

AGGREGATION INDUCED EMISSION (AIE) AND TRANSFORMATION FROM ACQ TO AIE BY DECORATING ACQ LUMINOPHORES WITH AIE CORES

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Abstract

Materials with aggregation-induced emission (AIE) properties have attracted much attention, due to their scientific importance and practical real-world applications. Until now, many researchers have worked on the structure-property relationships, working mechanisms of the AIE process to design and synthesize new AIE materials with efficient luminescence. One of the key factors to design new AIE materials is the transformation of ACQ (aggregation caused quenching) systems to AIE systems. In this review, we will focus on some typical AIE systems which demonstrate a successful transformation from ACQ to AIE by decorating ACQ luminophores with AIE cores.

Keywords: Aggregation, Emission, Luminophores

INTRODUCTION

Generally, conventional organic luminophores often show weak emission or even non-luminescent in dilute solutions.^{1,2} On the other hand, in the concentrated solution, chromophoric molecules often induce nonradiative energy transfer, resulting in emission self-quenching.^{3,4} The phenomenon of aggregation caused quenching (ACQ) was first observed in the fluorescence of pyrene by Forster and Kasper in 1954. Most organic dyes suffer from the ACQ effect, according to the summary by Birks in his classic book on *Photophysics of Aromatic Molecules* in 1970. Conventional luminophores often emit strongly when they are isolated as a single molecular. However, when they are aggregated or clustered, they meet with varying degrees of ACQ effect. The aromatic ring of the luminophore with the disc-like shape or rod-like shapes have strong π - π stacking interaction which promotes the formation of aggregates. The excited state of the aggregates decays mainly via non-radiative pathways caused by quenching of light emission. The ACQ is very common. Perylene is a typical example of the ACQ effect (Figure 1, left panel).⁵ When perylene was dissolved in a good solvent, e.g., pure tetrahydrofuran (THF), the dilute solution of perylene in THF shows strong luminescence. When increasing the fraction of water (f_w), the luminescence of perylene becomes weakened. At $f_w = 80$ vol %, the emission of perylene was significantly quenched. When the fraction of water is up to 90 vol %, its emission is quenched completely. In aggregate form, the planar aromatic ring of perylenes induces strong π - π intermolecular interaction which prompts the formation of such detrimental species as excimers, resulting in the emission quenching. In 2001, Tang et al. discovered an abnormal behavior of silole derivatives which is opposite to a common phenomenon.^{6,7} A series of silole derivatives were found to be non-luminescent in the solution but strong luminescent in the aggregate form. This phenomenon was termed "aggregation-induced emission" (AIE). Hexaphenylsilole (HPS) is non-emissive when its molecules are dissolved in a good solvent, e.g., THF. Its emission turned on when the fraction of water reached 80% (vol) (Figure 1, right panel) as a consequence of aggregation.

Practically, for the vast majority of applications, luminophores are often used as materials in the solid-state such as a thin-film layer in organic light-emitting diodes (OLEDs).⁸⁻¹⁰ Therefore, to reduce the ACQ effect, various chemical, physical and engineering approaches have been developed to hamper aggregate formation. For example, branched chains, bulky cycle, spiro links have been added to aromatic rings.¹¹⁻¹³ However, in many cases the aggregation was hampered partially or temporarily.^{11,13-15} Intrinsically, luminophores with conjugated structure aggregates in the condensed phase such as solid-state or concentrated solution. It is such a great innovation if their aggregates can luminesce efficiently.

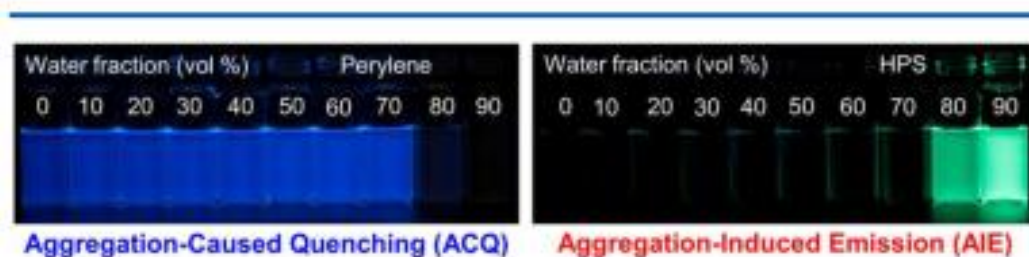


Figure 1. Fluorescence photographs of perylene and hexaphenylsilole (HPS) in THF/water mixtures with different fractions of water.⁵

According to the previous papers, the restriction of intramolecular rotation (RIR) has been proposed to be the main cause for most of the reported AIE systems.^{5,16} Based on the mechanistic understanding, structural design strategies for the development of efficient luminophores have been developed. It is envisaged that integrating AIE elements into ACQ might be an effective way to transform ACQ luminophores to AIE luminogens (whereas emissive chromophores as molecular species are called luminophores, those non-emissive as molecules but emissive under appropriate conditions, for example, as aggregates, are named luminogen⁵). The focus of this small review is on the studies undertaken by other research groups. We will present some typical examples of the AIE systems developed by various research groups.

