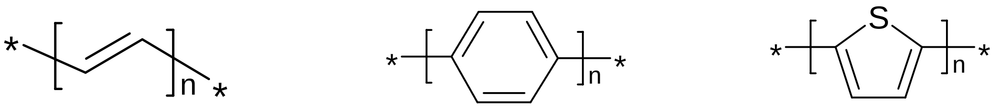
THEORETICAL INVESTIGATION ON STRUCTURAL AND ELECTRONIC PROPERTIES OF FLUORENE-PYRIDINE COPOLYMER

INTRODUCTION

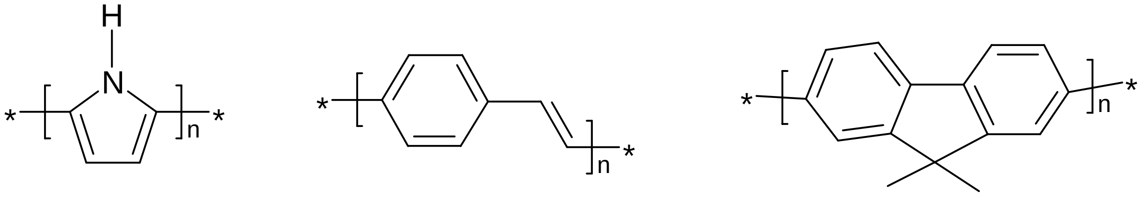
Organic polymers have traditionally found application in packaging and other structural applications as electrical insulators. Conjugated polymers are a class of polymer that possesses a π-bond network extending along the chain. In 1958, polyacetylene was first synthesized by Natta *et al*. (1954) as a black powder. This was found to be a semi-conductor with a conductivity between 7 x 10^{-11} to 7 x 10^{-3} Sm^{-1}, depending upon how the polymer was processed and manipulated. This compound remained a scientific curiosity until 1967, when a postgraduate student of Hideki Shirakawa at the Tokyo of Technology was attempting to synthesize polyacetylene, and a silvery thin film was produced as a result of a mistake. It was found that 1000 times too much of the Ziegler-Natta catalyst, $Ti(O\text{-}n\text{-}Bu^t)_4\text{-}EtAl$, had been used. When this film was investigated it was found to be semiconducting, with a similar level of conductivity to the best of the conducting black powders. Further investigations, initially aimed to produce thin films of graphite, showed that exposure of this form of polyacetylene to halogens increased its conductivity a billion fold. Undoped the polymer was silvery, insoluble and intractable, with a conductivity similar to that of semiconductors. When it was weakly oxidized be compounds such as iodine it turned a golden color and its conductivity increased about 10^4 Sm^{-1}. In the 1980's polyheterocycles were first developed. Polyheterocycles were found to be much more air-stable than polyacetylene, although their conductivities were not so high, typically about 10^3 Sm^{-1}. By adding various such groups to the polyheterocycles backbone, derivatives which were soluble in various solvents were prepared. Other side groups affected properties such as their color and their reactivity to oxidizing and reducing agents (Bradley, 1996).

Since the first successful demonstration of polymer light emitting diodes (PLEDs) from a conjugated polymer in 1990, PLEDs have attracted worldwide attention as a candidate for the next generation of emissive flat panel displays (Guo *et al*., 2000). Conjugated polymers are also widely investigated for use in organics transistors, photodiodes, solar cells and lasers (Wong *et al*., 2002). These materials constitute a fast growing field of fundamental research and technological applications due to their fascinating electronic and optical properties (Rohlfing *et al*., 1999). Much attention has been paid to their optical and conduction properties because of their scientific interest and their possible use in organic light emitting diodes as well as novel electronic applications. In light emitting diodes based on conjugated polymers, all three primary colors (red, blue, and green) required by full color displays have been demonstrated in PLEDs, only red (orange) and green PLEDs have sufficient efficiencies and lifetimes to be of commercial value. Pursuing efficient and stable blue LEDs based on conjugated polymers remains a challenge. The first blue LED has been fabricated from poly(*p-phenylene*) (PPP). Later on, polyfluorenes (PFs), polycarbazoles (PCs), polythiophene derivatives (PTs), derivatives of polyparaphenylene with ladder structures, and some copolymer based on fluorene or pyridine have also been introduced as blue emissive polymers. Figure 1 shows these typical conjugated polymers. Advantages of organic semiconductors are expected relative to traditional inorganic semiconductors in terms of fabrication, compatibility with shaped and flexible substrates and, ultimately, costs (Campbell *et al*., 2001).

