Modulating Molecular Aggregation of Luminogens: Bridging the Gap Between Solutions and Solids

Peng Meng,[a,d] Andreis Lau,[a] Daigo Miyajima,[a] Parvej Alam,[a,*] Zijie Qiu,[a,c,*] Ben Zhong Tang[a,b,*]

[a] Clinical Translational Research Center of Aggregation-Induced Emission, School of Medicine, The Second Affiliated Hospital, School of Science and Engineering, The Chinese University of Hong Kong, Shenzhen (CUHK-Shenzhen), Shenzhen 518172, China

[b] Department of Chemistry, Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration and Reconstruction, The Hong Kong University of Science and Technology, Kowloon, Hong Kong, China

[c] Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

[d] University of Science and Technology of China, Hefei, Anhui, 230026, China

Abstract:

In the past two decades, the advancement of aggregation-induced emission (AIE) has greatly advanced our understanding of organic luminescence and facilitated the application of organic luminescent materials. AIEgens emit weakly in solutions but strongly in aggregated states. This significant difference in luminescence between solutions and aggregated states of AIEgens has shown that there is much to explore in the mesoscopic world (the intermediary phase). Accordingly, the research paradigm is shifting towards aggregate science. The path to new aggregate materials relies not only on molecule syntheses but also on the control of molecular aggregation. Molecular aggregation bridges the gap between solutions and solids, which is of great significance for developing aggregate science. In this perspective, we outline three general strategies for managing molecular aggregation to stimulate new ideas and provide guidance on controllable molecular aggregation.

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1. Introduction

Solution and solid represent two fundamental states of matter. In solutions, substances dissolve into solvents, while solids form as solvents are removed. This solution-to-solid transition seems simple yet underlies many important natural phenomena, especially in molecular systems where properties in each state can vastly differ. This contrast unlocks rich molecular behaviors and provides ample opportunities for academic investigations. A typical example of this is found in organic luminescent materials.[1-4]

In the past two decades, organic luminescent materials have flourished with the development of modern application techniques, including flexible display,[5-8] imaging,[9-13] sensors,[14-18] disease diagnosis and therapy,[19-23] etc. One of the most significant advantages of organic luminescent materials is their excellent processability,[24-27] which is manifested by the easy transition between solutions and solids. However, the luminescent properties of organic materials displayed in solutions and solids can be different, which are summarized into two complementary phenomena: aggregation-caused quenching (ACQ) and aggregation-induced emission (AIE).[28-29] ACQ molecules exhibit bright emission in solutions but are quenched in aggregate states. In contrast, AIE molecules (AIEgens) are weakly emissive in solutions but become highly emissive upon aggregation. Compared to ACQ materials, AIEgens have attracted increasing attention because of their robust luminescence performance in the aggregate/solid state. This has made research on AIEgens a thriving research area.[2, 12, 30-34]

Significant progress has been made in understanding the working mechanism of AIE over the past two decades. Several theories have been proposed, among which restricted intramolecular motion (RIM) is the most popular.[3, 35] According to RIM, the excited molecules can readily dissipate their energy through nonradiative pathways at the molecular level due to active molecular motions. However, at aggregate levels, the motion of AIEgens is restricted, decreasing the nonradiative relaxation and consequently facilitating the radiative relaxation of AIEgens upon excitation. The RIM mechanism offers invaluable insights for tailoring AIEgens at the molecular level, which paves the foundation of AIE. Inspired by AIE, many new

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concepts have been discovered and proposed, such as crystallization-induced emission (CIE),[36-38] cluster-triggered emission (CTE),[39-42] vibration-induced emission (VIE),[43-44] etc. These fantastic research outcomes lead to a conclusion that the properties of molecules in solutions and aggregated states can be vastly different,[27] not just from the perspective of photophysics, but from the basic understanding of physical chemistry. In this context, our group proposed a new research paradigm of "aggregate science" and summarized four effects: antagonism, synergism, emergence, and divergence.[30] The four effects cover the basic principles of aggregate science, providing general guidance for researchers and stimulating new ideas from a broad readership.

