different starti positions: (1) at the 2.5 Å above the atom C8, and (2) at the 2.5 Å above the atom C These two beginning structures are then allowed to fully relax.

The binding energy is obtained with the counterpoise correction method, in ord to eliminate the basis set superposition error. The following expression is used:

$$\Delta E = E_{AB}(AB) - \left(E_{AB}(A) + E_{AB}(B)\right) - \Delta E_{A}(A)$$

where $E_{AB}(AB)$ is the energy of the complex in its relaxed geometry. $E_{AB}(A)$ a $E_{AB}(B)$ is the energy of the isolated molecule and Al in the basis set of the complex a the geometry of the complex. $\Delta E_{A}(A)$ is the energy difference due to the geomet change in the isolated and the complex environment.

3 Results and Discussion

3.1 Geometries

The optimized geometrical parameters for the DMO-OPV$_2$ with and without the atom are summarized in Table 1.

Table 1. Structural parameters of the isolated and complex molecule obtained from fu optimization. (bond lengths in Å, and angle in °)

	isolated	**complex**		**isolated**	**complex**
C7-C8	1.35	1.42	C6-C1	1.39	1.39
C15-C16	1.34	1.34	C6-C5	1.40	1.40
C3-C7	1.46	1.46	C4-C5	1.39	1.40
C8-C9	1.46	1.44	C4-C3	1.41	1.41
Al-C7	-	2.34	C3-C2	1.42	1.42
Al-C8	-	2.31	C2-C1	1.40	1.40
Al-C7-C8	-	71.07	C9-C14	1.41	1.40
Al-C8-C7	-	73.41	C14-C13	1.39	1.42
C4-C3-C7-C8	-13.95	-7.50	C12-C13	1.41	1.41
C10-C9-C8-C7	-12.83	-1.38	C12-C11	1.40	1.41
C3-C7-C8-C9	178.41	178.55	C10-C11	1.39	1.38
			C10-C9	1.42	1.43

We found that the Al atom, which were initially placed at the different positions, relaxd to exact the same final structure. The calculations indicate that when Al approaches to the DMO-OPV$_2$ molecule, it prefers to interact with the two carbon atoms at the vinylene linkage, i.e., the Al atom settles at about the central above the plane of vinylene unit (see Fig. 2). The distances of Al atom to the carbon atoms are observed to be 2.31 and 2.34 Å, which shows that Al forms two bonds to the carbon atoms. This observation is similar to the results of the Al$_2$/terthiophene complex calculated by V. Parente et al. [3].

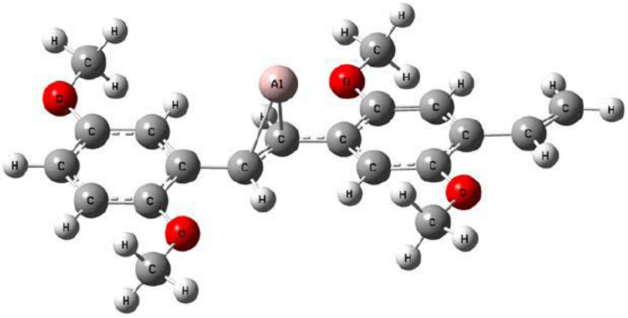


Fig .2. Calculated structure for the Al/DMO-OPV$_2$ complex.

We have calculated the potential energy curve to verify the result of optimization. The curve is obtained by varying the distance of the Al atom to the center of the vinylene linkage, perpendicular to the plane. The result of the potential energy scan (see Fig. 3) confirms that the most stable point is located at the distance about 2.3 Å above the vinylene plane.

The perturbation to the vinylene linkage by the Al-C bonding makes the C7-C8 bond length increases significantly from 1.35 Å in the isolated molecule to 1.42 Å in the complex. This can be considered as the double bond of the vinylene transform to the single-like bond, which shows the breaking of its interaction of π electrons. Furthermore, the C8-C9 bond length shorten a little bit, and the torsion angle C10-C9-C8-C7 become smaller. The explanation may be given by an occurrence of an interaction between Al and C9. More detail will be described in subsection 3.3.

The other parts of DMO-OPV$_2$ besides the vinylene segment appear to be undisturbed. Calculated C-C distances in the phenylene ring of the complex are almost equal to those of the isolated. Therefore, Al does not significantly affected on the geometry of phynelyne rings, and the aluminum interaction is localized to the carbon atom of the vinylene.

