APPENDIX B

Oral Presentation and Poster Contributions to Conferences

Oral Presentation

Chidthong, R, Poolmee, P., Suramitr, S. and Hannongbua, S. **Study of the Electronic and Absorption Properties of the Fluorene-Pyridine Conjugated Polymers by Theoretical Investigation.** Workshop on Modeling Interactions in Biomolecules II, Czech University of Agriculture, Prague, Czech Republic, September, 5-9, 2005

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

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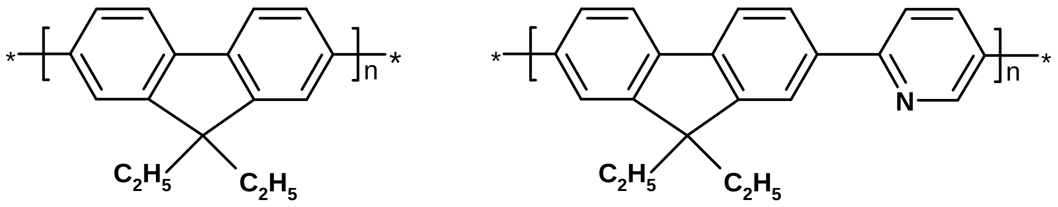
Geometric structure, vertical excitation energies (E_gs) and maximum absorption wavelengths (λ_{abs}) of fluorene-pyridine oligomer $(FPy)_n$, (Figure 1b) were studied by quantum chemical calculations. The geometrical optimizations of FPy was obtained by density functional theory (DFT) at the B3LYP/6-31G* level of calculations. It was found that the optimized geometry of FPy oligomers show nonplanar structure. 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* calculation (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 $(F)_n$ (Figure 1a.) It is indicated that pyridine monomer can reduce the excitation energies of polyfluorene. This information is important in a fine-tuning of the emitted color and at a significant improvement in quantum efficiency.



(a) (b)

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

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Chidthong, R., Aquino, A., Hannongbua, S., Wolchann, P., and Lischka, H. **Theoretical Study on Structural and Electronic Properties of Fluorene-Pyridine Copolymer.** 10th Annual National Symposium on Computational Science and Engineering, Chiang Mai University ,Chiang Mai, Thailand, March 22-24, 2006.

Theoretical Study on Structural and Electronic Properties of Fluorene-Pyridine Copolymer

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Abstract

The structural and electronic properties of fluorene-Pyridine copolymer $(FPy)_n$, (Figure 1) were investigated theoretically. Geometry optimizations of these oligomers were calculated at the DFT/SVP and TDDFT/SVP for the ground state and the first lowest excited states, respectively. It is found that $(FPy)_n$ is non-planar in its ground state whereas completely planarity in the S_1 state. The lowest excitation energy of this polymer carried out at the TDDFT/SVP and TDDFT/SVP+ are 2.66 and 2.64 eV, respectively which are good agreement as compared to the experimental data. The $S_1 \leftarrow S_0$ electronic transition of each oligomer possesses a much larger oscillator strength and is mainly described by the promotion of electron from HOMO to LUMO. The fluorescence energies and radiative lifetimes for the oligomers were calculated at the TDDFT/SVP. It is found that the fluorescence energy and radiative lifetime of $(FPy)_n$ are 2.41 eV and 0.25 s, respectively.

1. Introduction

Conducting polymers are now considered as a very important class as new materials for electronic and optoelectronic devices. Among such oligomers, polyfluorene and its derivatives are promising materials for light emitting diodes because of their high quantum efficiency and photoluminescence. Recently, novel fluorene-pyridine based copolymers revealing interesting blue electroluminescence were synthesized and characterized. Thus, it is very important to investigate the chemical structures and electronic properties of this copolymer. In this work, we investigated the ground state and excited properties of copol(2,5-pyridine-alt-fluorene) $(FPy)_n$, Figure 1. The ground and excited state conformational curves were determined using density functional theory and time dependent density functional theory, respectively. Then, the ground and excited structures were fully optimized using DFT and coupled cluster singles and doubles method (CC2) with the resolution of identity approximation and TD-DFT, respectively. Additionally, based on the ground state and excited state optimized structures, the vertical excitation energies and fluorescence spectra were determined. Moreover, on the basis of fluorescence energies and oscillator strengths, the radiative lifetimes were calculated.

