INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Thesis Title: **Chiroptical properties of helical-shaped π-conjugated systems based on five- and six-membered rings**

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SHORT ABSTRACT

This thesis talks about structure-property relations and excited-states properties including chiroptical properties of screw-shaped π-conjugated systems. Helical-shaped systems are inherently chiral due to their helical motifs. They have large applications in the various fields material chemistry such as, in organic light emitting diode, perovskite solar cell, bioimaging, fluorescent sensors, asymmetric synthesis etc.. In recent times, a large number of helical shaped systems have been developed and helicenes are widely studied examples of them. However, this thesis mainly focuses on absorption, circular dichroism (CD), and circularly polarised luminescence (CPL) properties studied in different levels of theories. Widely used pristine helicenes possess lower values of fluorescence quantum yield ($\Phi_{FL)}$ and dissymmetry factor for emission (g_{CPL}). Literature shows that designing of light-emitting molecules with higher values of Φ_{FL} and g_{CPL} is not an easy task. In recent times, various types of modified helical structures including multiple helicenes are reported. In case of single-helicenes, typical modifications are based on either increasing the number of π-conjugated rings (i.e., either helical length or lateral extension) or substitution of hydrogen atoms by other functionals groups. At this juncture, computational studies are very useful for studying and designing molecules with improved chiroptical properties. In this thesis, excited-states properties of screw-shaped pyridine-thiophene oligomers and various helicenes are reported. Effects of helical/lateral length extension and fluorine substitution on the ground and excited state properties are reported. The performance of these systems towards photoluminescence applications are measured by some key parameters, such as rotatory strength, g_{CPL}, and Φ_{FL}. Methods such as Density Functional Theory (DFT), time-dependent DFT (TD-DFT) and wavefunction based algebraic diagrammatic construction scheme of second order (ADC(2)) are used in these studies.

This thesis is divided into six chapters. Chapter 1 and Chapter 2 are about introduction, and theoretical and computational methodologies.

In chapter 3, structural and excited-state properties of pyridine-thiophene (PT) oligomers (n=1-5) are studied by using three different sets of DFT functionals. The DFT results are compared against the RI-ADC(2) result. Among the DFT functionals, CAM-B3LYP, M06-2X, and ωB97XD show results comparable to those obtained using RI-ADC(2). $(PT)_4$ shows the best results for both K_f and g_{CPL}.

In chapter 4, effects of heterocyclic ring fusion and chain elongation on structural and chiroptical properties of 9Ha are presented. Two laterally-extended (denoted as 9HaP and 9HaQ) and one helically-extended (denoted as 11Ha) derivatives are designed starting from the reported 9Ha molecule. Structural, charge transfer, and chiroptical properties of these four systems are studied at TD-DFT level. All the four compounds are found to be CD and CPL active. For 9HaQ and 11Ha, K_f values for the $S_1 \rightarrow S_0$ transitions get improved compared to that of the parent 9Ha, due to significant increase in the values of electric dipole transition moment. However, g_{CPL} follows the order of $|m|/|\mu|$, i.e., 9HaP>9Ha>11Ha>9HaQ.

In chapter 5, chiroptical properties of di-, tetra- and octafluorinated carbo[5-8]helicenes are explored at RI-ADC(2)/def2-TZVP level. Degree of fluorination is found to have different effect on different carbohelicenes. While K_f is found to increase with fluorination in 6H, g_{CPL} values in fluorinated 6Hs are foudn to be smaller than in 6H. However, in the cases of fluorinated 8H, both the g_{CPL} and K_f values improve simultaneously.

The last chapter contains a brief summary and concluding remarks of the thesis.