Aggregation-induced emission systems involving supramolecular assembly

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Funding information
National Natural Science Foundation of China, Grant/Award Numbers: 51673084, 21871108; Jilin Province-University Cooperative Construction Project—Special Funds for New Materials, Grant/Award Number: SXGJSF2017-3

Abstract
Aggregation-induced emission (AIE), as an exciting photophysical phenomenon, has been regarded as one frontier research topic within both ranges of molecular luminescence and materials science over the last two decades. Since controllable molecular ensembles with particular morphologies and tunable functions can be elegantly constructed in the realm of supramolecular chemistry, the integration of supramolecular assembly and AIE systems can expectedly bring about luminescent materials with tunable emission and tailorable well-ordered architectures. In this review, we will provide a summary of the creation and working mechanisms of AIE systems involving supramolecular systems that are driven by different supramolecular driving forces including hydrogen bonding, host–guest interactions, metal coordination, and π–π interactions. The morphological and photoluminescent features of these AIE-active supramolecular assemblies will be elucidated, and the regulated fluorescence properties of the AIEgens induced by the assembling–disassembling processes will be discussed in detail.

Keywords
aggregation-induced emission, fluorescence enhancement, luminescent materials, supramolecular assembly, synthetic macrocycles

INTRODUCTION

The manipulation of light has long been a captivating and challenging task in the development of human society since ancient times. On the molecular scale, light can be emitted by organic luminophores with conjugated π systems upon external irradiation, which is widely known as photoluminescence. However, conventional luminogens that are used to afford photoluminescence universally exhibit reduced or quenched emission because of their tendency to form excimers or exciplexes upon aggregation or in the solid state, and this phenomenon has been denoted as aggregation-caused quenching (ACQ),[1] marking a major blockade for the practical applications of many luminescent materials. Aggregation-induced emission, or AIE for short, has been a groundbreaking photoluminescent phenomenon within the field of light-emitting materials since its first discovery by Tang and coworkers in 2001.[2] In sharp contrast to traditional dyes, luminogens with nonplanar configurations, as known as AIEgens today, have been found to show poorly emissive features in dilute solutions while perform intense emission in the aggregated or solid states.[3] This inconsistency with conventional luminogens is contributed to the physically restricted intramolecular rotations or vibrations, or in other words, the restricted intramolecular motions (RIM), of the nonplanar conformations of AIEgens in the aggregated state, thus maximizing radiative relaxation pathway for the excited luminogens and exhibiting enhanced photoluminescence.[4] Definitely, the unearthing of AIE has dramatically stimulated the advancement of luminescent materials, offering unprecedented opportunities in a broad range of applications.[5]

Although plenty of luminescent materials based on AIE mechanism have already emerged, controlling the aggregation of AIEgens and tuning the aggregation patterns still remain indispensable topics and continue to attract much endeavor. Supramolecular assembling processes, driven by noncovalent intermolecular interactions including hydrogen bonding, electrostatic interactions, hydrophobic forces, metal coordination, Van der Waals forces, and π–π stacking are seminal for the creation of well-ordered architectures beyond molecular level built with fundamental building blocks, following the “bottom-up” approaches.[6,7] Due
to the dynamic and directional nature of the noncovalent driving forces, supramolecular assemblies are endowed with intriguing properties, such as good reversibility and stimuli-responsiveness, whereby the assembling processes can be adjusted by varying the basic molecular modules and/or exerting external actuations. Till today, a large number of AIEgen-containing supramolecular assemblies have been reported varying from simple complexes to sophisticated supramolecular ensembles, demonstrating adjustable features in various aspects including luminescence intensities, emission colors, and assembly morphologies, which relate closely to the altered strength or binding modes of supramolecular complexation.[8]

In this review, we try to cover the most recent and representative researches concerning AIE systems constructed via the approaches of supramolecular assembly driven by different types of supramolecular interactions, including hydrogen bonding, host–guest interactions, metal coordination, and \(π−π\) stacking. The construction methodologies of the AIE-active supramolecular assemblies will be discussed, accompanied by the structure–property connection between the resulted photoluminescent features of the AIE systems and the assembling patterns. Finally, the advantages of AIE systems involving supramolecular assembly will be highlighted, and we will also give our perspectives on the ongoing researches.

