

Aggregation-Induced Emission Properties in Polymers

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Aggregation-Induced Emission (AIE) is a phenomenon that consists of the appearance of fluorescence in solid state or aggregation greater than that of molecules in solution and has recently attracted the attention of the scientific community because of their potential applications in different fields. Compared to small molecules, little attention has been paid to polymers and oligomers that exhibit AIE, despite having excellent properties such as high emission efficiency in aggregate and solid states, signal amplification effect, good processability and the availability of multiple functionalization sites. In addition to these features, if the molecular structure is fully conjugated, intramolecular electronic interactions between the composing chromophores may appear, thus giving rise to a wealth of new photophysical properties. In this review, we focus on selected fully conjugated oligomers, dendrimers and polymers, and briefly summarize their synthetic routes, fluorescence properties and potential applications. An exhaustive comparison between spectroscopic results in solution and aggregates or in solid state has been collected in almost all examples, and an opinion on the future direction of the field is briefly stated.

aggregation-induced emission

AIE

aggregation induced emission enhancement

1. Introduction

George Gabriel Stokes, in 1852, coined the term “fluorescence” to describe the process of the emission of blue light produced by fluorspar ore when irradiated with ultraviolet light [1]. Since then, luminescence phenomena have attracted a great deal of attention in the scientific community [2]. Such is the importance that, in the last 40 years, nine Nobel Prizes in Chemistry or Physics have been directly related to the interaction between light and chemical compounds, mostly organic. Photosynthesis, conductive polymers, green fluorescent proteins, light-emitting diodes or optoelectronics would be some of these awarded discoveries [3]. Among all luminescent materials, organic compounds have the advantage of being easily prepared and tuned for specific properties. From a structural point of view, the organic molecules capable of both interacting with visible light and producing luminescence in their different forms, are constituted by a skeleton that contains π -type electrons or non-bonding orbitals. In addition, if double or triple bonds alternate with single bonds in the molecule, there is a delocalization of π -electrons from these orbitals throughout the structure known as conjugation [4]. If this conjugation extends throughout the molecular backbone, it is known as “fully conjugated” or “fully π -conjugated” systems.

A widespread geometrical parameter in conjugated systems is the Bond Length Alternation (BLA), defined by the average of the difference between the bond lengths of consecutive C–C single and double bonds. The determination of BLA allows us to estimate the degree of quinoidal or aromatic character in conjugated systems.

HOMO-LUMO energy gap, usually referred to band gap, is another important parameter closely related to BLA, which strongly determines the intrinsic optoelectronic properties in conjugated systems [4][5]. Nevertheless, these properties do not depend exclusively on the conjugation of the π - and non-bonding electrons. The molecular scaffold together with the functional groups that decorate it, can have a great impact when tuning these properties, resulting in the design of elegant structures for challenging applications.

Among all the properties exhibited by conjugated compounds, luminescence is undoubtedly one of the most studied and still with interesting issues to be resolved. One of them is the control over the emitting properties in different environments, and that is closely related to maintaining these characteristics in the final device. For example, in the construction of organic light-emitting diodes (OLEDs), it is essential that the luminescent properties are maintained in the solid state, as luminescence can change dramatically when going from solution to aggregated and/or solid states. Thus, the development of new emissive materials involves a rational design of the structure where not only intrinsic molecular properties must be considered, but also a wide range of intermolecular parameters that can be responsible of the mechanism involved in that phenomenon.

Despite the fact that dramatic changes in the fluorescence quantum yield (Φ) were described many years ago when going from solution to aggregated/solid states in early studies [6], in recent years the AIE (Aggregation Induced Emission), AIEE (Aggregation Induced Emission Enhancement), SLE (Solid-state Luminescence Enhancement) and ACQ (Aggregation Caused Quenching) acronyms have been widely used in literature to refer to a vast group of phenomena in which the luminescent properties are strongly affected by the molecular arrangement in solution and/or the packing in solid state. Although sometimes the acronyms AIE, AIEE or SLE are used indistinctly, the differences among them are well established. The AIE phenomenon refers to compounds that are not luminescent in solution but become emissive when aggregated or in solid state [7], AIEE refers to fluorescent compounds in solution with increased fluorescence when aggregated [8] or solid. SLE refers to compounds that are more fluorescent in solid state than in solution [9]. Parallel to the experimental observations, different theories and mechanisms have been proposed to decipher from a molecular and electronic point of view the origin of such intriguing phenomena [10]. In this respect, the theory of molecular excitons by Kasha et al. [11][12] has provided a successful description of the changes in luminescence after aggregation. According to it, luminescent properties depend on long range coulombic couplings due the interaction between molecular transition dipole moments of the neighbor molecules. Thus, the so-called J aggregates would produce bathochromic shift with respect to the non-aggregate state increasing or enhancing the emission, while the H aggregate would produce hypsochromic shifts and/or luminescence is suppressed. A more expanded Kasha's theory of H- and J-molecular aggregates was exhaustively described by Spano et al. [13] considering the effects of vibronic coupling and intermolecular charge transfer. As a conclusion, short- and long-range excitonic coupling could interfere with each other to produce HH, HJ, JH and JJ aggregates resulting in a vast range of photophysical behaviors.