2. Computational details

The ground and lowest excited state geometries of the fluorene-pyridine oligomers were optimized at the *ab initio* RI-CC2 and the DFT and TDDFT levels, respectively, using the B3LYP functional. Geometry optimizations were restricted to C_s symmetry. On the basis of the optimized geometries, the lowest excitation energies and fluorescence energies were obtained at the RI-CC2 and TDDFT. Lowest excitation energies were calculated at the ground state geometry. The fluorescence energies were performed at the optimized geometry of excited state. The polarized split valence (SVP) was used. The SVP basis set by a set of diffuse function which exponents was obtained from the lowest s, p and d exponents by division of a factor of 3 (denotes as SVP+). All calculations were done using the Turbomole program package.

3. Results and discussion

The sketch map and atomic numbering of the structure for copol(2,5-pyridine-alt-fluorene), $FPy)_n$ is shown in Figure 1.

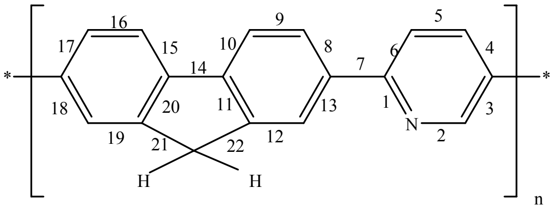

Figure 1: Molecular structure and atomic numbering scheme of $(FPy)_n$.

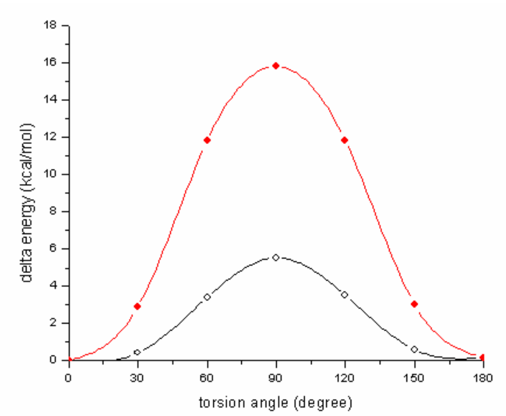

Figure 2: Potential energy curves for ground state as obtained from DFT/SV(P); (open circle) and excited state as calculated from TDDFT/SV(P); (solid square).

The ground and excited state potential energy curves of fluorene-pyridine monomer, (FPy) as obtained from DFT/SV(P) and TDDFT/SV(P), respectively are shown in Figure 2. The value from ground state indicated non-planar structure of fluorene-pyridine monomer whereas the excited state depicted absolutely planarity. The fully optimized at ground and excited state were performed using DFT/SV(P) and TDDFT/SV(P) respectively. From the oligomer in S_1 state, it was observed that the bond distances along the long axis of the molecule, bond nos. 2, 5, 7, 9, 12, 14, 16, 19, are significantly shortened. In contrast, the other bond distances are significantly elongated as compared to the respectively bond distances calculated for the pristine molecule in the ground state. This clearly denotes that, the lowest excited state structures lead to possess quinoidic-like structure.

TDDFT/SVP and TDDFT/SVP+ were used on the basis of the optimized structures to obtain the electronic excitation energy of all oligomers. Table 1 shown the calculated and the experimental excitation energies and oscillator strength (in parentheses) from TDDFT/SV(P), TDDFT/SV(P)+ and RI-CC2/SV(P). It is clearly indicated that the transition to S_1 state is predominantly by the promotion of electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) which is related to $\pi \rightarrow \pi^*$ electronic transition. The excellent agreement between the *Eexcit* and the experimental (electrochemical method) were observed.