Polydialkyfluorene and its derivatives (PFs) are one class of the most widely investigated PLEDs due to their high efficient blue emission in both photoluminescence (PL) and electroluminescence (EL). Poly(9,9-dialkyfluorene) exhibits very good, non-dispersive hole transport, but very poor electron transportation. The main drawbacks of PFs, such as aggregation and/or excimers formation in the solid state, which result in the appearance of an additional emission band in the long wavelength region of the spectrum and a concomitant drop in electroluminescence (EL) quantum efficiency, insufficient stability, relatively large energy band gaps and especially the high-energy barriers for hole injection, have limited their application in PLEDs. Thereafter, the search for novel fluorene-based polymer materials with improved properties, such as thermal stability and anti-oxidative stability, represents a continuing research challenge (Liu, S.-P. *et al.*, 2005).



Polyacetylene (PA) Poly(para-phenylene) (PPP) Polythiophene (PT)



Polypyrrole (PPy) Poly(para-phenylene vinylene) (PPV) Polyfluorene (PF)

Figure 1 Selection of conjugated polymers.

Poly(2,5-pyridinediyl) (PPy) and its derivatives, such as poly(pyridine vinylene) (PPyV) with electron accepting nature is a family of promising conjugated polymers because of their high luminescence, excellent electron transporting behavior and their general resistance to oxidation. The application of pyridine as the deficient moiety in our polymers is driven by the consideration that polypyridinyl (PPy) was used in blue emitting devices and that polymers based on pyridine have been demonstrated to be highly luminescent. Therefore, the incorporation of pyridinyl unit into polymer backbone increases the electron affinity of the polymers, which not only makes the copolymers to be *n*-dopable and capable of better electron transportation, but also makes the polymers more resistant to oxidation. These polymers with pyridine units will be expected to possess low LUMO energy levels for an easy electron injection from a cathode. It is well known that electroluminescence in conjugated polymers is afforded by the recombination of electrons injected at the cathode and holes injected at the anode in fluorescent polymer films. The charge balance for injection and transport of electrons and holes is a critical parameter in controlling quantum efficiencies. Ideally, electron and hole mobility should be of comparable magnitude. As a consequence, it is necessary to design and synthesize conjugated alternating polymers with high electron-donating and electron-accepting properties, which would aid to balance the rates of injection of electrons and holes naturally.

The copolymerization approach has been widely used in the preparation of conjugated polymers to achieve specific electronic and physical properties. It is also demonstrated that copolymerization of fluorene with various aryl partners allows for tunability of electronic properties with enhanced stability. Copolymers of fluorene-pyridine have been reported. Poly[2,7-(9,9'-dioctylfluorene)-*co-alt*-5,5'-(2,2'-bipyridine)] was designed and synthesized via the Suzuki reaction. This copolymer emitted blue light (Liu, B. *et al*., 2001). Liu, B. *et al*. (2001), also prepared the blue light emitting, poly[2,7-(9,9-dihexlyfluorene)-co-alt-2,5-pyridine] by palladium-catalyzed Suzuki coupling reaction. Next, a series of high molecular weight, readily soluble copolymers of 9,9-dioctylfluorene with pyridine (less than or equal to 50 mol%) were synthesized by Suzuki polycondensation. These copolymers emitted blue light and exhibited high PL efficiency (Yang *et al*., 2004). Subsequently, Aubert *et al*. (2004), reported the synthesis of poly[2,5-pyridine-alt-(9,9'-dioctylfluorene)]. Although there are many syntheses of copolymer, however, there have been only a few theoretical studies investigating of fluorene and copolymer.