ACQ TO AIE TRANSFORMATION BY DECORATING ACQ LUMINOPHORES WITH AIE CORES

As mentioned in the Introduction section, the integration of AIE elements into the ACQ system can work as an effective way to transform ACQ luminophores to AIE luminogens. One of the most potent ways is directly attaching well-known AIE archetypes onto ACQ cores. Typical examples have been selected and shown in Figure 2. Flat anthracene core suffers from ACQ effect while tetraphenylethene (TPE) was typical AIE archetype. Shu et al., attached 2 TPE moieties to both sides of the anthracene core, and ACQ luminophores were transformed into an AIE luminogen (compound **37**, Figure 2).¹⁷ Compound **37** showed weaker emission when dissolved in cyclohexane with fluorescence efficiency ϕ_F of 6 % and greatly enhanced intensity in its solid-state form. Probably, the increase of emission intensity in the solid-state can be interpreted by the influence of TPE moieties. The multiple phenyl groups of TPE are rotors that effectively dissipate the excited-state energy via intramolecular rotation in the solution state. In the aggregate or the solid-state form, these rotors were rigid and blocked the non-radiative decay channels. Additionally, the propeller of TPE moieties has increased bulky structure and nonplanarity of the whole molecule, therefore, preventing the π - π stacking interactions. Consequently, emission efficiency significantly. Compound **38** was weakly emissive in THF solution with a quantum yield of 0.28% due to the

intramolecular rotation process of the TPE unit but it emitted intensely in the condensed phase with quantum yield ϕ_F value up to unity (100%).¹⁸ Similarly, fluorescence quantum yield of compound **39** was low in the solution while approached to unity in the film state.¹⁹ Thus, the introduction of freely rotatable TPE to conventional luminophore anthracene quenched their emission in the condensed phase due to the RIR, and their emission efficiency achieved unity in the film state.

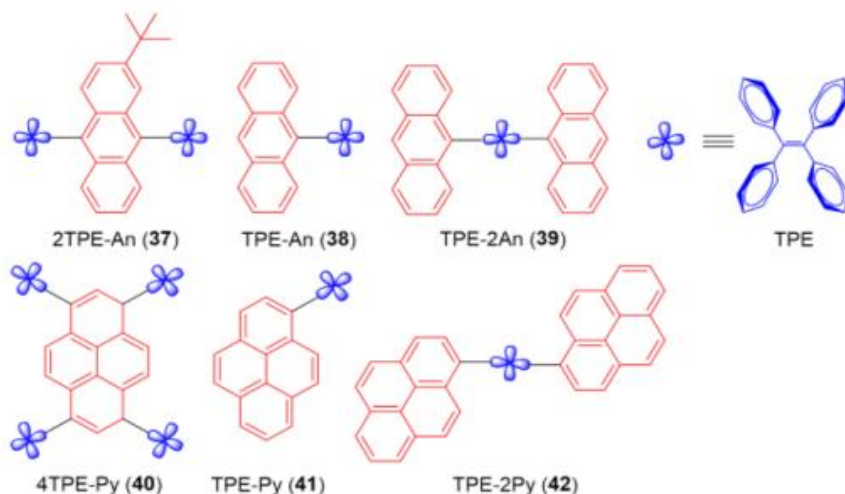


Figure 2. Examples of ACQ to AIE transformation by decorating ACQ cores with AIE archetypes whereas ACQ cores (anthracene, pyrene), AIE archetype (tetraphenylethene TPE).⁵

A series of TPE-decorated pyrene derivatives have been successfully synthesized with high emission quantum yield (Figure 2, compounds **40**, **41**, **42**) in the film state. Attaching 4 TPE units to pyrene core endows the resultant 4TPE-Py (compound **40**) with AIE effect; emission quantum yield in solid-state reached 70% while that in solution was estimated to be 9.5%.²⁰ The result in the solid-state indicated that intramolecular interactions were restricted and thus hampered non-radiative pathways. Similar observations were observed for compounds **41** and **42** (Figure 2).^{18,19} In film, emission quantum yield reached 100% for both these compounds. Another typical example of perylene bisimide (PBI) derivatives with 2 TPE attaching units (Figure 3, compound **43** and compound **44**).^{21,22} The emission efficiency of compound **43** rises from 0.07% in the solution to 6.3% in the film state while that of compound **44** enhances from 0.03% in the solution to 13% in the film state. The intramolecular rotations are the main cause of non-radiative decay channels in the solution. In the condensed phase such as solid-state or film state, these intramolecular rotors were hampered and the twisted conformation of TPE prevents strong π - π interactions, leading to highly effective emission. AIE effect was also observed for a series of TPE-containing boron dipyrromethene compounds **45**, **46**, **47**, **48** (Figure 3).^{23,24}