Table 1: Calculated and experimental excitation energies and oscillator strength of Fluorene-Pyridine oligomers.

	state	TDDFT/SV(P)	TDDFT/SV(P)+	RI-CC2/SV(P)
		excitation energy, (eV)	excitation energy, (eV)	excitation energy, (eV)
N=1	$S_0 \rightarrow S_1$	3.96 (0.852)	3.88 (0.831)	4.52 (0.754)
N=2	$S_0 \rightarrow S_1$	3.31 (0.994)	3.27 (1.967)	
N=3	$S_0 \rightarrow S_1$	3.09 (2.922)	3.05 (2.882)	
N=4	$S_0 \rightarrow S_1$	2.99 (3.640)	2.95 (3.584)	
N=∞		2.66	2.64	
exptl. [1]		2.87(thin film) 2.94(THF solution) 2.69 (electro chemistry)		

TDDFT/SVP and TDDFT/SVP+ were used on the basis of the excited state optimized structure to obtain the fluorescence energies of FPy oligomers. Table 2 exemplified the relationship between the fluorescence energies and relative lifetimes on the reciprocal chain lengths of FPy oligomers as calculated by TDDFT/SVP and TDDFT/SVP+. The fluorescence energies and oscillator strengths decreased with the extension of conjugated backbones. Interestingly, the TDDFT/SVP results showed lower fluorescence energy than that calculated from TDDFT/SVP+. The extension of conjugated backbone leads to a decrease of lifetimes. The calculated lifetimes from DFT/SVP and DFT/SVP+ are 0.25 and 0.19 ns, respectively. There is a slightly different (0.06 ns) between the two basis sets.

Table 2: Calculated fluorescence energies and radiative lifetimes of FPy oligomers as obtained from TDDFT/SVP and TDDFT/SVP+. Geometries were performed at the B3LYP/SVP level.

	TDDFT/SVP		TDDFT/SVP+	
	Fluorescence (eV)	Lifetime (ns)	Fluorescence (eV)	Lifetime (ns)
n=1	3.72 (0.996)	0.84	3.88 (0.831)	0.92
n=2	3.02 (2.335)	0.54	3.27 (1.967)	0.55
n=3	2.83 (3.202)	0.45	3.05 (2.882)	0.43
n=4	2.77 (3.786)	0.40	2.95 (3.584)	0.37
n=∞	2.41	0.25	2.65	0.19

4. Conclusion

Systematic investigations on $(FPY)_n$ were studied on both ground state and excited state from monomer up to tetramer repeat units. Fully optimizations on both ground and the first excited state were performed. B3LYP and RI-CC2 were used to investigate geometry optimization and excitation energies of FPy oligomers. In ground state, the torsional angles are larger than that obtained from the first excited state. In the first transition, the excited state structure has a strong coplanar tendency, that is, show much more quinoidic-like character. Electronic excitation from S_0 to S_1 state possesses a much higher oscillator strength which is corresponds to the promotion of an electron from the HOMO to the LUMO. TDDFT/SVP vertical excitation energies calculated in the basis of the ground state are in excellent agreement with the electrochemistry experimental data. Including the diffuse function leads to the same value of excitation energies by the DFT/SVP. On polymeric values from extrapolation, not only excitation energies but also fluorescence energies are in good linearity. The extension of conjugated length leads to a decrease of fluorescence energies and computed radiative lifetimes.

5. Acknowledgement

The Graduate School Kasetsart University (KU) is gratefully acknowledged for the financial support and research activities and the Cooperative Research Network (CRN) of Nanoscience and Nanotechnology under the Commission of Higher Education, for financial support via Grant-in-Aid for thesis. Generous supply of computing time and research facilities by the Postgraduate Education and Research Programs in Petroleum and Petrochemical Technology, LCAC, the computing Center of KU and the Schrödinger II cluster of the University of Vienna, Austria is gratefully acknowledged.

