THESIS

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

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The structural and electronic properties of the fluorene-pyridine copolymer, Poly[2,7-(9,9-diethylfluorene)-co-*alt*-2,5-pyridine] (PEFPy) and Copol(2,5-pyridine-*alt*-fluorene) (PFPy) were investigated by means of quantum chemical calculations. Geometry optimizations of these oligomers were performed for the ground state and the lowest excited state. HOMO-LUMO energy gaps, vertical excitation energies, absorption wavelengths and fluorescence energies are extrapolated to infinite chain length making use of their good linearity with respect to 1/n. It was found that fluorene-pyridine copolymers are non-planar in their ground state whereas a more pronounced trend toward planarity are observed in the S_1 state. Additionally, the quinoid-like structures are found in their lowest excited state. HOMO-LUMO energy gap calculated at B3LYP/6-31G* level is suitable for estimate the energy gap of PEFPy (3.14 eV). Furthermore, the vertical excitation energies as obtained from ZINDO/S and TDDFT give good agreement with experimental data. Vertical excitation energies of Copol(2,5-pyridine-*alt*-fluorene) (PFPy) as calculated by TD-B3LYP/SVP and TD-B3LYP/SVP+ are 2.64 and 2.66 eV, respectively, which are in good agreement with experimental results. Fluorescence energies and radiative lifetimes are calculated as well. The $S_1 \leftarrow S_0$ electronic excitation is characterized as a HOMO to LUMO transition and dominated in terms of oscillator strength. The obtained results indicate that the fluorescence energy and radiative lifetime of $(FPy)_n$ are 2.16 eV and 0.38 ns, respectively. The decrease of fluorescence energy and radiative lifetime with the increase in the chain length is discussed.

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