New tetraphenylpyridinium-based luminogens with aggregation-induced emission characteristics

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The research on aggregation-induced emission (AIE) has drawn increasing interests in the past decade. With the efforts scientists paid, a variety of AIE systems have been developed, among which the tetraphenylethylene and silole derivatives are the most studied. Development of new AIE systems could further enrich the AIE molecules and promote the development of AIE area. In this communication, we prepared a new AIE system based on 1,2,4,6-tetraphenylpyridinium ions according to the restriction of intramolecular rotation mechanism. These molecules could be facily synthesized via one-step and one-pot reaction. The ionic AIE-active molecules could find wide application in sensing and optoelectronic areas.

aggregation-induced emission, cation, restriction of intramolecular rotation, tetraphenylpyridinium

1 Introduction

Development of efficient luminescent materials in the solid-state is a hot research topic because of their promising practical applications in organic light-emitting diodes (OLEDs), organic solid-state lasers, chemical sensors, biological probes, logic circuitry, etc [1–6]. With the enthusiastic efforts scientists paid, tremendous fluorogenic dyes have been generated. However, many of them are highly emissive when dissolved in good solvents but faintly luminescent or totally nonemissive when increased the concentration or aggregated in poor solvents. This is the thorny problem of aggregation-caused quenching (ACQ) effect, which should be properly tackled because these materials are commonly

used as solid films in their real-world applications [7, 8]. Various chemical, physical, and engineering approaches (e.g. attachment of alicyclic pendants, encapsulation by amphiphilic surfactants, and blending with transparent polymers) have been taken to alleviate the ACQ effect. These attempts, however, have met with limited success [9–11]. Dye aggregation is a spontaneously occurred physical phenomenon in nature. It will be better if the dye aggregation plays a positive instead of negative role for its emission in condensed phase. Thus, researchers never need to painfully fight against this process but amusedly utilize it to generate efficient emitters in the solid state [12–14].

We have observed an unusual phenomenon of “aggregation-induced emission” (AIE) in 2001 [15], which is exactly opposite to the aforementioned ACQ effect. A series of propeller-shaped molecules are nonluminescent when molecularly dissolved but become highly emissive in the aggregate state. Restriction of intramolecular rotation (RIR) of their multiple phenyl rings in the aggregate or solid states

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has been proven experimentally and theoretically as the main cause for the AIE effect [16–25].

Attracted by the intriguing photophysical process of AIE effect, the researchers throughout the world have been actively involved in this area. As a result, a variety of AIE systems have been developed in the past decade, among which the tetraphenylethylene (TPE) and silole derivatives have been widely investigated and identified as the archetypal AIE systems [12, 13, 26]. They have been widely applied in fluorescent chemosensors and bioprobes, stimuli-responsive nanomaterials, and as active layers in efficient OLEDs [27]. However, the emission efficiency of TPEs and the tedious synthesis and purification procedures of siloles have greatly limited the expansion of the researches on AIE. To further promote the development of the AIE area, new AIE system is highly demanded. Furthermore, for biological applications, the AIE molecules have always been decorated with hydrophilic groups on their periphery to make them water soluble, which requires additional functionalization procedures. [28, 29].

We are interesting in exploring new AIE systems, especially the ionic AIE-active molecules because of their promising application in biological field. According to the RIR mechanism of AIE, a propeller-shaped molecule with multiple phenyl rotors could feature such characteristics, and pyridine derivatives could generate ionic species by substitution reaction with ease. Following these rules, a type of cationic molecules named 1,2,4,6-tetraphenylpyridinium drew our attention [30–32]. In such molecule, four phenyl rings are integrated on a pyridinium cation. We thus anticipated that the rotation of these phenyl rings in solution

would consume the energy of excited state and make the molecule nonemissive or weakly luminescent. While, in the aggregate or solid states, the rotations are greatly restricted physically, and the emission will turn on.