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Poster Presentations

Chidthong, R., Poolmee, P., Meeto, W. and Hannnongbua, S. **Ground State Geometry Analysis of 2-pyridine-(9,9'-diethylfluorene) Based Dyad Quantum Chemical Calculations Approach** 30th Congress on Science and Technology of Thailand (STT 2004), IMPACT Exhibition and Convention Center (Hall 1-8), Bangkok, Thailand, October 19-23, 2004.

GROUND STATE GEOMETRY ANALYSIS AND ELECTRONIC PROPERTIES OF 2-pyridine-(9,9'-diethylfluorene) BASED DYAD; QUANTUM CHEMICAL CALCULATIONS APPROACH

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Abstract:

The ground state geometries and electronic properties of Poly-2,5-pyridine-(9,9'-diethylfluorene) were investigated by quantum chemical calculations approach. Conformational analysis of 2-pyridine-(9,9'-diethylfluorene) was performed by using AM1, HF/3-21G*, HF/6-31G* and B3LYP/6-31G* methods. The obtained results were compared and it was found that there are two minima at 0-45 and 135-180 degrees. The electronic properties, HOMO-LUMO energy differences were calculated at B3LYP/6-31G* level. It was found that extrapolated HOMO-LUMO energy gaps at B3LYP/ 6-31G*//AM1 and B3LYP/6-31G*//HF/3-21G* were 3.35 and 3.52 eV respectively. The results shows that the HOMO-LUMO energy differences are overestimated with the experimental value.

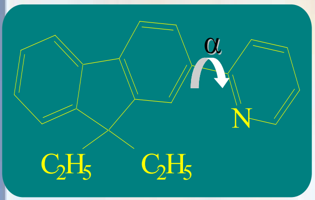

Figure 1: Molecular structure of 2-pyridine-(9,9'-diethylfluorene) used in this study.

Introduction:

In the past two decades, conducting polymers have been used in many applications such as light emitting diode. Poly-2,5-pyridine-(9,9'-diethylfluorene) is one of the conductive polymers which can emit light. Conformational analysis studies on monomer species, which serve as a model for polymeric systems, are of the fundamental importance. It can provide useful information that can enable to understand the behavior of the real polymer. In this work, we reported the conformational analysis of the ground state geometries and electronic properties of 2-pyridine-(9,9'-diethylfluorene).

Methods of Calculation:

The ground state geometries of fluorene-pyridine were partially optimized by Semi-empirical (AM1), the Restricted Hartree-Fock method (HF) at the 3-21G* and 6-31G* basis sets and the Density Functional Theory (DFT) at the 6-31G* basis set. The conformational analysis of the dyad was done by changing the torsional angle (α) by 15° steps. The geometries were fully optimized at each point. The electronic properties (HOMO-LUMO differences) were also studied using Density Functional Theory (DFT) at the 6-31G* basis set. The calculations were performed on a Pentium 4 (3.2 GHz) personal computer with 1 Gb of RAM using the GAUSSIAN 03 program, version 5.2.

Results and Discussion

1. Ground State Geometries :

The potential energy surfaces of fluorene-pyridine based dyad, calculated at the AM1, HF/3-21G*, HF/6-31G* and B3LYP/6-31G* levels were shown in Figure 2. It was found that there are two local minima were obtained. A similar potential surfaces at the same minima and similar potential energy barrier were obtained. Fully optimized ground-state geometries of fluorene-pyridine based dyad were obtained at the AM1, HF/3-21G*, HF/6-31G* and B3LYP/6-31G* levels. The optimized dihedral angles and interring distance between the subunits of the dyad are summarized in Table 1. The results were also indicated that the ground state geometries of fluorene-pyridine dyad give almost planar structures. These geometries will be used for estimate energetic properties of this dyad.

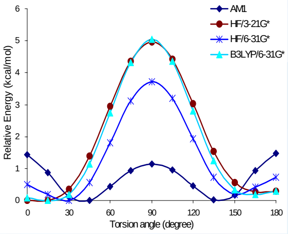

Figure 2: Ground-state potential energy surfaces of fluorene-pyridine based dyad as obtained from AM1, HF/3-21G*, HF/6-31G* and B3LYP/6-31G* calculations.