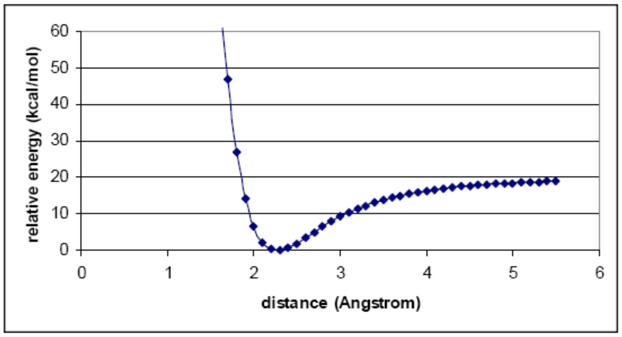


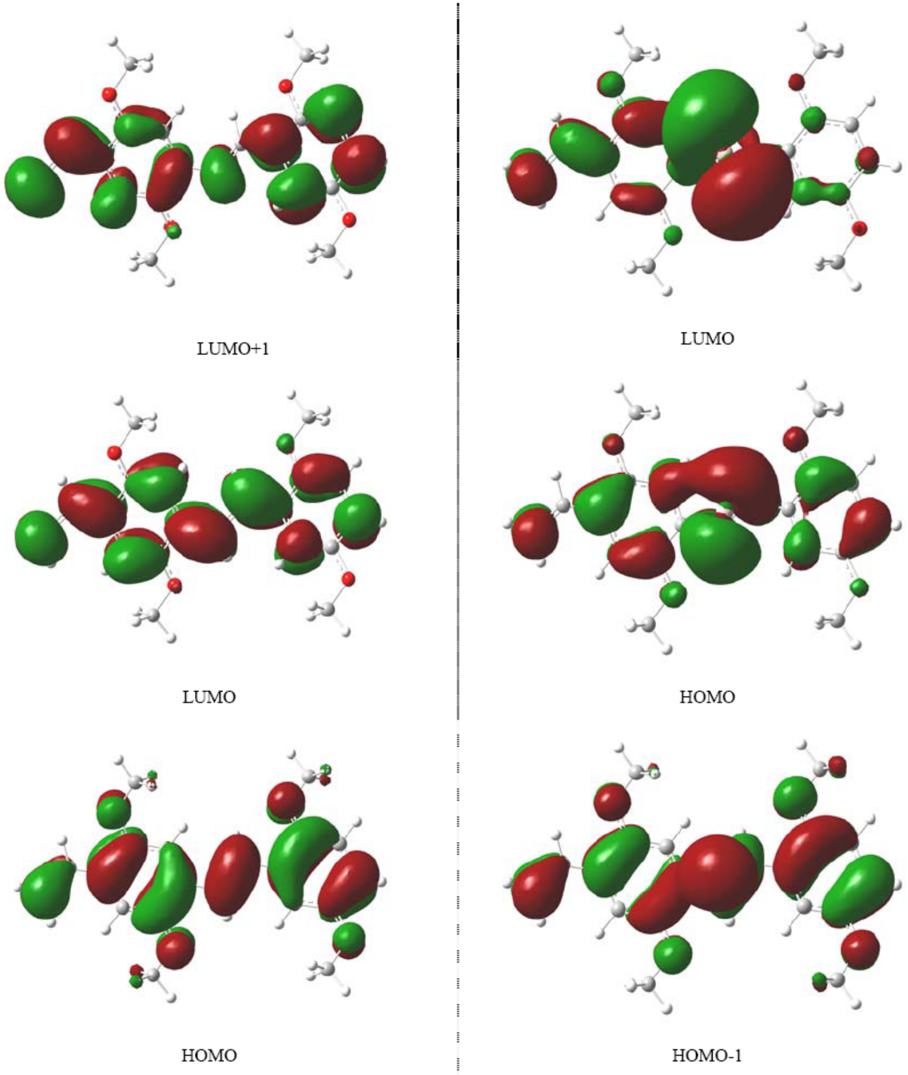
Fig .3. The potential energy curve of the distance between vinylene unit and Al

3.2 Binding Energies

The counterpoise corrected binding energy is found to be -19.8 kcal/mol. Although the binding energy is low, it is enough for the stability of Al-C bond. The bond is considered as a weak covalent bonding. In this case, the size of basis set superposition error is quite small, which is equal to 1.0 kcal/mol.

3.3 Molecular Orbitals

The results of molecular orbitals (MOs) of the isolated DMO-OPV$_2$ molecule and that of the complex with Al are shown in Fig. 4. We show only the spin-up orbitals of the complex system; however, the spin-down orbitals are essentially same as those of spin up. Considerable contributions from Al 3*s* and 3*p* are found in the HOMO-1, HOMO and LUMO molecular orbitals in the Al/DMO-OPV$_2$ complex. By comparing the shape of MOs, we observed that the HOMO and LUMO in the isolated molecule is similar to HOMO-1 and HOMO in the complex, respectively.


LUMO+1

LUMO

LUMO

HOMO

HOMO

HOMO-1

Fig. 4. Schematic representation of the MOs of the isolated DMO-OPV$_2$ (left-hand side) and that of complex with Al atom (right-hand side).

According to the calculation, the HOMO and LUMO of the isolated DMO-OPV$_2$ have a very clear π character and are delocalized over the carbon backbone of the molecule, which is a typical characteristic of conjugated polymers. An important observation is that the MOs of the complex are still delocalized over the conjugated chain. This contradicts to the case of polythiophene [2] that Al induces the localization of MOs at the interaction site and severe loss of the conjugation. Large modification due to the interaction of Al occurs at the LUMO of the DMO-OPV$_2$ system. The Al 3*p* contributes into the the LUMO which thereby lower its energy and becomes the HOMO of the complex system. This HOMO is the result of the Al 3*p* forming hybridization orbital with the C=C anti-π-bonding orbital, as well as the LUMO. The HOMO-1 of the complex corresponds to Al 3*s* orbital formimg an anti-bond with the π orbital. Moreover, some extent of the Al 3*s* as well as 3*p* overlaps with the π orbital of phenylene rings, and results in the shorter C8-C9 bond and the stiffer torsion angle.

The calculated HOMO-LUMO gap of the complex system appears to be narrower, i.e., 3.3 and 1.4 eV for the isolated and the complex system, respectively. Although we cannot rely on the absolute values, this gives us a trend of lower excitation energy in the complex system.

3.4 Charge Density Distribution

Important modifications in the charge density distribution of the conjugated system are also induced by the formation of the Al-C bonds. According to the Mulliken population analysis, the charge density of Al decreases by about 0.4 $|e|$, while the charge density of the carbon atoms around the vinylene segment largely increases when compare to the charges of the isolated molecule. This observation relates to the electron transfer from Al atom to the carbon chain. In addition, the interaction with Al leads to some loss of charge in the phylene rings.

4 Conclusions

We have used *ab initio* Density-functional theory methods to investigate the interaction between Al and MEH-PPV interface. The results of this DFT study confirm that Al interacts with the back bone of conjugated system by forming weak covalent bonds with two carbon atoms at the vinylene linkage. This interaction weakens the conjugation of the polymer chain by inducing a transformation of the double bond to the single bond. The charge transfer from Al to the carbon atoms occurs around the interaction unit. The valence orbitals of Al contribute to the HOMO and LUMO of the polymer, forming hybridized molecular orbital with the π conjugation of the chain. However, the delocalization of π-molecular orbital is maintained along the chain.

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Oral Presentation IV

Songwut Suramitr, Wichanee Meeto, and Supa Hannongbua,
Theoretical Investigation of Ground and Excited States Geometry of Conjugated Based on Carbazole Copolymers.
The International Conference on Modeling in Chemical and Biological Engineering Sciences held in Bangkok from October 25-27, 2006, The Rama Gardens Hotel Bangkok, Thailand.

Theoretical Investigation of Ground and Excited States Geometry of Conjugated Based on Carbazole Copolymers Songwut Suramitr, Wichanee Meeto and Supa Hannongbua*

1Department of Chemistry, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand.

