LITERATURE REVIEW

The field of semiconducting polymers has its root in the 1977 discovery of the semiconducting properties of polyacetylene. This breakthrough earned Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa the 2000 Noble Prize in Chemistry for "the discovery and development of conductive polymers" (Braun *et al*., 2002). Due to the unique characteristics: electronic, optical, magnetic properties of semiconductors and metals, and processing advantages of conducting polymers so conducting polymers can be use in many applications for examples light emitting diodes (LEDs), transistors, photodiodes, laser and solar cells.

Poly(dialkylfluorene)s are promising materials for light emitting diodes because of their high photoluminescence (PL), quantum efficiencies and thermal stability. The fluorene structural unit provides both rigidly planarized biphenyl units within the polymer backbone and the possibility of remote functionalization at C-9, the latter offering the prospect of improving both polymer processability and mediating potential interchain interactions in films (Lee *et al.,* 1999). Polyfluorenes were first synthesized by Yoshino and coworkers in 1989 from a simple chemical oxidation of the monomers using $FeCl_3$. However, this polymer has low molecular weight (DP $\sim$10) and it was difficult to remove all traces of the oxidant. Nevertheless, devices were fabricated with these polymers. Next, in 1993 Masahiko and coworkers synthesized polyfluorene derivatives with alkyl chains. These polymers are found to be soluble in common organic solvents such as chloroform. However, the degree of polymerization was still low. This polymer was found to be fusible and the thermal properties of the polymer have been characterized by differential scanning calorimetry (DSC). The glass transition was found to be decrease with an increasing of the alkyl chain length. The electronic structure of poly(9,9-dioctylfluorene) (PFO) film on a Au-coated Si substrate was investigated by ultraviolet photo electron spectroscopy (UPS) and x-ray photoelectron spectroscopy (XPS). From the UPS measurement, the obtained ionization potential (IP) of the PFO film was 5.60 $\pm$ 0.05 eV. From the XPS shake-up peaks, the electron energy band gap

(E_g) of the film, $E_g = 3.10 \pm 0.10$ eV. By comparing the E_g with the optical absorption gap, Masahiko and coworkers also found that the value of E_g was closer to the optical absorption maximum than to the optical absorption edge. Moreover, they also suggested that the optical absorption maximum may be a better approximation than the optical absorption edge in estimating E_g (Liao *et al.,* 2000). The poly(2,7-(9,9-dioctylfluorene) was produced in good yields (85-90%) via palladium-catalyzed Suzuki coupling reaction (Blondin *et al.*, 2000). The quantum efficiency in blue-light emitting polymer/dielectric nanolayer nanocomposite light-emitting devices was enhanced by the blending poly(di-citylfluorene) with organo-clay. By reducing the excimer formation that leads to long wavelength tails, the photoluminescence (PL) and electroluminescence (EL) color purity of the device was also enhanced. The ratio of PDOF/organo-clay was regulated from 2:1 to 0.5:1 (w/w). The light-emitting device of 0.5:1 (w/w) blend demonstrated the highest quantum efficiency (QE), 0.72% (ph/el), which is ~ 500 times higher value compared with that of the pure PDOF layer device (Park *et al.* 2004). Moreover, poly[(2,7'-(9-9-dioctylfluorene)] was prepared through palladium-catalyzed coupling. In solution, this neutral yellow polymer exhibited blue emission (maximum of emission around 410 nm) with high quantum yields (up to 0.87). Additionally, Poly[(1,4-phenylene)-2,7-(9,9-dioctylfluorene)], Poly[2,7'-(9,9-dioctyl-2',7-bifluorene)], Poly-2,7'-(diethyl 9,9-dioctyl-2,7'-bifluorene-9',9'-dicarboxylate)], Poly[2,7'-(ethyl 9,9-dioctyl-2,7'-bifluorene-9'-carboxylate)] and Poly[2,7'-[(methoxyethoxy)ethyl 9,9-dioctyl-2',7-bifluorene-9'-carboxylate]] were also synthesized. All of these polymers exhibited blue emission with high quantum yield in the yellow neutral phase. All these interesting electrical and photophysical properties make these materials quite promising for applications in blue-light-emitting devices as emitting units as well as novel air-stable electron-injecting electrodes (Ranger *et al.* 1997). Therefore polyfluorene and its derivatives are used as electron transport materials for organic light-emitting diodes (Kulkarni *et al.,* 2004)

Due to the drawbacks of polyfluorene and its derivatives such as aggregation and excimers formation in the solid state, insufficient stability and high energy barrier for hole injection, limit their application in polymer light emitting diodes. In the

attempt of tuning the physical properties of PFs by molecular modification, one has to face the problem that the only available possibility of remote functionalization is at the C-9 position, and any other performing functional chemical reactions. In 1988 Kreyenschmidt and coworkers found that copolymerization of fluorene with various aryls allows for tunability of electronic properties and enhanced thermal stability. A variety of high molecular weight, thermally stable, blue-light-emitting random copolymers of 9,9-di-*n*-hexylfluorene by nickel(0)-mediated polymerization were prepared. The electronic properties of copolymers were altered somewhat as a function of comonomer structure and composition. The formation of excimers depended on the polymer composition and the morphology of the polymer films, the latter of which in turn depended on the processing conditions. The copolymers were readily soluble and easily processable from organic solvents (Kreyenschmidt *et al.*, 1998). The cyclic voltammetry measurements for the blue electroluminescent conjugated polymer poly(9,9-dioctylfluorene) were also reported. Both oxidation and reduction potentials were measured and thus estimated of both the ionization potential, IP and electron affinity EA of the polymer were obtained for the same sample under the same experimental condition. The estimated IP = 5.80 eV and EA = 2.12 eV. These results disagree with the common assumption that E_a is, to good approximation, given by the difference between IP and the optical gap (Janietz *et al.*, 1998). An alternating copolymer composed of fluorenedivinylene as the light emitting unit and pyridine as the electron transporting was synthesized by employing the Wittig reaction. The copolymer which has conjugation throughout the molecular chain is soluble in both polar and nonpolar solvents. The copolymer has a band energy gap of 3.85 eV deduced from an ultraviolet-visible absorption spectrum, and the ionization potential and electron affinity of -5.67 and -2.82 eV, respectively, deduced from a cyclic voltammogram. The photoluminescence (PL) emission maximum was observed at 440 or 540 nm depending on the solvent used in making the solution for spin casting. The copolymer was also capable of transporting electrons and could be used as an electron transporting layer (Kim *et al.,* 1999).

