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The Mechanistic Understanding of the Importance of Molecular Motions to Aggregation-induced Emission

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1.1 Introduction

Molecular motions drive most natural processes, ranging from the formation and annihilation of astronomical objects to the metabolism of microbes. All kinds of intra- or intermolecular interactions induce molecular motions in specific forms, through which the energy is generated and transformed. Mechanistic understanding and manipulation of molecular motions can lead to the effective design of smart molecular systems to achieve programmed tasks, as well as dynamic control of multiple processes. Indeed, by employing the light as a stimulus, researchers have developed a variety of functional molecular machines (e.g. molecular motors, molecular switches, molecular shuttles, and supramolecular assemblies) to achieve effective control of catalysis activity and chirality transfer in various practical applications, in which the dynamic manipulation of diverse molecular motions is critical [1].

For organic luminescence processes, molecular motions also extensively affect the photophysical behaviors for organic luminophores and govern the excited-state decay pathways, including vibrational relaxation, internal conversion, intersystem crossing, kinetic quenching, etc.[2]. Upon photoexcitation, the coupled nuclear and electronic motions will drive the excited molecules to evolve through radiative and nonradiative pathways [3]. However, traditional photophysical research usually focuses on the highly rigid and conjugated molecules and investigates the targets in the gas phase or solution, in which the importance of intramolecular motions to the luminescence is less considered, and the variation of molecular motions in the solid state is often ignored [4]. In 2001, the discovery and proposal of aggregation-induced emission (AIE) triggered the research on molecular motions and photophysical studies in the aggregate or the solid state [5]. The luminogens with the AIE property (AIEgens) often show different scales of molecular motions in different phases. Vigorous intramolecular motions in the solution can nonradiatively dissipate excited-state energy and always result in weak light emission, whereas such motions can be restricted in the solid state due to the environmental constraints so that the emission can be strongly enhanced [6].

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The restriction of intramolecular motion (RIM) has been concluded as the most widely accepted and applicable mechanism for the AIE phenomenon through numerous experimental and theoretical exploration, and the strong electron-vibration coupling (EVC) between the excited and the ground state has been revealed to be the quantum origin of the weak emission of AIEgens in the solution [3, 7]. Recently, the connotation of RIM has been further clarified with deeper mechanistic insights into various novel AIEgens. The nonadiabatic excited-state molecular dynamics [8] and theoretical model based on multiple electronic states [9] have been employed to elucidate the dynamic evolution of excited states through molecular motions of tetraphenylethylene (TPE) derivatives and heteroatom-containing AIEgens. Meanwhile, the aromaticity reversal in the excited state [10] and the anti-Kasha emission from higher excited states [11] have provided another proof for the enhanced emission efficiency in the solid state for AIEgens. Apart from the critical effect on the nonradiative decay, molecular motions have also been verified to promote the electronic transition process [12, 13]. The excited-state through-space conjugation facilitated by excited-state molecular motions has been proved to contribute to the enhanced visible light emission of a series of nonconjugated AIEgens [13].

In this chapter, we will take a journey of mechanistic studies for AIE from the general RIM to mechanisms developed recently and propose the perspective on the further exploration in the future.

1.2 Restriction of Intramolecular Motion

When we look into the AIE phenomenon, two essential questions arise: why do the AIEgens show none or weak emission in the solution? Why does the aggregation brighten the light emission of AIEgens? Enthusiastic efforts have been devoted to deciphering the AIE mechanism. Several possible mechanisms have been proposed, including intramolecular conformation planarization, J-aggregate formation, *E*/*Z* isomerization, and excited-state intramolecular proton transfer, but they are only applicable for specific molecular systems [6c]. A general working mechanism for AIE is highly desired for fundamental understanding and material designing.