*Corresponding author: Tel. 662-942-8900 ext 217, Fax 662-942-8900 ext 324
E-mail: *fscisph@ku.ac.th*

ABSTRACT

We report the ground state and the lowest singlet excited-state properties of carbazole-based molecules. Geometry optimizations have been performed for the ground state and for the first electronically excited state using density functional theory (DFT) and time-dependent density functional theory (TDDFT) levels using the B3LYP functional. Electronic excitation leads to quinoide type distortions, in particular to a shortening of the inter-ring bonds. Vertical excitations and the fluorescence transition from the lowest excited state have been calculated. The absorption and luorescence energy agree very well with the available experimental data.

INTRODUCTION

Recently, novel well-defined 2,7-carbazole-based (Cz) polymers were synthesized by Leclerc et al. Luminescent materials spanning the entire visible range have been prepared from these polymers, and can be used in Organic Light Electronic Devices (OLED). The absorption and emission energies of these copolymerized derivatives were correlated with their electronic transitions. Therefore for this work, the ground state and the lowest singlet excited-state for the carbazole-based molecules (Figure 1) were investigated using various theoretical approaches and basis sets. They were used here to study five carbazole-based molecules: Cz-dimer (Cz2), Cz-co-Fluorene (Cz-co-FL), Cz-co-Phenyl (Cz-co-P), Cz-co-Thiophene (Cz-co-Th) and Cz-co-Furan (Cz-co-F).

METHODOLOGY

The ground state and the lowest singlet excited-state geometries of the fluorene-based oligomers were optimized at the DFT and TDDFT levels, using the B3LYP functional. On the basis of the optimized geometries, the electronic absorption and luminescence spectra were calculated at TDDFT levels. Vertical excitations are computed at the ground-state geometry. The fluorescence transition is obtained as the vertical de-excitation at the optimized geometry of the excited state. The polarized split-valence (SVP) and the triple-ζ valence-polarized (TZVP) basis sets have been used. All calculations were done using the Turbomole version 5.7 program packages.

RESULTS and DISCUSSION

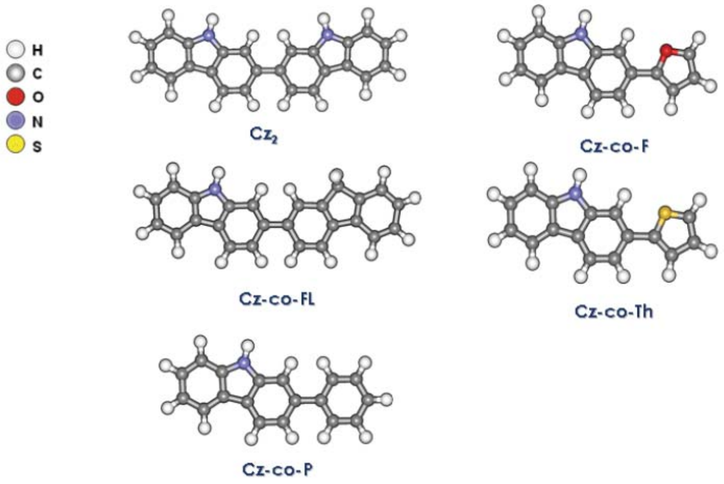

Figure 1. Chemical structure of carbazole dimer and carbazole-based copolymers.

In the ground state, Cz-copolymerized with five-membered aromatic rings are more stable in a planar configuration than with six-membered aromatic ring monomers. The excited state distances of the inter-ring bonds are slightly shorter (about 0.03 Å) than the ground stat geometry. The electronic excitation leads to formation of a quinoide type structure. The calculations at SVP and TZVP theoretical levels show the changes in distances at about 0.04 Å. It is noted that the SVP calculations predicted relative energies of the carbazole-based conformations in good agreement with TZVP methods. Taking this into account, it can be conclude that the B3LYP/SVP and TD-B3LYP/SVP method are appropriate, in terms of both accuracy and computing time, for the ground state and excited state geometry optimization and, therefore, it can be used for further analysis. The vertical excitations and the fluorescence transition excitation energies calculated by TDB3LYP/ SVP are agreed with experimental data to within 0.10 eV. In addition, based on the method used, TD-B3LYP/SVP calculations can increase 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. This structural and electronic information can be applied in the designing of novel conducting polymer materials.

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ACKNOWLEDGMENTS

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Poster Presentations I

Songwut Suramitr, Teerakiat Kerdcharern, Toemsak Srikhirin, Supa Hannongbua, **Structure and electronic properties of the alkoxy derivatives of poly(para-phenylenevinylene) as explained by TD-DFT calculations.** Theory and Applications of Computational Chemistry, February, 15-20, 2004, Gyeongju, Republic of Korea.

Electronic Properties of Alkoxy Derivatives of Poly(para-phenylenevinylene), Explained by Time Dependent Density Functional Theory Calculations

***Songwut Suramitr*[1], *Teerakiat Kerdcharoen*[2], *Toemsak Srikhirin*[2] and *Supa Hannongbua*[1]**
[1]Department of Chemistry, Faculty of Science, Kasetesart University, Bangkok 10900
[2]Department of Physic, Faculty of Science, Mahidol University, Bangkok 10900. E-mail fscisph@ku.ac.th

Abstract

Geometries and energy gaps of poly(*para*-phenylenevinylene) oligomer (OPV_N) and its alkoxy derivatives were investigated, based on quantum chemical calculations. This oligomer series includes poly(*para*-methoxy-PV) (DMO-OPV_N), poly(*para*-hexoxy-PV) (DHO-OPV_N) and poly(2-methoxy,5-(2'-ethyl-hexyloxy)-PV) (MEH-OPV_N). Linear correlations were employed to semiquantitatively estimate first excitation energy. We introduce the relationships with the working function of $E_{expt} = 0.604E_{TDDFT\text{-}B3LYP/6\text{-}31G} + 0.947$ and $E_{expt} = 0.604E_{TDDFT\text{-}B3LYP/6\text{-}31G^*} + 0.983$, based on the geometry obtained from HF/3-21G for correction of the extrapolated energy gaps of DMO-OPV_N, DHO-OPV_N and MEH-OPV_N. It was found that satisfied linear relationship and TDDFT method can be used to predict the lowest excitation energies for compounds in these systems and applicable to the design of new conducting polymers.