Table 1: Dihedral angles and interring distance of fluorene-pyridine based dyad as obtained by AM1, HF/3-21G*, HF/6-31G* and B3LYP/6-31G* level of calculations.

Method/basis set	Dihedral angle, α (degrees)	Interring distance (°)
AM1	40.2	1.470
HF/3-21G*	10.3	1.480
HF/6-31G*	27.1	1.490
B3LYP/6-31G*	17.4	1.487

2. Ground State Electronic Properties:

The electronic properties, HOMO-LUMO energy differences were calculated at B3LYP/6-31G* level. The optimized geometries (AM1 and HF/3-21G*) have been used in the calculations. It was found that extrapolated HOMO-LUMO energy gaps at B3LYP/ 6-31G*//AM1 and B3LYP/6-31G*//HF/3-21G* were 3.35 and 3.52 eV respectively. The results shows that the HOMO-LUMO energy differences are overestimated with the experimental value (2.82 eV). The HOMO-LUMO energy gaps at B3LYP/ 6-31G*//HF/6-31G*, B3LYP/ 6-31G*//B3LYP/6-31G* and excitation energies of this dyad were then performed.

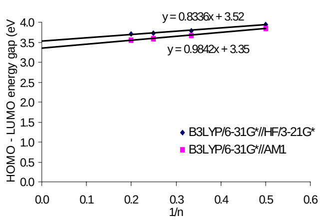

Figure 3: Energy gap extrapolated from the HOMO-LUMO energies of the 2-pyridine-(9,9'-diethylfluorene) oligomers versus the inverse number of monomer units(Eg expt. = 2.82 eV).

Conclusions:

Semi-empirical ab-initio and density functional theory were used to study the ground state geometry of 2-pyridine-(9,9'-diethylfluorene). Conformational analysis of 2-pyridine-(9,9'-diethylfluorene) was performed by using AM1, HF/3-21G*, HF/6-31G* and B3LYP/6-31G* methods. The obtained results were compared and it was found that there are two minima at 0-45 and 135-180 degrees. The electronic properties, HOMO-LUMO energy differences were calculated at B3LYP/6-31G* level. It was found that extrapolated HOMO-LUMO energy gaps at B3LYP/ 6-31G*//AM1 and B3LYP/6-31G*//HF/3-21G* were 3.35 and 3.52 eV respectively. The results shows that the HOMO-LUMO energy differences are overestimated with the experimental value.

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- Nakhon Pathom Rajabhat University are gratefully acknowledged.
- LCAC and Computing Center of Kasetsart University

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Chidthong, R. and Hannongbua, S. **Ground State Geometry Analysis and Energy Gap of Poly-2,5-pyridine-alt-(9,9'-dihexlyfluorene); Quantum Chemical Approach** 2nd Asia Pacific Conference on Theoretical & Computational Chemistry, Chulalongkorn University, Thailand, May 2-5, 2005.

GROUND STATE GEOMETRICAL ANALYSIS AND ENERGY GAP OF Poly-2,5-pyridine-alt-(9,9’-diethylfluorene), QUANTUM CHEMICAL APPROACH

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INTRODUCTION

In the past two decades, conducting polymers have been used in many applications such as light emitting diodes and flat panel displays. Poly-2,5-pyridine-(9,9’-diethylfluorene) is one of the conductive polymers which can emit blue light. In this work, we reported the conformational analysis and electronic properties of fluorene-pyridine copolymer using quantum chemical approach and compared with experimental data.

MODEL

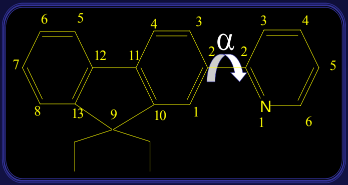

Fig. 1 Molecular structure of 2-pyridine-alt-(9,9’-diethylfluorene) used in this study.