Exploring and characterizing novel aggregates /solid-state materials is the foundation of materials science. Each of these materials has unique properties that make them particularly desirable. Developing robust techniques for controlled aggregation of molecules is crucial, especially when multiple aggregates or solid forms can be derived from identical or closely related molecular constituents. This ability to manage molecular aggregation bridges the gap between solutions and solid-state materials, constituting an essential element within the overarching framework of aggregate science and should not be overlooked.
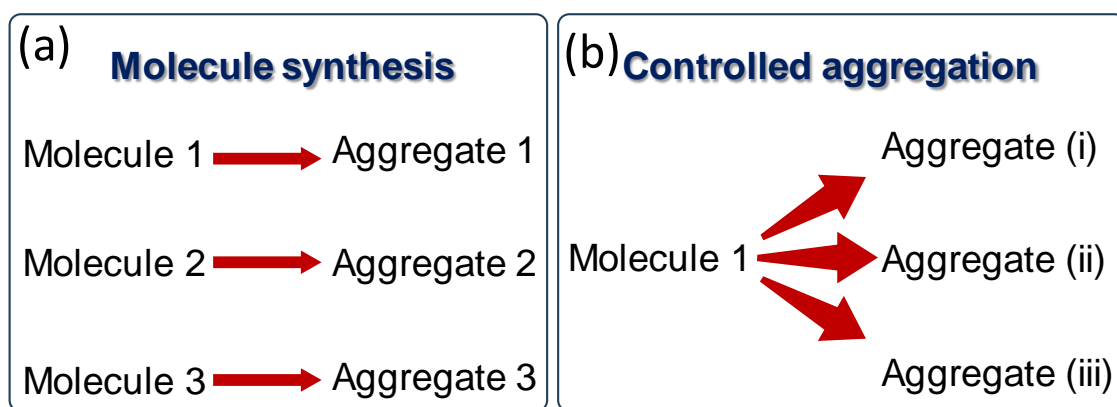

Figure 1. Two general ideas for obtaining new aggregates: (a) by molecular synthesis and (b) by controlled aggregation.

Controllable molecule aggregation aims to create various structures at aggregate level using single molecules, generally from the corresponding solutions

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(Figure 1). The molecular composition at aggregate levels, in both microscopic and macroscopic scales, can be categorized into two subtypes: amorphous states and crystalline states. Thus, controllable molecular aggregation involves manipulating the formation of amorphous and crystalline states to achieve a desired orientation.

In this perspective, we aim to summarize the current progress made in manipulating molecular aggregation. We have identified three general paths/methodologies based on the different stages of molecular aggregation (**Figure 2**). These paths include (i) molecule modification before aggregation, (ii) manipulation during aggregation, and (iii) post-processing after aggregation. Our goal is to provide guidance on controlling molecular aggregation from solutions to diverse aggregates/solids.

① Molecule modification before aggregation   ② Manipulation during aggregation   ③ Post-processing after aggregation

Solution state   **Aggregated State**
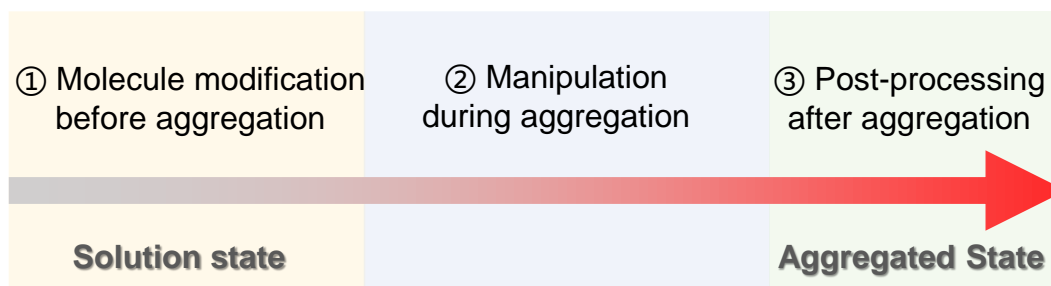
Figure 2. Three general methodologies for molecular aggregation: (1) molecule modification before aggregation, (2) manipulation during aggregation, and (3) post-processing after aggregation.

