METHODS OF CALCULATIONS

Part A: Gaussian Calculations

1. Model Setup

In this study, fluorene-pyridine copolymers were investigated theoretically. The molecular structure of fluorene-pyridine derivatives is shown in Figure 3. Fluorene-pyridine oligomers were constructed by Gaussian View 03. The structural and electronic properties of fluorene-pyridine copolymers were performed using Gaussian03 (Frisch *et al.*, 2003) running on Linux PC 3.2 GHz.

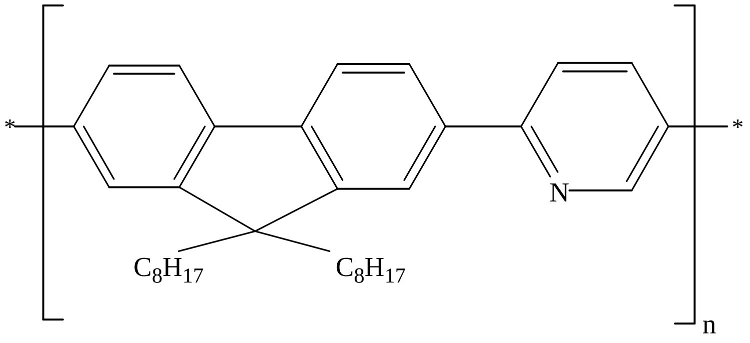

Figure 3 Molecular structure of Poly[2,7-(9,9-dioctylfluorene)-co-*alt*-2,5-pyridine] (POFPy), used in this study.

It has been proven that, long alkyl chains, such as hexyl or octyl groups that are often attached to fluorene units or hexyloxy or decyloxy groups on phenylene units, can be replaced with ethyl or ethyloxy groups respectively to reduce computational time. The presence of these long alkyl chains may enhance the solubility of these molecular systems or prevent unwanted aggregation effects, however, from a computational point of view, their replacement with shorter chains does not effect the optimized structures of backbones in their ground or excited states (Belletete *et al.*, 2000; Yang *et al.*, 2005). There is also experimental evidence (Zeng *et al.* 2002) that the length of the alkyl chain does not affect their optical properties such as the locations of absorption maxima. However, it can affect their emission spectra since some improvement in reducing the aggregation effect is observed as the alkyl chains get longer (Gong *el al.* 2005). Table 1 shows the HOMO-LUMO energy difference of 2-pyridine-(9,9'-diethylfluorene) (EFPy) monomer when the alkyl groups at 9-positions of fluorene increases. Consequently, the models used in this study are shown in Figure 4. In these calculations, the structural and electronic properties of Poly[2,7-(9,9-diethylfluorene)-co-*alt*-2,5-pyridine] (PEFPy) were investigated.

Table 1 HOMO-LUMO gap (ΔE, eV) of 2-pyridine-(9,9'-dioctyllfluorene) (FPy) monomer when alkyl groups (R) at fluorene unit increase. AM1 and HF/3-21G were carried out.

substituents	energy gap (eV)	
	AM1	HF/3-21G
H	8.06	8.37
C_1	8.04	9.80
C_2	8.04	9.80
C_3	8.04	9.81
C_4	8.04	9.81
C_5	8.04	9.81
C_6	8.04	9.81
C_7	8.04	9.81
C_8	8.04	9.81

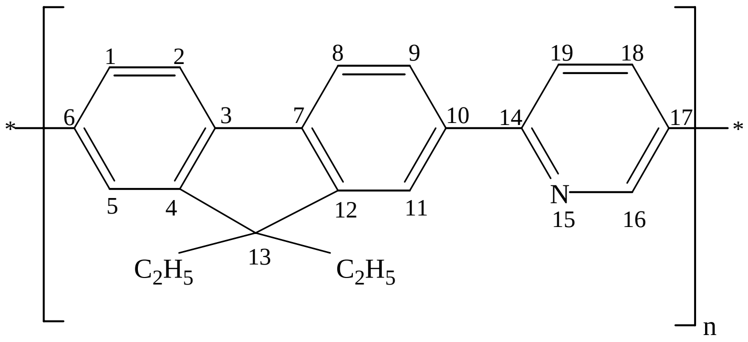

Figure 4 Molecular structure of Poly[2,7-(9,9-diethyllfluorene)-co-*alt*-2,5-pyridine] (PEFPy) and its atomic numbering used in this study.