Introduction

Poly(*para*-phenylenevinylene) (PPV) is one of the most important conductive polymers studied world wide because of the ease of processing and tuning of electronic and optical properties by modifying the polymer side chain. Derivatives of PPV have been synthesized by attaching alkoxy side groups onto the phenylene ring at the 3 and 6 carbons (Figure 1), leading to increasing both their solubility and stability. Thus, the unique structures of the PPV derivatives yield an attractive combination of electronic and mechanical properties that represent promising materials from an engineering viewpoint.

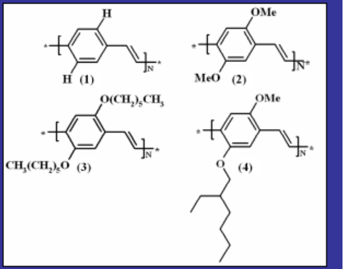

Figure 1. Illustration of the chemical structure of OPV_N alkoxy derivatives.
(1) Poly(para-phenylenevinylene) OPV_N : R1= R2= H,
(2) Poly(para-methoxy)-PV) DMO-OPV_N : R1= R2= O-CH3
(3) Poly(para-hexoxy-PV) DHO-OPV_N : R1= R2= O-(CH2)5-CH3,
(4) Poly(2-methoxy,5-(2'-ethyl-hexyloxy)-PV) MEH-OPV_N :
R1=OCH3,
R2=O-$CH_2CH(C_2H_5)(C_4H_9)$.

Methods of calculations

Starting geometries of the oligomer were constructed by SciPolymer 3.0 program. The OPV_N derivatives were modified by attaching alkoxy groups onto the phenylene ring at the C3 and C6 atoms. In this work, the notation OPV_N represents the oligomers of PPV with N corresponding to the total number of phenylene rings in the oligomers. The oligomers of OPV_N derivatives are denoted by DMO-OPV_N, DHO-OPV_N and MEH-OPV_N. Their chemical structures are illustrated in Figure 1.

The ground state geometries of oligomers, OPV_N derivatives, were fully optimized by using AM1 and HF/3-21G implemented in Gaussian98, running on a Linux-PC 2.4 GHz. The calculations of the excitation energies were then performed based on the ground-state geometries. Excitation energies were calculated by using the TDDFT(B3LYP/6-31G) and TDDFT(B3LYP/6-31G*) methods.

Results and discussion

The extrapolated energy gaps of OPV_N and derivatives obtained from the TDDFT(B3LYP/6-31G//AM1, B3LYP/6-31G*//AM1, B3LYP/6-31G//HF/3-21G and B3LYP/6-31G*//HF/3-21G) calculations were then predicted as shown in Table 1. The predicted energies are lower than that of the experimental values for each OPV_N derivatives which are 2.38, 2.18, 2.08 and 2.10 eV, respectively. It was found from our study that the energy gaps of OPV_N obtained from density functional theory (TDDFT(B3LYP/6-31G//HF/3-21G and B3LYP/6-31G*//HF/3-21G)) are in good agreement with the experiments. However, the energy gaps of DMO-OPV_N, DHO-OPV_N and MEH-OPV_N show overestimate energy gaps of about 0.3 eV as found inherent in TDDFT calculations.

Table 1. TDDFT excitation energies (eV) of oligomers with B3LYP functional and two basis sets (6-31G and 6-31G*), based on the ground-state geometries from AM1 and HF/3-21G methods.

Polymers	Energy gap (eV)				
	TD(B3LYP/ 6-31G//AM1)	TD(B3LYP/ 6-31G*//AM1)	TD(B3LYP/ 6-31G//HF/3-21G)	TD(B3LYP/ 6-31G*//HF/3-21G)	Expt. [1]
OPV_N	2.01	1.90	2.38	2.32	2.38
DMO-OPV_N	1.93	1.87	2.01	1.95	2.18
DHO-OPV_N	1.89	1.82	1.89	1.83	2.08
MEH-OPV_N	1.90	1.83	1.92	1.86	2.10

Table 2. Linear fits between the experimental and calculated excitation energies based on the ground-state geometries from AM1 and HF/3-21G methods.

Methods	Linear equations	Energies gap$_{correction}$ (eV)			
		OPV_N	DMO-OPV_N	DHO-OPV_N	MEH-OPV_N
TD(B3LYP/6-31G//AM1)	$E_{expt} = 2.518E_{TD} - 2.682$ ($r = 0.999$)	2.38	2.18	2.08	2.10
TD(B3LYP/6-31G*//AM1)	$E_{expt} = 3.537E_{TD} - 4375$ ($r = 0.910$)	2.35	2.24	2.06	2.10
TD(B3LYP/6-31G//HF/3-21G)	$E_{expt} = 0.604E_{TD} + 0.947$ ($r = 0.991$)	2.38	2.16	2.09	2.11
TD(B3LYP/6-31G*//HF/3-21G)	$E_{expt} = 0.604E_{TD} + 0.983$ ($r = 0.991$)	2.38	2.16	2.09	2.11

Llinear fits between the experimental and calculated values for the excitation energies based on the ground-state geometries from AM1 and HF/3-21G methods are summarized in Table 2. Based on the correction, the predicted energy gaps of all derivatives are improved and estimated to be consistend with the experimental data.

Conclusions

It was found that satisfied linear relationship and TDDFT method can be used to predict the lowest excitation energies for compounds in these systems. The trend in energy gaps observed for OPV_N and its derivatives may be useful for the design of novel conducting polymer materials. In addition, this TDDFT method with B3LYP functional can be applied to the large molecular system such as OPV_N derivatives and the correction excitation energy is required for reasonable energetic properties.

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Poster Presentations II

Songwut Suramitr, Supa Hannongbua and Alfred Karpfen, **Electronic properties of conjugated polymers based on fluorene, carbazole, dibenzofuran and dibenzothiophene.** 40th Symposium for Theoretical Chemistry. Computational Chemistry, September, 19-23, 2004, Suhl, Germany.