2. Strategies for Modulating Molecular Aggregation

2.1. Molecule Modification Before Aggregation

Molecule modification before aggregation refers to chemically altering the intended molecules prior to aggregation. This is a chemical process that does not physically change the molecules themselves. However, as the luminescent properties of molecules are generally dependent on their chromophores, modifications that do not alter the electron distribution on chromophores will not affect the optical properties at the molecular level.

On the other hand, molecule modification inevitably changes molecular size, leading to different steric effects during aggregation and, thus, aggregate structures. Therefore, this methodology provides a way to manipulate molecular

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aggregation through chemical means. A typical example is size chain engineering, where the size and shape of side chains are altered to influence intermolecular interactions and control aggregation.[45-47]

Differing from moving the linked point of the alkyl chain to the backbone, which will change the electron distribution on the backbone and thus shift the emission at the molecular level, [48-49] side chain engineering by prolonging the alkyl chain generally will not affect its absorption/emission properties at the molecular level as the chromocenters are intact. However, due to different steric hindrance, the different length of the alkyl chain does affect the molecular packing at aggregate levels, which endows it a valuable strategy to tune the absorption and emission properties at aggregate levels for multiple functions.[50-52] For example, Yingping Zhou and co-workers synthesized three A-DA'D-A (acceptor–donor–acceptor'–donor– acceptor) type molecules, namely Y6, Y6-C4, and Y6-C5, to illustrate how side-chain engineering can manipulate molecular stacking in films (**Figure 3a,b**).[50] The central backbone of **Y6** possesses a twisted DA'D framework, owing to the branched alkyl chain 2-ethylhexyl with the opposite manner attaching to the two sp^2-hybridized nitrogen atoms in the pyrrole motif. All three acceptors had similar absorption spectra, with the maximum absorption peak located at 731 nm in solution, indicating that the absorption properties of **Y6**, **Y6-C4**, and **Y6-C5** were barely affected by different alkyl chains in dilute solution. However, the changes from solution to film exhibited large differences in molecular packing. **Y6** displayed an obvious red shift of about 100 nm, while **Y6-C4** and **Y6-C5** showed a red shift of only ~50 nm from solution to film absorption. Grazing-incidence wide-angle X-ray scattering results indicated that the **Y6** film adopted the preferential face-on orientation. By moving the branching point of the pyrrolic alkyl chain from second to fourth, the **Y6-C4** film exhibited favorable edge-on orientation to the substrate. On the other hand, **Y6-C5,** which has alkyl chains branched in the fifth position, showed a relatively higher face-on orientation than **Y6-C4**. Consequently, **Y6-C5** behaved as a rather crystalline solid aggregate, compared with **Y6-C4** in both pristine and blend systems, which leads to the lower non-radiative energy loss of

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0.26 eV with the highest open circuit voltage of 0.88 V among the three photovoltaic devices.

Side-chain engineering can be used to adjust the optical properties of films and bulk crystals. Meizhen Yin et al. reported that the minor modification of the alkyl groups of cyanostilbene derivatives (**CSEt** and **CSPr**) allows control of the solid-state fluorescence and photomechanical behaviors in the crystal state (**Figure 3c**).[53] In dimethyl sulfoxide (DMSO) solutions, **CSEt** and **CSPr** showed identical patterns of UV-vis absorption at 325 nm. Meanwhile, the fluorescence spectra expressed the same peaks at 400 nm with a low fluorescence quantum yield of 0.3% and 0.5% for **CSEt** and **CSPr**, respectively. Those results indicated that the alkyl groups did not affect the electronic structure of the cyanostilbene core. However, in their crystalline state, the **CSPr** crystal powder with longer alkyl groups emitted intense blue fluorescence emission at 455 nm under UV light with a quantum yield of 84%. In contrast, the **CSEt** crystal with shorter alkyl groups exhibited weak emission. The **CSPr** crystals demonstrated excellent photostability when subjected to UV light. However, the **CSEt** crystal exhibited high reactivity to [2+2] photocycloaddition, leading to light-driven crystal bending and cracking. Furthermore, the fluorescence of the **CSEt** crystal underwent a significant increase upon exposure to UV irradiation and force grinding. This unique feature enabled the crystal to exhibit dual stimuli-responsive fluorescence that turned on. Single crystal X-ray diffraction and DFT calculation demonstrated that this was due to the different stacking modes in which the **CSEt** adopted a mixed stacking with significant intermolecular overlap and strong π-π interactions (interplanar distance: 3.32 Å). In contrast, **CSPr** adopted a lamellar-like stacking with weak π-π couplings (interplanar distance: 3.67 and 3.42 Å).