A variety of light emitting diodes from fluorene-based π-conjugated polymers are prepared. The alternated incorporation of phenylene or thiophene moieties in

fluorene-based π-conjugated polymers were synthesized in order to the tunability of the electroluminescent properties. The spectral emission varied from blue to green or yellow, depending on the composition of the copolymer. To enhance the luminous efficiency of the devices, the hole injection and hole transport into the polymer were improved by insertion of an insulating buffer layer and the incorporation of efficient hole transport material in the polymer. The insertion of a charge injection layer such as LiF and a hole transport layer such as *N,N*-diphenyl-*N,N*-bis(3-methylphenyl)-1,1-biphebyl-4,4'-diamine significantly improved the electroluminescence efficiency of the diode from 4.5 to 125 cd/m^2 (Donat-Bouillud *et al.*, 2000). In addition, Liu *et al.* (2000) reported the synthesis of a novel series of soluble alternating conjugated copolymers of 9,9-dihexylfluorene and substituted bithiophene by palladium-catalyzed Suzuki coupling reactions. They found that in the backbone structure of the polymers, the thiophene rings in the bithiophene moieties were *β*-substituted with decyl chains, and the bithiophene moieties were in two different coupling configurations of head-to-head and tail-to-tail regioregularities. By means of the controllable structure modifications, the electric properties of the polymer were tuned. In addition all polymers demonstrated efficient blue-to-green light emission, good thermal stability, and relatively high glass transition temperature ($T_g \sim 78^oC$). For the green-light emitting polymers, they comprised of bithiophene units. On the other hand, the polymer composed of thiophene produced bluish green emission with high fluorescence quantum efficiency.

In 2001, Liu, B. *et al*. presented a new series of fluorene based alternating copolymers by copolymerization with 10 different aryl comonomers. The same main chain structure polyfluorene-co-alt-phenylene with different functional groups attached at the 2- and/or 5-positions of the phenylene ring were synthesized by a palladium-catalyzed Suzuki coupling reaction. The electronic properties of the resultant polymers are tuned in a wide range, while the blue emission is well maintained. Moreover, comonomers provide the opportunity of bonding different functional side chain groups so that the electronic and physical properties of the polymers may be further tunable. The structure-property relationships within the blue alternating copolymers are also studied. Through controllable modification for both

the main chain structures and the side chains, not only optical and electronic properties of the blue emissive polymers had been tuned, but also the structure-properties relationships, especially the HOMO and LUMO energy level engineering, have been studied. Relatively high PL efficiency in both solution and film states, good thermal stability, and relatively high glass transition temperatures were demonstrated on these polymers. In general, polymers with the main chain structure of polyfluorene-co-alt-phenylene were found to have higher Φ_{fl} both in solution and in solid states than those copolymers with other main chain structures. The results showed that all of 10 copolymers had the band gaps ranging from 2.81 to 3.35 eV, corresponding to blue-light emission. For poly[2,7-(9,9-dihexlyfluorene)-co-alt-2,5-pyridine] has E_g = 2.82 eV (stand for the band gap energy estimated from the onset wavelength of the optical absorption) and E_g = 2.86 eV (from cyclic voltammetry). The spectroscopic properties of poly[2,7-(9,9-dihexlyfluorene)-co-alt-2,5-pyridine] was measured both in solution ($CHCl_3$) and in thin films. In solution, the maximum absorption at 385 nm was obtained whereas its PL spectrum peaked at 416 nm, with small shoulders around 440 and 475 nm. In thin films, poly[2,7-(9,9-dihexlyfluorene)-co-alt-2,5-pyridine] exhibited the absorption maximum and emission wavelength at 395 and 426 nm. A small shoulder at 447 nm was obtained. It can be summarized that when pyridine was chosen as comonomer, both absorption and emission spectra had shown a slight red shift in comparison with those of poly(9,9-dihexylfluorene). Although there was no obvious difference between the absorption and emission spectra of this copolymer as compared to those of poly(9,9-dihexlyfluorene), both the HOMO and LUMO energy levels were reduced greatly when they were compared with those of poly(9,9-dihexlyfluorene). Liu, B. *et al*. also synthesized the conjugated polymer, poly[2,7-(9,9'-dioctylfluorene)-co-alt-5,5'-(2,2'-bipyridine)], comprised of 9,9-dioctylfluorene and 2,2'-bipyridine via the Suzuki reaction. It was found that the optical, electrochemical and other physical properties of the polymer are depending on the linker. Poly[2,7-(9,9'-dioctylfluorene)-co-alt-5,5'-(2,2'-bipyridine)] exhibited the absorption maximum at 386 nm. Its PL spectrum peaked at 413 nm with a shoulder around 435 nm. In comparison with poly[2,7-(9,9'-dioctylfluorene)-co-alt-5,5'-(2,2'-bipyridine)], poly(9,9'-dioctylfluorene) had shown an obvious spectral red shift. This obvious spectral difference could be understood in

terms of the inserting of pyridine units. The film of poly[2,7-(9,9'-dioctylfluorene)-co-alt-5,5'-(2,2'-bipyridine)] emitted intensive blue light by excitation of UV light. The E_g, estimated from the onset wavelength of the optical absorption was 2.88 eV.

The improving of doped π-conjugated polymers for use in organic light-emitting diodes was reported by Gross *et al.* (2000). OLED devices are typically fabricated using one transparent electrode. The material most commonly employed for this purpose is indium tin oxide (ITO), which serves as the anode. The electronic work function ϕ_w of ITO is generally smaller than the highest occupied molecular orbital (HOMO) level of most organic semiconductors, resulting in a barrier φ_h for hole injection. The work function of ITO has been shown to depend strongly on the manufacturing process and any pretreatment, which makes the reproducibility of device fabrication rather difficult. Yang, Y., *et al.* (1994) have shown that coating the ITO with "doped" (that is oxidized) polyaniline reduced φ_h and consequently, lowered the onset voltage and operating voltage of the devices.

The aggregation phenomena and the luminescence of blue-light emitting of polyfluorene were also improved by the introducing of carbazole into the polymer backbone. The disordered polyfluorene was made though a Ni-catalyzed reaction, which resulted in high yield and high molecular weight polymers. The copolymers exhibited better spectral properties both in solution and in film compared to the polyfluorene homopolymer. And the cyclic voltammetry studied showed a slightly lower highest occupied molecular orbital (HOMO) than the homopolymer (Xia *et al.*, 2001). Consequently, in 2002, a novel series of conjugated polymers having oxadiazole, quinoline, quinoxaline, and phenylenecyanovinylene moieties in the main chain based on fluorene were synthesized in good yields by palladium-catalyzed Suzuki coupling reaction, a new approach different from the traditional polyhydrazide precursor route (oxadiazole-containing polymers), acid-catalyzed Friedländer condensation reaction (polyquinolines), and Knoevenagel condensation polymerization (poly(phenylenecyanovinylene)). The thermal, electrochemical, and optical properties of these copolymers were examined. All these polymers possess excellent thermal stability with glass transition temperatures of 114-208 °C and onset

decomposition temperatures of 387-415 °C. Cyclic voltammetry studies reveal that these copolymers possess low-lying LUMO energy levels ranging from -3.01 to -3.37 eV and low-lying HOMO energy levels ranging from -6.13 to -6.38 eV and may be promising candidates for electron-transporting or hole-blocking materials in light-emitting diodes. The polymers in thin films emit strong blue luminescence around 414-476 nm with narrow bandwidth upon photoexcitation. Photoluminescence spectra of the polymers in the films are only red-shifted by 7-11 nm compared to those in the solution, indicating that the aggregation and the excimer fluorescence are suppressed (Zhan *et al.*, 2002 and Lee *et al.* 2002).

