Aggregation-induced emission: right there shining

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The emergence of fluorescent probes has enabled researchers to find and observe invisible matter from the investigated object without light emitting. For example, green fluorescent protein (GFP), an invention that received the Nobel Prize for Chemistry in 2008, works as a visible fluorescent reporter to monitor the localization and movement of protein-GFP chimeras, protein-protein interactions, gene expression, and many other biological events in living cells in real time. GFP and its analogs have innovated research techniques and features in biological and life sciences.

A recent breakthrough in these research areas is the discovery of fluorescent probes with characteristics of aggregation-induced emission (AIE) [1]. With their unique emission mechanism and distinct emission behavior from classical luminogens, AIE-active luminogens (AIEgens) have contributed new insights into the photo-physical process in organic luminescent materials. AIEgens have also been applied as fluorescent probes in the monitoring of cellular physiological processes, as emitting agents in the fabrication of organic light-emitting diodes, and as light concentrators in the construction of organic/polymer photovoltaic cells [2–5]. In 2016, AIE-based luminescent dots were deemed to be among the four fundamental nanomaterials in supporting the coming “nanolight revolution,” and the “virus-sized particles that fluoresced in every color could revolutionize applications from television displays to cancer treatment” [6]. In 2017, Prof. Tang and colleagues received the first-class prize in the National Natural Science Awards for their distinguished work on the mechanism study, molecular design and preparation, and material applications of AIEgens. In recent years, AIE has become one of the

top five major research areas in chemistry and material sciences, according to data on the Web of Science.

The AIE system turns from a faintly emissive to a brightly emissive state when molecular aggregates originate from individual molecules that have a sufficient degree of motion freedoms. When tetraphenylethene (TPE) is used as a representative [7,8], the aggregate formation process must be accompanied by conformation rearrangements of phenyl groups attaching to the central ethylene moiety. A series of AIEgens showing mechano-fluorochromic effect have revealed the dependence of emission features (emission peak λ_{em} , efficiency Φ , and lifetime τ) on the molecular conformation (e.g., dihedral angle change). However, this finding only involves information on the original and terminal states. Since the AIE phenomenon was first reported, limited direct evidence was available to demonstrate the dynamic details of conformational changes.

In a recent work, Zhang *et al.* [9] contributed a subtle design to expose the analytical actions of intramolecular rotations under spotlight. In this design, a TPE unit is covalently and directly attached to the 3- or 6-position of a (*R*)-1,1'-binaphthyl-unit to derive four different polymers (Fig. 1a). When the polymer chain coils collapse in poor solvent mixtures, the restricted intramolecular rotations in the TPE units induce the fluorescence (FL) emission (P-1, Fig. 1b), which is a common observation for TPE-related molecules and macromolecules. However, the conjugation of TPE with a (*R*)-1,1'-binaphthyl-unit makes uncommon sense from all of the previous studies. As shown in Fig. 1c, d, the aggregation process or the conformational variation scenario is reflected by the subtle changes of the circular dichroism (CD) spectra of

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Figure 1 *In situ* monitoring of molecular aggregation using CD. (a) Chemical structure of designed TPE and 1,1'-binaphthyl-containing polymers P-1 to P-4. (b) Photoluminescence (PL) spectra of P-1 in tetrahydrofuran (THF)/water mixtures with different water fractions (f_w). Concentration: $10^{-5} \text{ mol L}^{-1}$, $\lambda_{\text{ex}} = 355 \text{ nm}$. (c) Simulated CD spectra of (R)-1,1'-binaphthol with θ varying from -45° to -110° in 1° intervals. (d) Schematic of polarization directions of main electronic transition moments and torsion angle θ of (R)-1,1'-binaphthyl derivatives. (e) CD spectra. P-1 in THF/water mixtures with different water fractions. Concentration: $10^{-4} \text{ mol L}^{-1}$. (f) Schematic representation of conformational change of (R)-1,1'-binaphthyl moieties during aggregation process. Reproduced with permission from Ref. [9]. Copyright 2018, Nature Publishing Group.

(R)-1,1'-binaphthol unit. As shown in Fig. 1f, a refined model is generated using the dihedral angle (θ), Davydov splitting width ($\Delta\lambda$), and negative CD couplet intensity ($\Delta\epsilon$) as estimation parameters, combined with theoretical

calculation for a number of states, and finally compared with the experimental data (Fig. 1c–e).