2 Results and discussion

The 1,2,4,6-tetraphenylpyridinium-based ionic molecules could be facilely synthesized. As shown in Scheme 1, the reactions between 2,4,6-triphenylpyrylium tetrafluoroborate and mono- or di- amines in the refluxed ethanol solutions readily furnished corresponding compounds **1**, **2** and **3** after simply workup procedures [33]. Unlike other ionic AIE-active luminogens, which were prepared via post-functionalization reactions, the cationic pyridiniums are formed in situ with the substitution reactions of oxygen by nitrogen. The molecules are soluble in dichloromethane and other polar solvents like DMSO and DMF, but partially soluble in water. The molecules were fully characterized by ^1H (Figure S1) and ^{13}C (Figure S2) NMR and mass spectra (Figure S3), and satisfactory data corresponding their structures were obtained [see Supporting Information for details].

Then, we studied their photophysical properties. As can be seen from Figure S4, the dilute DMSO solutions of **1**, **2** and **3** show absorption maximum (λ_{max}) at 309, 313, and 317 nm, respectively. The red-shift of the λ_{max} is probably due to the conjugation extension from **1** to **3**.

According to the RIR mechanism of AIE, the 1,2,4,6-tetraphenylpyridinium derivatives should possess such

Scheme 1 Synthetic routes to 1,2,4,6-tetraphenylpyridiniums **1**, **2** and **3**.

Figure 1 (a) PL spectra of 1,2,4,6-tetraphenylpyridinium derivative **2** in the DMSO/H₂O mixtures with different fractions of water (f_w). Concentration: 10 μ M; excitation wavelength: 313 nm. (b) Plot of the change in PL intensity with f_w of 1,2,4,6-tetraphenylpyridinium derivative **2**, where I_0 and I are the maxima PL intensity. Inset: Plots of the changes in PL intensity with f_w of 1,2,4,6-tetraphenylpyridinium derivatives **1** and **3**.

characteristics. We thus investigated the photoluminescence (PL) behaviors of **1**, **2** and **3** in the solution and aggregate states. The aggregates were prepared by adding water into their DMSO solutions under vigorous stirring. The resultant mixtures are visually transparent and macroscopically homogenous, suggesting that the molecular aggregates are nanometer-sized [34].

Variations of the PL spectra of **2** with f_w in the DMSO/water mixtures are shown in panel (a) of Figure 1 as an example. When excited at 313 nm, the PL spectrum of the diluted DMSO solution of **2** gives almost a flat line parallel to the abscissa, manifesting that **2** is a weak emitter when molecularly dissolved. In contrast, when a large amount of water is added into the solution, intense emission

was recorded. Furthermore, the emission peaks were gradually red shifted from 422 to 446 nm under the same measurement conditions, which is probably due to the solvent polarity effect with more water added. Since **2** is partially soluble in water, addition of large amount water into its DMSO solution will make the molecules aggregated. **2** was thus induced to emit by aggregate formation, *i.e.* **2** is AIE-active. While, for **1** and **3**, their DMSO solutions could emit weak light but the intensities were strengthened upon addition of water (Figures S5 and S6). In other words, they feature the characteristics of aggregate-enhanced emission (AEE).

The plots of relative emission intensity of the molecules in DMSO/water mixtures vs. f_w further confirm their AIE/AEE features. As shown in Figure 1(b), the emission intensity of **1**, **2** and **3** was gradually increased with addition of water, and the highest values were all recorded in DMSO/water mixtures with f_w of 90%, which are 12.6, 85.0, and 6.1-fold higher than that those in their DMSO solutions, respectively. The relatively low intensity enhancement of **1** and **3** is because their solutions are weakly emissive. These results indicate that the emission behaviors of 1,2,4,6-tetraphenylpyridinium-based molecules could be easily fine-tuned through molecular engineering.

3 Conclusions

In summary, according to the RIR mechanism, we have developed a new AIE system based on 1,2,4,6-tetraphenylpyridinium ion. Compounds **1**, **2** and **3** could be facily synthesized from commercially available starting materials of 2,4,6-triphenylpyrylium tetrafluoroborate and mono- or di-amines in the refluxed ethanol solutions. The photophysical measurements showed that these molecules possess AIE/AEE characteristics, which in turn proves the reasonability of the RIR mechanism. Unlike the reported ionic AIE-active molecules, in which the charges were on their periphery, these molecules have charges on their cores, which are promising to be applied as chemosensors and bioprobes with high sensitivity. The generation of more AIE-active 1,2,4,6-tetraphenylpyridinium ions and exploration of their applications are on-going in our research groups.

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