Electronic and Structural Properties of Conjugated Polymers Based on Fluorene, Carbazole, Dibenzofuran and Dibenzothiophene

Songwut Suramitr[1,2], Supa Hannongbua[1] and Alfred Karpfen[2]
[1]Department of Chemistry, Faculty of Science, Kasetsart University, Bangkok 10900
[2]Institute for Theoretical Chemistry and Structural Biology, University of Vienna, Währinger straße 17 A-1090 Vienna, Austria

Abstract

Equilibrium structures and excitation energies of fluorene (F), carbazole (Cz), dibenzofuran (DBF) and dibenzothiophene (DBTh) (see figure 1) were computed using the density functional theory (B3LYP and BHandHLYP). Four basis sets, 6-31G, 6-31G(d), 6-311G(d,p) and 6-311++G(2d,2p), were used for this purpose. ZINDO and TDDFT calculations of the excitation energies were then performed at the optimized geometries of the ground states. We have investigated the basis set dependence of excitation energies calculated with TDDFT for fluorene, carbazole, dibenzofuran and dibenzothiophene. The application of TDDFT gives results for the first singlet excitation energies that agree very well with the experimental data. These results show that TD-B3LYP/6-311++G(2d,2p) is a good predictive tool for the first excitation energy of molecules. The same comparison can be done for the HOMO and LUMO of fluorene which turns out to be similar to the HOMO and LUMO of dibenzofuran. Carbazole is similar to dibenzothiophene. This suggests that the pairs fluorene/dibenzofuran and carbazole/dibenzothiophene should have similar characteristics of their lowest excitation. The ordering and electronic configurations of the orbitals calculated agree with previous theoretical studies for fluorene, carbazole, dibenzofuran and dibenzothiophene.

Methods of calculations

Since the properties of the polymers depend greatly on their constituent monomers, we begin by studying the properties of the four molecules that will form the repeated unit of the polymers under consideration. These molecules are Fluorene (FL), Carbazole (CZ), Dibenzofuran (DBF) and Dibenzothiophene (DBTh). Their atomic structures are depicted in Figure 1.

The ground-state geometries of monomers were fully optimized using the density functional theory (B3LYP and BHandHLYP) calculations, starting from structural data, regularized in order to satisfy the C_{2v} symmetry. ZINDO and TDDFT calculations of the excitation energies were then performed at the optimized geometries of the ground states. We have investigated the basis set dependence of excitation energies calculated with TDDFT for Fluorene, Carbazole, Benzofuran and Benzothiophene.

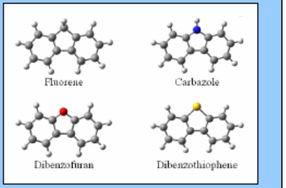


Figure 1. Structures of monomers.

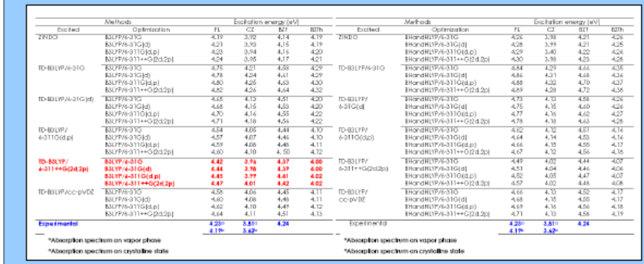
Introduction

The use of conjugated polymers for the development of electronic devices has been, and still is, fruitful and varied. Many applications such as organic light emitting diodes and even solid state organic lasers use poly(p-phenylene) (PPP) or its derivatives. It is interesting to consider polymers with variations of the atomic structure of PPP. The polymers based on the molecules of Fluorene, and Carbazole all possess the sequence of bonded benzene rings characteristic of the geometry of PPP. The similarity in the atomic structure of the polymers and molecules suggests a resemblance in their electronic and optical properties

First-principles methods, for which no experimental parameters are necessary, enable us to study systems where few or no data are available. The knowledge acquired about the electronic structure gives us information on the interesting optical properties of the polymers under consideration. Many theoretical studies were done on PPP and some on poly(2,7-fluorene). However, we are not aware of any theoretical work on poly(2,7-carbazole), which is a very recently synthesized polymer, and poly(α,γ-borafluorene), which has not been synthesized yet. We propose a comparative study of electronic and structural properties of these systems.

Results and discussion

Table 1. Calculated and experimental first excitation energies of FL, CZ, BZF and BZTh monomers from B3LYP and BHandHLYP optimized



Methods		Excitation energy (eV)			
Excited	Optimization	FL	CZ	BZF	BZTh
ZINDO	B3LYP/6-31G	4.19	3.92	4.14	4.19
	B3LYP/6-31G(d)	4.21	3.93	4.15	4.19
	B3LYP/6-311G(d,p)	4.23	3.94	4.16	4.20
	B3LYP/6-311++G(2d,2p)	4.24	3.95	4.17	4.21
TD-B3LYP/6-31G	B3LYP/6-31G	4.75	4.21	4.58	4.29
	B3LYP/6-31G(d)	4.78	4.24	4.61	4.29
	B3LYP/6-311G(d,p)	4.80	4.25	4.63	4.30
	B3LYP/6-311++G(2d,2p)	4.82	4.26	4.64	4.32
TD-B3LYP/6-31G(d)	B3LYP/6-31G	4.65	4.13	4.51	4.20
	B3LYP/6-31G(d)	4.68	4.15	4.53	4.20
	B3LYP/6-311G(d,p)	4.70	4.16	4.55	4.22
	B3LYP/6-311++G(2d,2p)	4.71	4.18	4.56	4.22
TD-B3LYP/ 6-311G(d,p)	B3LYP/6-31G	4.54	4.05	4.44	4.10
	B3LYP/6-31G(d)	4.57	4.07	4.46	4.10
	B3LYP/6-311G(d,p)	4.59	4.08	4.48	4.11
	B3LYP/6-311++G(2d,2p)	4.60	4.10	4. 50	4.12
TD-B3LYP/ 6-311++G(2d,2p)	**B3LYP/6-31G**	**4.42**	**3.96**	**4.37**	**4.00**
	B3LYP/6-31G(d)	**4.44**	**3.98**	**4.39**	**4.00**
	B3LYP/6-311G(d,p)	**4.45**	**3.99**	**4.41**	**4.02**
	B3LYP/6-311++G(2d,2p)	**4.47**	**4.01**	**4.42**	**4.02**
TD-B3LYP/cc-pVDZ	B3LYP/6-31G	4.58	4.06	4.45	4.11
	B3LYP/6-31G(d)	4.60	4.08	4.48	4.11
	B3LYP/6-311G(d,p)	4.62	4.10	4.49	4.12
	B3LYP/6-311++G(2d,2p)	4.64	4.11	4.51	4.13
Experimental		4.23[a] 4.19[b]	3.81[a] 3.62[b]	4.24	

