CONCLUSIONS

Poly[2,7-(9,9-diethyllfluorene)-co-*alt*-2,5-pyridine] (PEFPy) was studied both in structural and energetic properties. The conformational analysis of 2-pyridine-(9,9'-diethylfluorene) (EFPy) monomer was performed at the semi-empirical (AM1), *ab initio* (HF/3-21G, HF/3-21G*, HF/6-31G, HF/6-31G*, HF/6-31G**) and density functional theory (B3LYP/6-31G and B3LYP/6-31G*). The results indicated that *ab initio* and density functional theory methods gave very similar potential energy curves and potential barriers. The local minima located around 0-30^{o} and 150-180^{o}. Whereas, semi-empirical (method) (AM1) revealed a different minima located around 30-45^{o} and 135-150^{o}

The ground-state geometries of PEFPy were fully optimized using semi-empirical (AM1), *ab initio* (HF/3-21G* and HF/6-31G*) and density functional theory (B3LYP/6-31G*). It was found that all molecules possess nonplanar structures. On the basis of ground state geometries, the HOMO-LUMO energies were calculated using density functional theory (DFT) method. The HOMO-LUMO energy gaps (Δ_{H-L}) were evaluated by the extrapolation of HOMO-LUMO energy differences to infinite chain lengths. It was found from the results that the extrapolation of HOMO-LUMO energy gaps, calculated by B3LYP with 6-31G, 6-31G*, 6-31G**, 6-31+G*, 6-31++G* and 6-311G* basis sets, based on AM, HF/3-21G* and HF/6-31G* optimized geometries gave an overestimated results as compared with experimental data (2.87 eV). On the contrary, B3LYP/6-31G* method with the B3LYP/6-31G* optimized geometries was found to be a suitable method to estimate the HOMO-LUMO energy gaps of PEFPy. The HOMO-LUMO energy gap calculated is 3.14 eV which is agree well with the experimental data.

ZINDO and TD-B3LYP using the optimized geometry (AM1, HF/3-21G*, HF/6-31G* and B3LYP/6-31G*) were found to be a method to estimate the energy of the singlet-singlet electronic transitions and maximum absorption wavelengths of PEFPy. The vertical excitation energies and maximum absorption wavelengths of PEFPy were obtained by extrapolating of those of the oligomers to the chain length

equal to zero (1/n = 0). Our polymeric values are in good linearity. Excitation to the S_1 state corresponds almost exclusively to the promotion of an electron from the HOMO to the LUMO. The first electronic excitation gave a large value of the oscillator strength. The HOMO possesses an antibonding character between subunits, which may explain the nonplanarity observed in ground state. On the other hand, the LUMO shows bonding character between the two adjacent rings, in agreement with the more planar S_1 state. TDDFT theoretical electronic transitions showed a good agreement with the experimental value. Whereas ZINDO/S gave the reasonable results which can be used to calculate the vertical excitation energy of large molecule.

The lowest singlet state was studied with the Singles Configuration Interaction (CIS). The results showed that the single bond inter-ring distances decrease while the double bond distances increase in the excited states and the polymer becomes quinoidal. Moreover, it is clearly to indicate that the lowest singlet excited state becomes nearly planar (CIS results) and more rigid.

Finally, the good agreement between the theoretical results and the experimental data seems to indicate that a rational design of the tunable light-emitting fluorescence derivatives and related polymers is possible and should then contribute to the development of organic light emitting diodes.

Systematic investigations on $(FPy)_n$ oligomers were performed for ground and several excited states starting from the monomer up to four repeat units. Full TD-DFT geometry optimizations on both the ground state and the lowest excited state were performed. The behavior of torsional angles has been discussed in detail. For the ground state, the computed torsional angle for the monomer is 14.4^o. A hydrogen bonded interaction between the hydrogen atom of the fluorene and the nitrogen atom of the pyridine is found. In the first excited state, a strong tendency to coplanarity is observed, which is in good agreement with the quinoide-like character of that state.

Electronic excitation from S_0 to S_1 corresponds to the HOMO-LUMO transition and possesses much higher oscillator strength than the other electronic

excitations. The HOMO shows antibonding character between rings, which explains the nonplanarity in the ground state. In contrast, the LUMO possesses bonding character between two adjacent subunits explaining the above-mentioned strong trend to planarity in the S_1 state.

Vertical excitation energies and fluorescence energies show very good linear relationship with 1/n (n is the number of repeat units). The extrapolated vertical excitation energies of 2.66 and 2.64 eV are somewhat lower than the experimental data. Increase of conjugation length leads to a decrease of fluorescence energies and computed radiative lifetimes. The values extrapolated to infinite chain length obtained from TDDFT/B3LYP/SVP and TDDFT/B3LYP/SVP+sp are 2.41 and 2.16 eV. The computed values are lower than the experimental results. Our investigations have shown that detailed and reliable calculations on the properties of electronically excited states of oligomer sizes relevant for comparison with experiment are possible nowadays. These investigations should also be regarded as a first step toward the dynamical simulation of absorption and fluorescence spectra under particular consideration of torsional broadenings.[41]