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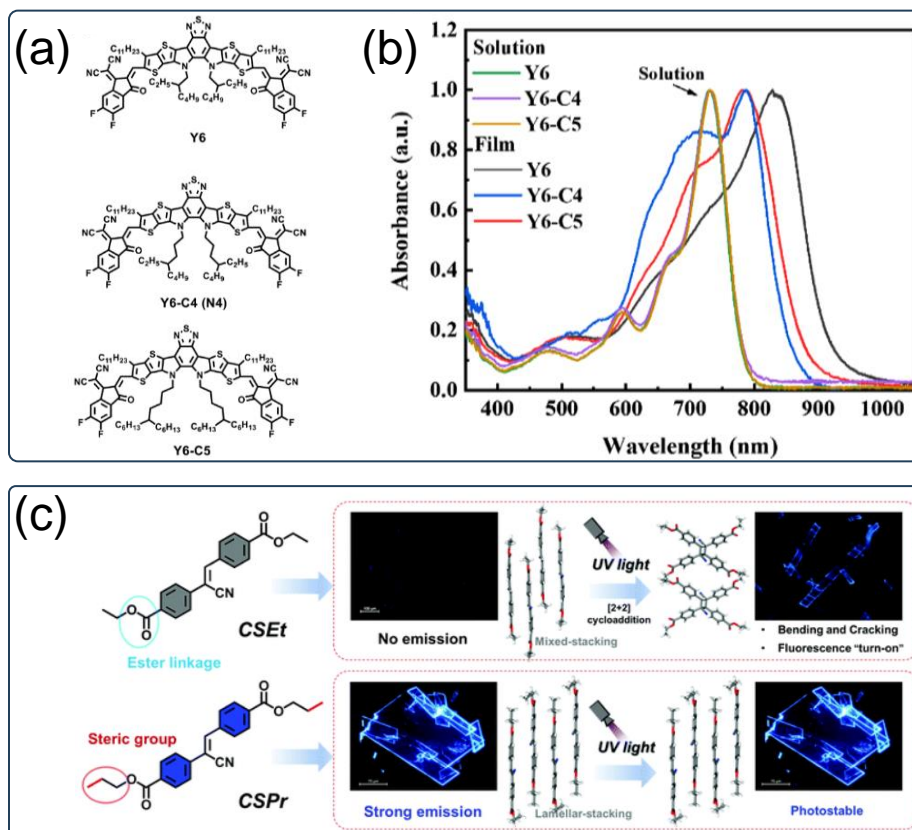
Figure 3. Side-chain engineering demonstrating (a,b) the change of emission wavelength (Copyright: CC BY license)[50] and (c) the change of quantum yield (Copyright: Royal Society of Chemistry).[53]

2.2. Manipulation During Aggregation

Manipulation during aggregation is to control the structure of molecular precipitation from solutions by adding poor solvents and evaporating solvents. [54-56] Both thermodynamic and kinetic factors control this process and can be regarded as controllable polymorphism,[57-59], which is of great challenge. The precipitation of molecules can be either amorphous or crystalline, depending on the practical implications. The approaches of controllable polymorphism include (i) transformation from the amorphous to crystals and (ii) induction of crystals with multiple phases.