RESULTS AND DISCUSSION

1.Conformational Analysis

The potential energy surfaces of fluorene-pyridine based dyad, calculated at the AM1, HF/3-21G*, HF/6-31G* and B3LYP/6-31G* levels were shown in Fig. 2. The obtained results among these methods were compared and it was found that there are two minima at 0-45 and 135-180 degrees and nonplanar conformations for this molecule.

Table 1 Energy gaps obtained from various methods

Methods of calculation	Energy gaps (eV)
B3LYP/6-31G*//AM1	3.35
B3LYP/6-31G*	3.16
ZINDO//AM1	3.22
ZINDO// B3LYP/6-31G*	3.13
TD-DFT//AM1	2.92
TD-DFT//B3LYP/6-31G*	2.75
Expt.	2.94[1]

CONCLUSIONS

Overall, the semi-empirical ab-initio and density functional theory were used to study the ground state geometry of 2-pyridine-(9,9’-diethylfluorene). The optimized structures show non-planar structure. The HOMO-LUMO energy differences were studied using DFT with the 6-31G* level whereas the lowest excitation energy were calculated by ZINDO and time-dependent density functional theory at the B3LYP/6-31G* level. The extrapolation results are in good linearity and good agreement with experimental data. Moreover, the obtained results indicated that TDDFT with B3LYP functional is expected to be a relatively reliable tool for evaluating the excitation energies of low-lying excited states.

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2. Yang, S., Olishevski, P., Kertesz, M., *Synth. Met.*, **2004**, *141*, 171-177.

MOTHODS OF CALCULATION

Construct the structure using Gaussview 3.0

Conformational analysis using AM1, HF/3-21G*, HF/6-31G*, B3LYP/6-31G* by Gaussian03

Ground state geometries were fully optimized with AM1 and B3LYP/6-31G*

B3LYP/6-31G*, ZINDO and TD-DFT were performed at the ground state geometries

HOMO-LUMO energy differences and excitation energies were obtained by extrapolating the resultant linear relationship to infinite chain length

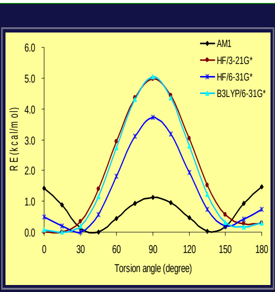

Fig. 2 Ground-state potential energy surfaces of fluorene-pyridine based dyad as obtained from AM1, HF/3-21G*, HF/6-31G* and B3LYP/6-31G* calculations.

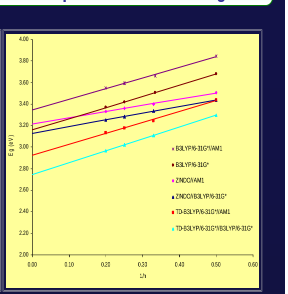

Fig. 3 The E_g and excitation energy by B3LYP/6-31G*, ZINDO and TD-B3LYP as a function of reciprocal chain length on oligomers of (PFPy).

2.Electronic Properties

HOMO-LUMO energy differences were calculated at B3LYP/6-31G* level. From Table 1, the results indicated that the HOMO-LUMO energy differences are overestimated with the experimental value (2.94 eV). However, the predicted HOMO-LUMO energy differences can be useful to estimate the energy differences of large molecule. In addition, the excitation energies were done using the ZINDO method and TDDFT at B3LYP/6-31G* level. From Table 1, it was found that the ZINDO predictions also provide an overestimated as compared with experimental data whereas the inverse chain length approximation by TD-B3LYP/6-31G*//AM1 shown excellent agreement with experimental data.

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- Postgraduate Education and Research Programs in Petroleum and Petrochemical Technology (ADB-MUA)
- Nakhon Pathom Rajabhat University
- LCAC and Computing Center of Kasetsart University

Chidthong, R., Rotpradit, K. and Hannongbua, S. **Study of the Structural and Electronic Properties of the Fluorene-Based Conjugated Polymers** CBES 2006 International Conference on Modeling in Chemistry and Biological Engineering Sciences, The Rama Garden Hotel, Bangkok, Thailand, October 25-27, 2006.