Jin *et al.* (2003) reported the synthesis of a new green electroluminescence copolymer, CN-poly(dihexylfluorenevinylene) (CN-PDHFV), which denoted poly(9,9-dihexyl-9*H*-fluorene-2,7-diyl)(1-cyanoethene-1,2-diyl)(9,9-dihexyl-9*H*-fluorene-2,7-diyl)(2-cyanoehtene-1,2-diyl) by condensation polymerization utilizing the Knoevenagel reaction. The resulting polymer exhibited good stability in common organic solvents such as chloroform, THF and ODCB. The polymer was also easily cast on a glass plate to green film. The UV-vis spectrum of the polymer showed characteristically a broad absorption band at 440 nm. This polymer exhibited photoluminescence around λ_{max} = 535 nm (exciting wavelength 410 nm) and green electroluminescence around λ_{max} = 530 nm. The blue-emitting polymer is still prepared. The alternating F-alt-X-copolymers, where F was 9,9-bis(2'-ethyl)fluorene unit and the X comonomer varies from vinylene to thiophene and to thiophene-S,S-dioxide unit were synthesized and characterized (including structural, optical, electrochemical and electroluminescence properties). Among these X-monomers, the phenylene group is at the origin of a blue-emitting polymer with unitary luminescence efficiency in solution, while thiophene-S,S-dioxide promoted the highest electron affinity. These copolymer are also used in fabrication of light emitting diodes (Charas *et al.*, 2003. The other blue light emitting polyfluorene derivatives, poly[9,9-bis(4'-*n*-octyloxyphenyl)-fluorene] (PBOPF) was synthesized through Ni90) mediated polymerization and its light emitting properties were investigated. This polymer showed the maximum UV-visible absorption and band edge at about 380 and 440 nm, respectively. PBOPF showed PL emission maximum at about 424 nm. And it was

found that no significant excimer emission, however, was observed in the PL spectra of the PBOPF even after thermal annealing suggesting that BOPF unit significantly suppressed the excimer emission (Hwang, D.-H., *et al.*, 2004).

In order to overcome the drawbacks of polyfluorenes, it is convenience to add charge carriers into the luminescence chromophore to get easier charge transfer at the interfaces and to obtain the radiative recombination into the polymer. Pyridine units may act as electron charge carrier. Therefore, the synthesis of alternated copolymers appears to be a common way to introduce this carrier into a polyfluorene material and to combine the properties of the respective homopolymer. A novel poly[2,5-pyridine-*alt*-(9,9'dioctylfluorene)] poly-PyF8 was synthesized by Suzuki polycondensation reaction. The characterization of the copolymer by size exclusion chromatography reveals chains lengths of about 20-30 repeat units (40-60 rings), leading to a good processability for potential optical applications. The 1:1 ratio between the two units improved the solubility of the material in common organic solvents such as methylene chloride, chloroform, THF, dichloroethane and chlorobenzene, allowing for physicochemical characterizations. Raman and FT-IR experiments indicated that the electronic structure of the backbone is rather benzenic in the neutral (undoped) state, as opposed to a quinoic oxidized structure. This copolymer exhibited interesting electrochromic properties as attested by cyclic voltammetry and UV-vis experiments. The Eg obtained from cyclic voltammetry, film and in THF solution were 2.69, 2.87 and 2.94 eV, respectively. The pyridine-containing copolymer showed a maximum absorption wavelength λ_{max} around 380 nm. This copolymer exhibited strong photoluminescence (PL) spectra. The PL spectra showed the main emission maxima at 416 nm with a shoulder at 438 nm. Poly-PyP8 has a starting degradation around 325^{o}C and completed before 500^{o}C. It reversibly switches among the entire visible spectra, which is of particular importance for display applications (Aubert *et al.*, 2004). The alternating fluorene-pyridine copolymers were also studied by Liu and coworkers (2004). A novel series of well-defined alternating poly[2,7-(9,9-dihexyl-uorenyl)-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.

To enhance the color purity in blue-emitting fluorene-pyridine-based copolymers, the controlling the chain rigidity and effective conjugation length were investigated. 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. Copolymers emitted blue light and exhibited high PL efficiency. PL efficiencies showed the maximum at 3,5-pyridine content of around 30 mol% in the copolymer. With further the increase of meta-linkage contents, PL efficiencies decreased rapidly to 15% for alternating copolymer. Cyclic voltammetry investigation revealed that LUMO levels of copolymers increased with the increasing pyridine content. The introduction of pyridine unit at 3,5-position into polyfluorene backbone significantly depressed the excimer formation. The intensity of excimer emission decreased with the increased of 3,5-pyridine contents. Narrow and pure blue EL emission was obtained for copolymer with pyridine content of 40 mol%. External quantum efficiency was moderately high (0.4–0.5%) for such a pure blue emitter. The threshold voltages of devices from copolymers with the pyridine content of less than 40 mol% were low in the range of 5–6 V based on the device configuration: ITO/PEDOT/polymer/Ba/Al. The results indicated that fluorene-co-3,5-pyridine copolymers are promising blue-emitting electroluminescent materials (Yang, W., *et al.,* 2004).

Moreover, beside from light-emitting devices, polyfluorene copolymer can be used as solar cells. Bulk heterojunction solar cells based on blends of photoactive layers of polyfluorene copolymer Poly((2,7-(9-(29-ethylhexyl)-9-hexyl-fluorene)-*alt*-5,5-(49,79-di-2-thienyl-29,19,39-benzothiadiazole))-*co*-(2,7-(9-(29-ethylhexyl)-9-hexyl-fluorene)-*alt*-2,5-thiophene)) (LBPF3) acting as electron donor, and [6,6]-phenyl-C_{61}-butyric acid methylester (PCBM), acting as electron acceptor, were constructed and studied. The power conversion efficiency for a 1:4 (by weight) blend of LBPF3:PCBM under simulated solar light illumination having light intensity of 100 mW/cm^2 was 1.7%, and 9.2% under monochromatic (565 nm) light illumination with light intensity of 0.145 mW/cm^2 . The maximum external quantum efficiency (incident photons to converted electrons) for this device was found to be above 40% from 400 to 560 nm. The effects of blend composition and film thickness on the photovoltaic parameters were also studied. The incident light intensity dependence of the short circuit current showed a linear relationship (Yohannes *et al.*, 2004).