Upon absorption of photons, the excited molecule will decay through radiative and nonradiative paths or the photochemical process [2]. Hence, AIEgens in the solution may mainly undergo nonradiative decay or photochemical reaction to dissipate the majority of energy. Once aggregation occurs, the nonradiative decay paths can be blocked, or the radiative paths can be facilitated so that the emission can be enhanced. As the structure determines the property, typical AIEgens own flexible structures, containing multiple rotor or vibrator substituents, like hexaphenylsilole (HPS) and TPE, which endow them with high flexibility and potential to consume energy through intensive intramolecular motion, whereas multiple intermolecular interactions exist in the aggregate state, which can serve as constraints to molecular motions detrimental to the emission [6]. Continuous experimental exploration has been made through manipulation of the molecular motions by adjusting environmental factors, including hydrophobic interaction, temperature, viscosity, pressure, host–guest interaction, and intramolecular constraints such as substituent steric hindrance, ring closing, conjugation effect, and so on [14]. With persistent effort, Tang and coworkers have proposed the restriction of intramolecular rotation (RIR), the restriction of intramolecular vibration (RIV), and, finally, concluded that the restriction of intramolecular motion (RIM) was the general working principle for AIEgens [15].

1.2.1 Restriction of Intramolecular Rotation

Investigation of the effect from molecular motions on luminescence processes has drawn increasing interests. The less conjugated structures and intrinsic steric congestions are responsible for the high conformational flexibility of AIEgens.

Taking HPS as the model AIEgen [14a] as shown in Figure 1.1, when HPS is fully dissolved in the THF solution to form the isolated molecular species, it shows almost no emission. With increasing water gradually into the dilute solution and keeping the same concentration, the HPS molecules tend to aggregate due to the hydrophobicity. When the water fraction reaches 60%, notable aggregate forms and the quantum yield of the whole system starts to increase. Further increasing the water fraction, the light emission is continuously enhanced due to the further aggregation. According to general physics, any form of motion can consume energy. When we look into the structure of HPS analyzed from the X-ray diffraction, it can be found that six phenyl rings are attached to the central silole ring through single bonds with large dihedral angles, which allow free torsion or twisting motions, indicating that motions of phenyl rings are responsible for the energy dissipation in the solution state. With increasing the solvent viscosity by adding the glycerol into the solution or decreasing the temperature of the solution from room temperature to −196 °C, the emission of HPS-2 can be gradually enhanced due to the constraints coming from the highly viscous solvent or rigidified solvent environment at the low temperature. Furthermore, introducing