The solid states of AIEgens (both in nanoparticles and films) can easily be amorphous due to the rotatable parts present in the molecules. In 2017, a seminal work reported by Liu Bin and co-workers regarding the transformation of

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nanocrystals from amorphous state as an effective method to enhance the brightness of AIE materials.[60] They synthesized a new AIEgen by adding a tetraphenylethene (TPE) moiety to dicyanomethylene-benzopyran (DCMB), named **TPE-FN**, which had a moderate brightness in the amorphous state, but became highly emissive when it formed crystals (**Figure 4a**). The amorphous state of **TPE-FN,** which was the immediately precipitated products after adding water (f_w: 60–90%), emitted a moderate orange emission under UV light excitation, while the nanocrystals which were obtained by aging the amorphous particles for 24 hours, showed bright greenish yellow emission. Since transforming from nanoaggregates to nanocrystals is a thermodynamic process, they developed an ultrasound-assisted technique to shorten the transformation time and make it more controllable. In addition, there was no significant difference between the absorption spectra of both. At the same time, the PL intensity of nanocrystals showed more than a 4-fold increase with a 50 nm blueshift compared to that of amorphous nanoaggregates. The bright fluorescence of nanocrystals resulted from the tightly packed arrangement of **TPE-FN** molecules within a crystal matrix. This ordered structure restricts intramolecular motion to a greater extent than the disordered structure of amorphous aggregates, suppressing nonradiative relaxation pathways and activating the radiative decay channels.

Moreover, during the amorphous-to-crystal transformation, the crystalline structures can be tuned. For example, Jianjun Wang *et al*. adopted a freeze assembly strategy to manipulate the molecular assembly process of 1,1,2,2-tetra(4-methoxyphenyl) ethene (**TMOE**) through the regulation of the evolution of solvent crystal grain recrystallization (**Figure 4b**).[61] Two achievements were realized: (i) size-customizable nanocrystals (from ~3 nm to hundreds of nanometers) by simply adjusting the assembly temperature; (ii) the same AIEgen could be assembled into different packing structures by regulating the change rate of temperature. The crystal packing data demonstrated that no π−π interactions or any H- or J-aggregation existed in either crystal due to the propeller shape of TPE units. The average value of the torsion angles of the phenyl rings was 49.3° for the $\alpha_{1.0}$ crystal, whereas 54.35° for the $\alpha_{0.3}$ crystal. The densities of the two crystals