**AIE SYSTEMS INVOLVING HYDROGEN BONDING–DRIVEN SUPRAMOLECULAR ASSEMBLY**

Hydrogen bonding is one of the most fundamental noncovalent interactions in the scope of supramolecular chemistry, which also broadly exists and plays vital roles in life systems. Originating from the dipole–dipole forces between hydrogen atom and electronegative atoms like oxygen and nitrogen, hydrogen bonding can be attained easily via facile functionalization. Therefore, constructing AIEgen-containing supramolecular assemblies via hydrogen bonding has proven a feasible approach to obtain fluorescent supramolecular materials, such as self-healing fluorescent materials and luminescent liquid crystalline polymers. For example, in 2019, Zhang and coworkers reported a photo-deformable fluorescent polymer, namely, P4VP(Z-TCS)\(_x\), with an \(α\)-cyanostilbene derivative tethered to poly(4-vinyl pyridine) side chains as the AIE-active chromophore via hydrogen bonding O–H…N (Figure 1A), affording yellow fluorescent supramolecular fibers.[9] On account of the Z/E- isomerization of the \(α\)-cyanostilbene moieties upon irradiation of UV light, the as-prepared fibers displayed an excellent photo-induced deformation feature by shifting to a bending shape, which could be reversibly tuned by alternate operation of stretching and heating (Figure 1B). Without labor-taking
FIGURE 2 AIE systems involving quadruple hydrogen bonding–driven supramolecular assembly based on TPE stereoisomers. (A) Chemical structures of (Z)-TPE-UPy and (E)-TPE-UPy, and their supramolecular polymerization patterns. (B) The controlled photoisomerization yields and the resulted emission intensities by altered solvent conditions. Inset: fluorescence signals for the photoisomerization. Reproduced with permission. [13] Copyright 2017, American Chemical Society; Reproduced with permission. [14] Copyright 2019, American Chemical Society

synthetic procedures, a convenient method for the fabrication of smart fluorescent materials is provided in this work by simply attaching AIEgens into polymer backbones through hydrogen bonding-driven supramolecular assembly. Apart from acting as the binding forces basically, the application of hydrogen bonding can also take part in adjusting fluorescent properties of the inherent AIEgens. Wang, Xie, and coworkers demonstrated a liquid crystalline polymer assembled by hydrogen bonding named PPA(PTPEC$_4$)$_x$ (Figure 1A), which consisted of TPE derivative PTPEC$_4$ grafted to the side chain and showed reversible color tuning of fluorescence emission.[10] As PTPEC$_4$ content decreased, the emission color of the polymer in the solid state showed a red shift from 510 nm to 551 nm (Figure 1C and 1D). This phenomenon was attributed to the less restricted conformation of PTPEC$_4$ when less hydrogen bonds were formed within the polymer. The color could also be tuned upon fuming of proton acid and removal since the breakage of hydrogen bonding was caused by the protonation of the pyridine groups in PTPEC$_4$ (Figure 1E).

Especially, although the preparation and fluorescence adjustment of AIE systems involving hydrogen bonding–driven supramolecular assembly can be facile and expedient, higher binding selectivity and directionality are more possibly achieved by multiple hydrogen bonding, resulting in fluorescent supramolecular assemblies with well-ordered architectures, which are undoubtedly more applicable for the construction of tailor-made fluorescent materials with specific functionality. For instance, Yang and coworkers reported a series of light-harvesting supramolecular materials, including supramolecular polymeric nanoparticles, microfibers, and fluorescent films, constructed via quadruple hydrogen bonding using 2-ureido-4-[1H]-pyrimidinone (UPy)-modified donors and acceptors, presenting application potentials in in vitro and in vivo imaging.[11] Similarly, in 2020, another hydrogen bonding–driven supramolecular polymeric AIE material was fabricated by Wang and coworkers for light harvesting.[12] Supramolecular nanoparticles with intense emission at 480 nm were generated by assembling UPy-functionalized TPE molecules via quadruple hydrogen bonding followed by a mini-emulsion method. Upon loading the acceptor dye Nile Red into the nanoparticles, efficient light harvesting process was achieved within the material with a high Förster resonance energy transfer (FRET) efficiency and antenna effect.