STUDY OF THE STRUCTURAL AND ELECTRONIC PROPERTIES OF THE FLUORENE-BASED CONJUGATED POLYMERS

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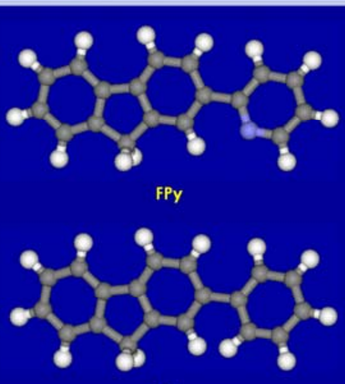
Introduction

During the past two decade, many studies on organic light emitting materials have been focused on developing efficient, stable, and pure blue-light-emitting polymers. Among these polymers, polyfluorene derivatives show interesting, unique chemical and physical properties because they contain a rigid planar biphenyl unit, and facile substitution at the remote C-9 position. Polyfluorene derivatives have high luminescence and phosphorescence efficiencies. In this regard, various fully conjugated polyfluorenes have been studied for light emitting diode applications. In this work, we report the ground and excited state structures of fluorene-pyridine and fluorene-phenylene oligomers. The ground state and excited structures of fluorene-pyridine (FPy) and fluorene-phenylene (FP) oligomers determined using B3LYP/SVP and TD-B3LYP/SVP, respectively. The TD-B3LYP/SVP and TD-B3LYP/SVP+ were used to calculate the lowest excitation energies of FPy and FP oligomers. Finally, the vertical excitation energies of polymers were obtained using linear extrapolating plot.

Methodology

Ground state and excited state of fluorene-pyridine and fluorene-phenylene monomers were calculated using B3LYP and TD-B3LYP calculations with SVP functional. The electronic absorption and luminescence spectra were computed at the TD-B3LYP/SVP and TD-B3LYP/SVP+ levels. Vertical excitation energies were obtained based on the ground state optimized geometries. The SVP (polarized split-valence) and SVP+ basis sets were used to calculate vertical excitation transitions. The first 3 singlet-singlet electronic transitions ($S_0 \rightarrow S_n$) were calculated at TD-B3LYP/SVP and TD-B3LYP/SVP+ levels. All calculations were performed with the Turbomole program package.



FPy

FP

Figure 1: Sketch map of FPy and FP.

Results, Discussion and Conclusions

1. Structural properties

The sketch map of fluorene-pyridine and fluorene-phenylene copolymers is depicted in Figure 1. Table 1 shows the inter-ring torsional angle (θ, deg) and inter-ring distance (Å) of FPy and FP at ground and excited state obtained by using B3LYP/SVP and TD-B3LYP/SVP level of calculations. It was found that both FPy and FP possess nonplanar structures in their ground states. However in their excited states, they possess planarity geometry. The stable ground state geometry of FPy is achieved by twisting the pyridine ring by 14.4° whereas the obtained torsion angle between fluorene and phenyl units is 34.8°. The replacement of a pyridine group by a phenyl ring (FP) hardly affects the torsion angle between the subunits due to the presence of carbon atom. Additionally, the torsion angle of FPy is slightly smaller compared to that of FP, which suggests that the electronic conjugation across the rings is enhanced for FPy.

Table 1: Inter-ring torsional angle (θ, deg) and inter-ring distance (Å) of FPy and FP at ground and excited state obtained by using B3LYP/SVP and TD-B3LYP/SVP level of calculations, respectively.