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were 1.248 and 1.259 g/cm^3, respectively. This resulted in different restriction degrees of intramolecular twisting and molecular packing according to the RIM mechanism, leading to different emission properties.
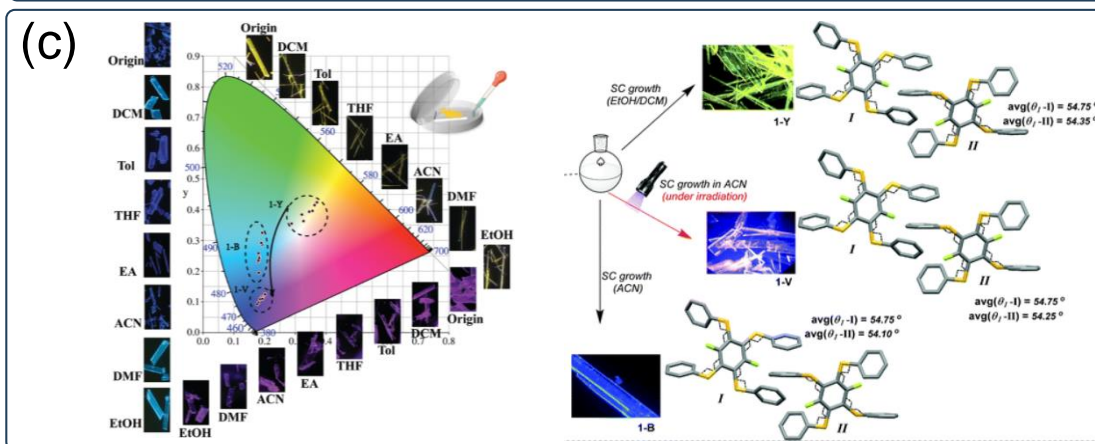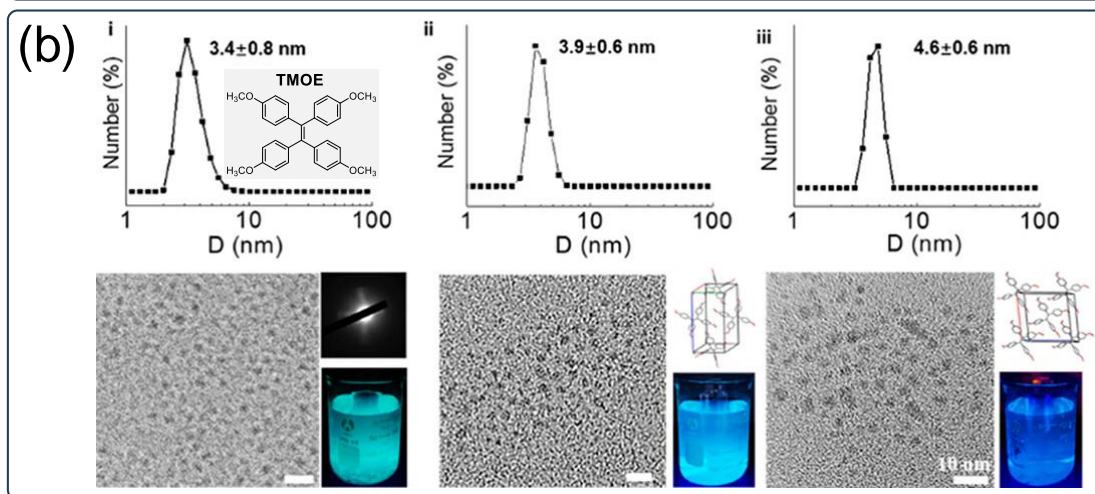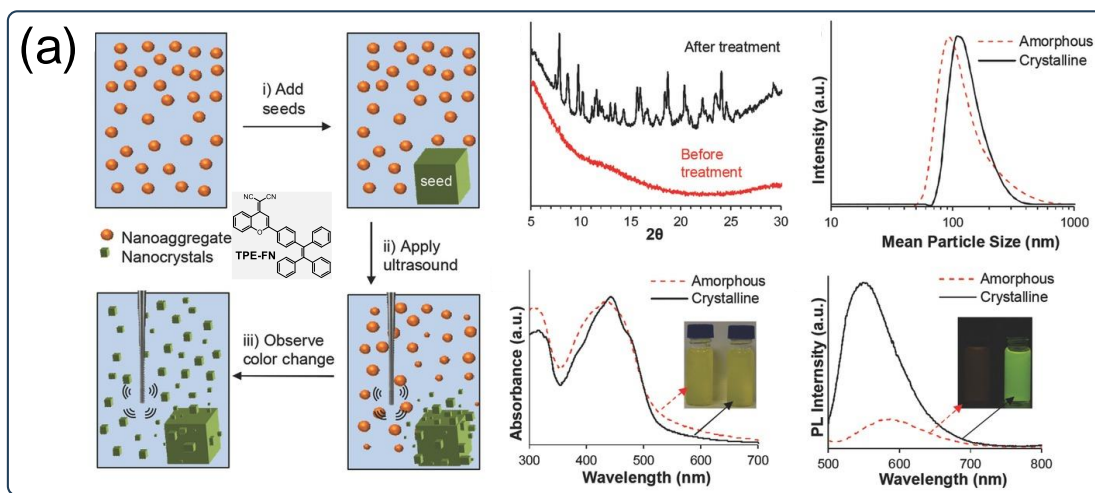
Figure 4. (a) Illustration of amorphous-to-crystal transformation of **TPE-FN**, demonstrating how nanocrystallization can be used as an effective method to increase the brightness.[60] Copyright: Wiley-VCH. (b) Size control of **TMOE** in nanocrystals during amorphous-to-crystal transformation.[61] Copyright: American Chemical Society. (c) Solvent induction polymorphism of a fluorosubstituted tetrakis-(arylthio) benzene molecule.[62] Copyright: Royal Society of Chemistry.