2. Conformational Analysis and Geometrical Optimization

The conformational analysis of all 2-pyridine-(9,9’-diethylfluorene) (EFPy) monomer was done by changing the torsional angle ϕ by 15° steps. The geometries were fully optimized at each point. To obtain the final torsional angles of the conformer, calculations of these geometries were performed without constraint on the dihedral angles. The rotation angle, (θ = C_{10}-C_{11}-C_{14}-C_{15}) defines the relative orientation of the dyad subunits. The ground-state geometries of monomer was fully optimized using semi-empirical (AM1), *ab initio* (HF/3-21G* and HF/6-31G*) and density functional theory (B3LYP/6-31G*). The excited state of 2-pyridine-(9,9’-diethylfluorene) (EFPy) monomer was optimized by *ab initio* CIS/3-21G*, as implemented in GAUSSIAN 03 program running on Linux PC 3.2 GHz. The alkyl groups at 9 positions were replaced by ethyl groups to reduce the computational time.

3. Electronic Properties

3.1 HOMO-LUMO Energy Gaps and Vertical Excitation Energy

On the basis of ground state geometries, HOMO-LUMO energy gaps (Δ_{H-L}) of poly(2,5-pyridine-*alt*-(9,9’diethylfluorene) $(EFPy)_n$ were performed using the density functional theory (DFT). Additionally, the vertical excitation energies were calculated by ZINDO and TDDFT (B3LYP/6-31G*) calculations.

The estimated HOMO-LUMO energy gaps of the polymer were obtained by plotting the HOMO-LUMO energy differences of the oligomers against the reciprocal chain lengths. Correspondingly, the vertical excitation energies were also investigated in the same plot.

3.2 Optical Properties

The absorption spectra of poly(2,5-pyridine-alt-(9,9’diethylfluorene) $(FPy)_n$ were calculated using the ZINDO and TDDFT (B3LYP/6-31G*) calculations on the ground state optimized geometries. On the basis of excited state geometry, the emission wavelength of EFPy monomer was obtained by ZINDO and TDDFT (B3LYP/6-31G*) calculations. Absorption wavelengths of the corresponding polymers were obtained by extrapolating absorption wavelengths to infinite chain length (1/n = 0).

PART B: TURBOMOLE CALCULATIONS

1. Model Setup

Copol(2,5-pyridine-*alt*-fluorene) (PFPy) was constructed using Molden program. Figure 5 shows the molecular structure and atomic numbering of copol(2,5-pyridine-alt-fluorene) (PFPy) used in this calculation. The structural and electronic properties of copol(2,5-pyridine-alt-fluorene) (PFPy) were calculated using Turbomole program package.

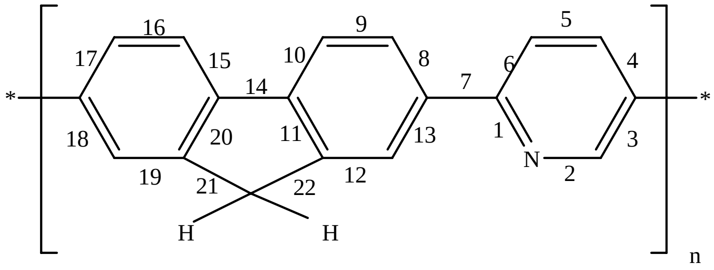

Figure 5 Molecular structure and atomic numbering of copol(2,5-pyridine-alt-fluorene) (PFPy) used in Turbomole study.

2. Conformational Analysis and Geometrical Optimization

Ground state and excited state potential energy curves of monomer and dimer along torsion angle were calculated using DFT and TDDFT with the B3LYP functional (Becke, 1992), respectively. In this calculation, the conformation analyses of monomer and dimer were done by changing the torsion angle by 30^{o} steps. Geometry optimizations were fully optimized using *ab intio* RI-CC2, DFT for the ground state and TD-DFT for excited state geometries with the B3LYP functional and the SVP basis set.

3. Electronic Properties (Vertical excitation energy and fluorescence transition)

The electronic absorption and luminescence spectra were computed at the TDDFT level. Vertical excitation energies were obtained based on the ground state optimized geometries. The fluorescence transitions were calculated at the vertical de-excitation based on the optimize structure of the excited states. The SV(P) (polarized split-valence) and SVP+sp (+diffuse) basis sets were used to perform vertical excitation transitions. Diffuse functions (one s and one p) which obtained from the lowest s and p exponents by division of a factor of 3 were added to the standard SVP basis set to improve the description of negatively charged molecular regions. The first 5 singlet-singlet electronic transitions were applied by TD-DFT approximations. The linearity between the calculated vertical excitation energies of the oligomers and the reciprocal chain length is excellent for all homologous series of oligomers.