By means of tuning the modification of the AIE modules, fluorescent supramolecular assemblies driven by quadruple hydrogen bonding can be constructed bearing distinct assembling fashions and luminescent features concurrently. In 2017, Tang and coworkers reported two types of supramolecular assemblies that were composed of (E)- and (Z)-isomers of TPE molecules equipped with UPy groups, namely, (E)-TPE-UPy and (Z)-TPE-UPy, respectively (Figure 2A).[13] Efficient self-assembly was driven by quadruple hydrogen bonding between two TPE moieties. The assembly of different isomers of TPE modules resulted in different architectures depending on the adjacent or opposite locations of UPy groups in the TPE configurations, where (Z)-isomers
formed spherical assemblies and (E)-isomers assembled into nanofibers. Additionally, the nanospheres showed green emission at 495 nm due to the loose arrangement, while the fibers, with more ordered structures, exhibited blue fluorescence at 479 nm, demonstrating the impact of AIEgen packing modes on the fluorescence properties of the assemblies. Interestingly, these UPy-modified TPE molecules can also undergo photoisomerization as controlled by the different polymerizability of the monomers and visualized by the altered fluorescence of the system (Figure 2B).\(^{14}\) By comparing the isomerization yields in different solvent conditions, higher assembly degree obviously contributed largely to the inhibition of backward reaction and promoted the isomerization efficiency, further causing the sphere-to-fiber transformation and the fluorescence change from weak green to bright blue, providing real-time monitoring of the photoisomerization processes.

AIE SYSTEMS INVOLVING HOSTGUEST–DRIVEN SUPRAMOLECULAR ASSEMBLY

Host–guest interactions universally involve the formation of inclusion complexes between two or more molecular entities via multiple noncovalent forces. Common macrocyclic host molecules used in supramolecular assemblies include crown ethers,\(^{15}\) cyclodextrins (CDs),\(^{16}\) cucurbit[n]urils (CB[n]s),\(^{17}\) calixarenes (CAs),\(^{18}\) and pillar[n]arenes (pillararenes),\(^{19}\) whereas guest modules of each host vary according to the different cavity properties and side-chain substituents. Particularly, well-defined supramolecular structures have been fabricated via the integration of AIEgens and host–guest chemistry, whereby the aggregation state of the chromophores are directed by the highly tunable and reversible assembly–disassembly processes of host–guest complexation that are responsive to various external stimuli.\(^{20}\) Three strategies are mainly applied to introduce host–guest chemistry into AIE systems for effective manipulation of the AIEgen emission, that is, (i) encapsulating AIEgens into macrocycle cavities, (ii) functionalizing macrocyclic hosts or guest entities covalently to AIEgens, and (iii) weaving AIEgens into the skeleton of macrocycles.

AIEgens modified by host or guest entities

Covalently equipping AIEgens with host and/or guest entities has been a widely used approach for the construction of tunable AIE materials that are manipulated by supramolecular assembly, whereby either macrocyclic hosts or guest groups can be functionalized onto the side chains of inherent AIEgens and further result in the supramolecular complexation or polymerization. Remarkably, the functionalization of the AIEgens by host–guest entities can be rationally selected according to the particular design, which largely attributes to the important advantages of supramolecular assembly–induced AIE systems that valid fluorescence enhancement can be realized in both solid and solution phases without suffering the limitation of solvent constituents and that the luminescence properties can be controlled precisely by excretion of specific stimuli.

