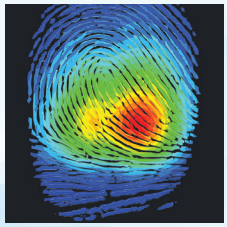
HORIBA

Fluorescence

Understanding the Relationship Between Molecular Structure and Aggregate Behavior in Nonconjugated Rhodamine Derivatives Unlocks Their Potential in Food Spoilage Detection



Application Note
Agricultural Sciences
FL-2024-4-4

Introduction

In the realm of materials science, the bottom-up molecular design paradigm has long been a cornerstone for developing new functional materials. However, recent studies have unveiled that the properties of certain organic molecules can dramatically change upon aggregation, leading to a new research frontier focusing on the relationship between molecular structure and aggregate behavior.

This application note summarizes a groundbreaking study in the world of food safety and conservation that delves into the aggregation-induced emission (AIE) phenomenon of nonconjugated rhodamine derivatives, sheds light on the underlying mechanism driving their luminescent properties and unlocks their potential in food spoilage detection.

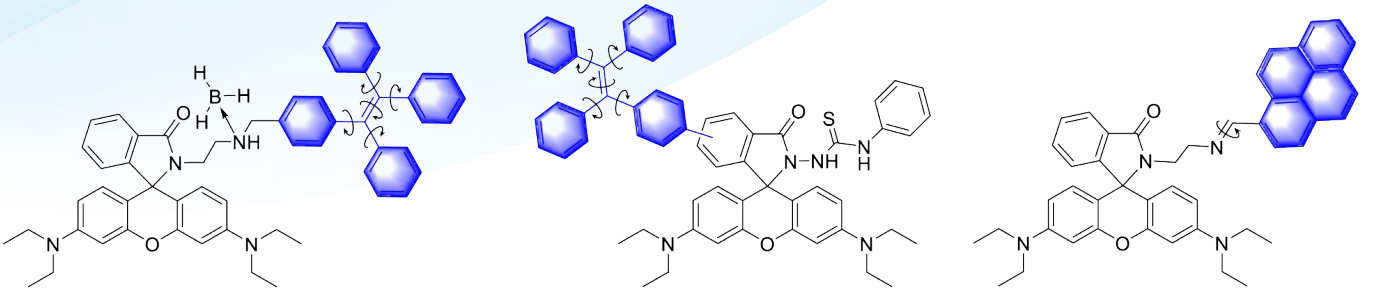
Study Overview

The study investigates the AIE properties of closed-form rhodamine-based compounds (Figure 1), which typically lack emissive behavior due to the absence of conjugated chromophores. Surprisingly, these compounds exhibit strong luminescence in the aggregate state, challenging conventional understanding. The research explores the mechanism behind this phenomenon and its implications for materials design and applications, particularly in food spoilage detection.

Methodology

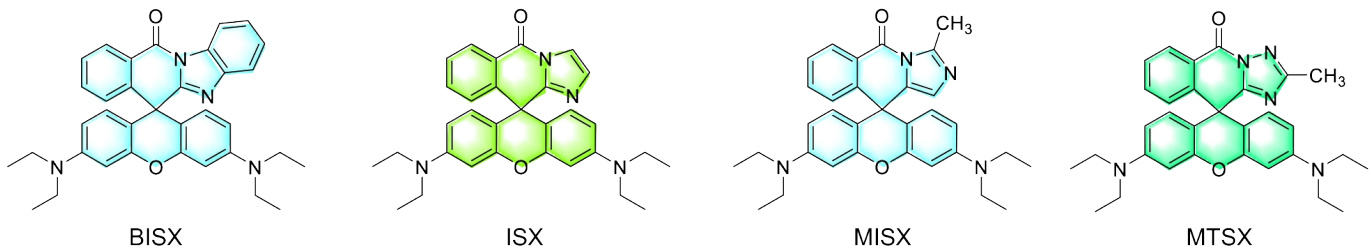
Fluorescence spectra were performed on a HORIBA QuantaMaster 8000. Fluorescence lifetimes were carried out with FluoroMax-TCSPC. Quantum efficiencies were acquired on a QuantaMaster 8000 using an integrating sphere apparatus.