According to the experimental and theoretical results, the chiral AIE-active polymers containing 1,1'-binaphthyl

and TPE units provided an unprecedented model for the real-time and *in situ* monitoring of the molecular aggregation process. With an “open” structure, polymers P-1 and P-2 exhibited an effect of aggregation-annihilated CD (AACD) signal, and their CD couplet intensity was also largely annihilated by the aggregate formation. On the contrary, the AACD effect was suppressed in both P-3 and P-4 where the “openings” of the binaphthyl moieties were locked by methylene groups. Specifically, the dihedral angle θ of “open” polymers P-1 and P-2 decreased largely and part of the conformers relaxed from *cis* ooid to *trans*-oid following the change from the solution to aggregate state. By contrast, the “locked” polymers P-3 and P-4 showed a slightly larger θ and their *cis* ooid conformations were preserved during the aggregation process. These observations were consistent with the molecular dynamic simulation results and analysis of the change of CD couplet intensity and Davydov splitting during the aggregation process.

In the preceding example, the collapse of the polymer chain was triggered by the addition of a sufficient amount of non-solvent into a real dilute polymer solution. In some cases, the solubility of a macromolecule decreases or even vanishes in the mixture of two good solvents. This phenomenon is called cononsolvency effect, which has been widely applied in the physicochemical, green chemical, and pharmaceutical industries [10–12]. Dynamic light scattering, neutron scattering, isotope labeling, and molecular dynamic simulation techniques have been used in the relevant investigation, but the landscape for cononsolvency effect is elusive. Through the aid of an AIE-active fluorescent probe, a clear picture was drawn by a collaborative study and careful analysis of the emission behaviors of the TPE-crosslinked thermo-sensitive microgels in a nano-confined environment [13].

The molecular design, macromolecular structure, and working mechanism are illustrated in Fig. 2a. The crosslinking networks are formed through the acylhy-

Figure 2 *In situ* sensing of cononsolvency effect with AIE-active fluorescent probe. (a) Molecular structure of AIE-active probe and monomer, and schematic of cononsolvency behavior of a crosslinked thermo-sensitive microgel. (b) FL spectra of N-AH-TPE microgels in water (H₂O)/N,N-dimethylformamide (DMF) mixtures with various water molar fractions (χ_{water}). (c) Plots of emission intensity at maximum emission wavelength of microgels in H₂O/ethanol (1), H₂O/methanol (2), H₂O/DMF (3), H₂O/DMSO (4), and H₂O/THF (5) mixtures as a function of water molar fraction. Reproduced with permission from Ref. [13]. Copyright 2018, American Chemistry Society.

drazone bonds resulting from the condensation of aldehyde groups of TPE-4ALD and acylhydrazine group of 4-acylhydrazine-(2-hydroxy-3-(methacryloxypropyl))pyridine hydrochloride (AH monomer). By considering the hydrodynamic diameter of 302 nm for *N*-AH-TPE microgels in aqueous suspension at 25°C, we can estimate that one TPE-4AH moiety exists for approximately 394 nm³ for the swollen *N*-AH-TPE microgels. The self-aggregation of TPE moieties can be ruled out of the analysis because the TPE moieties are confined in the crosslinked network of microgels, and the change in FL intensity could be solely attributed to the variation of the restriction degree of the intramolecular rotations. In aqueous solution, the poly(*N*-isopropylacrylamide) (polyNIPAM) chains are dissolved and the hydrophobic TPE moieties are almost insoluble. In addition, a TPE moiety is localized at the crosslinking point of the resultant microgel network. In this condition, the intramolecular motions of TPE are restricted. Thus, strong emission could be observed from the microgels.

The TPE moieties are held within the niches of *N*-AH-TPE microgels and cannot diffuse freely even in good solvent. Five organic solvents, namely, DMF, THF, *N,N*-dimethyl sulfoxide (DMSO), ethanol, and methanol, which are good solvents for TPE and polyNIPAM, as well as miscible with water, have been attempted to examine the cononsolvency effect. Here water/methanol mixture is used as an example. Water and methanol are individually good solvents for polyNIPAM. However, precipitate is observed in a water/methanol mixture with a certain water fraction (χ), which is a typical phenomenon in cononsolvency. As shown in Fig. 2b, the relative FL of *N*-AH-TPE microgels intensifies with the decrease of χ from 1.0 to approximately 0.85 (black symbols), which indicates greater restriction of molecular motions (rotations and vibrations) of the TPE units. Correspondingly, the hydrodynamic diameter of the *N*-AH-TPE microgels in water/methanol mixtures becomes continuously small in the χ range, suggesting that the co-solvent changes from good to not so good. As χ decreases from 0.8 to 0.6, the FL intensity decreases and the hydrodynamic diameter of the microgels increases monotonously. The solvency improves and the molecular motions are less restricted; these two trends show consistency. Only a narrow χ window exists between 0.85 and 0.80, in which the FL intensity diminishes but the hydrodynamic diameter increases. This finding can be explained as follows. As methanol is more hydrophobic than water, the hydrophobicity is weakened when the χ value is reduced. This condition leads to the activation of the rotations and vi-