Importantly, the design of assembling modules plays an important role in the major characteristics of the resulted AIE materials, including morphological and photophysical properties. Herein, we take AIE systems involving pillar[n]arene-based host–guest–driven supramolecular assemblies as models to illustrate that different assembly types with altered morphological and fluorescent properties can be formed via tuning the basic modules. For example, a linear supramolecular polymer with enhanced yellow emission upon assembly was reported by our group, which consisted of a 9,10-distyrylanthracene (DSA)-bridged pillar[5]arene dimer (DSA–(P5)\(_2\)) and a ditopic neutral guest linker (Di-G) with a 2:2 unit ratio of the effective host and guest binding moieties/sites, that is, each pillarene ring in one dimeric host binds to one triazole-cyano binding site in a ditopic guest linker (Figure 3A, note: the apparent host–guest binding stoichiometry is 1:1).\(^{21}\) Larger ensembles can be obtained by increasing the amount of host or guest binding sites functionalized in the AIE systems. Multidimensional AIE-active fluorescent supramolecular polymer was fabricated through assembling TPE-bridged pillar[5]arene tetramers (TPE-4C-(P5)\(_4\)) by Di-G with a unit ratio of 4:2 for the effective host and guest binding moieties/sites, that is, each pillarene ring in one tetrameric host binds to one triazole-cyano binding site in a ditopic guest linker (Figure 3B, note: the apparent host–guest binding stoichiometry is 1:2).\(^{22}\) Supramolecular gels with intense blue fluorescence were afforded, and performed reversible sol–gel transition and switchable fluorescence intensity upon temperature variation, presenting excellent stimuli-responsive features. Notably, via the integration of the two AIEgens by modifying them with host and guest moieties, respectively, a color-tunable fluorescent supramolecular assembly can be afforded due to the efficient FRET processes between TPE-4C-(P5)\(_4\) or TPE-2C-(P5)\(_2\) and DSA-G upon complexation at the unit ratio of 4:2 for the effective host and guest binding moieties/sites (Figure 3C, note: the apparent host–guest binding stoichiometry is 1:2),\(^{21}\) which performed tuned emission both in solution and in solid state, thanks to the host–guest interaction facilitated FRET, holding promise in smart optical devices. Apart from ditopic guests, linkers with tritopic guest entities (Tri-LG and Tri-SG) were synthesized with different carbon chain lengths and were used to interact with TPE-4C-(P5)\(_4\) or TPE-2C-(P5)\(_2\) at the unit ratio of 4:3 for the effective host and guest binding moieties/sites to construct a series of AIE-active supramolecular assemblies (Figure 3D, note: the apparent host–guest binding stoichiometry is 3:4).\(^{24}\) The assemblies fabricated by these building blocks possessed more intense fluorescence compared with the 4:2 systems, demonstrating an elevated enhancement effect endowed by the increased binding sites in each host and guest. Interestingly, assembly with shorter carbon chains showed stronger fluorescence, while no gelation activity was observed. On the contrary, despite that Tri-LG \(_c\) TPE-4C-(P5)\(_4\) displayed less emission enhancement, this assembly with longer carbon chains was successfully constructed into blue fluorescent supramolecular gel. These phenomena can be ascribed to the higher compactness induced by the shorter chains and the looser assembly structures formed by the longer chains that can include solvent molecules, respectively. Furthermore, assemblies in larger scales, such as supramolecular polymeric networks, have also been reported.
and proved to possess even higher enhancement degree in the respect of fluorescence intensity and quantum yields.\cite{25,26}

Definitely other supramolecular macrocycles have also been used in the supramolecular assemblies for AIEgens and are able to present their unique features in the assembling processes. For instance, crown ethers can lead to assemblies by specifically chelating with $K^{+}$ at a 2:1 host guest binding stoichiometry and in a sandwich mode, thus weaving AIEgens into the structures,\cite{27} while CAs can assemble several guest-bearing AIEgens concurrently and achieve emission enhancement, which is known as calixarene-induced aggregation.\cite{28} CB[n]s (especially when $n = 8$) can form 1:2 host–guest complexes with monocationic guests,\cite{29} and sometimes even the AIEgens can be included into their cavities and be put into the packing arrangements.\cite{30}

Benefitting from this fundamental knowledge, AIE-active host–guest-driven supramolecular assemblies with promoted functionalities have been constructed for various real-world applications. Because of the enhanced fluorescence properties of AIE systems and responsive features of host–guest–driven complexes, AIE-active supramolecular assemblies with good water dispersity and biocompatibility are considered ideal materials for biomedical applications. In 2020, Ding and coworkers reported the fabrication of a type of CD-based supramolecular AIE dots prepared by host–guest coassembly between the tumor-targeting enzyme-responsive PEG-peptide and $\alpha$-CD modified by AIEgen entities ($\alpha$-CD-TPR) and anticancer drug molecules ($\alpha$-CD-GEM), respectively (Figure 4A).\cite{31} Enhanced fluorescence was originated from the formation of compact nanoparticles caused by host–guest interactions, thus lighting up the targeted tumor sites after precise accumulation, while drug release was achieved within the tumor cells simultaneously in response to the reductive microenvironment, realizing effective image-guided drug delivery.

