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Aggregation induced emission (AIE) characteristics and main working mechanism for AIE: Restriction of intramolecular rotation

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Abstract

Luminogenic materials with aggregation-induced emission (AIE) have been paid much attention since it was first discovered by Tang *et al* in 2001. Attracted by fascinating potential, many groups have worked on the structure-property relationships, working mechanisms, and operating principles of the AIE process to design and synthesize new AIE luminogens with efficient luminescence. Restriction of intramolecular rotation (RIR) was proposed as the main mechanism for the AIE phenomenon. In this review, we will focus on this mechanism, discuss more details about the structure-property relationship of several typical compounds to deep insight into the RIR mechanism.

Keywords: Aggregation induced emission, working mechanism, restriction of intramolecular rotation

Introduction

Light is not only useful but also a mysterious process to humankind. Classic studies of organic luminescence have generally been conducted in the solution state. For example, photophysical parameters, such as exciton lifetime, decay rate, and luminescence efficiency, have usually been studied in very dilute solutions where luminogens molecules can be approximate as isolated single molecular. The investigation in solution has made great contributions to the fundamental understanding of the luminescence process at a molecular level.

However, the use of dilute solutions caused many problems. For example, emission efficiency in dilute solution is often weak, leading to poor sensitivity in the sensor ability of the system [1, 2]. The sensitivity cannot be enhanced by using high fluorophore concentration due to the notorious concentration-quenching effect. A molecule quenches its fluorescence at a high concentration due to aggregation formation [3, 4]. The phenomenon of aggregation-caused quenching (ACQ) was first observed in the fluorescence of pyrene by Forster and Kasper in 1954 [5]. Common organic dyes show marked concentration quenching effects, which are summarized by Birks in his classic book on Photophysics of Aromatic Molecules in 1970. Even in the dilute solutions, concentration-quenching still occurs. For example, the small fluorophore molecules may accumulate on the surfaces of the biomacromolecules and cluster in the hydrophobic cavities, leading to the increase of local fluorophore concentration and causing the concentration-quenching problem [6, 7]. The aromatic ring of the fluorophore with discs-like shapes have strong π-π stacking interaction which promotes the formation of aggregates. The excited state of aggregates decays mainly via non-radiative pathways caused quenching of light emission [8, 9]

The luminescence of molecules is normally investigated in the solution state. However, in practical application, they are often used as materials in the solid-state, such as thin-film layer in organic light-emitting diodes (OLEDs) [10-13], and fluorescent diagnostic kits [6, 7, 14]

To reduce the ACQ effect, various chemical, physical, and engineering approaches have been developed. For example, branched chains, bulky cycle, spiro links, and dendritic wedges have been covalently attached to aromatic rings to hampered the aggregation formation [15-17] Research efforts to obstruct chromophore aggregation have been investigated and ended with limited success because organic luminophores with conjugated structures naturally aggregate in the solid-state and aqueous media. In many cases, aggregation was impeded only partially or temporarily [16–19] the difficult fact is that aggregation formation is an intrinsic phenomenon when luminogenic molecules are in the condensed phase. It will be great if chromophore aggregates can luminescence efficiently. In 2001, Tang *et al*. found the uncommon emission behavior of silole derivatives which is opposite to common law: a series of silole molecules were found to be non-luminescent in the solution state but emissive in the aggregated state [20, 21]. Tang *et al*., stated the term "aggregation-induced emission" (AIE) for this phenomenon. The AIE effect is opposite to the notorious ACQ effect, which makes it possible for the technologist to actively utilize the aggregation process. After the first discovery of AIE by Tang *et al*., more research on AIE processes has been investigated such as structure-property relationships, working mechanisms [22-24]. This information was very useful to design the molecular structure for the development of efficient luminogens. In the previous research, different classes of AIE luminogens and briefly discussed their plausible working principles have been presented [25] Especially, the restriction of intramolecular rotation (RIR) has been proposed to be the main cause for most of the reported AIE systems even though detailed mechanisms need to be further elaborated.

This small review focuses on the working mechanisms and operating principles of AIE processes, mainly paying attention to the restriction of intramolecular rotation.

Restriction of intramolecular rotation

It is well known that all movements consume energy [26, 27]. Generally, typical AIE luminogens include several small aromatics and constituent small aromatic rings which acts as excitation-energy dissipater. The majority of AIE luminogens in the solution phase are none missive or weakly emissive because of strong interactions between flexible AIE luminogens and neighboring solvent molecules [28, 29]. On the other hand, after aggregation formation of AIE luminogens, the restricted intramolecular motions of constituent small aromatic rings in aggregates induce structural rigidity. Consequently, the nonradioactive decay processes decelerated and the portion of radiative decay during excitation energy relaxation increased.

