

Efficient Luminescence from Nanostructured Aggregates of Organic Luminogens

Ben Zhong Tang*, Yuning Hong, Jacky Wing Yip Lam

Department of Chemistry, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China.

Department of Polymer Science & Engineering, Zhejiang University, Hangzhou 310027, China E-mail: tangbenz@ust.hk

Abstract- It has been a textbook knowledge that chromophore aggregation generally quenches light emission. Here, we present an opposite phenomenon termed aggregation-induced emission (AIE) and identified the restriction of intramolecular rotation as a main cause for the AIE effect. Based on the mechanistic understanding, we explored the technological applications of the AIE luminogens as light-emitting and sensoric materials.

I. INTRODUCTION

Development of new organic luminescent materials has attracted considerable interest among scientists owing to their potential applications in organic light-emitting diodes (OLEDs).¹ Conventional organic conjugated molecules often exhibit remarkably bright emissions in their dilute solutions but become weakly or even nonemissive when fabricated into thin solid films.² The close proximity of the chromophores in the solid state often induces nonradiative energy transfer, resulting in self-quenching of the light emission. This has greatly limited the scope of their applications and it is therefore highly desirable to develop luminophores that can overcome this notorious “aggregation-caused emission quenching” problem.

Our group is interested in developing new organic chromophores that can emit efficiently in the solid state and have discovered an unusual phenomenon: a series of silole molecules are found nonluminescent in the solution state but emissive in the aggregate state (as nanoparticle suspensions in poor solvents or as thin films in the solid state).³ We coined “aggregation-induced emission” (AIE) for this novel phenomenon, because the nonemissive silole molecules are induced to emit by aggregate formation.⁴

Attracted by the intriguing phenomenon and its fascinating perspectives, we embarked on a program directed towards the decipherment of the working principle behind the AIE process, because the mechanistic understanding would help guide us to design new AIE luminogens and to explore their technological applications. In this paper, we briefly summarized what we have done in the area in the past years. We have identified the restriction of intramolecular rotation (RIR) in the aggregates as a main cause for the AIE phenomenon (Fig. 1), developed a large variety of new AIE luminophores based on the RIR mechanism, and demonstrated their utilities as multifunctional materials.

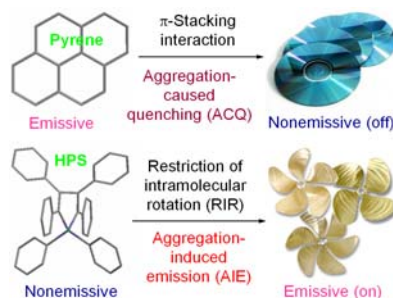


Fig. 1. Planar luminogens such as pyrene tend to aggregate just as discs pile up due to strong π - π stacking interaction, which commonly turns “off” light emission, whereas nonplanar propeller-shaped luminogens such as hexaphenylsilole (HPS) behave oppositely, with their light emissions turned “on” by aggregate formation, due to the restricted intramolecular rotation in the aggregates.

II. PHENOMENA

Hexaphenylsilole (HPS) is the first AIE luminogen developed in our laboratory. Solutions of HPS in its good solvents, e.g. acetonitrile, are nonemissive. Addition of large amounts of water into the acetonitrile solution of HPS causes its molecules to aggregate and induces them to emit efficiently (Fig. 2). Particle size analyses reveal the existence of particles with average sizes of 100–200 nm in the solvent mixtures with high water fractions, confirming that the HPS molecules have indeed aggregated into nanoparticles. In the solvent mixtures with water contents $\leq 50\%$, no nanoparticles are detected by the particle size analyzer, proving that the HPS molecules are genuinely dissolved as isolated species in the solvent mixtures with “low” water contents.

Closely related to the ACQ effect is the crystallization of dye molecules, which normally weakens their emissions. The crystals of the AIE molecules, however, emit in higher

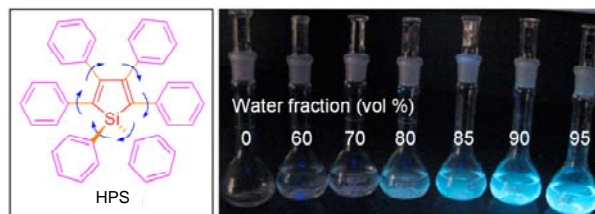


Fig. 2. (Left) Chemical structure of HPS. (Right) HPS solutions in the acetonitrile/water mixtures containing different volume fractions of water; photographs taken under illumination of a UV lamp.