Another important aspect in the biomedical field is cell identification. In 2020, Tang and coworkers constructed a series of fluorescent supramolecular assemblies based on host–guest interaction between TPE derivatives and CB[8]s, which showed optimized fluorescence properties after host–guest binding and also possessed superior cell staining ability (Figure 4B).\cite{32} Particularly, the material hold

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**FIGURE 3** AIE systems involving host–guest driven supramolecular assembly with pillar[5]arene-based AIE supramolecular assemblies as models. (A) Linear supramolecular assemblies by DSA-(P5)$_2$, Di-G at a unit ratio of 2:2. (B) Multi-dimensional supramolecular assemblies by TPE-4C-(P5)$_4$, Di-G at a unit ratio of 4:2. (C) Color-tunable supramolecular assemblies with host–guest interaction facilitated FRET process by TPE-4C-(P5)$_4$ or TPE-2C-(P5)$_4$ and DSA-G at a unit ratio of 4:2. (D) Supramolecular assemblies by TPE-4C-(P5)$_4$, TPE-2C-(P5)$_4$, Tri-LG, Tri-SG at a unit ratio of 4:3. Note: the ratios were obtained by counting the pillararene ring numbers in each host and the triazo-cyano binding site numbers in each guest during compact and ideal supramolecular assembly, just for better understanding, which do not represent the host-guest binding stoichiometry. Reproduced with permission.\cite{21} Copyright 2015, Royal Society of Chemistry; Reproduced with permission.\cite{22} Copyright 2014, Royal Society of Chemistry; Reproduced with permission.\cite{23} Copyright 2020, Royal Society of Chemistry; Reproduced with permission.\cite{24} Copyright 2018, Wiley-VCH VerlagGmbH&Co. KGaA, Weinheim.\cite{25,26}

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FIGURE 4 AIE systems involving host–guest driven supramolecular assemblies in aqueous media for biomedical applications. (A) Supramolecular AIE dots constructed via the host–guest co-assembly of α-CD-TPR and α-CD-GEM with PEG-peptide chains for image-guided drug delivery. (B) Supramolecular assemblies constructed via host–guest interaction between TPE-based guests and CB[8] for cell line identification. (C) Supramolecular assemblies constructed via host–guest interaction between TPE-based photosensitizer and WP5 for controlled ROS generation. (a) Fluorescence spectra of G, G (pH 5), WP5 + G (pH 5), and WP5 + G. (b) Changes of fluorescence intensities of WP5 + G at varied pH. Reproduced with permission. [31] Copyright 2020, American Chemical Society; Reproduced with permission. [32] Copyright 2020, American Chemical Society; Reproduced with permission. [33] Copyright 2020, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

the ability of cell identification between normal cells and cancer cells due to different affinity of the supramolecular assemblies toward different cell lines, whereby cell pollution can also be tracked with the aid of the tunable emission of the supramolecular assemblies.

Apart from supramolecular assemblies with sophisticated structures, simple complexes can also be utilized for important biomedical applications. For example, in 2020, a host–guest complex with switchable AIE fluorescence and adjustable generation of reactive oxygen species (ROS) was established containing water-soluble pillar[5]arene (WP5) and a TPE-based photosensitizer as the guest (Figure 4C). [33] The complex showed weak red fluorescence under neutral conditions, but dramatic emission enhancement upon acidification due to the reduced solubility caused by the pH-responsive feature of the pillar[5]arene. Concurrently, ROS was annihilated because of the photoinduced electron transfer (PET) between host and guest, while upon acidification the host–guest binding site can be tuned through a shuttle movement, thus recovering the ROS generation. The supramolecular complex achieved switch on–off processes for both fluorescence and ROS and showed potential in cancer imaging and therapy.