(a). Previous Work (AIE active)



Angew. Chem. Int. Ed. 2016, *55*, 519 | *Chem. Sci.* 2017, *8*, 2047 | *ACS Appl. Mater. Interfaces* 2017, *9*, 8910

(b) This Work (AIE active)



BISX | ISX | MISX | MTSX

Figure 1. Chemical structures of the Rhodamine B-based AIEgens
(a) Previously reported work on Rhodamine B-based AIEgens via introducing rotors. (b) Unique rotor-free Rhodamine B-based AIEgens (BISX, ISX, MISX and MTSX) reported in this work. The filled colors indicate their crystal emission, respectively.

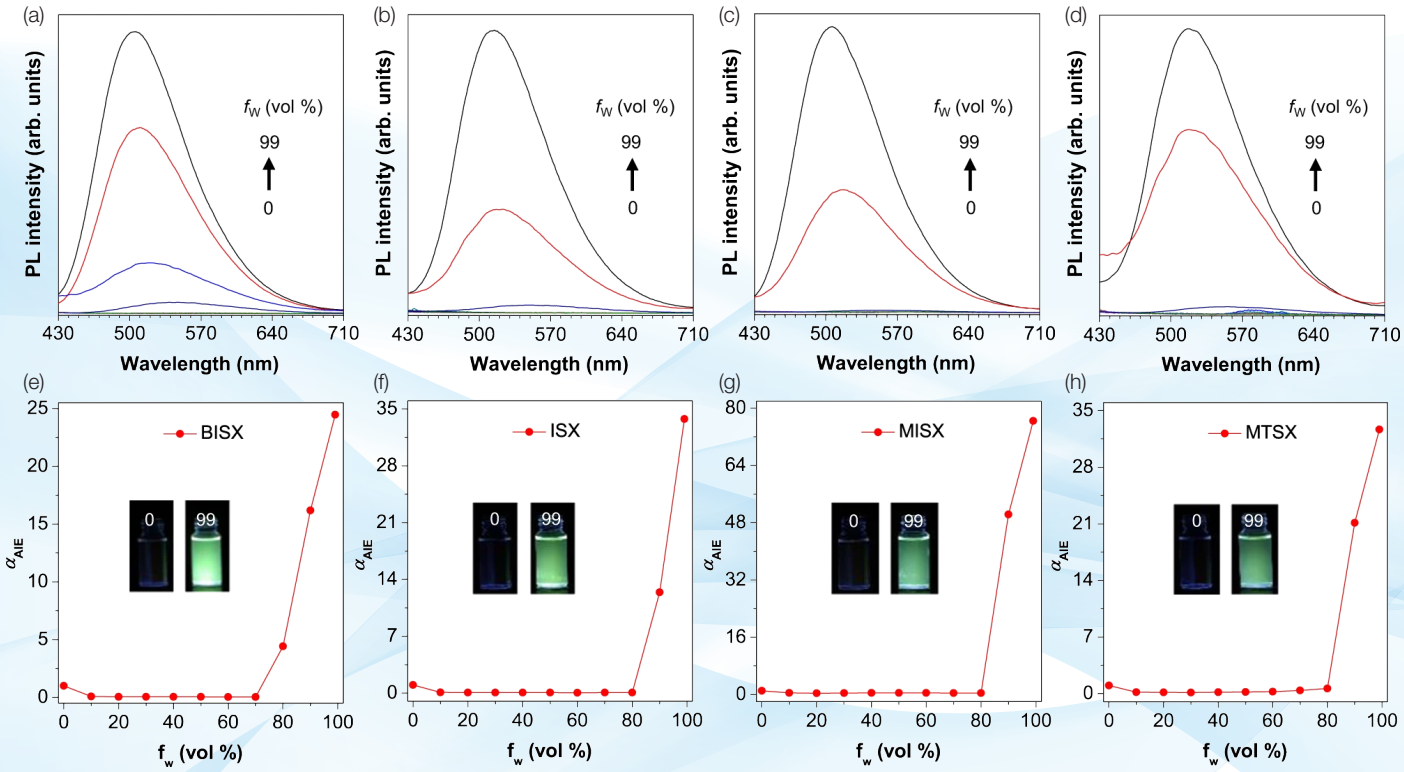


Figure 2. AIE features of BISX, ISX, MISX and MTSX
(a-d) PL spectra of BISX, ISX, MISX and MTSX in THF/water mixtures with different water fractions (f_w). Concentration (c) = 1x10^{-5} M, excitation wavelength (λex)=365nm. (e-h) Plots of relative PL intensity αAIE(I/I_0) versus f_w, where I_0 was the maximal PL intensity in the THF solution. Inset: fluorescence images of BISX, ISX, MISX and MTSX in THF/water mixtures with f_w = 0% and 99%, respectively.

Key Findings

Unique AIE Behavior: The closed-form rhodamine derivatives show AIE characteristics (Figure 2), with luminescence intensity increasing significantly upon aggregation, contrary to expectations based on their molecular structure.

Mechanism Investigation: Traditional explanations, such as the restriction of intramolecular motion (RIM) mechanism, fail to fully account for the observed AIE behavior. Instead, the study proposes a novel mechanism involving intramolecular charge transfer induced by molecular conformation changes upon aggregation.

Experimental Validation: Structural analysis, optical property investigations, and theoretical calculations support the proposed mechanism, highlighting the role of intermolecular interactions and molecular conformation changes in driving AIE.

Application in Sensor Development: The study demonstrates the practical utility of these AIE-active compounds by developing a sensitive food spoilage sensor based on their "turn-on/off" emission response to acid-base treatments (Figure 3).

Implications and Future Directions

The findings of this study provide valuable insights into unconventional AIE systems and offer a deeper understanding of the interplay between molecular structure, aggregation, and luminescent properties. By leveraging these insights, researchers can explore novel materials design strategies and develop innovative applications in various fields, including sensing, imaging, and optoelectronics.

Conclusion

The study represents a significant advancement in the understanding of AIE phenomena in nonconjugated rhodamine derivatives. By elucidating the underlying mechanisms and demonstrating practical applications, it paves the way for future research endeavors aimed at harnessing the unique properties of aggregated molecular systems for diverse technological applications.