In theoretical points of view, due to the limitation of experimentally synthesis, the theoretical investigations of conducting polymer are also interesting to obtain the structural, optical and electronic properties of conjugated polymers. The ground state geometry of poly(2,7-(9,9-dioctylfluorene)) was studied. The ground state potential curve of bifluorene (BF) as computed by HF/6-31G(d) level of calculation showed the two minima at 45^o and 135^o whereas three maxima were observed on the potential energy curves, two for the planar conformations and one for the perpendicular one. This potential energy curve is very close to that obtained for biphenyl using the same level of calculation. Moreover, the observed results showed that the presence of alkyl chains (ethyl groups) at the 9-position of BF does not significantly change its potential energy curve. This strongly suggested that the presence of octyl chains in the corresponding polymer should not intrinsically change the conformation behavior of each of the repeat units as far as they remain isolated (Blondin *et al.*, 2000). The structural properties of poly(2,7-fluorene), (PF) was also studied by Brière *et al.* (2004). The ground state optimization was done using DFT with plane wave basis set. The obtained dihedral angle of PF was 26^o which was well agree with experimental data.

The ground state of covalently linked fluorene-based dimers (fluorene derivatives: 1-(9,9-dioctylfluoren-2-yl)phenylene (FP), 2-(9,9-dioctylfluoren-2-yl)thiophene (FT), 2-(9,9-dioctylfluoren-2-yl)-3-methylthiophene (FMT), 2-(9,9-dioctylfluoren-2-yl)-3,4-(ethylenedioxy)thiophene (FEDOT), and 9,9,9',9'-tetraoctyl-2,2'-bifluorene (FF) were investigated by HF/6-31G(d) *ab initio* calculations. The octyl groups at the 9 position were replaced by ethyl groups to reduce the time to calculation. The alkyls group at the 9 position does not significantly affect the equilibrium geometry of the fluorene derivatives. These derivatives showed nonplanarity in their ground electronic states. The extent of nonplanarity depended on the nature of the aromatic ring bonded to the fluorene unit. From the geometry optimization, the dihedral angle of FP was 45.3^{o}. A distance of 1.491 Å between the subunit was computed for FP. This geometry was very close to that obtained for biphenyl using the same level of calculation ($\theta = 46.0^{o}$). The ground state of FT was slightly less twisted than that of FP. Accordingly, the inter-ring distance (*d*) was slightly shorter (*d* = 1.478 Å). As expected, five-membered aromatic rings create less steric hindrance than six-membered rings. Accordingly, the interring distance of FMT was slightly increased, compared to that of FT (Belletête *et al.*, 2000). Dkhissi *et al.* (2003) calculated the geometric and electronic structure of 3,4-ethylenedioxythiophene oligomers, ranging in size up to decamer with density functional theory according to Becke's three-parameter exchange functional and the gradient-corrected functional of Lee, Yang and Parr (DFT/B3LYP/6-31G) and ab initio Hartree-Fock (HF/6-31G) methods. A comparison between the energetic of the aromatic and quinoid dorms in the neutral state showed as expected that the former was more stable. The optical properties calculated at the semiempirical level (intermediate neglect of differential overlap/single configuration, (INDO/SCI)) on the basis of the geometries provided by DFT and HF were also analyzed. Using the linear relationships, the optical energies of 2.10 and 1.65 eV were extrapolated for an infinite chain on the basis of HF and DFT geometries, respectively.

In order to investigate the excited states geometries, the singles configuration interaction (CIS) theoretical approach is used. It has been shown that the CI-singles wave function can be used to compute efficiency the analytic first derivatives of the

energy in order to obtain accurate properties and optimized geometries for a wide range of molecules in their excited states. In addition, a computer program is described which allows CI computations to be done in a "direct" fashion, with no disk storage required for the two-electron integrals. Moreover, the CI approximation can be corrected via second-order Møller-Plesset perturbation theory to produce a level of theory for excited states which further includes some effects of electronic correlation (Foresman *et al.,* 1992). Chakraborty and coworker (2001) reported the study of ground state configurations of thiophene and its cyano derivatives oligomers which were carried at the restricted Hartree-Fock (RHF/3-21G(d)) level of calculation. The first (lowest) singlet excited states were followed performed by CIS/3-21G(d) level of calculation. The results revealed that the delocalized first singlet excited states (CIS) were accompanied by a strong geometry relaxation in comparison to their ground-state (HF) geometries. And the shape and the location of the relaxation depended on the oligomer length.

In 2003, Tirapattur *et al.* reported the geometry optimizations of the ground and first lowest (singlet) excited state (S_1) of fluorene derivatives: 1-(fluoren-2-yl)phenylene (FP), 2-(fluoren-2-yl)thiophene (FT), and 2-(fluoren-2-yl)-3-methylthiophene (FMT) using the restricted Hartree-Fock (RHF/6-31G(d)) and the restricted configuration/singles (RCIS/6-31G(d)), respectively. It was found that these molecules were nonplanar in the ground state, whereas the almost reached planarity in their S_1 excited state. they almost reach planarity in their S_1 excited state. CIS calculations produce singlet excitation energies in good agreement with the 0-0 absorption peaks measured in cyclohexane (differences less than 0.2 eV). The RCIS/6-31G(d) calculations also showed that delocalized first single excited states (CIS) were accompanied by a geometry relaxation in comparison to their ground-state (HF) geometries. The geometry relaxation energies were estimated to be approximately 1 eV for these derivatives. From the CIS vertical transition energies taken at the minimum of the S_1 torsional potentials, the emission energies were computed. It is found that these transition energies were very close to those determined from the emission spectra measured in cyclohexane.

In 2004, Belletête *et al.* investigated the ground and excited states of covalently linked 2-carbazole-based dimers by theoretical methods. Geometry optimizations of the ground state of *N*,*N*'-diethyl-2,2'-bicarbazole (CC), 2-(*N*-ethylcarbazole-2-yl)thiophene (CT), and 2-(*N*-ethylcarbazole-2-yl)-9,9-diethylfluorene (CFl) were carried out at the restricted Hartree–Fock level (RHF/6-31G*). The three derivatives were non-planar in their ground electronic states. The optimization (relaxation) of S_1 and S_2 electronic states were done using the RCIS/6-31G* method. For the three oligomers, S_2 is much more stabilized than S_1 causing a crossing of the singlet excited states (S_2 becomes lower in energy than S_1). It was observed that the three dyads reach almost planarity in their first relaxed excited state. Belletête *et al.* (2004) also studied the ground and excited states of covalently linked 2-carbazole-based dimers, N,N'-diethyl-2,20-bicarbazole (CC), 2-(N-ethylcarbazol-2-yl)thiophene (CT), and 2-(N-ethylcarbazol-2-yl)furan (CF). The ground state geometries were carried out using the restricted Hartree–Fock level (RHF/6-31G*). It was found that CC and CT are nonplanar in their ground electronic states (S_0), whereas CF is completely planar in the S_0 state. The optimization (relaxation) of S_1 and S_2 electronic states was done using the RCIS/6-31G* method. For all the oligomers investigated, S_2 is much more stabilized than S_1 causing a crossing of the singlet excited states (S_2 becomes lower in energy than S_1). It was observed that the three dyads reach planarity in their S_1 relaxed excited state. The structures of polyfluorene (PF) and poly(2,7-fluorene-*alt*-*co*-5,7-dihydrodibenz[*c*,*e*]oxepin) (PFDBO) were studied by quantum chemical approach. The ground state geometries were fully optimized using the density functional theory (DFT) with the 6-31G basis set. CIS/3-21G level of calculation was used to obtain the excited state geometries. It was found that the basic structures of polymer can be described as their oligomers. The addition of seven-membered ring leaded to the dramatical twisted in the structure of $(FDBO)_n$ compared with PF. The character of $(FDBO)_n$ will block the conjugation for conjugated backbone between the fluorene cells. In their excited state, it was obvious that the excited structure had a strong coplanar tendency: that is the conjugation is better in their excited structure. It will be useful to examine the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) for these oligomers and polymers to provide the framework for the excited