AIEgens encapsulated by macrocycles

Compared with modifying AIEgens with macrocycles or guest entities, the straightforward encapsulation of the luminophores into the macrocycle cavities can be a more facile method to achieve enhanced fluorescence. A representative model of macrocycle-encapsulated AIEgen was presented by Tang and coworkers in 2014, where TPE molecules were first covalently bonded to α-CDs, β-CDs, and γ-CDs, respectively, and then formed a self-inclusion complex due to the hydrophobic cavities of CDs, among which the complex TPE-α-CD showed the most intensified fluorescence resulting from the efficient restriction of TPE motions by the host compared with the other two CDs, because of the relatively small cavity of α-CDs (Figure 5A). [34] With strong emission and improved water solubility, this self-inclusion complex was endowed with application potential in intracellular imaging. Interestingly, the macrocycle-encapsulated AIEgens does not necessarily show enhanced fluorescence in all cases. Another work concerning the inclusion of amphiphilic TPE into γ-CD cavity presented the conflicting phenomenon. [35] TPE modified by two sulfonate groups formed one-dimensional aggregates in water and performed
bright emission due to the aggregated state, yet the addition of \( \gamma \)-CDs led to fluorescence turn-off by preventing the TPE molecules from aggregation. Since the cavity of \( \gamma \)-CDs are too large to apply effective restriction for TPE motions, the host–guest interaction only caused the discrete state of the AIEgens. From this result, it can be deduced that enhanced emission cannot be achieved based on mere inclusion but the valid restriction on the intramolecular motions of the AIE luminogens. Similarly, CB[n]s also have been used as the “containers” for AIEgens to achieve assembly-induced emission enhancement. For instance, TPE cationic derivatives can be encapsulated into CB[10]s via host–guest interaction in two plausible modes and thus exhibited fluorescence enhancement (Figure 5B).[36]

**AIEgen-based macrocycles or molecular cages**

Creation of macrocycles with controllable fluorescent features has been a hot topic in the field of supramolecular chemistry and also a meaningful task for broadening the species of functional fluorescent materials.[37–41] Recruiting AIEgens as monomers for the design of macrocyclic or shape-persistent cage-like structures can afford inherent restriction for the intramolecular motions and hence promote the fluorescence properties, while the further introduction of the guest molecules into the AIE-based macrocycles can act as an effective regulator for the emission features.[42] On this basis, Tang and coworkers described the design and construction of an amphiphilic organic cage with the AIEgen tetraphenylpyrazine (TPP) weaved into the cage structure covalently (TPP-cage), which performed intense blue emission and brilliant guest uptake ability toward a planar yellow-emissive luminophore, thus exhibiting stable white light emission (Figure 6A).[43] Binary light harvesting was achieved in this host–guest system on account of the synergetic effect that the restriction on the intramolecular motions of TPP units was largely elevated upon formation of the cage and that intermolecular stacking of the planar guest molecules was prevented due to the encapsulation by the cage, enabling the TPP-cage to emit enhanced blue fluorescence in the solution and allowing the guests to display strong yellow emission in the assembled state.

Further self-assembly of the AIEgen-based macrocycles may lead to supramolecular nanostructures with interesting fluorescent properties. Inspired by the famous cyclophane “Blue Box” reported by the Stoddart group, Cao and coworkers reported the synthesis of a TPE-based tetracationic dicyclophane with three TPE units integrated into one macrocycle (Figure 6B).[44] The tetracationic macrocycle could self-assemble into crystalline nanospheres in an aqueous solution with bright emission at 580 nm and a high quantum yield of 97.7%. The nanospheres can encapsulate red-emitting dye molecules, Nile Red, to realize light harvesting via efficient energy transfer.

Remarkably, the integration of AIEgens and existing macrocycle units into one macrocycle skeleton provides another feasible strategy for generating AIEgen-based macrocyclic compounds with unexpected structural and optical features. A new fluorescent dual macrocycle, denoted as bowtiearene, was recently reported by Cong and coworkers as a combination of TPE moieties and pillar[5]arene rings (Figure 6C(a)).[45] Possessing double pillar-like cavities, bowtiearene showed adjustable fluorescence response to multiple stimuli including mechanical forces (grinding) and vapor fuming (\( p \)-xylene) in the solid state, attributing to the altered molecular packing modes of its crystals, whereby the less ordered packing structure led to the red shifts of fluorescence emission (Figure 6C(b)).