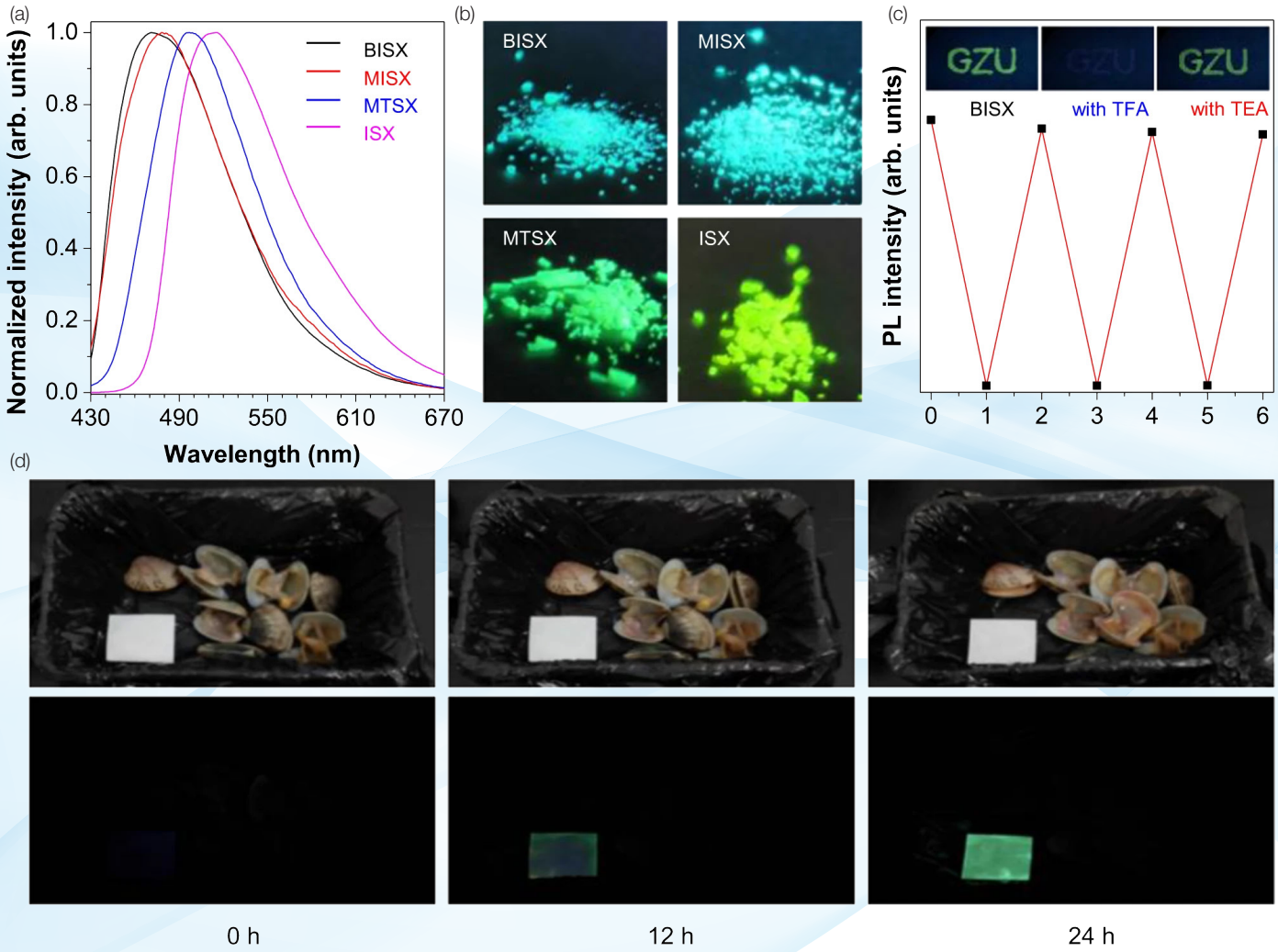


Figure 3. Dynamic responses of BISX to external stimuli
Normalized PL spectra (a) and fluorescence images (b) of BISX, ISX, MISX and MTSX in the aggregate state. Excitation wavelength (λex) = 365 nm. (c) Maximal PL intensity of BISX treated with trifluoroacetic acid (TFA) and triethylamine (TEA). Inset: fluorescence images taken under 365 nm UV irradiation, respectively. (d) Spoilage detection of clams in sealed packages for 24 h at room temperature using BISX. Photographs taken under daylight (upper) and 365 nm UV irradiation (bottom).

Availability

All data supporting the findings of this study, including experimental procedures, computational methods, and supplementary information, are available within the manuscript and supplementary files. The X-ray crystallographic coordinates for the reported structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and can be accessed via https://www.nature.com/articles/s41467-024-45271-6

This application note is based on the study Understanding the AIE Phenomenon of Nonconjugated Rhodamine Derivatives via Aggregation-Induced Molecular Conformation Change. Yang, LL., Wang, H., Zhang, J. et al. Understanding the AIE phenomenon of nonconjugated rhodamine derivatives via aggregation-induced molecular conformation change. Nat Commun 15, 999 (2024). https://doi.org/10.1038/s41467-024-45271-6 https://rdcu.be/dAP43