state TDDFT calculations in the subsequent section. The results indicated that the relative ordering of the occupied and virtual orbitals provided a reasonable qualitative indication of the excited properties. The HOMO and LUMO of both molecules were localized predominantly on the phenyl rings. For both $(F)_2$ and FDBO, there was antibonding between the bridge atoms and there was bonding between the bridge carbon atom and its conjoint atoms in the same benzenes in the HOMO. On the contrary, there were bonding in the bridge single bond and the antibonding between the bridge atom and its neighbor in the same phenyl ring in the LUMO. The electronic cloud distributing in the front orbitals of FDBO was similar to that of $(F)_2$ on the fluorene ring. However, the electronic cloud in the benzene on the left side of the seven-membered ring was distributed less than that of other benzenes in FDBO. FDBO was bonding relaxation in the seven-membered ring compared with the fluorene ring from the electronic cloud picture. For the polymers, this implied the conjugation blocked in the seven-membered ring in PFDBO compared with PF (Wang, J.-F., *et al.,* 2004).

The ground and excited states of fluorene-phenylene (FP) based oligomers and polymers were studied. The ground state optimized structures were obtained at a restricted (closed-shell) Hartree-Fock level (RHF) and the density functional theory (DFT) as approximated by the various hybrid functionals (RB3LYP, RB3P86, RB3PW91, RMPW1PW91). The ground state potential energy curves or surfaces of FP and its derivatives were obtained using RHF. All derivatives were nonplanar in their electronic ground state. The lowest singlet state was studied with the configuration interaction (singles) approach (CIS). For each monomer, the $S_1 \leftarrow S_0$ electronic transition involved primarily the promotion of an electron from the HOMO to the LUMO, and was strongly polarized along the monomer backbone. CIS results also suggested geometry relaxation in the first singlet excited state (Gong *et al.* 2005).

Due to the limitations of CIS, so TDDFT and RI-CC2 are interesting methods to perform the excited state optimization (Aquino e*t al.,* 2005, Beenken *et al.,* 2005, Lukeš e*t al.,* 2005 and Serrano-Andrés *et al.,* 2005). They reported TDDFT and RI-

CC2 calculation performed on the excited state intramolecular proton transfer in malonaldehyde, *o*-hydroxybenzadehyde, salicylic acid, 7-hydroxy-1-indanone, and 2-(2'hydroxyphenyl)-benzothiazole. The results indicated that TDDFT and RI-CC2 methods were good candidates for the description of excited-state intramolecular proton transfer potential energy surface. TDDFT and RI-CC2 also provided excited state structures of methylene-bridged oligomers constructed of two, four, six and eight aromatics rings. It was found that the elongation of the molecular chain leaded to only small changes in the interring distances and to a slight increased in the bond length alternation in comparison to the fluorene molecule. The largest change occurred for a terminal ring becoming an inner one. After further extension the bind-length differences seem to be quite well converged. Moreover, the electronic excitation led to formation of a quinoide-type structure (Lukeš e*t al.,* 2005).

Theoretical studies on the electronic structures of polymer have contributed a lot to rationalize the properties of known polymers and to predict those of yet unknown one. There are two different theoretical approached to evaluate the band gaps of polymers. One is the polymer approach in which the periodic structures are assumed for infinite polymers. Another one, the oligomer extrapolation technique, has acquired the increasing popularity in this field, however. In this approach, sequence of increasing longer oligomers is calculated, and extrapolation to infinite chain length is followed. A distinct advantage of this approach is that it can provide the convergence behavior of the structural and electronic properties of the oligomers. In practice, both the oligomer extrapolation and the polymer approached are generally considered to be complementary to each other in the understanding of the properties of polymer. The theoretical band gap is the quantity for energy from the ground state to the first dipole-allow excited state. There exist a variety of theoretical approached for evaluating this quantity for oligomers as well as infinite polymers. The crudest estimate is the orbital energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), obtained from Hartree-Fock (HF) or density functional theory (DFT). In addition, the orbital energy difference between HOMO and LUMO is still an approximate estimate to the transition energy since the transition energy also contains significant contributions

from some two-electron integrals. However, the real situation is that an accurate description of the lowest singlet excited state requires a linear combination of a number of excited configurations, although the one mentioned above often plays a dominant role. The calculated HOMO-LUMO gap agrees fairly well with the experimental band gap in many cases, probably due to the error cancellations. Hence, it is desirable to obtain more rigorous information on the nature of the lowest singlet excited state by employing other elaborate theoretical methods. Among those theories, Hartree-Fock (HF)-based methods such as configuration interaction singles (CIS) and the random phase approximation (RPA), which is equivalent to the time-dependent HF (TDHF), usually only provide the qualitative or semiquantitative descriptions for the low lying excited states (Ma *et al.,* 2002 and Yang, S., *et al.,* 2004).