[a]Absorption spectrum on vapor phase
[b]Absorption spectrum on crystalline state

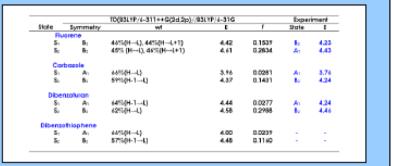
Methods		Excitation energy (eV)			
Excited	Optimization	FL	CZ	BZF	BZTh
ZINDO	BHandHLYP/6-31G	4.26	3.98	4.21	4.26
	BHandHLYP/6-31G(d)	4.28	3.99	4.21	4.25
	BHandHLYP/6-311G(d,p)	4.29	3.40	4.22	4.26
	BHandHLYP/6-311++G(2d,2p)	4.30	3.98	4.23	4.28
TD-B3LYP/6-31G	BHandHLYP/6-31G	4.84	4.29	4.66	4.35
	BHandHLYP/6-31G(d)	4.86	4.31	4.68	4.36
	BHandHLYP/6-311G(d,p)	4.88	4.32	4.70	4.37
	BHandHLYP/6-311++G(2d,2p)	4.89	4.28	4.72	4.38
TD-B3LYP/ 6-31G(d)	BHandHLYP/6-31G	4.73	4.13	4.58	4.26
	BHandHLYP/6-31G(d)	4.75	4.15	4.60	4.26
	BHandHLYP/6-311G(d,p)	4.77	4.16	4.62	4.27
	BHandHLYP/6-311++G(2d,2p)	4.78	4.18	4.63	4.28
TD-B3LYP/ 6-311G(d,p)	BHandHLYP/6-31G	4.62	4.12	4.51	4.16
	BHandHLYP/6-31G(d)	4.64	4.14	4.53	4.16
	BHandHLYP/6-311G(d,p)	4.66	4.15	4.55	4.17
	BHandHLYP/6-311++G(2d,2p)	4.67	4.12	4.56	4.18
TD-B3LYP/ 6-311++G(2d,2p)	BHandHLYP/6-31G	4.49	4.02	4.44	4.07
	BHandHLYP/6-31G(d)	4.51	4.04	4.46	4.06
	BHandHLYP/6-311G(d,p)	4.52	4.05	4.47	4.07
	BHandHLYP/6-311++G(2d,2p)	4.57	4.02	4.48	4.08
TD-B3LYP/ cc-pVDZ	BHandHLYP/6-31G	4.66	4.13	4.52	4.17
	BHandHLYP/6-31G(d)	4.68	4.15	4.55	4.17
	BHandHLYP/6-311G(d,p)	4.69	4.16	4.56	4.18
	BHandHLYP/6-311++G(2d,2p)	4.71	4.13	4.58	4.19
Experimental		4.23[a] 4.19[b]	3.81[a] 3.62[b]	4.24	

[a]Absorption spectrum on vapor phase
[b]Absorption spectrum on crystalline state

For molecules, it is also possible to calculate the excitation energies using ZINDO, and TDDFT. The application of TDDFT gives quantitative results for the first singlet excitation energies that agree very well with the experimental data (Table 1 and 2). These results show that TD-B3LYP/6-311++G(2d,2p) is a good predictive tool for the first excitation energy of molecules.

For the result, the same comparison can be done for the HOMO and LUMO of Fluorene that is similar to the HOMO and LUMO of Dibenzofuran. Carbazole is similar with Dibenzothiophene. This suggests that Fluorene/Dibenzofuran and Carbazole /Dibenzothiophene should have similar characteristics for their lowest excitation. The ordering and electronic configurations of the orbital calculated agree with previous theoretical studies for Fluorene, Carbazole and Dibenzofuran.

Table 2. Calculated and experimental first excitation energies of FL, CZ, BZF and BZTh monomers from B3LYP optimized



	TD(B3LYP/6-311++G(2d,2p))//B3LYP/6-31G				Experiment	
State	Symmetry	wt	E	f	State	E
Fluorene						
S_1	B_2	46%(H→L), 44%(H→L+1)	4.42	0.1539	B_2	4.23
S_2	B_2	45% (H→L), 46%(H→L+1)	4.61	0.2834	A_1	4.43
Carbazole						
S_1	A_1	66%(H→L)	3.96	0.0281	A_1	3.76
S_2	B_2	59%(H-1→L)	4.37	0.1431	B_2	4.24
Dibenzofuran						
S_1	A_1	64%(H-1→L)	4.44	0.0277	A_1	4.24
S_2	B_2	62%(H→L)	4.58	0.2988	B_2	4.46
Dibenzothiophene						
S_1	A_1	66%(H→L)	4.00	0.0239	-	-
S_2	B_2	57%(H-1→L)	4.48	0.1160	-	-

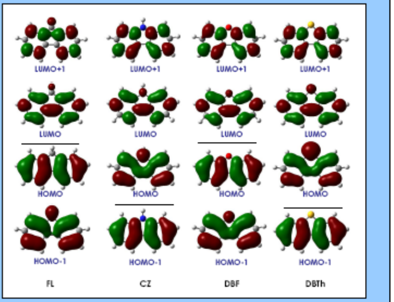


Figure 2. Calculated HOMO and LUMO of Fluorene, Carbazole, Dibenzofuran, and Dibenzothiophene. Depicted are two isosurfaces of equal values but opposite sign.

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Poster Presentations III

Songwut Suramitr, Supa Hannongbua, Peter Wolschann and Alfred Karpfen, **Time-dependent density functional theory calculations to study the electronic properties of polycarbazole and carbazole-based copolymers.** The 2nd Asian Pacific Conference on Theoretical and Computational Chemistry (APCTCC-2), May, 2-6, 2005, Chulalongkorn University, Bangkok, Thailand.