As discussed above, traditional luminogens are usually flat disk-like aromatic molecules which lead to the ACQ effect due to strong π-π intermolecular interaction in concentrated solution or in aggregate form. Introduction of freely rotatable tetraphenylethene (TPE) to conventional luminogens quenched their light emission in the solution but endows the resultant molecules (TPEArs) with AIE characteristics in the condensed phase with fluorescence quantum yield values up to unity (Figure 1, Table 1) [29]. The restriction of intramolecular rotation is responsible for such a molecular rotor system.

Internally, a covalent linkage can change molecular conformation, hinder intramolecular rotation and hence, block the radiation less relaxation channels and enhance the emission intensity. The fluorescence intensity of biphenyl (47) increased 4.4 times when a methylene linkage was introduced (48) (Figure 2) [30]. Similar effect was observed for pair of compounds 49 and 50 [31]. Therefore, Methylene Bridge made 48 more planar and rigid, resulting in enhance the fluorescence intensity. Additionally, the quantum yield compounds 49 and 50 are respectively lower than those of 47 and 48, probably due to the introduction of flexible 2, 2-diphenylethylenne units to the molecular structures 49 and 50. Thus, the emission efficiency change rapidly when adding the flexible rotors to the molecular structure. Another similar example was observed in pair of silolle derivatives (Fig 3) [32, 33]. The emission is completely quenched when two more phenyl rings were added to the 3,4-position of silole core.

Table 1: Opticle properties of TPEArs in solution (Soln), [a] crystalline (Cryst), [b] and film (Film) [c] states

	λabc (nm) SoIn	λcm (nm)			ϕ_F (%)	
		SoIn	Cryst	Film	SoIn[d]	Film[e]
TPEPy[f]	348	432	443	468	0.34	100
TPEAn[g]	387	423	428	450	0.28	100
TPEPa	323		444	481	0.033	88
TPENp	321		452	469	0.022	83
TPECa	337		440	468	0.045	100
TPEIq	331		445	471	0.019	20

A, in THF (10 μM) solution. b) Grown from methanol-dichloromethane mixture. e) Film drop-casted on quartz plates. d) Quantum yields determined in THF using 9, 10-diphenylanthracence (ϕ_F = 90% in cyclohexane) as standard. e) Quantum yields of the films measured by integrating sphere. f) For its pyrene parents, ϕ_F = 32% in solution. g) For its anthracence parent, ϕ_F = 36% in solution [29]

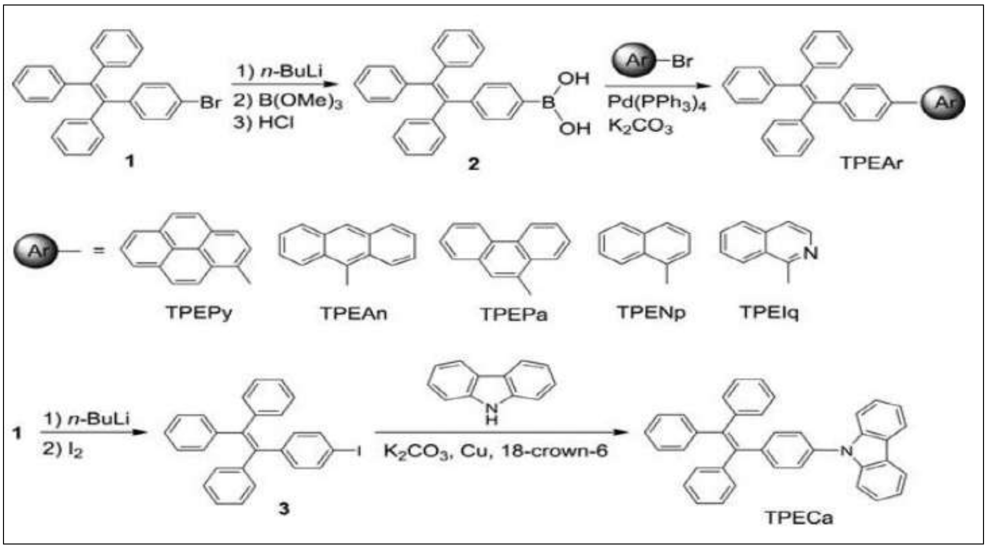

Fig 1: Synthetic routes to the TPE-substituted planar luminogens (APEArs) [29]

A series of experiments have been performed on model luminogens hexaphenylsilole (HPS) to externally and internally modulate the intramolecular rotations. Several parameters were investigated such as solvent viscosity, temperature, and pressurizing solid film. The results showed HPS emitted more efficiently in a more viscous solvent, at a lower temperature, and under high pressure, indicating that RIR was the main cause for the AIE effect of HPS [34-36] Nonplanar geometry of constituent aromatic rings in AIE luminogens was very useful to prevent the ACQ due to strong intermolecular π-π interactions between AIE luminogens and RIR [35, 37, 38].