The estimated band gaps, ionization potentials and electron affinity for polyacetylene, polythiophene, polypyrrole, polythiazole and a thiophene-thiazole copolymer were investigated by DFT using a slightly modified hybrid functional. The results showed that the band gaps are within 0.1 eV of experimental solid-state values. (Salzner *et al.,* 1998). The electronic properties of poly(2,5-pyridine) (PPy) were studied by density functional method with the linear muffin-tin orbitals (LMTOs) as basis functions. From this calculation, the $n \rightarrow \pi^*$ transition was around 3.2 eV and $\pi \rightarrow \pi^*$ was around 2.5 eV. The latter value was in good agreement with the experimental value of about 3 eV, when taking the common band gap underestimate of density functional calculations into account (Vaschetto *et al.,* 1999). The Density Functional theory (DFT) is developing rapidly as a cost-effective general procedure for studying physical properties of molecules (Becke *et al.*, 1992 and Jahnson *et al.,* 1992). Belletête *et al.* (2000) reported the HOMO and LUMO of fluorene-based dimers (fluorene derivatives: 1-(9,9-dioctylfluoren-2-yl)phenylene (FP), 2-(9,9-dioctylfluoren-2-yl)thiophene (FT), 2-(9,9-dioctylfluoren-2-yl)-3-methylthiophene (FMT), 2-(9,9-dioctylfluoren-2-yl)-3,4-(ethylenedioxy)thiophene (FEDOT), and 9,9,9',9'-tetraoctyl-2,2'-bifluorene (FF). It was found that the HOMO of each compound possessed an antibonding character between subunits, while the LUMO showed bonding character. The nature and the energy of the first 10 singlet-

singlet electronic transitions were obtained by ZINDO/S semiempirical calculations performed on the HF/6-31G* optimized geometries. All electronic transitions were of the $\pi\pi^*$ type and involved both subunits of the molecules. For each derivative, excitation to the S_1 state corresponded mainly to the promotion of an electron from the HOMO to the LUMO, and the $S_1 \leftarrow S_0$ electronic transition was strongly favored and polarized along the long axis of the molecular frame. The energy of the first electronic transition of all derivatives followed the HOMO-LUMO energy gap computed from HF/6-31G* ab initio calculations. The absorption and fluorescence spectra of the fluorene derivatives were recorded in cyclohexane. The first absorption band of each derivative can be assigned to the $S_1 \leftarrow S_0$ electronic transition computed from ZINDO/S calculations. The overall shape of the absorption and fluorescence spectra suggested a smaller distribution of conformers in the S_1 state than in the ground state. The fluorescence quantum yield and lifetime in cyclohexane were obtained. In these systems, the photophysical properties were mainly governed by nonradiative processes.

Polythiophene and its derivatives are have been most widely studied because of their good environmental stability, small band gap (~2.0 eV) and easy electrochemical preparations. In 2000, Kwon *et al.* computed the band gaps of polythiophene (T) and the related polymers with a fused benzene ring (TB, polythieno[3,4-*b*]-benzene) or a fused pyrazine ring (TN, polythieno[3,4-*b*]pyrazine) using a variety of methods. The excitation energies were computed using ZINDO (INDO/S), configuration interaction singles (CIS), and time-dependent density functional theory (TDDFT). Band gaps were extrapolated from excitation energies. It was found that the band gap in the TN polymer was predicted to be smaller than in TB polymer (Kwon *et al.*, 2000). The properties of polythiophene and its derivatives are also investigated by Chakraborty *et al.*, (2001). The first singlet excitation energies of thiophene and its cyano derivative oligomer were studied using CIS/3-21G* method. This investigation indicated that the cyano substituted thiophene polymer has a smaller intrinsic band gap than its parent polymer. CIS calculations produced singlet excitation energies in excellent agreement with the experimental values (~0.1 – 0.5 eV). The spectroscopic and photophysical properties of thiophene-

fluorene oligomers were studied by Belletête *et al*., (2001). The first absorption band of each derivative can be assigned to the calculated $S_1 \leftarrow S_0$ electronic transition computed from ZINDO/S calculations performed on the optimized geometries (HF/6-31G*). Excitation to the S_1 state corresponds mainly to the promotion of an electron from the HOMO to the LUMO. The HOMO possesses an antibonding character between neighboring rings which should contribute to the nonplanarity observed for these derivatives in their ground states. On the other hand, the LUMO showed bonding character between adjacent rings in agreement with more planar S_1 excited state. The energy of the $S_1 \leftarrow S_0$ electronic transition follows the HOMO-LUMO energy gap of each derivative. Addition of ester groups at both ends of the thiophene-fluorene oligomers induces a red-shift of the absorption and fluorescence bands. In 2004, Poolmee *et al.* performed quantum chemical calculations to obtain the HOMO-LUMO gap and the lowest excitation energy of poly[2,7-(9,9-dihexylfluorene)-co-alt-2,5-(decylthiophene). The obtained results indicated that TDDFT(B3LYP/6-31G*)//B3LYP/6-31G* calculations can be useful to provide reliable energetic and structural results of this polymer. The HOMO-LUMO predictions were not accurately obtained as compared to the experimental results. The inverse chain length approximation by using TDDFT(B3LYP/6-31G*)//B3LYP/6-31G* calculations provided energy gap of 2.50 eV, which was in an excellent agreement with the experimental data. However, it was found that the HOMO-LUMO energy gaps obtained from B3LYP calculations were still far from the experimental data.

In 2002, Belletête *et al*. presented the spectroscopic and photophysical results on phenylene-fluorene oligomers as well as corresponding polyester. From ZINDO/S calculations preformed on the optimized geometries (HF/6-31G*), the first absorption band of each derivatives is assigned mainly to the electronic excitation from the HOMO to the LUMO, which is strongly allowed and polarized along the long molecular axis (*x*). The increase of the oligomer length and/or the addition of carbonyl groups at both ends of the molecules induce a red shift of the absorption and fluorescence spectra due to an increase in the electronic delocalization along the molecular frame. From optimized geometries performed at the HF/6-31G* level, it is observed that the ground state molecular conformation was not much affected by the

length of the oligomer and/or the presence of end substituents (carbonyl groups). On the other hand, according to fluorescence spectra, all derivatives relaxed more planar conformations in the first singlet excited state. The luminescence of the polyesters was intense (ϕ_F = 0.6) making these polymers promising materials for blue LED materials. The influence of donor and acceptor substituents on the electric characteristics of poly(fluorene-phenylene) was studied by Zeng *et al.* (2002). They investigated theoretically the influence of electron acceptors such as cyano groups and donors such as methoxy and amino groups on the geometric and electronic properties of the poly(9,9-dihexylfluorene-1,4-phenylene) unit cells. The HOMO and LUMO levels were calculated by AM1. The results showed that the use of diamino or dicyano substituents on the phenylene ring allowed the bandgaps to decrease significantly. This information is of prime important in the design of new chemical structures aimed at a fine-tuning of the emitted color and at a significant improvement in quantum efficiency. Belletête *et al*. (2004) also investigated absorption and emission properties of covalently linked 2-carbazole-based dimer. The nature and the energy of the first five singlet–singlet electronic transitions and fluorescence spectroscopies of *N*,*N*'-diethyl-2,2'-bicarbazole (CC), 2-(*N*-ethylcarbazol-2-yl)thiophene (CT), and 2-(*N*-ethylcarbazol-2-yl)-9,9-diethylfluorene (CFl) were obtained by ZINDO/S semi-empirical calculations performed on the HF/6-31G* optimized geometries. For all oligomers, the first electronic transition ($S_1 \leftarrow S_0$) is weakly allowed and polarized along the *y*-axis (short axis), whereas the $S_2 \leftarrow S_0$ electronic transition possesses a much larger oscillator strength and is polarized along the *x*-axis. The $S_2 \leftarrow S_0$ electronic transition can be correlated to the first absorption band of each derivative measured in *n*-hexane. Electronic transition energies from the relaxed excited states were carried out from ZINDO/S calculations performed on the optimized geometries of S_1 and S_2. It was found that the electronic transition energies from the first relaxed excited state were close to those determined experimentally from the fluorescence spectra recorded in *n*-hexane. This study is believed that a rational design of tunable light-emitting materials based on polycarbazoles is possible and should then contribute to the development of organic light-emitting diodes. Moreover, Belletête *et al*. (2004) reported the nature and the energy of the first two singlet–singlet electronic transitions of N,N'-diethyl-2,2'-bicarbazole (CC), 2-(N-