brations of the phenyl groups on the TPE units, thereby reducing the FL efficiency. However, methanol is a good solvent for polyNIPAM, and the polymer chains can be swollen in the water/methanol mixtures with suitably reduced χ values. In other words, TPE units and polyNIPAM chains have a distinct sensing ability to hydrophobicity and hydrogen bond formability. Similarly, cononsolvency was observed for polyNIPAM microgels in water-methanol mixtures and other water-miscible polar solvents including THF, DMF, and DMSO (Fig. 2c). These primary achievements imply that AIE-active fluorescent probes can be a general method to investigate the interactions between solvent molecules and polymer chains.

The cononsolvency effect results from mixing two good solvents and leads to movement frozen of polymer chains. The freezing process in a good solvent can also be triggered by temperature change and/or other external stimuli. Sol-gel transition, a typical freezing process of polymer chains, is one of the most important topics in processing and practical application of polymeric materials. Chitosan (CS), a representative polysaccharide, has attracted considerable attention for its application as a resource-renewable and eco-friendly macromolecule [14–16]. In a recently developed technique for the fabrication of CS-based materials and devices, CS alkali (LiOH)-urea aqueous solutions have been applied as precursor [17]. After thermal gelation process in a mold and a post-rinsing treatment, the final products can be obtained. Compared with traditional techniques, this method of CS hydrogel preparation has shown advantages such as considerable improvement in hardness, strength, and toughness. In addition, the distinct gelation behavior offers innovative hydrogel design strategies. Thus, the study of gelation possesses high industrial and academic value. However, understanding of the gelation mechanism has been limited for a long time due to the shortage of suitable techniques for monitoring of the *in situ* gelation process.

In 2016, Wang *et al.* [18] introduced AIE-active fluorescent probe as an *in situ* reporter for gelation. As demonstrated in Fig. 3a, TPE units are covalently attached onto the side chain of the polysaccharide, and the trace amount of probe has no effect on the solubility and processability of TPE-modified CS (TPE-CS) due to the high sensitivity of FL technique. After thermal gelation and rinsing treatment, the TPE-CS in the LiOH-urea solution emits strong blue FL under UV light (Fig. 3b). Time-dependent confocal laser scanning FL microscope images reveal details of the gelation process (Fig. 3c). The

Figure 3 Real-time and *in situ* visualization of gelation process of CS by using AIEgen as fluorescent probe. (a) Molecular structure of TPE-CS. (b) Digital images of formation of hydrogel with TPE-CS: solution of TPE-CS, TPE-CS gel after thermal gelation, and TPE-CS hydrogel after complete removal of LiOH and urea; scale bar, 5.0 mm. The fluorescent photographs were taken under ultraviolet illumination (365 nm). (c) Confocal laser scanning FL microscope images of gelation process of TPE-CS. (I) Solution; (II) gel after thermal gelation; (III, IV) hydrogel after rinsing. Scale bar, 250 nm for (I–III); 25 nm for (IV). Reproduced with permission from Ref. [18]. Copyright 2016, Nature Publishing Group.

fluorescent image of the solution shows no specific patterns (I). However, some bright areas start to appear as heating starts, corresponding to the thermal gelation stage. The bright areas continue developing over time. Then, the development slows down, and finally the pattern stabilizes (II), implying that the thermal gelation of the system possesses a certain terminal point. The gel structure evolves further after LiOH and urea were completely removed by rinsing (III), suggesting that a further gelation process occurs after the terminal point of thermal gelation. After the rinsing stage, the bright areas subdivide and contract, and dark textures form. Eventually, a reticular structure is generated in the final CS hydrogel (IV). Combined with an analysis of the mechanical, dynamic mechanical property measurements and X-ray diffraction patterns, a three-stage gelation model was proposed: (1) thermal-induced formation of inter/intra-macromolecular hydrogen bonds, (2) microcrystallization-induced junction generation and primary gel formation, and (3) further formation of hydrogen bonding and final CS hydrogel formation due to the removal of LiOH and urea. This study represents a unique attempt to visualize the entire gelation process of the CS LiOH-urea aqueous system by using the AIE-active fluorescent probe. A detailed mechanism for the gelation

process was demonstrated, which shed new light on the intermolecular interactions in complex biomacromolecular systems. With the growth of the AIE and biomaterials field, various AIE fluorogens could be used to visualize various gelation systems.