Additionally, apart from the covalent pathway, the coordination of tailored AIEgens with metal ions can also afford macrocycle or cage structures, that is, well-defined metallacycles and metallacages,[46–51] which can also exhibit satisfying fluorescence enhancement because of the rigid immobilization of the AIEgens within the coordination structures. Considering that these metal–organic materials are categorized into the scope of supramolecular coordination complexes and have already been elucidated comprehensively in previous literature,[52] we will not cover the detailed illustrations on the subject in this review.
AIE SYSTEMS INVOLVING COORDINATION-DRIVEN ASSEMBLY

Coordination-driven assemblies of AIEgens have been extensively investigated with versatile design methods, thanks to the relative ease of luminophore functionalization and the multiple choices of metal ions. Similarly, coordination-driven assembly-induced emission enhancement has been realized mainly by the construction of AIE-active coordination supramolecular polymers and the fabrication of discrete coordination complexes.

Regarding the AIE systems involving coordination-driven supramolecular assembly, the application in the design and exploitation of fluorescent probes for metal ions can hardly be ignored. In 2019, we reported a supramolecular approach to achieve fluorescence enhancement via constructing a supramolecular polymer connected by metal ion coordination and host–guest interactions, which possessed superb abilities of sensing and removing Hg$^{2+}$ in aqueous media (Figure 7A). TPE molecules dually functionalized by quaternary ammonium groups were linked via host–guest complexation with thymine-modified [2]biphenyl-extended pilarenes, as the macrocycle cavity included two quaternary ammonium moieties, leading to the formation of linear supramolecular assemblies. Because of the strong binding affinity between thymine groups and Hg$^{2+}$ through thymine–Hg$^{2+}$–thymine pairing, the addition of mercury ions can result in cross-linked supramolecular polymers with stronger fluorescence. Reusability of the material was proved by removing Hg$^{2+}$ upon addition of S$^{2-}$, thus quenching the turned-on fluorescence (Figure 7B).

Discrete coordination complexes normally concern one or several AIEgen-based ligands coordinated to metal ions without polymerization. Yan and coworkers reported the facile preparation of a type of fluorescent metallo-organic vesicles assembled by a red-emitting AIEgen, triaryleamine carboxylate, after being coordinated to Zn$^{2+}$ as the ligand at a ratio of 2:1. The ligand was found to coordinate exclusively to Zn$^{2+}$ compared with other divalent metal ions and showed remarkable emission enhancement after coordination, which was attributed to the firm confinement within the vesicles formed by the coordination complex. Another discrete AIE coordination complex was developed by the same group in 2020, whereby various alkaline-earth metal ions were adopted to coordinate with an AIE-active ligand, diphenylidibenzofulvene modified with a coordination head (PBFL), and the complex further assembled into lamellar packing structures, achieving well-tuned emission color via hydration and dehydration processes. All complexes showed intense yellow emission under dry conditions, yet noticeable color changes occurred upon hydration, because the inherent tight packing of the complexes were loosened by varying degrees and caused changes of the AIEgen from relatively planar conformation to a more torsioned structure. In addition, reversible conformation and color tuning of the complexes can be realized by water removal via either heating or grinding, demonstrating a facile method of adjusting fluorescence properties of AIEgens, especially in the solid state.
AIE SYSTEMS INVOLVING–INTERACTION-DRIVEN SUPRAMOLECULAR ASSEMBLY

The $\pi-\pi$ interactions have been broadly investigated in the range of conjugated molecules as a universally existing intermolecular binding forces that occur among the inherent luminogens instead of effecting via postmodified functional groups, thus rendering it particularly effective in tuning fluorescence properties by straightly altering the packing modes. For many supramolecular architectures containing $\pi$-conjugated molecular entities, even though the assemblies are principally jointed by other intermolecular driving forces, $\pi-\pi$ interactions are still indispensable within the structures,[56–59] which we will not discuss in detail in this section.

Particularly, it is worth noting that an important class of $\pi-\pi$ interaction–driven supramolecular assembly is the formation of luminescent crystals owning well-ordered molecular arrangements. Specifically, AIEgen-containing crystal systems with simple components can perform enhanced fluorescence and tunable emission colors highly depending on the crystal packing modes. For example, Tian, Xu, and coworkers reported the creation of two types of luminescent cocrystals grown by controlling crystallization solvents, consisting of a typical AIEgen, 9,10-bis(E)-2-(pyridin-4-yl)vinyl)anthracene (BP4VA), and a halogenated conformer, 1,3,5-trifluoro-2,4,6-triiodobenzene (FIB) (Figure 8A).[60] Dominated by halogen bond and $\pi-\pi$ interactions, respectively, the two crystalline structures can be transformed to each other reversibly by grinding, THF fuming, or heating, resulting from the adjustable intermolecular arrangements, and the fluorescence color was also altered from green to yellow in accordance with the packing modes (Figure 8A and 8B).