ethylcarbazol-2-yl)thiophene (CT), and 2-(N-ethylcarbazol-2-yl)furan (CF) which obtained by ZINDO/S semi-empirical calculations performed on the HF/6-31G* optimized geometries. For all the oligomers, the first electronic transition (pp*) was weakly allowed and polarized along the y-axis (short axis) of the molecule. On the other hand, the $S_2 \leftarrow S_0$ electronic transition of each oligomer possesses a much larger oscillator strength, was polarized along the x-axis, and was mainly described by the promotion of one electron from the HOMO to the LUMO. Additionally, these calculations produced $S_2 \leftarrow S_0$ vertical transition energies in fair agreement with the absorption bands maxima measured in n-hexane. Moreover, the electronic transition energies from the first relaxed excited state were close to those determined experimentally from the fluorescence spectra recorded in n-hexane.

Recently, time-dependent density functional theory (TDDFT) was developed and formulated for a variety of purposes. A significant quantitative improvement in the excitation energies from TDDFT over those from HF-based methods has been demonstrated, but at roughly comparable computational cost. The failure of TDDFT with the pure exchange-correlation functionals in the large systems is attributed to the fact that the exchange-correlation potentials generated by the current approximate exchange-correlation functionals decay too rapidly in the asymptotic region. This problem is partially overcome in TDDFT with the HF/DFT hybrid functionals such as B3LYP, since the incorporated HF exchange potential decays correctly. So TDDFT with the B3LYP functional is expected to be a relatively reliable tool for evaluating the excitation energies of the low-lying excites states for small- and medium-sized molecules. Moreover, the TDDFT band gaps can still convey very useful information for designing novel polymers with narrow band gaps (Ma *et al.* 2002). However, for high/lying excited states or Rydberg excited states, TDDFT underestimates the excitation energies by up to 1 eV or more (Hirata *et al.*, 2003).

In 2001, Hsu *et al.* applied TDDFT to calculate vertical excitation energies of *trans*-1,3-butadiene, *trans*-*trans*-1,3,5-hexatriene, all-*trans*-1,3,5,7-octatetraene, and all-*trans*-1,3,5,7,9-decapentaene. Attachment and detachment densities for transitions in butadiene and decapentaene from the ground state to the $2\ ^1A_g$ and $1\ ^1B_u$ excited

states were also calculated and analyzed. For the 1 ^1B_u state, TDDFT underestimates the excitation energy by 0.4-0.7 eV. In this case, TDDFT has performed very well indeed in describing the excitation energies to the 2 ^1A_g state across this series of molecules. The time dependent density functional theory (TDDFT) was also used to calculate the absorption ($S_0 \rightarrow S_1$) and emission ($S_1 \rightarrow S_0$) transition energies of poly(*p*-phenylene vinylene) (PPV). The absorption and emission energies were estimated to be 2.44 and 2.16 eV, respectively, from the extrapolation of calculated results of oligomers. Comparison with available experimental data demonstrated that TDDFT is a very reliable tool for investigating the electronic transitions of PPV (Han *et al.* 2004).

The electronic and optical properties of poly(2,7-fluorene) were obtained using density functional theory (DFT and time dependent density functional theory (TDDFT) with a plane-wave basis set, pseudopotentials and local exchange-correlation energy. The obtained first excitation energy of bifluorene as obtained from DFT and TDDFT were 3.58 and 4.24 eV, respectively. These analyses are in accordance with the experimental data (excitation in vapor and crystal are 4.19 and 4.07-4.10 eV, respectively). The calculated energy gaps of poly(2,7-fluorene) as obtained from DFT was 2.0 eV whereas the calculated values are around 3.25-3.3 eV (Brière *et al.*, 2004). The ionization potentials (IP), electron affinity (EA) and HOMO-LUMO gaps (Δ_{H-L}) of polyfluorene (PF) and poly(2,7-fluorene-*alt*-*co*-5,7-dihydrodibenz[*c*,*e*]oxepin) (PFDBO) were investigated using density functional theory with B3LYP functional. The lowest excitation energies (E_gs) and the maximum absorption wavelength,λ_{abs} of oligomers were studied employing the time-dependent density functional theory (TDDFT) and ZINDO. Band gaps of the corresponding polymers were obtained by extrapolating HOMO-LUMO gaps and the lowest excitation energies to infinite chain length. The IP, EA and λ_{abs} were also obtained by extrapolating those of oligomers to the inverse chain length equal to zero (1/n = 0). For PFDBO, IP and EA were higher and the band gap was larger than those of PF's from the extrapolation. The outcome showed that the dramatically twisted structure of PFDBO in the seven-membered ring results in the decreased conjugation in the chain. These caused both the maximal absorption and emission wavelengths of

PFDBO blue shift compared with PF (Wang *et al.,* 2004). Because of the good candidates for organic blue-light emitting diodes of fluorene and its derivatives, fluorene-phenylene (FP) based oligomer and polymers were studied. The character and energy of the first 20 singlet-singlet electronic transitions were investigated by applying the time-dependent DFT approximations, TD-B3LYP, TD-B3P86 and TD-B3PW91, to the corresponding optimized ground state geometries. Excitation energies were red shift when side chains were attached to the basic FP unit or when the unit was extended longitudinally. Similar shifts were observed in the HOMO-LUMO gaps as obtained from the ground state DFT calculations (Gong *et al.*, 2005).