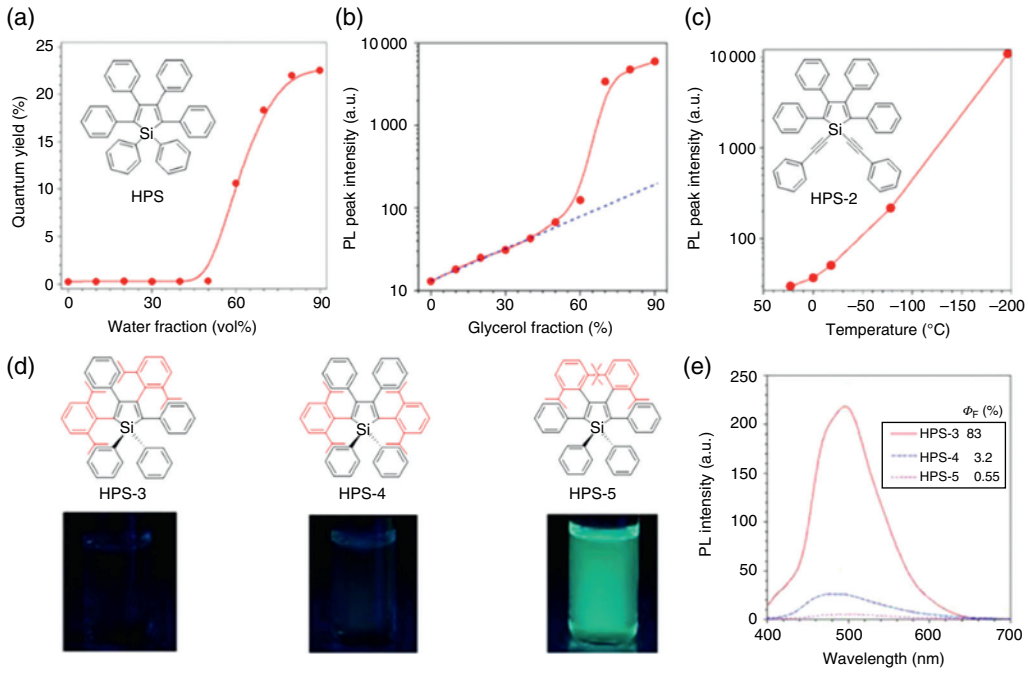

Figure 1.1 (a) Fluorescence quantum yield of HPS in the acetone/water mixtures with different water fraction. (b) Photoluminescence peak intensity of HPS in the glycerol/methanol mixtures with different glycerol fraction [HPS] = 10^{-5} M. (c) Photoluminescence peak intensity of HPS-2 in the 1,4-dioxane solution at different temperatures. [HPS-2] = 10^{-5} M. *Source:* Adapted from Ref. [14a] with permission from American Chemical Society. (d) Chemical structures and fluorescence photos. (e) Photoluminescence spectra of HPS 3–5 in the acetone solution (10^{-5} M). *Source:* Adapted from Ref. [14c] with permission from American Chemical Society.

internal steric hindrance shows a similar effect by attaching the isopropyl groups onto the 2,3,4,5-positions of the central silole as presented in Figure 1.1d and e [14c]. Crowdedness induced by the bulky groups hampers the torsion of the phenyl rings, then the nonradiative decay process can be restricted, and the emission can be restored.

TPE is another prototype of AIEgens with a similar intrinsic structure as HPS. Four phenyl rings are connected with the central double bond in a highly twisted conformation. As presented in Figure 1.3a, upon excitation, four phenyl rings can drastically twist against the double bond. Meanwhile, the C=C double bond will be weakened due to the photoexcitation, which endows it with strong twisting ability to reorganize the conformation. All these intramolecular motions result in the undetectable emission for TPE in the dilute solution. However, its emission can be dramatically boosted once the aggregation occurs. Further locking the adjacent phenyl rings through chemical bonds or attaching bulky groups onto the phenyl rings of TPE, its emission can be enhanced even in the solution [16]. All these experiments of controlling the internal or external constraints to the intramolecular motions have proved that the RIR mechanism is responsible for the AIE effect of the rotor-based AIEgens.

1.2.2 Restriction of Intramolecular Vibration

Apart from the intramolecular rotation, the intramolecular vibration in the luminogens-lacking rotors can also cause emission quenching in the dilute solution. Bu et al. have found that two coumarin derivatives fused with five-membered and seven-membered alkyl rings, respectively, show totally different photophysical behaviors, despite their similar conjugation degrees in the ground state, as indicated by the similar ultraviolet (UV)–vis absorption spectra presented in Figure 1.2 [10a].

The compound CD-5 with a five-membered ring is much more rigid and can show strong light emission in the dilute solution, but its emission is weakened in the solid, whereas the CD-7 is almost nonemissive in the dilute solution, but it can show enhanced light emission in the solid state. The calculated conformations of these two derivatives have revealed that the CD-7 with seven-membered ring owns much higher vibrational flexibility in the excited state. The central π-conjugated plane of CD-7 will suffer the vibrational motion with a dihedral angle of around 18°, so its emission can be easily quenched in the dilute solution. But such intramolecular vibration can be efficiently restricted in the solid state, which finally leads to the AIE phenomenon. The mechanism for such AIEgens-lacking rotors has been concluded as the RIV.

However, it remains unclear what the driving force is for the vigorous molecular motions on the excited state. Zhao et al. have recently systematically investigated the structure–property relationship of a series of annulene-based AIEgens and figured out the driving force of the strong vibrations in the excited state [10]. The parent cyclooctatetrathiophene (COTh) contains an eight-membered ring fused by four thiophene rings and takes a noncoplanar and saddle-like conformation as presented in Figure 1.3b. Such a highly twisted structure makes COTh nonaromatic in the ground state. The COTh shows typical AIE behavior that it can only emit negligible light in the dilute solution but shows enhanced green emission in the aggregate and solid film. The optimized structure of COTh in the ground state is similar to its single crystal structure, whereas it can relax to a transition state with a planar conformation, and finally decay through fast nonradiative pathways to the ground state. Through the calculation of the nucleus-independent chemical shift (NICS) and anisotropy of the induced current density (ACID) to characterizing the aromaticity of the structures, it has been revealed that the aromaticity reversal from the ground state to the excited