	Ground state		Excited state	
	Inter-ring distance (Å)	Torsion angle (°)	Inter-ring distance (Å)	Torsion angle (°)
FPy	1.490	14.4	1.448	0.0
FP	1.488	34.8	1.443	7.6

2. Vertical excitation energies

TD-B3LYP/SVP and TD-B3LYP-SVP+ were used to obtain the first 3 singlet-singlet electronic transitions of FPy and FP oligomers. Table 2 shows the calculated and experimental excitation energies and oscillator strength of Fluorene-Pyridine and Fluorene-Phenylene oligomers. It was found that all transitions are of the ππ* type and involve both subunits of the molecule. It can be seen that the excitation from S_0 to S_1 state corresponds almost exclusively to the promotion of an electron from the HOMO to the LUMO, which are both delocalized over the whole molecule. Consequently, the large oscillator strengths along the long axis of the molecule (x) are obtained. From Figure 2, there are good linear relation between the excitation energies and the inverse chain length. From TD-B3LYP/SVP and TD-B3LYP/SVP+, the extrapolated values are 2.66 and 2.64 eV for $(FPy)_n$ and 2.89 and 2.87 eV for $(FP)_n$, respectively.

Table 2: Calculated and experimental excitation energies and oscillator strength of Fluorene-Pyridine and Fluorene-Phenylene oligomers.

	States	(FPy)n		(FP)n	
		TD-B3LYP/SVP	TD-B3LYP/SVP+	TD-B3LYP/SVP	TD-B3LYP/SVP+
		excitation energy, (eV)	excitation energy, (eV)	excitation energy, (eV)	excitation energy, (eV)
n=1	$S_0 \rightarrow S_1$	3.96 (0.852)	3.88 (0.831)	3.99 (0.904)	3.91 (0.873)
	$S_0 \rightarrow S_2$	4.36 (0.019)	4.26 (0.032)	4.33 (0.009)	4.23 (0.025)
	$S_0 \rightarrow S_3$	4.47 (0.006)	4.45 (0.009)	4.66 (0.004)	4.60 (0.003)
n=2	$S_0 \rightarrow S_1$	3.31 (0.994)	3.27 (1.967)	3.33 (2.040)	3.28 (1.990)
	$S_0 \rightarrow S_2$	3.78 (0.055)	3.74 (0.053)	3.81 (0.000)	3.77 (0.000)
	$S_0 \rightarrow S_3$	3.93 (0.082)	3.85 (0.082)	3.95 (0.091)	3.87 (0.082)
n=3	$S_0 \rightarrow S_1$	3.09 (2.922)	3.05 (2.882)	3.28 (3.015)	3.24 (2.969)
	$S_0 \rightarrow S_2$	3.48 (0.239)	3.44 (0.286)	3.66 (0.163)	3.62 (0.172)
	$S_0 \rightarrow S_3$	3.52 (0.178)	3.47 (0.123)	3.71 (0.032)	3.67 (0.014)
n=4	$S_0 \rightarrow S_1$	2.99 (3.640)	2.95 (3.584)	3.19 (3.909)	3.16 (3.843)
	$S_0 \rightarrow S_2$	3.26 (0.739)	3.22 (0.744)	3.46 (0.441)	3.42 (0.440)
	$S_0 \rightarrow S_3$	3.36 (0.138)	3.32 (0.124)	3.58 (0.006)	3.54 (0.003)
n = ∞		**2.66**	**2.64**	**2.89**	**2.87**
Expt. [1]		2.87 (thin film)		2.92 (thin film)	
		2.94 (THF solution)		-	
		2.89 (electro chemistry)		2.89 (electro chemistry)	

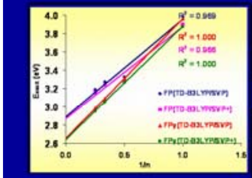
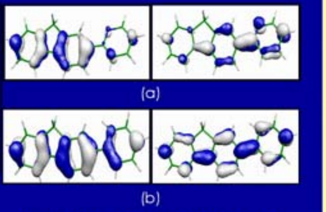


Figure 2: Lowest excitation energies (E_{excit}) by TD-B3LYP/SVP and TD-B3LYP/SVP+ as a function of reciprocal chain length *n* in oligomers of $(FPy)_n$ and $(FP)_n$.



(a)

(b)

Figure 3: Plots of HOMO (left) and LUMO (right) of (FPy) and (FP) obtained by TD-B3LYP/SVP calculations.

References

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