Aggregation-Induced Emission and Fluorescent Mechanochromism

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Mechanochromic fluorescent polymers are defined as materials that are able to detect a mechanical stress through a fluorescence output. This feature has evoked a growing interest in the last decades, thanks to the progress of fluorogenic molecules whose optical characteristics and chemical functionalities allow their effective insertion in many thermoplastic and thermoset matrices. Among the different types of fluorogenic probes able to detect mechanical solicitations, those with aggregation-induced emission (i.e., AIEgens) have attracted tremendous interest since their discovery in 2001. In this contribution, the main principles behind the AIEgens working behavior are introduced along with the current state of knowledge concerning the design and preparation of the derived mechanochromic fluorescent polymers. Examples are provided concerning the most ingenious solution for the preparation of chromogenic materials, starting from dierent types of commodity plastics or synthetic polymers and combined with the latest AIE technology to provide the most sensitive response to mechanical stress.

Aggregation Induced Emission polymers mechanochromism mechanochromic fluorescence

1. Introduction

A revolutionary class of fluorescence materials featuring emission triggered by aggregation has received great attention in sensor applications since their discovery by Ben Zhong Tang in 2001.[1] The effect, called aggregation induced emission (AIE), arises from the restriction of fluorophore intramolecular motions (RIM) that is typical of those molecules whose structure consists of two or more units that can dynamically rotate against each-other. Moreover the presence of a twisted propeller-shaped conformation renders intermolecular π–πinteractions difficult in the aggregate state. Noteworthy, by allowing light emission in the aggregate and solid state, AIE fluorophores (AIEgens) show a striking impact on energy, optoelectronics, life science and environment.[2][3] Fluorescent sensors based on the AIE mechanism take advantages from the ordinary fluorescent sensors thanks to the very brilliant emission in the solid state that allows for the development of efficient ON-OFF and, more interestingly, OFF-ON optical response towards several interferences. The detection of mechanical stress through optical variations, referred to as *mechanochromism*,[4] have therefore gained great importance also in the AIE technology field, since it enables the identification of *in-situ* materials failure also at early stage damage, thus suggesting applications as anti-counterfeit systems and self-diagnostic materials.[5] The intense luminescence coming from supramolecular aggregates triggered the research in the field of mechanochromic and piezochromic fluorescent materials, since the colour of the emission could possibly change by external compression or mechanical grinding. Recently, many reports have been published on the effective mechanism of piezochromic fluorescence based on the molecular aggregation state of AIE luminogens.[6][7] Many AIEgens actually show crystallization-induced emission or crystallization-enhanced emission and a mechanical solicitation applied to the chromophoric ordered structures possibly promote the deaggregation of the fluorescent units. This process favours the reduction of the barrier energy associated to the AIEgen rotors thus ending up with the typical ON-OFF behaviour. Even more interesting, if the mechanical stress is provided by compression or pressurization to amorphous conformations of AIEgens with loosely packing patterns, an enhanced emission intensity occurs due to crystallization phenomena triggered by the increased molecular interactions. Therefore, the more attractive OFF-ON behavior is provided.

2. Aggregation-Induced Emission (AIE) and Fluorescent Mechanochromism

An intriguing solution aimed at providing a more sensitive fluorogenic response is provided in literature profiting of the accessible modification of the AIE core with push-pull functional groups (Figure 1).[8] The several stacking modes in such AIE functionalized crystals result in the formation of J- or H-aggregate that are characterized by different luminescence features and affected by the diverse supramolecular state. Notably, the closer the two or more neighbouring molecules are, the stronger the intermolecular π-πinteractions among them, and also exciton coupling and orbital overlap between chromophores.

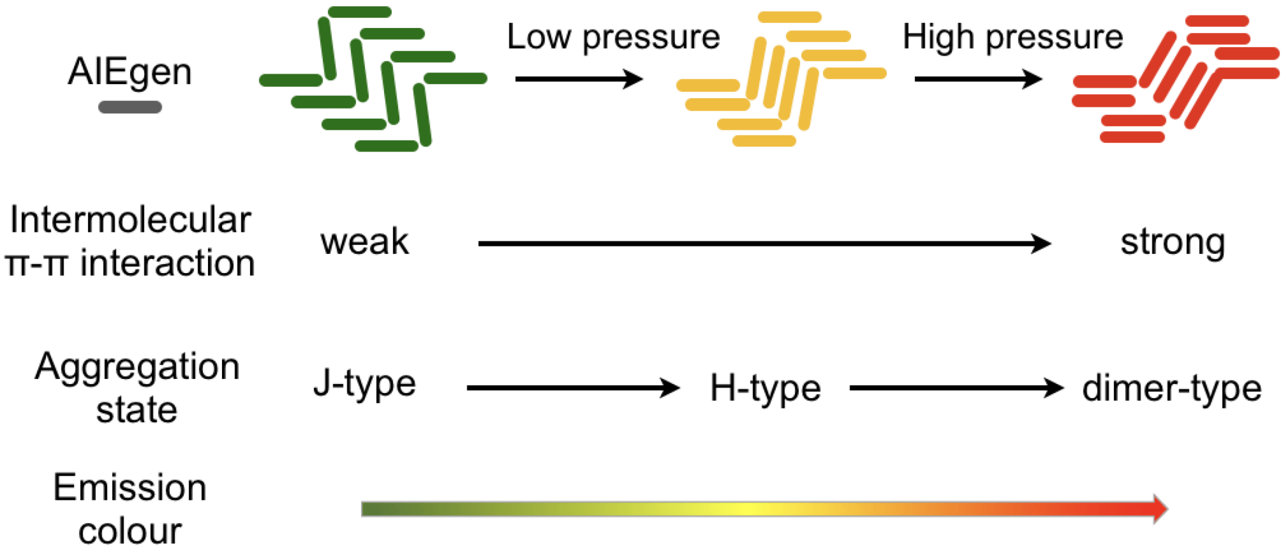

Figure 1. Schematic diagram of stacking mode and emission colour with various molecular aggregation states in a generic AIE luminogen. Adapted with permission. Copyright (2013) John Wiley and Sons.

In contrast to small AIE luminogens, macromolecules with AIE characteristics have been less investigated so far. Notably, AIE polymers have many advantages over low mass AIEgens, such as processability, easy functionalization, good thermal stability and possess structural complexity and phase ordering that can be easily modulated by external solicitations.[9] On this account, AIEgens can be also utilized as piezochromic fluorescent additives in commodity polymers. The AIE behaviour possibly enables the formulation of more sensitive mechanochromic response with respect to the traditional planar ACQ fluorophores.

The easy functionalization of the AIE core appears also very useful for the introduction of the chromogenic probe in both thermoplastic and thermoset polymer matrices by a covalent pathway. Dispersion into polymers is certainly a sustainable procedure and largely applied to commodity plastics, but the covalent approach has the advantage to prevent AIEgen segregation and diffusion and also for conferring to amorphous elastomeric matrices a clear fluorescent variations towards mechanical stimuli.

Both ON-OFF and OFF-ON chromogenic behaviors were taken into account, albeit this last considered promising for the development of highly sensitive mechanocromic fluorescent polymers. AIEgen dissolution into core-shell particles was actually proposed as a modern method for the development of useful mechanochromic OFF-ON fluorescent response.[10] The extreme sensitivity of the AIEgen core to minimum deformation extent combined with their encapsulation within ductile microcapsules appear so far the best solution for the preparation of auto-diagnostic polymer systems with a ratiometric response that gives access to quantitative assessment.

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