Therefore, many AIE systems can be explained by the RIR mechanism [39]. However, some AIE systems cannot be fully interpreted by the RIR process (Fig 4) [40, 41]. THBA molecule is composed of two flexible parts; in each part, two phenyl rings are attached by a bendable flexure. The flexure of the molecule allowed 2 phenyl rings to vibrate dynamically. In the aggregate form, the intramolecular vibrations (RIV) become restricted. As a result, the radiation less pathway was blocked and the radiative decay channel was opened, which enhance the emissive intensity of the compound.

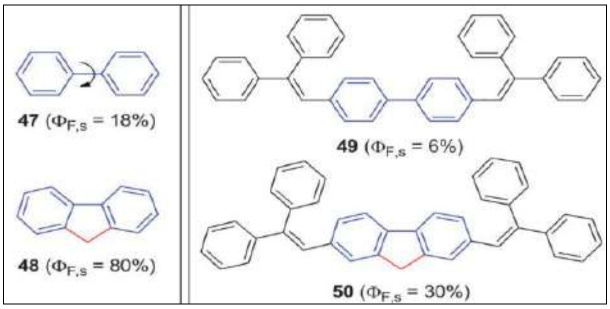

Fig 2: Examples illustrating RIR effect on luminescent behaviors of biphenyl-based luminogens [30, 31].

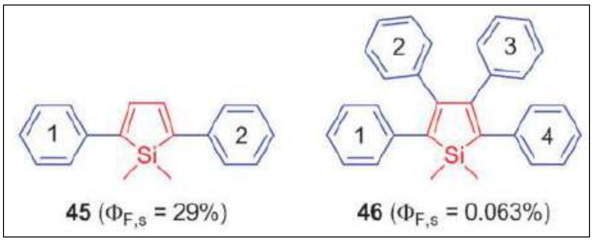

Fig 3: Effect of number of peripheral phenyl rotors on luminescence behavior of silole luminogens [32, 33].

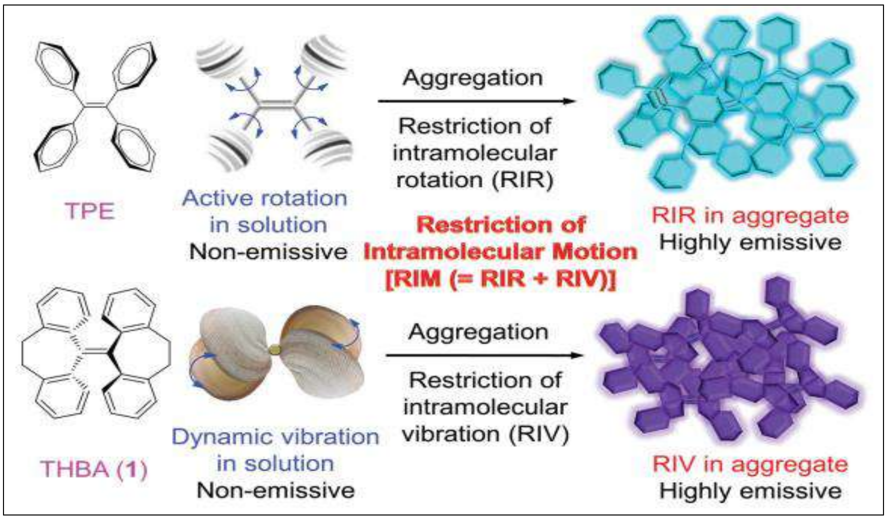

Fig 4: Propeller-shaped luminogens of tetraphenylethene (TPE) is non-luminescent in a dilute solution but becomes emissive when its molecules are aggregated. Shell-like luminogens of 10, 10', 11, 11'-tetrahydro-5,5'-bidibenzo[a, d] [7] annulenylidene (THBA) behaves similarly due to restriction of intramolecular vibration [40, 41]

Until now, various AIE mechanisms were proposed by different research groups to draw a picture on the light emission processes such as the restriction of intramolecular rotation (RIR), restriction of intramolecular vibration (RIV), J-aggregate formation (JAF), twisted intramolecular charge transfer (TICT) and excited-state intramolecular proton transfer (ESIPT) which are summarized more detailed in several highly qualified reported paper [42-44]. It is shown that restriction of intramolecular rotation is the major cause to explain AIE phenomena.

Conclusion

The study of the AIE phenomenon is of academic value. In this review, we briefly look at the ACQ effect as well as the AIE effect. In addition, we discussed several typical AIE compounds whose emission intensities are well explained by RIR. The mechanistic picture of the AIE process has become clear: The restriction of intramolecular rotation in the aggregate form suppresses their molecular motions and rigidifies their molecular structure, which activates the radiative decay channels and passivates the non-radiative decay channels. As a result, the emission intensity increase when the molecules are in the aggregate form.

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