INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

Name of the Student	:	Indraneel Debnath
Roll Number	:	186122012
Programme of Study	:	Ph.D.
Thesis Title	:	Synthesis and tunable self-assemblies of *peri*-naphtho dyes
Name of Thesis Supervisor(s)	:	Dr. Kingsuk Mahata
Thesis Submitted to the Department/ Center	:	Chemistry
Date of completion of Thesis Viva-Voce Exam	:	20/11/2024
Key words for description of Thesis Work	:	Dye, supramolecules, self-assembly, *peri*-naphthoindigo, aldrone condensation

SHORT ABSTRACT

The thesis entitled "Synthesis and tunable self-assemblies of *peri*-naphtho dyes" is based on the derivatization of *peri*-naphthoindigo (**PNI**) dye, an analogue of popular and historic dye indigo. The results of the derivatization process are summarized in to four chapters.

Chapter 1 : In the first chapter, a boron difluoride complex of *peri*-naphthoindigo (**PNIBF$_2$**) was prepared, and its supramolecular chemistry was studied in both non-polar and polar solvent mixtures. In non-polar solvent mixtures, **PNIBF$_2$** aggregates into emissive and linear nanofibres, which have a higher extinction co-efficient compared to the monomer. On the other hand, in polar solvent mixtures, the molecule exhibited supramolecular polymorphism at a specific composition (76/24 water/THF) in which conversion from ellipsoidal to spherical shape was seen via heating and subsequent slow cooling. The polymorphism was accompanied by pathway complexity, and kinetic and thermodynamic forms of the aggregates were identified. This work highlights the potential of **PNI** derivatives as motifs in dynamic and functional supramolecular systems.

Chapter 2 : In the next chapter, a derivative of **PNI** was prepared with butyl groups attached to the *peri*-position of the naphthalene rings. The dye's (**BuPNI**) supramolecular interactions in non-polar solvent mixture were studied, providing fibre-like morphologies. The assembled fibrous aggregates responded to stimuli of both acid and fullerene. Toggling between the different morphologies was attempted via the action of both fullerene and acid together. A method was used to switch between two different supramolecular morphologies via introduction of acid from a remote location; diffusion of acid to and from an aqueous layer was used as the procedure for both removal and introduction of acid into the organic layer. This research work is compiled as an imitation of biological self-assemblies in that are sensitive to various stimuli, and rely on indirect input of said stimuli, thereby also ensuring both chemical and spectrosocopical reversibility of the dye solution.

Chapter 3 : A new class of dyes, *peri*-naphthoisatogens or **PNTI**, was developed, via an acid mediated reaction, and its preliminary photophysical properties were studied. Optimization of reaction conditions were carried out at different temperatures and with different acids. The dye **PNTI** was unique due to the absence of any C2 substitution, which was previously unknown. The reaction was carried out in acid mediated conditions, which was quite unique for a nucleophilic attack of the enol form of the acetyl group to the N-atom of the group, both of which are attached to the *peri*-positions of naphthalene. The reaction and successful isolation of product was only possible with an amine substituent at *para* to the nitro group. A derivative was also prepared for the **PNTI**, utilizing the reaction of 1,3-dipolar cycloaddition and ethyl acrylate as diene, to provide an aza-phenalenone. Both **PNTI**s and the aza-phenalenone derivative are moderately emissive and absorb in the visible region.

Chapter 4 : In the last chapter, the self-assembly property of **PNTI**s were investigated in details. The aggregation tendency of the dyes is highly dependent on the nature of the alkyl chain. Dye with short alkyl chain produced only J-aggregate in THF-water mixture. On the other hand, **PNTI**s with long alkyl chains produced both J- and H-aggregates, depending upon the composition of the THF-water in the solution. Up to a solvent mixture of 7:3 (v/v) water-THF, such **PNTI** only produced J-aggregate. But, the formation of H-aggregate was noticed when the solvent composition was changed in to 9:1 (v/v) water-THF. In an intermediate solvent composition, 83:17 (v/v) water-THF, the interconversion between the two aggregates were observed upon heating and cooling. Temperature induced switching between the aggregates also led to the change in the fluorescence properties. The non-emissive H-aggregates were converted into emissive J-aggregate upon heating. The change in fluorescence intensity as a function of temperature could be applied to the fabrication of fluorescence thermometer.