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# Luminogenic polymers with aggregation-induced emission characteristics

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ABSTRACT

Aggregation-induced emission (AIE) is a newly developed phenomenon that is exactly opposite to the aggregation-caused emission quenching effect observed with some conventional luminophores. The AIE phenomenon was first realized in propeller-like small molecules and now has extended to polymeric systems. In this review, we summarize the recent progress on the preparation of luminogenic polymers with AIE or aggregation-enhanced emission (AEE) characteristics, which are generally prepared by attaching AIE-active luminogens, such as tetraphenylethene and silole, as pendants to the polymer backbones or utilizing them as skeletons for main chain polymers. An AIE phenomenon was observed in succinic anhydride-containing nonconjugated polymers bearing no luminogens, presumably due to the agglomeration of carbonyl groups. The AIE/AEE-active polymers show unique properties, such as emission superquenching, high and tunable light refractivity, and aggregation-enhanced two-photon excited fluorescence, and have found potential applications as fluorescent sensors, biological probes, and active layers for the fabrication of light-emitting diodes.



**Contents**



*Abbreviations:* ACQ, aggregation-caused quenching; AEE, aggregation-enhanced emission; AETPEF, aggregation-enhanced two-photon excited fluorescence; AIBN, azobisisobutyronitrile; AIE, aggregation-induced emission; $Alq_3$, tris(8-hydroxyquinolinato)aluminum; BCP, bathocuproine; BPO, benzoyl peroxide; BSA, bovine serum albumin; CSA, camphorsulfonic acid; DCM, dichloromethane; EL, electroluminescence; fwhm, full width at half-maximum; ITO, indium tin oxide; HPS, hexaphenylsilole; LCST, lower critical solution temperature; NIPAM, *N*-isopropylacrylamide; PA, picric acid; PATA, poly(aroyltriazole); PDPA, poly(diphenylacetylene); PIBSA, polyisobutene succinic anhydride; PL, photoluminescence; PNIPAM, poly(*N*-isopropylacrylamide); PPA, poly(1-phenyl-1-alkyne); PVK, poly(9-vinylcarbazole); RD, rhodamine; RI, refractive indices; RIR, restriction of intramolecular rotation; SEM, scanning electron microscope; TPB, triphenylbenzene; TPE, tetraphenylethene; TPEF, two-photon excited fluorescence.

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## 1. Introduction

Organic and polymeric luminophores are promising materials for applications in various areas, such as light-emitting diodes [1–6], plastic lasers [7–9], and fluorescent chemosensors and bioprobes [10–16]. To respond to the demand, scientists have synthesized a large number of luminescent materials. Many of them have been found to be highly emissive in dilute solutions, with fluorescence quantum yields reaching unity. For most practical applications, the luminescent materials have to be used in the solid state (e.g. as thin films), where the luminophores tend to form aggregates. However, it is known that aggregation of organic luminophores often leads to partial or even complete quenching of their light emissions. This aggregation-caused quenching (ACQ) effect has limited the scope of technological applications of the luminophoric molecules. To alleviate the ACQ effect in the condensed phase, various chemical, physical, and engineering approaches have been developed. For example, branched chains, bulky cyclics, spiro kinks, and dendritic wedges have been covalently attached to aromatic rings to impede aggregate formation [17–28]. Luminogens have also been physically passivated via surfactant encapsulation, doped into matrices of nonconjugated transparent polymers such as poly(methyl methacrylate), and blended with different inorganic or organic or polymeric materials [29–34]. Although various approaches have been taken to interfere with luminogen aggregation, the attempts have met with only limited success and they, however, are often accompanied by severe side effects. The steric effects of bulky cyclics, for example, can twist the conformations of the chromophoric units and thus partially jeopardize the electron conjugation in the luminophores. The nonconjugated encapsulates and the transparent matrices used in the physical processes are nonemissive and insulating, and can dilute the luminophore density and obstruct the charge transport in electroluminescence (EL) devices. The spatial distribution of the fluorophore dopants in a doped film suffers from temporal instability: the luminogens dispersed in the polymer matrices gradually migrate together over time, eventually emerging phase separation and forming large aggregates [2].

As aggregation is an inherent process when luminogenic molecules are in the condensed phase, it would be useful to develop a system in which aggregation plays a constructive, rather than destructive role, in the light-emitting processes of luminogens [35–51]. In their search for efficient luminescent materials, Tang and co-workers were attracted by a group of organometallic molecules called siloles. A silole molecule named hexaphenylsilole (HPS or **1**) is shown in Fig. 1 as an example, whose electronic structure looks extensively conjugated. However, the silole molecules were found to be virtually nonluminescent when molecularly dissolved in good solvents, but became highly emissive when aggregated in poor solvents or fabricated into thin solid films. They coined the term of "aggregation-induced emission (AIE)" for this phenomenon because the silole molecules were induced to emit by aggregate formation [52,53]. Since then, many organic fluorogens have been found to show the AIE effect [54–62] and behave like HPS. For example, a dilute THF solution of tetraphenylethene (TPE or **2**) is practically nonluminescent (Fig. 1), but addition of a poor solvent, such as water, induces aggregation and results in light emission.

Some luminogenic materials exhibit "turn-on" photophysical properties when utilized as chemo- and biosensors due to metal complexation, hydrogen-bond formation, electrostatic interaction, chemical reaction, etc. [63–66]. What is the working principle for the AIE effect? A number of possible mechanistic pathways, including conformational planarization, J-aggregate formation, twisted intramolecular charge transfer (TICT), and restriction of intramolecular rotation (RIR), have been proposed for

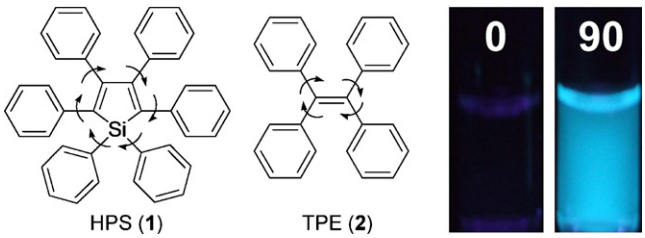


**Fig. 1.** Molecular structures of HPS and TPE and fluorescent images of TPE in THF/water mixtures with water fractions of 0 and 90%. The bright rim at the top of the blue image is caused by an optical effect due to the container. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)