The restriction of intramolecular motions (RIM) mechanism is another model of more simplicity that has been successfully proposed to interpret the enhancement or the quenching of emission in many luminogens [14]. According to it, the absorbed energy by the molecules would be dissipated in solution through intramolecular vibrations (RIV) and rotations (RIR). However, when molecules are aggregated or in solid state, or the viscosity of

the medium is increased, these molecular motions are blocked, and the molecules relax radiatively. A similar description is proposed when the luminescent properties are affected by the Z/E-photoisomerization through a C–C double bond. In solution, the photoisomerization is favored by the torsional motions of the molecule and, consequently, the emission is quenched. In contrast, when molecules become aggregated or the viscosity of the medium is increased, the photoisomerization is blocked resulting in bright states in solid state [15].

In addition to all these mechanisms, the presence of conical intersections between the potential energy surfaces of the ground and excited states has been also identified in many molecular systems to be responsible for non-radiative electronic relaxations. Thus, when the access to this intersection is restricted because of a consequence of significant geometry changes after excitation, the intersection is canceled, and the molecules relax radiatively. This effect has been called as Restricted Access to Conical Intersection (RACI) [10].

The interest aroused by this fascinating research field has led to the study and description of a many fluorescent chemical structures in the solid or aggregate state, as it is proven by the fact that in the last two years, at least forty reviews have been published related to this topic [16][17][18][19][20][21]. However, most of the molecular structures are discrete molecules or independent luminescent units within a non-conjugated skeleton. In the latter case, the ultimate properties of the integrated fluorescent moieties are, in most cases, very similar to those of the lead luminogens because the HOMO and LUMO molecular orbitals are essentially the same. On the contrary, when these luminogens are electronically connected through a conjugated structure, the effects produced on them are more important and the final photophysical properties can significantly change with respect to the initial luminogen.

2. Strength, Weakness, Opportunities and Threats in AIE Polymers.

Although a full SWOT analysis would be very useful to reflect the current and future prospective of the AIE compounds in order to commercialize them, nowadays, the information available is very scarce and focused on fundamental research about their synthesis and photophysical characterization. Currently, only a very limited offer of TPE-derived molecules is marketed by Merck KGaA [22] or AIEgen BioTech Co. [23] but there is nothing concerning oligomers, dendrimers or polymers. Thus, its development is still in a very preliminary stage and not very oriented to an applied or commercial development. However, some ideas about Strengths, Weaknesses, Opportunities or Threats can be enumerated without being an exhaustive SWOT study.

Strengths: The applications of p-conjugated compounds cover areas ranging from the development of light-emitting devices, either lighting or display, solar cells, or sensors. The technological implementation of these compounds requires, in most cases, that they are in solid state in which polymers with AIE properties enhance their luminescent properties. The increasing interest expressed by the community in these compounds is evidenced by the progressive increase in the number of patents over the last 10 years (Figure 1, left), moreover, around 38% of the patents on AIE in 2020 were of polymeric materials. Probably, the advantages of polymers over other materials, such as versatility, low-cost of production, ease of manufacture, lightweight, portable, durable and more affordable products, make them good candidates for use in technological devices.

Weaknesses: However, despite these advantages, there are many questions still to be resolved about the control of AIE properties in macromolecular systems. As we have tried to collect in this review, most of the papers describe the luminescent properties of compounds but rarely try to provide a thorough explanation of why the phenomena occur, which complicates making correlations between molecular structure and photophysical properties. On the other hand, luminescent compounds are chemically constituted by highly hydrophobic elements. Since environmental sustainability has of great social interest worldwide, both the synthesis of compounds and their processability require the use of organic solvents, mostly pollutants such as THF, dichloromethane, ortho-dichlorobenzene, etc. This aspect is something that should be technologically solved in order to make the development of these materials more environmentally friendly.