Address: Hong Kong, China

*Contacting Author: Ben Zhong Tang

efficiencies than their amorphous counterparts.

III. MECHANISM

The novel AIE effects challenge our understanding of the photoluminescence processes. We have proposed that the restriction of intramolecular rotation of the peripheral phenyl rings in the aggregate state is the main cause for the AIE effect.

In the solutions, the multiple aryl blades of the silole molecules rotate around the single-bond axes linking the peripheral aryl rotors and the central stator of silacyclopentadiene core. The intramolecular rotation converts photonic energy to heat and deactivates the excited states nonradiatively, thus making the molecules nonemissive. In the aggregates, the intramolecular rotation is restricted and the nonradiative relaxation channel is obstructed. Owing to their propeller-like shapes, the silole molecules experience little π - π stacking interactions in the condensed phase and thus have little chance to form excimer species. The activated RIR process and the reduced likelihood of excimer formation cooperatively make the silole molecules highly emissive in the solid state.

This hypothesis has been verified by our experimental evidence. External controls by lowering the temperature, increasing the solution viscosity, and pressurization have boosted the emission of AIE molecules efficiently. Internal structural perturbation by molecular structural endeavour can also alter the photophysical behaviors of the AIE molecules, turning them into AIE-inactive. All the imposed stimuli restrict the intramolecular rotations of the phenyl rotors, which block the nonradiative channels and thus populate the radiative decay of the excitons.

Based on the mechanistic understanding, we developed a series of new fluorescent and phosphorescent AIE systems, examples of which include fulvene, tetraphenylethylene, and butadiene (Fig. 3). By attaching different substituents, dye molecules with emission colours covering the entire visible spectral region with high luminescence solid-state quantum yields up to unity are generated.

IV. APPLICATIONS

The AIE luminogens are highly emissive in the aggregate state. This unique characteristic differentiates them from the conventional luminophores and makes them ideal candidates for high-tech applications in practically useful solid state. While many possibilities can be imagined for the AIE systems, we have mainly explored their high-tech applications as luminescence sensors and in light-emitting devices.

The applications of the AIE luminogens are exemplified in Fig. 3, which include fluorescence sensors (for explosive, ion, pH, temperature, viscosity, pressure, etc.), biological probes (for protein, DNA, RNA, sugar, phospholipid, etc.), immunoassay markers, PAGE visualization agents, polarized light emitters, monitors for layer-by-layer assembly, reporters for micelle formation, multistimuli-responsive nanomaterials,

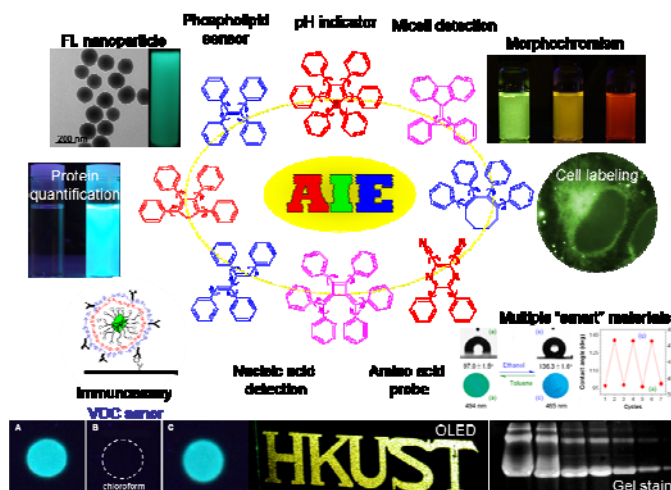


Fig. 3. Examples of AIE-active luminogens and their applications.

and active layers in the fabrication of organic light-emitting diodes.

V. CONCLUSION

In this work, we have discovered a novel AIE phenomenon. We have proposed that the RIR process accounts for the AIE effect and have designed a series of experiments to validate our hypothesis. On the basis of our mechanistic understanding, we have developed a variety of new AIE luminogens and explored their potential applications as chemical sensors, biological probes, smart nanomaterials, and solid-state emitters. The AIE effect offers a new platform for study of solid-state luminescence. We enthusiastically expect new discoveries by other and our research groups and are looking forward to new exciting advancements in the area of AIE research.

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