A series of triphenylamine (TPA) derivatives were also successfully synthesized with high emission efficiency by integrating ACQ luminophore TPA with AIE cores, for instance, tetraphenylethene TPE and triphenylacrylonitrile TPAN (Figure 4). One TPA core has been attached with three and one TPE units to form compounds **49**, **50** respectively while TPE acted as a bridge to connect 2 TPA cores to form compound **51**.^{25,26} All compounds had small emission efficiency, but they were highly emissive in the solid-state, the emission efficiency reached to 91.6% for compound **49** and 100% for 2 compounds **50** and **51**. It is worthy to note that the TPA core is emissive in the solution.²⁵

Thus, the non-luminescent nature of compounds all these compounds in the solution suggested that the TPE unit quenched the light emission. In the solution, the active phenyl rotors of the TPE unit effectively deactivated the excited energy via the rotational energy relaxation channels, thus they were non-emissive in the solution. On the other hand, in the condensed phase (aggregate or solid-state), the restriction of intramolecular rotations occurred which blocked the nonradiative decay pathways. Consequently, the emission efficiency was enhanced rapidly.

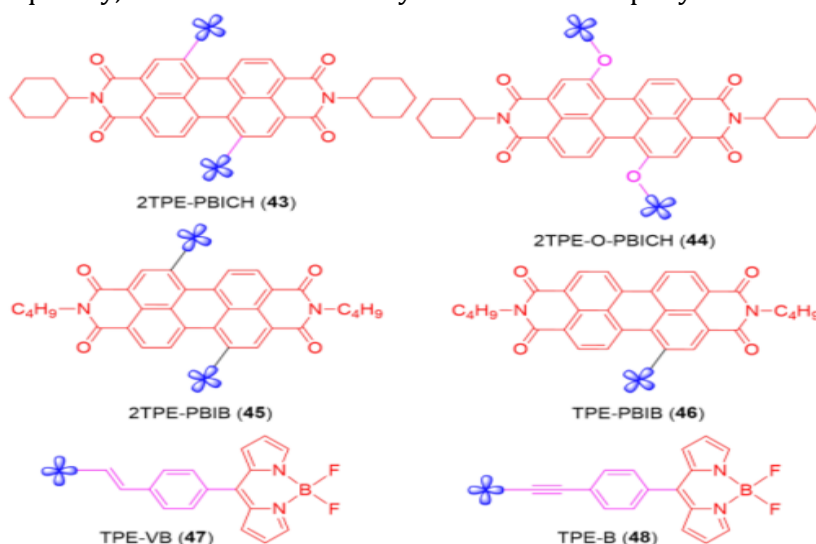


Figure 3. Examples of ACQ to AIE transformation by decorating ACQ cores with AIE archetypes whereas ACQ cores (perylene bisimide, and boron-dipyromethene), AIE archetype (tetraphenylethene TPE).⁵

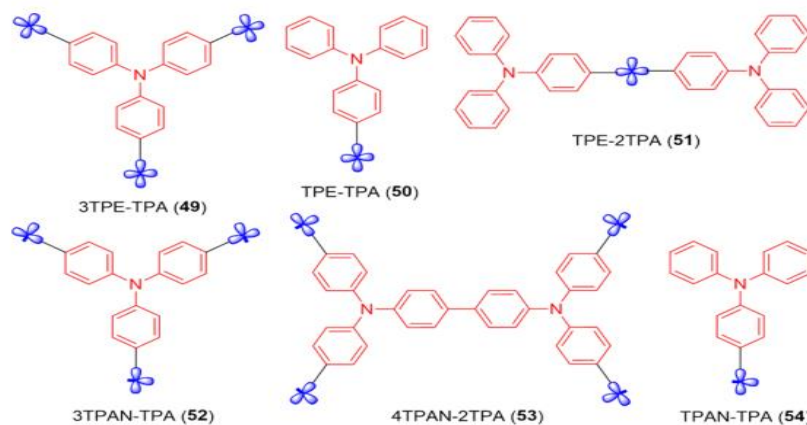


Figure 4. Examples of ACQ to AIE transformation by decorating ACQ cores with AIE archetypes whereas ACQ core (triphenylamine TPA), AIE archetypes (tetraphenylethene TPE, triphenylacrylonitrile TPAN).⁵

Another AIE core used to transform ACQ luminophore TPA into new AIE luminogens is triphenylacrylonitrile TPAN. The ratio of TPAN to TPA are 1, 2, 3 for compounds TPAN-TPA (**54**),²⁷ 4TPAN-2TPA (**53**),²⁸ and 3TPAN-TPA (**52**),²⁸ respectively (Figure 4). All these compounds are active-AIE compounds. The successful conversion from ACQ to AIE in these compounds is interpreted similarly to the previous systems. AIE effect was induced because of RIR.

CONCLUSION

In this review, we summarize several typical AIE luminogens which have been successfully synthesized and exhibited excellent emission efficiency. ACQ to AIE transformation through modular addition of AIE units to ACQ cores. These systems are non-emissive in the solution if attached AIE units can effectively consume the excited-state energy. In the condensed phase, the intramolecular rotations of AIE units were blocked which are the main cause of effective emission. Thank restriction of intramolecular rotations, various active AIE systems were designed for many applications in optoelectronic devices and sensory systems, for instance, they are promising materials for the fabrication of efficient OLEDs.

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