Opportunities: Considering the above weaknesses, improvement opportunities could focus on two main areas: Search for new structures and search for new applications. The synthesis of new structures has other two clear objectives: to help to better understand how AIE processes occur in complex macromolecular systems, and to search for compounds that emit in less exploited regions of the emission spectrum or with low quantum yields. Figure 39 (on the right) shows the emission wavelengths and fluorescence quantum yields in solid state for all the compounds collected in this article as a representative sample. It can be seen how there is a great variety of compounds with different quantum yields between the blue and green regions in the spectrum. However, there are more limited compounds that emit with high quantum yields in purple, yellow, orange or red. As an alternative to these opportunities focused on the development of new molecular structures, the use of these compounds can also be extended to other areas such as biomedicine. Work has already begun in this area that focuses on the use of compounds with AIE properties for cell imaging, theranostics or phototherapy. The characteristics and requirements of the compounds for these applications are completely different from those used for the technologies mentioned above. This opens a wide field of research and development still to be explored.

Threats: Other types of materials with good luminescent properties are being developed in parallel and/or in competition with AIE polymers, such as quantum dots, graphene, borophene, phosphorene, transition metal dichalcogenides, perovskites, rare-earth-doped luminescent materials, among others (see references [22] and [23] and references therein). The great expectations placed on graphene have resulted in a disappointing eternal promise and borophene emerges as an alternative to overcome graphene. [24] The potential of both materials is very great, but also the disadvantages of processability and technology needed to reach the levels of polymers. On the other hand, quantum dots are more technologically developed, and it is possible to find electronic devices with this technology in the market. As a result of the development of quantum dots, AIE dots have been created to combine the advantages of quantum dots and AIE compounds in nanoscopic aggregates of AIE molecules.

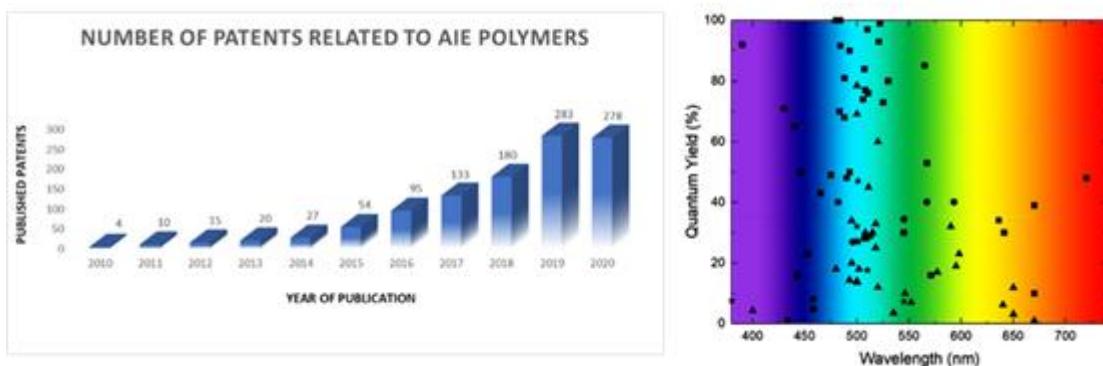


Figure 1. On the left, the number of patents published in the last ten years with AIE polymers in the description (source: Google Patents). On the right, representation of quantum yield vs. maximum emission wavelength of the oligomers (square), dendrimers (circle), linear polymers (triangle) and hyperbranched polymers (star) summarized in this review.

3. Conclusions

In this review, we have tried to give a holistic vision about the development of fully conjugated structures in which luminogen units are repeated and combined to give compounds with AIE or AIEE properties, a perspective never treated in the bibliography. We have started with oligomeric structures whose level of molecular complexity is low and allows establishing easy correlations between the molecular structure and the final optical properties. Progressively, we have increased this degree of complexity to dendrimers, then to polymers with only one luminogen, polymers with more than one luminogen and finally to highly branched structures, such as CMP or COF. As it has been shown, as the level of complexity of the structures increases, the constitutive luminogens lose their individual character because new intramolecular electronic interactions appear between the luminogens and the conjugated scaffolds, or even between the luminogens themselves, giving rise to more complicated systems from an electronic point of view allowing the construction of novel applied materials. Different luminogens have been shown throughout this work and, clearly, TPE is the mainstay as the directing agent for the induction of the RIM phenomenon as the main responsible for the AIE and AIEE effects. Although the synthetic reactions and mechanisms involved in those effects are well explored for conjugated molecules and macromolecules, there is still much room for improvement in the development of new fully conjugated structures with AIE and AIEE properties. In this sense, the study of the role of other phenomena alternative to RIM, such as *cis-trans* photoisomerization, RACI or intermolecular interactions in conjugated polymers, could help in finding new compounds with challenging applications. On the other hand, new AIE-active materials such as CMP, COFs or self-assembling compounds still need further exploration in the development in this field. In the case of the latter systems, aggregation is produced by an adequate and intelligent functionalization of the AIE molecule rather than by adding a mixture of solvents, a feature that would open the use of these compounds in fields such as biomedicine.

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