Besides the amorphous-to-crystal transformation, crystals with multiple phases can also be directly formed during molecular aggregation. A widely used strategy is solvent induction to control the structure of final crystals. There are many examples of crystallization in different solvents leading to polymorphs. For instance, a fluoro-substituted tetrakis-(arylthio) benzene could form a series of single crystals under different solvent conditions (**Figure 4c**).[62] Two crystals, including **1-Y** and **1-B**, were chosen for detailed studies. **1-Y** and **1-B** were obtained by the crystal growth of the molecules in ethanol (EtOH)/dichloromethane (DCM) mixed solvent and in acetonitrile (ACN), respectively. Interestingly, **1-Y** displayed yellow emission under UV light excitation (Φ_{PL} = 30.6%), and **1-B** showed blue emission (Φ_{PL} = 16.3%). More interestingly, the authors found that prolonged UV irradiation during molecular aggregation in ACN solution or EtOH/DCM (1:2,v/v) solvent mixture yielded an extraordinary crystal structure (**1-V**). This violet-emitting crystal **1-V** exhibited a remarkably high photoluminescence quantum yield of 30.6%.

Further analysis showed that the molecular structure of **1-V** remained unchanged during irradiation, identical to those in **1-B** and **1-Y**. X-ray structure analysis and DFT calculation indicated that the differences among these single crystals could be attributed to the synergistic effect of molecular conformations, including the bond lengths of the central aromatic core and the C–S and C–F bonds. These results demonstrated that the symmetric and asymmetric conformations of molecules during molecular aggregation could be controlled and monitored.

2.3. Post-Processing After Aggregation

Distinctive luminescent properties can also be achieved by post-processing the solids, for example, stimuli-responsive materials, after the completion of aggregation.[63] The two most widely studied approaches are light-induced transformations [64-67], known as photochromism, and force-induced transformations,[57, 68-71] called mechanochromism.