The motions of the polymer chains or segments with temperature changing involve a centurial and global problem—the glass transition problem [19], which can be considered as the case of a pure and glassy (or amorphous) polymer without any solvent. Glass transition temperature (T_g), is a fundamental physical and structural parameter that is related to various physical properties of a polymer. Thus, each physical property change during glass transition provides a measurement method for T_g determination. These methods, such as differential scanning calorimetry, dilatometry, and dynamic mechanical analysis, rely on the integral change because glass transition is an intrinsic phase transition. On the molecular level, T_g defines a threshold temperature at which the motion of the segments in polymer chains is liberated or frozen by a heating or cooling thermal treatment. In principle, such a thermal-induced process can be sensed by an AIE-active fluorescent probe because the activated segment motion pushes the motions of the probe molecules and then deactivates the FL emission or weakens the

emission intensity if AIE-active molecules exist in the polymer matrix.

This assumption was validated by a rational experimental design, which was reported by Qiu *et al.* [20] in 2017. The researchers named their T_g detection technique as ADEtect, which combined the terms “AIE” and “detect”. As shown in Fig. 4a, the setup and measurement procedures are simple. TPA-BMO and polystyrene (PS) were used as AIE-active fluorescent probe and polymer matrix, respectively. The PS film with 1 wt% TPA-BMO was prepared according to the standard procedure. The fluorescent images were captured by a charge-coupled device camera in a preset temperature window, and representative photos were selected as shown in Fig. 4b. The images showed that the emission intensity or brightness decreased with rising temperature.

To quantify the information captured by fluorescent images, the red, green, and blue values were obtained using Matlab, by which the brightness of an image was quantified as grayscale (G) (Fig. 4c) in a standard formulation. The relative value (G/G_0) against temperature was plotted (in Fig. 4d, where G_0 was the grayscale at time 0 s). The curve of G/G_0 declines steadily with temperature, and the point at which a slope change occurs is assigned to T_g . Using the relative FL intensity (I/I_0) seems to be a direct method, but in fact, the slope change on the I/I_0 curve is usually more ambiguous than that on the G/G_0 curve. The reason for this accuracy improvement is

that the full spectrum is recorded in the fluorescent image and calculated as G/G_0 , but for I/I_0 , only the peak intensity at a certain wavelength is analyzed, thereby leading to partial loss of spectral information. Based on the description, ADEtect has shown a series of advantages, including easy operation, high sensitivity, good reliability, and low cost. More importantly, this new method allows the measurement of multiple samples in parallel, showing great potential for high-throughput T_g measurement. Thus, ADEtect has demonstrated its great potential in the academic and industrial fields.

Besides the application in the study of chain movements of classical polymers, copolymers, and biomacromolecules, AIEgens have been also used in investigating dynamic polymers. These polymers, which are constructed through the self-assembly of supramolecular building blocks, have received considerable attention in recent years [21]. This type of polymers often exhibits hierarchically ordered structures, high stimuli responsiveness, and smart functions. Understanding the dynamic assembly process is important, but we are short of such techniques. Although scanning electron microscope, transmittance electron microscope, and atomic force microscope can help us view the microstructure and morphology at nanometer level, the information that corresponds to the end products or final assemblies, and the initial step and kinetic stimuli-responsive behavior of self-assemblies have hardly been visualized. A unique

Figure 4 (a) Schematic of equipment setup of ADEtect measurement system. (b) Photographs of TPA-BMO-doped PS-1 films taken at different temperatures (from 50 to 130°C). (c) Illustration of data processing method. (d) Change of relative grayscale (G/G_0) of TPA-BMO-doped PS-1 film with temperature and associated fitting curve as well as second derivative of the fitting curve to reveal the change in G/G_0 at different temperatures. Heating rate: 6°C min^{-1} . G_0 is the grayscale at time of 0 s, and G is calculated according to the equation of $G = 0.2989 \times \text{Red} + 0.5870 \times \text{Green} + 0.1140 \times \text{Blue}$. The inset shows the molecular structure of fluorescent probe TPA-BMO. Reproduced with permission from Ref. [20]. Copyright 2017, American Chemistry Society.

characteristic of the AIE-active fluorescent probe is that it can dynamically change the emission intensity. Thus, it is an ideal probe to monitor the self-assembly process.