In 2004, a novel series of well-defied alternating poly[2,7-(9,9-dihexylfuorenyl)-alt-pyridinyl] (PDHFP) with donor-acceptor repeat units were synthesized using palladium(0)-catalyzed Suzuki cross-coupling reactions in good to high yields. In this series of alternating polymers, 2,7-(9,9-dihexyl-uorenyl) was used as the light emitting unit, and the electron deficient pyridinyl unit was employed to provide improved electron transportation. These polymers were characterized by ^{1}H-NMR and ^{13}C-NMR, gel permeation chromatography (GPC), thermal analyses, and

UV-vis and fluorescence spectroscopy. The glass transition temperature of copolymers in nitrogen ranged from 110 to 148^{o}C, and the copolymers showed high thermal stabilities with high decomposition temperatures in the range of 350 to 390^{o}C in air. The difference in linkage position of pyridinyl unit in the polymer backbone has significant effects on the electronic and optical properties of polymers in solution and in film phases. Meta-linkage (3,5- and 2,6-linkage) of pyridinyl units in the polymer backbone is more favorable to polymer for pure blue emission and prevention of aggregation of polymer chain than *para*-linkage (2,5-linkage) of the pyridinyl units (Liu, B. *et al.*, 2004).

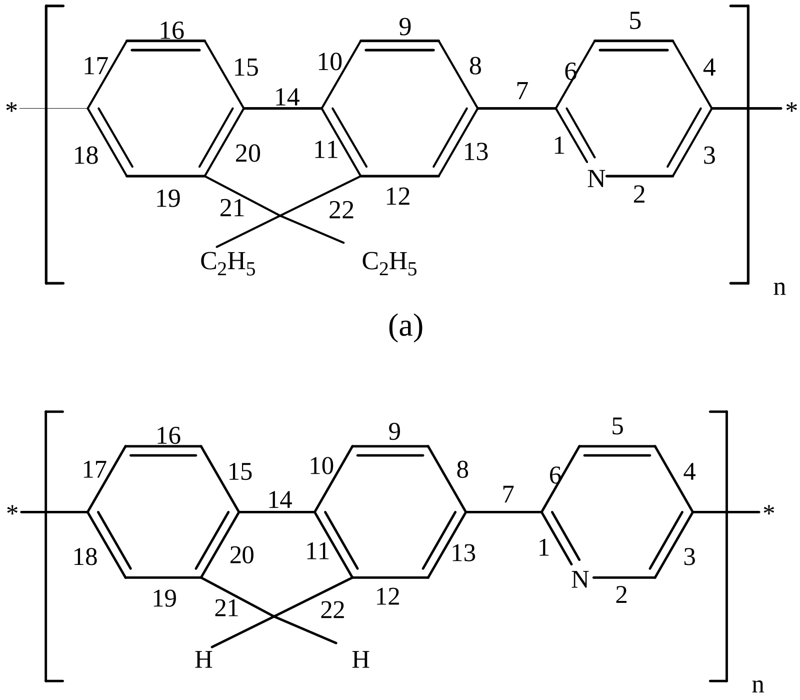
Recently, Liu, B. *et al.* (2005) reported the synthesis of a novel series of well-defined soluble poly[2,7-(9,9'-dialkyfluorenyl)-*alt*-pyridinyl] using palladium-catalyzed Suzuki cross-coupling reactions in good to high yields. In the series of alternating copolymers, 2,7-(9,9'-dialkylfluorenyl) was used as the light emitting unit and the electron deficient pyridinyl unit was employed to provide improved electron transportation. All these polymers were characterized by ^{1}H-NMR, ^{13}C-NMR, GPC, thermal analyses, UV–vis and fluorescence spectroscopy. The shorter pendant 9,9-dihexyl at fluorenyl unit is better to polymer for higher thermal stability and higher T_g than 9,9-dioctyl at fluorenyl unit. The meta-linkage (3,5- or 2,6-linkage) of pyridinyl units in the polymer backbone is more favorable to polymer for pure blue emission and prevention of aggregation of polymer chain than the para-linkage (2,5-linkage) of the pyridinyl units. In addition, the copoly(2,5-pyridine-*alt*-9,9'-dimethylfluorene) (PPyF) was investigated using quantum chemical techniques to improve the recombination of charge carrier. The results shown that the additional of pyridine, electron-withdrawing group, moiety greatly improve the electron-transporting and electron-accepting properties by the low LUMO energy levels.