On the other hand, single-component luminescent crystals can also be constructed with stimuli-responsive emission properties by regulating the stacking manners of the AIE molecules. In 2020, a piezochromic crystal was developed employing a TPE-modified anthracene molecule with a meta-linkage (mTPE-AN), which showed pressure-induced blue shift and fluorescence enhancement (Figure 8C).[61] Compared to its counterpart with a para-linkage that formed planar assembly (pTPE-AN), mTPE-AN took a more asymmetric conformation and thus favored the formation of dimers with antiparallel $\pi-\pi$ stacking. The mTPE-AN crystals, under ordinary pressure, displayed green yellow emission originated from the anthracene dimers, benefiting from the energy transfer from TPE moieties. However, as pressure increased, the fluorescence color was tuned from green to yellow, and finally changed to blue, which was rationally ascribed to the simultaneous energy transfer suppression and AIE effect induced by the tighter packing (Figure 8D and 8E). In contrast to common piezochromic materials, the integration of $\pi$-stacked dimers and AIEgens into one molecule highly promoted the fluorescence properties of the resulted supramolecular assemblies, including pressure-induced emission enhancement and multicolor fluorescence.

CONCLUSION

The design, syntheses, and photophysical properties of AIEgens have been under intense investigation for two decades. From the view point of molecular aggregates, an important topic in the scope of AIE systems is to yield well-defined aggregate structures with adjustable morphologies and tunable fluorescence. In recent years, the integration of supramolecular chemistry and AIEgens has emerged as an important approach for effectively controlling the aggregation activities of AIEgens. By modulating the aggregation of AIEgens with the supramolecular assembling processes that are driven by hydrogen bonding, host–guest interactions, metal coordination, and $\pi-\pi$ interactions, the fluorescence properties of the AIEgens, including fluorescence intensities and emission wavelengths, can be nicely regulated, accompanied by the reversible formation and dissociation of supramolecular ensembles. Compared with achieving fluorescence enhancement of AIEgens via the formation of...
random aggregates, the major advantages of fabricating AIE systems involving supramolecular assembly are as follows:

Instead of being lightened up only upon aggregation, fluorescence enhancement can be obtained in both dilute solutions and solid states because of the valid RIM effect endowed by the assembly.

By rationally selecting the building blocks of the supramolecular assemblies, the morphologies and stimuli-responsive features of the constructed architectures can be tailor-made according to the targeted scenarios.

Due to the versatile modification by supramolecular modules, the AIEgens can be endowed with diverse functionalities that allow the AIE systems to be applied as multifunctional luminescent materials in more broadened fields.

For the further advancement of AIE systems involving supramolecular assembly, one important aspect lies in the deeper understanding of the structure–property relationship. Systematic studies are required to shed more light on how assembling patterns specifically influence the photoluminescent properties of the AIEgens by means of proper characterization techniques and theoretical calculations. AIE-active supramolecular assemblies with even higher conformational regularity will also be pursued, including supramolecular organic frameworks (SOFs) with controllable properties, and metal-organic frameworks (MOFs) constructed by metal coordination. For another, since the exertion of supramolecular assembly in AIE systems can build a bridge to various functionalities, myriad possibilities beyond emission enhancement should arise, necessitating more efforts to be dedicated to promoting the performances of supramolecular assembly–driven AIE systems in many different fields, such as circular polarized luminescence, light harvesting systems, and thermally activated delayed fluorescence. We believe that the combination of AIEgens and supramolecular assembly can bring benefits to both research areas, and as novel constructing methods
continue to sprout, the births of luminescent materials that possess highly manipulated morphologies and emission properties can hopefully be anticipated.

ACKNOWLEDGMENTS

The authors acknowledge the National Natural Science Foundation of China (51673084, 21871108), the Jilin University Talents Cultivation Program for financial support. X.-Y.L. drafted the article and Y.-W.Y. revised and finalized the article.

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How to cite this article: Lou X-Y, Yang Y-W. Aggregation-induced emission systems involving supramolecular assembly. Aggregate. 2020;1:19–30. https://doi.org/10.1002/agt2.1