In 2005, The syntheses, spectral measurements and the theoretical study of 2-((9H-fluoren-9-ylidene)methyl)thiophene(**A**) , ((9H-fluoren-9-ylidene)methyl)5(thiophen- 2- yl) thiophene (**B**), 1-(5-((9H-fluoren-9-ylidene)methyl)thiophen-2-yl)propan-1-one (**C**), 1- (5-((9H-fluoren-9-ylidene)methyl)thiophen-2-yl)pentan-1-one (**D**), 1,2-bis(1-(5-((9H-fluoren-9-ylidene) methyl)thiophen-2-yl)propylidene)hydrazine (**E**) and 1,2-bis(1-(5-((9H-fluoren-9-ylidene)methyl)thiophen-2-yl)pentylidene)hydrazine (**F**) were presented. The influence of the conformation (e.g. *cis*- and *trans*-forms in the case of E and F molecules) on electronic spectra was interpreted by ZINDO/S method. The results indicated that the thiophene rings connected with terminal fluorene chromophores through the double bonded carbon atom seem to be suitable candidates for the subsequent preparation of the electro-optical materials (Lukeš *et al.,* 2005). In 2006, Yang *et al.* applied quantum chemical techniques to investigate a series of oligomer and polymers based on end-capped oligofluorene-thiophenes. The characterization of frontier orbitals, HOMO-LUMO gaps ($\Delta_{H\text{-}L}$), in addition to the ionic potentials (IP) and electron affinity (EA) were obtained by B3LYP/6-31G density functional theory (DFT) calculations. The lowest excitation energies (E_g) and the maximal absorption wave lengths λ_{abs} of the oligomers were studied employing the time dependent density functional theory (TDDFT). The $\Delta_{H\text{-}L}$, E_g, IP and EA of the polymers were obtained by extrapolating those of the oligomers to the inverse chain length equal to zero (1/n = 0). The outcome shown that the hole and electron accepting and transporting properties in polymers were better than that in oligomers. As the conjugation lengths increased the energy gaps decreased and thus the

absorption spectra exhibited bathochromic shift. Additionally, the singlet and triplet excitation energies in oligothiophene (up to five rings) using time-dependent density functional theory (TDDFT) with different exchange-correlation functionals were reported and compared those results with results from the approximate coupled-cluster singles and double model (CC2) and experimental data. Form the results, it was shown that TDDFT methods underestimate photoluminescence energies but the energy difference between singlet and triplet states shows trends with the chain-length similar to CC2. The results also indicated that the second triplet excited state was below the first excite state for long oligomers (Fabiano *et al.,* 2005).

The vertical excitations and the fluorescence transition from the lowest excited state of methylene-bridged oligomers constructed of two, four, six and eight aromatics rings were calculated using TDDFT, RI-CC2 and ZINDO/S. The RI-CC2 and ZINDO/S absorption and fluorescence spectra agreed very well with the available experimental data. On the other hand, TDDFT calculations underestimate excitation and fluorescence energies systematically for larger systems (N>4). The effective conjugation length was estimated to 13-14 repeated units. The computed radiative lifetimes for the fluorene molecule show good agreement with the experiment within realistic expectations (Lukeš *et al.*, 2005).

Theoretical study can also provide the information for the improvement of the polyfluorene drawbacks. In 2003, Cornil *et al.* reported a quantum-chemical characterization of the electric and optical properties of polyfluorene chains and compared them to those in copolymer containing a alternating fluorene and benzothiadiazole or ethylenedioxythiophene units. On the basis of the optimized geometries, the electronic excitation energies of the oligomers were computed using the spectroscopic version of the semiempirical Hartree-Fock INDO (intermediate neglect of differential overlap) hamiltonian developed by Zerner and coworkers. It can be concluded that the introduction of the comonomer can strongly modified the electronic properties as well as the efficiency of charge- and energy-transfer processes. And the choice of the comonomer is thus critical in targeting specified optical properties while maintaining good transport properties. One of the drawbacks

of light-emitting diodes based on polyfluorene derivatives is the injection of holes from the anode due to the high ionization potential (IP) of most derivatives. Substitution by electron-donating alkoxy substituents or by adding charge carriers on the conjugated polymer's backbone produces a remarkable influence on its electrical and optical properties. In this contribution, Yang *et al.* (2005) applied quantum-chemical techniques to investigate a family of π-conjugated polymers with substituted dimethoxy groups at the 3,6 positions of the fluorene ring, namely, poly(2,7-(3,6-dimethoxy-fluorene) (PDMOF), poly(2,7-(3,6-dimethoxy-fluorene)-*co*-alt-fluorene (PDMOFF), and poly(2,7-(3,6-dimeth-oxy-fluorene)-*co*-alt-2,5-thiophene (PDMOFT). The electronic properties of the neutral molecules, HOMO-LUMO gaps (¢H-L), in addition to the positive and negative ions, were studied using the B3LYP functional. The lowest excitation energies (E_g) and the maximal absorption wavelength λ_{abs} of PDMOF, PDMOFF, and PDMOFT were studied by employing time-dependent density functional theory (TD-DFT) and the ZINDO semiempirical method. The IP, EA, and E_g values of each polymer were obtained by extrapolating those of the oligomers to the inverse chain length equal to zero ($1/n = 0$). The influence of the presence of methoxy groups on the fluorene moiety on the ionization potential was especially emphasized. The outcomes show that the HOMO energies of these systems under study increased by about 0.4 eV and the IP values decreased by about 0.3 eV compared to those of the corresponding polyfluorene. Both effects result in a reduction of the energy barrier for the injection of holes in related polymeric light-emitting devices and should contribute to the enhancement of their performances. Because of the cooperation with thiophene in PDMOFT, which results in a good planar conformation, both the hole-creating and electron accepting abilities were improved.

Yang *et al.* (2005) reported the incorporation of the carbazole units into polyfluorene chain in order to efficiently suppress the keto defect emission. The quantum chemical approaches were used to investigate the two series of alternating fluorene/carbazole oligomers and copolymers poly[2,7-(n-(2-methyl0-carbazole0-co-alt-2,7-m(9,9-dimethylfluorene), namely PFmCz (m-1,2) and gain a detailed understanding of the influence of carbazole units on the electronic and optical

properties of fluorene derivatives. The electronic properties of the neutral molecules, HOMO-LUMO gaps ($\Delta_{H\text{-}L}$), in addition to the positive and negative ions, were studied using B3LYP functional. The lowest excitation energies (E_g) and the maximal absorption wavelength λ_{abs} of PFmCz (m-1,2) were studied, employing the time-dependent density functional theory (TDDFT). The properties of the two copolymers, such as λ_{abs}, E_g, IP and EA were obtained by extrapolating those of the oligomers to the inverse chain length equal to zero (1/n = 0). The outcome showed that the carbazole unit is a good electron-donating moiety for electronic materials, and the incorporation of carbazole into polyfluorene (PF) backbone resulted in a broadened energy gap and a blue shift of both the absorption and photoluminescence emission peaks. Most importantly, the HOMO energies of PF1Cz and PF2Cz were both a higher average (0.4 eV) than polyfluorene (PF), which directly resulted in the decreasing of IP of about 0.2 eV more than PF, indicating that the carbazole units significantly improved the hole injection properties of the copolymers. In addition, the energy gap tended to broaden and the absorption and emission peaks were gradually blue-shift to shorter wavelengths with an increase in the carbazole content in the copolymers. This was due to the interruption of the longer conjugation length of the backbone in the $(F1Cz)_n$ series (Yang *et al.*, 2005).