*T*ime-dependent density functional theory investigations on electronic properties of polycarbazole and carbazole-based copolymers

Songwut Suramitr[1,2], Supa Hannongbua[1], Peter Wolschann[2] and Alfred Karpfen[2]

[1]Department of Chemistry, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand
[2]Institute for Theoretical Chemistry and Structural Biology, University of Vienna, Währinger Straße 17 A-1090 Vienna, Austria

Introduction

Experimental studies focusing on carbazole homopolymer and carbazole copolymers have been increasingly reported in the literature due to conjugated polymer polycarbazole (PCz) could have as good hole-transport properties. It would be advantageous for as a host segment in copolymerization with various narrow energy gap comonomers. Recently, a new class of polycarbazoles, with tunable emission color (blue, green and red), were synthesized. Therefore, the aim of this work is to study the electronic properties of polycarbarzole-based copolymers by several time-dependent density functional theory methods (TD-DFT).

Methods of calculations

The ground-state geometries of each carbazole homopolymer and copolymers, Cz-dimer, Cz-co-Phenyl (Cz-co-P), Cz-co-Fluorene (Cz-co-FL), Cz-co-Thiophene (Cz-co-Th) and Cz-co-Furan (Cz-co-F), were fully optimized using the density functional theory (DFT). The vertical excitation energies of carbazole-based copolymers are employed by the time-dependent density functional theory (TD-DFT) at the BLYP, BP86, BHandHLYP, B3LYP and PBE1PBE functional with 6-311++G(2d,2p) basis sets based on B3LYP/6-311G(d,p) optimized geometries of the ground states. All calculations were implemented in Gaussian03.

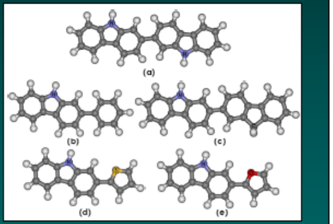
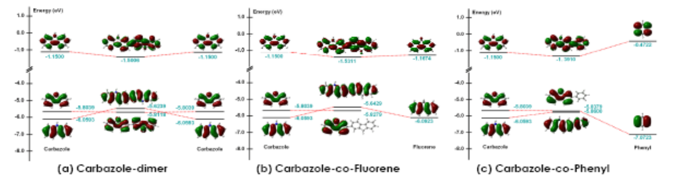


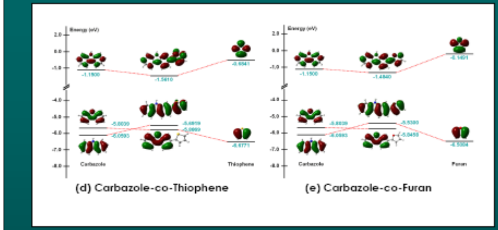
Figure 1. Chemical structure of carbazole dimer andcarbazole-based copolymers:
(a) carbazole combined with carbazole (Cz-co-Cz), (b) phenyl (Cz-co-P), (c) Fluorene (Cz-co-FL),
(d) Thiophene (Cz-co-Th) and (e) Furan (Cz-co-Fu).

Results and discussion

Figure 2. Energy diagram of (a) Carbazole-dimer and (b) Carbazole-co-Fluorene, (c) Carbazole-co-Phenyl, (d) Carbazole- co-Thiophene and (e) Carbazole-co-Furan calculated by B3LYP/6-311++G(2d,2p) calculation.



(a) Carbazole-dimer (b) Carbazole-co-Fluorene (c) Carbazole-co-Phenyl



(d) Carbazole-co-Thiophene (e) Carbazole-co-Furan

Table 1. The vertical excitation energy (Ex) and oscillator strength (f) of carbazole derivatives as obtained by TD-DFT calculations at 6-311++G(2d, 2p) basis set based on B3LYP/6-311G(d,p) geometry.

Methods	S_1		S_2	
	Ex/eV	f	Ex/eV	f
Cz-dimer				
TD-BLYP	3.36	0.8120	3.21	0.0022
TD-BP86	3.32	0.8061	3.18	0.0020
TD-B3LYP	3.72	1.0723	3.76	0.0050
TD-PBE1PBE	3.91	1.1337	3.96	0.0059
TD-BHandHLYP	4.21	1.3004	4.40	0.0076
	(HOMO)→(LUMO)		(HOMO-1)→(LUMO)	
Experimental*	3.85		-	
Cz-co-Fluorene				
TD-BLYP	3.29	0.9230	3.14	0.0104
TD-BP86	3.32	0.9184	3.16	0.0107
TD-B3LYP	3.72	1.1870	3.75	0.0288
TD-PBE1PBE	3.83	1.2589	3.87	0.0309
TD-BHandHLYP	4.11	1.3665	4.31	0.0311
	(HOMO)→(LUMO)		(HOMO-1)→(LUMO)	
Experimental*	3.83		-	
Cz-co-Phenyl				
TD-BLYP	3.37	0.0179	3.69	0.4925
TD-BP86	3.39	0.0177	3.72	0.4955
TD-B3LYP	3.83	0.0245	4.05	0.5964
TD-PBE1PBE	3.94	0.0262	4.16	0.6279
TD-BHandHLYP	4.33	0.0354	4.38	0.6747
	(HOMO)→(LUMO)		(HOMO-1)→(LUMO)	
Experimental*	-		-	

Methods	S_1		S_2	
	Ex/eV	f	Ex/eV	f
Cz-co-Thiophene				
TD-BLYP	3.25	0.0149	3.43	0.5371
TD-BP86	3.28	0.0149	3.47	0.5438
TD-B3LYP	3.73	0.0220	3.78	0.6700
TD-PBE1PBE	3.91	0.0254	3.98	0.7265
TD-BHandHLYP	4.26	0.0299	4.12	0.7578
	(HOMO-1)→(LUMO)		(HOMO)→(LUMO)	
Experimental*	-		3.04	
Cz-co-Furan				
TD-BLYP	3.30	0.0168	3.41	0.5972
TD-BP86	3.32	0.0166	3.44	0.6008
TD-B3LYP	3.74	0.2391	3.76	0.5630
TD-PBE1PBE	3.86	0.2974	3.84	0.5468
TD-BHandHLYP	4.25	0.0356	4.05	0.8773
	(HOMO-1)→(LUMO)		(HOMO)→(LUMO)	
Experimental*	-		-	

*Absorption wavelengths taken at the maximum of the absorption band [1].

The results of Figure 2 show frontier electronic levels of the five molecules.

All Figures can be easily rationalized by analyzing how the nature of the frontier electronic levels of the carbazole chains is affected by the incorporation of FL, P, Th or F units.

