

# **Investigation of Intramolecular Aggregation Induced Fluorescence in Different Molecular Scaffolds**

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## **Abstract**

Aggregation-Induced Emission (AIE) represents a paradigm shift in fluorescence studies, where certain materials show enhanced luminescence upon aggregation, contrasting with the typical aggregation-caused quenching (ACQ) observed in most fluorophores. These unique emissive aggregates present opportunities for developing advanced fluorescent materials with tailored functionalities. This research provides a detailed molecular-level understanding of AIE processes, particularly within novel deep eutectic solvents (DESs), which are environmentally friendly alternatives to traditional solvents. The study employs various pyrene (Py)-appended molecules to explore intramolecular aggregation and the folding of long-chain entities, including macromolecules, in both hydrophilic and hydrophobic DESs as well as other common solvents. Additionally, the thesis introduces two innovative systems: a dipyranyl compound with strong fluorescence in its excited-state aggregate, and a novel peptidomimetic demonstrating unprecedented intramolecular aggregation of tryptophan (Trp) units.

The work systematically investigates hydrophilic and hydrophobic DESs, particularly those based on choline chloride and monoterpene mixtures, respectively. Each DES system provides different viscosity landscapes, making it possible to analyze both ground- and excited-state interactions. The first study in this thesis marks the inaugural experimental investigation of a dipyranylalkane [1Py(3)1Py] dissolved in choline chloride (ChCl)-based DESs. Two specific DESs were utilized: ChCl:Urea and ChCl:Glycerol (1:2 mole ratio). The research also examined glycerol alone and polydimethylsiloxane (PDMS2000) for comparison. In PDMS2000, 1Py(3)1Py exhibits exclusive excited-state aggregation, forming a classical intramolecular excimer. However,

in high-viscosity DESs and glycerol, intramolecular aggregation occurs but is not exclusive to the excited-state. Ground-state heterogeneity is evident, indicating weak Py-Py interactions in the ground-state. The high viscosity and/or extensive hydrogen-bonding network within DESs/glycerol are proposed as reasons for the observed ground-state interactions. Building on these findings, the second investigation explores the solvation characteristics of the industrially relevant polymer, PDMS, in ChCl-based DESs using a dipyrenyl fluorescence probe (Py-PDMS-Py). The study reveals that intramolecular aggregation of pyrenyl groups is influenced by the dissolution state of PDMS (coiled or uncoiled). In PDMS2000, dimerization occurs exclusively in the excited-state, while in DESs and glycerol, ground-state heterogeneity is observed. PDMS is predominantly in a coiled/tangled state in DESs and glycerol, while it prefers an uncoiled state in PDMS2000. Consequently, ChCl:Urea and ChCl:Glycerol are characterized as "bad" solvents for PDMS, while PDMS2000 acts as a "good" solvent.

Subsequently, the study extends the investigation to hydrophobic DESs (HDESs), introducing them into chemical reactions involving cyclization. A series of DESs composed of decanoic acid (DA), menthol (Men), and thymol (Thy), with varying molar compositions were investigated using a pyrene-labeled diene probe. Classical excimers form in all eleven studied DESs, with excimer formation dynamics adhering to the standard Birks' scheme at temperatures  $\geq 333.15$  K. Rate constants for intramolecular excimer formation ( $k_a$ ) are slightly higher than previously reported for the same probe in ionic liquids and tetraethylene glycols. An excellent linear correlation between  $\ln k_a$  and  $1/T$  indicates conformity to the Arrhenius expression for each DES, suggesting the suitability of HDESs for chemical applications.

A novel dipyrenyl compound (DTP), featuring disulfide and diamide functionalities, was introduced next. DTP exhibits high excimer-to-monomer intensity ratios  $I_E/I_M$  and rapid excimer

formation kinetics, particularly in polar solvents.  $I_E/I_M$  and  $k_a$  values strongly depend on solvent polarity and protic/aprotic nature. DTP demonstrates high sensitivity and selectivity for  $H^+$  recognition, making it an effective proton chemosensor. The compound also serves as an efficient microfluidity probe, demonstrated through monitoring of solvent mixtures and trace water detection in an ionic liquid and DES. The final study reveals a breakthrough in Trp-Trp intramolecular aggregate formation using a bispidine-derived bicyclic scaffold. The research observes the formation of a newly established Trp-Trp dimer and a low-energy absorbance band (320-420 nm) in both polar and non-polar solvents at low probe concentrations (25  $\mu$ M). Evidence of a "dark aggregate" is found in neat solvents. The study also demonstrates proton-induced modulation of fluorescence, resulting in a new low-energy fluorescence band upon  $H^+$  addition, with high selectivity and sensitivity of the probe towards  $H^+$ . These findings hold promise for future applications in areas such as fluorescence-based sensing, imaging in polar environments, and the development of stimuli-responsive systems. The thesis demonstrates the versatility of DESs in a variety of chemical processes, highlighting their potential as eco-friendly alternatives to traditional solvents. It provides a roadmap for future studies on molecular aggregation and the development of next-generation fluorescent materials in green solvent systems.