Recently, Tang *et al.* [22] reported visualizing the initial step of self-assembly process and phase transition by using stereogenic and amphiphilic AIE-active molecules (Z)-TPE-OEG and (E)-TPE-OEG (Fig. 5a), which were constructed by a hydrophobic TPE core and six thermo-responsive hydrophilic oligoethylene glycol (OEG) monomethyl ether chains. (Z)-TPE-OEG molecules self-assemble into vesicles, and (E)-isomers form micelles in water (Fig. 5a). The initial step of their self-assembly processes can be visualized based on AIE characteristics, with a sensitivity much higher than that of the method based on transmittance measurement. A continuous phase transition from microscopic self-assembly to macroscopic aggregation has been recorded by the (Z)-type

amphiphile due to the intrinsic thermo-responsive behavior of OEG chains. The entire process can be successfully visualized *in situ* by confocal laser scanning microscopy (CLSM). Based on the analysis of the fluorescent images, the kinetic process of the self-assembly shows different stages (Fig. 5b), which can never be observed by examining the appearance of precipitates (FL and CLSM images in Fig. 5a).

These instructive studies show the uniqueness of AIE-active fluorescent probes. Distinct from the traditional fluorescent probes, the fluorescent probes characterized by AIE activity are not emissive lookers that simply stand by and report the events, but rather actively participate in the events. These probes can sense the emancipated segment motions in solid amorphous polymer matrix by concomitantly activated intramolecular rotations and vibrations and report the glass transition temperature.

Figure 5 (a) Molecular structures of (Z)-TPE-OEG and (E)-TPE-OEG and visualization of their self-assembly and thermo-responsive behaviors. (b) Illustration of self-assembly and phase transition of (Z)-TPE-OEG. As the temperature increases, packing morphology of (Z)-amphiphiles changes from vesicles to large aggregates due to dehydration of OEG chains. c: concentration, and T: temperature. The photographs in (a) show the microstructures formed in the aqueous solution taken by CLSM and digital camera. Reproduced with permission from Ref. [22]. Copyright 2019, American Chemistry Society.

These probes can localize in the nano-scale networks of polymeric microgels and *in situ* sense the cononsolvency effect by the enhancement of their emission. Furthermore, these probes can be labeled to the polysaccharide side chains to monitor the CS hydrogel formation process in an *in situ* and real-time manner, and to fluorescently illustrate a step-by-step scheme of H-bond formation, microcrystalline generation, urea–LiOH release, and further shrinkage.

With such an unmatched nature, AIE-active fluorescent probes may shed light on a greater number of specific spaces that are dark and deep. For example, AIEgens are assumed to be the best candidates to visualize interface structures and monitor the interfacial dynamic processes because the restriction and liberation of intramolecular motion usually occur at the interface. Some recent publications have shown the potential of this research area [23–26]. According to the restriction of intramolecular motion mechanism of AIE activities, various external stimuli can easily interfere with the sensing of dynamic processes. Subtle changes in micro-environment can be reflected in FL fluctuation. Incorporation with other signals besides emission intensity is a valuable method that has been validated in studies in which the dichroism signal has been engaged to monitor the dynamic process in an *in situ* and real-time manner [27–30]. Considering the importance of visually monitoring biological events in life science and that the relevant processes occur under tissues or inside organisms, we find that the AIEgens brightly emitting in near-infrared II region represent a highly demanding subject that will become a thriving research area.

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Conflict of interest The authors declare no conflict of interest.

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在哪里运动受限, 就在那里发光

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摘要 本文通过典型研究实例列举了具有聚集诱导发光(AIE)性能的荧光探针分子的一些新用途, 如监测分子聚集体形成细节、双亲高分子链的共非溶剂效应、壳聚糖溶液中的多步溶胶-凝胶转变、测量玻璃化转变温度的新方法以及原位显示动态高分子组装过程的初始阶段等。在这些研究中, AIE-型荧光探针充分显示了其原位、实时、动态变化大和对比度高的特点, 揭示了其他研究手段难以提供的动态信息细节。这类工作机理独特的荧光探针将在未来的材料结构与性能的内在关系研究中发挥越来越重要的作用。