- There are antibonding between the bridge atoms and there are bonding between the bridge carbon atom and its conjoint atoms in the same benzenes in the HOMO.
- The HOMO orbital of Cz-dimer, Cz-co-FL, CZ-co-Th and Cz-co-F are fully delocalized over the conjugated backbone, a wile Cz-co-P, the orbital delocalized on the HOMO-1 orbital.
- There are bonding in the bridge single bond and the antibonding between the bridge atom and its neighbor in the same phenyl ring in the LUMO.
- It is indicated that the delocalization of the LUMO orbital of Cz copolymer are depended on the electronic of monomer which combine with carbazole.

The vertical excitation energies of Cz-co-Cz and Cz-co-FL cases,

- The first electronic transition ($S_0 \rightarrow S_1$) is much larger oscillator strength the $S_0 \rightarrow S_2$ electronic transition. Whereas the $S_0 \rightarrow S_1$ electronic transition of Cz-co-P, Cz-co-Th.
- Cz-co-F copolymers are weakly allowed, a while the $S_0 \rightarrow S_2$ electronic transition possesses a much larger oscillator strength.
- Excitation to the S_1 for Cz-co-Cz and Cz-co-FL and excitation to the S_2 state of Cz-co-Th and Cz-co-F copolymers corresponds almost exclusively to the promotion of an electron from the HOMO to the LUMO.

Acknowledgments

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Poster Presentations IV

Songwut Suramitr, Supa Hannongbua and Alfred Karpfen. ***Ab initio* studies on structural and vibrational frequencies of butadiene derivatives.** 31st Congress on Science and Technology of Thailand (STT31) 2005, 18 - 20 October 2005, Nakhon Ratchasima.

AB INITIO STUDIES ON VIBRATIONAL FREQUENCIES OF 1-CIS-BUTADIENE WITH DONOR AND ACCEPTOR SUBSTITUENTS

Songwut Suramitr, Witchanee Meeto, Supa Hannongbua*
Department of Chemistry, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand,
e-mail address g4684002@ku.ac.th and fscisph@ku.ac.th

Introduction:

The importance of hydrogen bonding, particularly in organic polymer systems, has led to continuing studies, both experimental and theoretical. In some polymer systems, hydrocarbons containing π-conjugation have attracted great attention for a long time. Butadiene is the simplest conjugated hydrocarbon molecule and therefore has been studied most extensively by *ab initio* calculations. In this work, vibrational frequencies for Hydrogen bond intrainteraction system of 1-cis-butadiene derivatives have been studied. The frequencies of 1-cis-butadiene derivatives, such as methoxy, fluoro, chloro and bromo (in Figure1.), have been more clerer understood and explained by two major effects: π-electron delocalization (conjugation) and steric interactions.

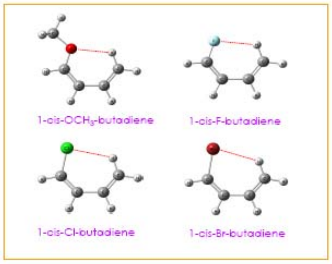


Figure 1. Molecular structures of the 1-cis-butadiene derivatives.

Method of calculations

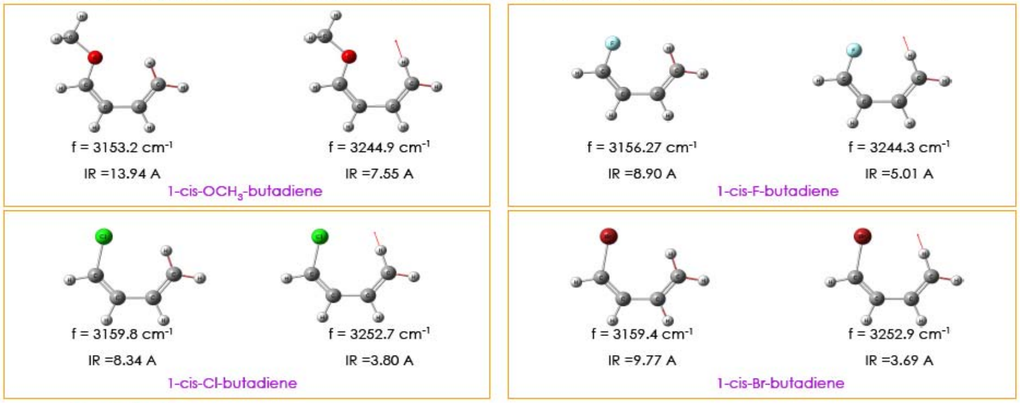
Starting geometries of the 1-cis-butadiene derivatives were constructed by SciPolymer 3.0 program. The 1-cis-butadiene derivatives were modified by attaching alkoxy groups onto the phenylene ring at the C1 atoms. The 1-cis-butadiene derivatives are denoted by 1-cis-OCH$_3$-butadiene, 1-cis-F-butadiene , 1-cis-Cl-butadiene and 1-cis-Br-butadiene. Their chemical structures are illustrated in Figure 1.

The vibrational frequencies and infrared (IR) intensities for the 1-cis-butadiene derivatives, such as methoxy, fluoro, chloro and bromo are calculated at hybrid density functional theory (B3LYP) level with GAUSSIAN03 series of programs. The vibrational characteristics are predicted using the cc-pVTZ Dunning's basis set.

Results and discussion:

The changes in the vibrational frequencies, and infrared intensities arising from the hydrogen bonding have been investigated by B3LYP/cc-pVTZ basis set. The calculations show that the stretching C-H vibrations of 1-cis-butadiene derivatives are changed, or shifted to higher frequency than those vibrations of 1-cis-butadiene (Exp. =3140 and 3221 cm^{-1}).

Figure 2. Calculated frequencies (f) of C-H stretching (red arrow) and infrared intensities (IR) of 1-cis-butadiene derivatives by B3LYP/cc-pVTZ method.



Conclusion

The results indicated that the effect of substitution groups play important role for structure of 1-cis-butadiene. It was found that the most sensitive to the strong interaction are the stretching C-H vibrations for hydrogen bonding. The predicted infrared intensities of hydrogen-bond for 1-cis-OCH3-butadiene vibrations are shifted to higher than the vibrations of 1-cis-F-butadiene, 1-cis-Br-butadiene and 1-cis-Cl-butadiene, respectively. At the same time their IR intensities increase essentially.

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