Wichanee Meeto 2010: Investigation on Electronic Structures and Properties of Poly(fluorenevinylene) Derivatives: Theoretical Studies. Doctor of Philosophy (Chemistry), Major Field: Chemistry, Department of Chemistry. Thesis Advisor: Associate Professor Supa Hannongbua, Dr.rer.nat. 136 pages.

A systematic study on the structural and photo-physical properties of model bifluorene-vinylene compounds based on the density functional theory (DFT) and its time-dependent version was presented (TD-DFT). The main aim of this work was the investigation of the direct influence of substitution using electron acceptor (CN) or electron donor (NH_2, OCH_3, OH) groups on the optimal geometry, torsional potentials and photo-physical properties. The ground state and the lowest singlet excited-state geometries of poly-(9,9-dialkylfluorene-2,7-vinylene) copolymer or PFV and its derivatives PFV-NH_2, PFV-CN, PFV-OCH_3 and PFV-OH were investigated based on density functional theory (DFT) and time-dependent DFT using B3LYP functional. The ground state and the lowest singlet excited-state geometries of the oligomers were optimized at the B3LYP/6-31G(d) and TD-B3LYP/SVP levels, respectively. The calculated ground state geometries favor the aromatic type structure, while the electronic excitations lead to quinoid type distortion, which exhibited a shortening of the inter-ring bonds (about 0.03 Å). Substitution on vinylene bridge, from the structural point of view, leads to the twisting of molecular fragment on the side of added group. Absorption and fluorescence energies were extrapolated to infinite chain length making use of their good linearity with respect to 1/n. The predicted energy gaps of the copolymer derivatives were calculated and compared to available experimental data. Fluorescence energies are 1.78, 1.77, 1.74, 2.00 and 1.73 eV and the predicted radiative lifetime are 0.6, 0.6, 1.0, 0.8 and 1.0 ns for PFV, PFV-NH_2, PFV-CN, PFV-OCH_3 and PFV-OH, respectively. The presented fundamental structural and electronic information can be useful in designing of novel optical materials as well as understanding of excitation-relaxation phenomena.

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