Theoretical calculations have also proved to be of importance in this field because of the various limitations of experiments. Due to the high level of disorder associated with most of these materials, structural information is hard to come by experimentally. There may be various uncertainties related to experimentally determined band gaps and geometries, sometimes the evidence is contradictory. These uncertainties may arise from various problems, such as the characterized distribution of conjugation lengths and oligomer sizes, solvent effects, the presence of impurities or unrecognized dopants, variations in morphology and packing patterns, disorders and defects, three-dimentional cross-links, etc. These problems hamper the direct comparison of theoretically predicted intrinsic properties with those observed experimentally. Theoretical studies can help establish relationships between the structure and the electronic properties of conjugated polymers, and hence contribute to a better understanding of the structural variables and help to realize bandgap control (Yang *et al*., 2001).

Theoretical studies have been a valuable instrument in the elucidation of the relationships between electronic structure and electrical properties. The electronic properties of a conjugated polymers is primarily governed by the chemical structure of the backbone itself; a number of additional tools have also been employed to further adjust the HOMO and LUMO energy levels of the conjugated so far, their relatively large band gaps and especially the high-energy barriers for hole injection have limited their applications in PLEDs. It is well-known that the balanced charge injection from both electrodes and the comparable mobility of electrons and holes within the polymers are crucial for achieving high device efficiency. Several strategies, such as introducing hole injection and/or a hole transporting layer to balance the injection of the two types of electrical charges, have been established to improve the EL efficiencies of PLEDs, including blue PLEDs. Alternatively, a more attractive way to achieve high efficiency in PLEDs is to develop new conjugated polymers with the desire injection ability for electrons and/or holes. To succeed, it is essential to find an effective synthetic methodology to adjust the HOMO and LUMO energy levels of the conjugated polymer. In this respect, however, because of the lesser amount of freedom of chemical modification compared to other backbone-structure conjugated polymers, for PFs, the only available possibility of remote functionalization is at C-9 position; any other position of the fluorene unit is difficult for performing conventional chemical modifications (Liu, B. *et al*., 2001).

Up to now, the standard for calculating excited-state equilibrium properties of larger molecules in the Gaussian program package is the configuration interaction singles (CIS) method. However, due to the neglect of electron correlation, CIS results are not accurate enough in many applications. So Turbomole package with the time dependent density functional theory (TDDFT) were applied successfully for excited-state calculations. Major methodological progress was achieved by the variational formulating of the TDDFT method by Furche *et al*. (2002) facilitating the calculation of analytical TDDFT gradients, thus allowing geometry optimizations in excited states. The possibilities and limits of TDDFT are much less documented. Therefore, support for TDDFT by ab initio methods is highly desirable. The approximate coupled-cluster singles and doubles methods (CC2) is a very interesting alternative. The implementation of the resolution of the identity (RI) method allows the efficient treatment of larger molecules. However, it should be noted that neither the TDDFT nor the CC2 methods are applicable in the case of avoided crossings or conical intersections where the single-reference approach breaks down.

This research will perform structural and electronic properties, based on quantum chemical calculations of the fluorene-pyridine based copolymers. Figure 2 shows the molecular structure of (a) poly[2,7-(9,9-diethylfluorene)-co-*alt*-2,5-pyridine] and (b) copol(2,5-pyridine-*alt*-fluorene) and atomic numbering, used in this study.



(a)

(b)

Figure 2 Molecular structure of poly[2,7-(9,9-diethylfluorene)-co-*alt*-2,5-pyridine] and copol(2,5-pyridine-*alt*-fluorene) and their atomic numbering, used in this study.

Objectives

In this study, the conformational analysis, ground state geometry, energy gap, excitation energy, excited state geometry and fluorescence energy and radiative lifetime of fluorene-pyridine copolymer will be studied using quantum chemical approach with the aims of:

1. To study the torsional angles of the ground and excited states for fluorene-pyridine monomer using quantum chemical calculations.

2. To obtain the ground and excited states geometries of fluorene-pyridine based copolymers by quantum chemical calculation.
3. To understand the relationship between the structural and electronic properties of fluorene-pyridine copolymer.
4. To calculate the HOMO-LUMO energy differences and excitation energies of fluorene-pyridine based copolymers by quantum chemical approach.
5. To investigate the fluorescence and radiative lifetime of fluorene-pyridine based copolymers.
6. To validate the quantum methods from calculations of fluorene-pyridine based copolymers as compared to the experimental data such as energy gap.