Photochromism describes the phenomenon where solid materials change their luminescent color or intensity as a result of exposure to light.[72] Photochromism is generally related to reversible chemical and physical changes upon light irradiation.[73-75] For example, diarylethenes can rapidly switch between closed and open forms upon exposure to UV and visible light. Bernard L. Feringa and co-workers reported a series of dissymmetric chiral diarylethene derivatives that could switch between open forms of (*M*)-**1o**, (*M*)-**2o** and closed forms (*S*,*S*)-**1c**, (*S*,*S*)-**2c** (**Figure 5a**).[76] The (*M*)-**1o** and (*M*)-**2o** have intrinsic axial chirality, while the (*S*,*S*)-**1c**, (*S*,*S*)-**2c** have central chirality. The microstructures fabricated by those molecules featured colour-tunability, erasability, reversibility, and multi-stability. Furthermore, the molecular conformation and intermolecular packing in aggregates can change upon excitation without bond formation, leading to diverse luminescent behaviors. For instance, 1,2-diphenylethane (**s-DPE**) was reported to be capable of performing light-driven solid-state molecular motion to form excited-state through-space complexes (ESTSC) (**Figure 5b**).[77] The radiative decay of ESTSC could generate an unexpected visible emission due to the clusteroluminescence. Meanwhile, the original packing structure could be recovered from ESTSC after the removal of light irradiation.
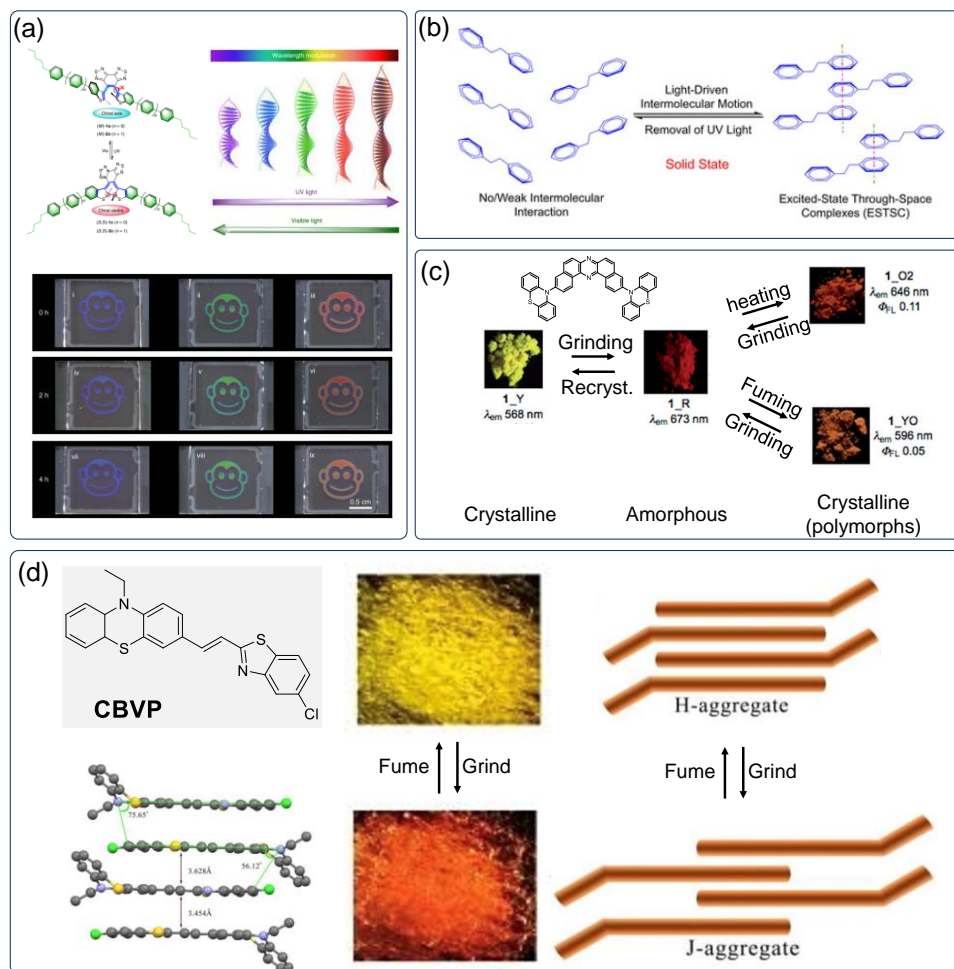
Figure 5. (a) light-induced switchable closed-form and open form of diarylethene derivatives,[76] Copyright: Springer Nature. (b) light-induced molecular packing changes of s-DPE resulting in clusteroluminescence,[77] Copyright: American Chemical Society. (c) crystallization-amorphization transformation induced by mechanic forces,[78] Copyright: Royal Society of Chemistry. (d) mechanic forces caused H-type into J-type aggregation in the solid state,[79] Copyright: Elsevier.

Post-processing by mechanical force is another widely adopted approach for modulating the luminescent properties of solid materials, known as mechanochromism.[79-81] In general, the effects of mechanical forces exerted on solids can be divided into two categories: (i) crystal-to-amorphous transformation and (ii) molecular stacking alteration.[82-84] Because of the flexible nature of most AIEgens, their molecular packing in crystals can be easily disturbed by mechanical

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forces such as grinding. This facilitates an easy transformation from crystals to amorphous.

Unlike the easy reversibility of photochromism, the emission response in mechanochromism is usually irreversible by simply releasing the applied force. This is because the original structure of the solid sample becomes altered and damaged under vigorous mechanical forces. Instead, the recovery back to the original state can be achieved by external stimuli such as solvent fuming or heating.

Takeda Minakata and co-workers reported tricolor mechanochromic luminescence of phenothiazine-dibenzo[*a,j*]phenazine-phenothiazine (**PDPP**) molecules at aggregated states (**Figure 5c**).[78] The as-synthesized crystals were yellow-emissive (λ_{max} = 568 nm). Upon grinding, the emission peak of the amorphous powder was red-shifted to 673 nm. After recrystallization from hexane/CHCl$_3$ (3:1) or CH$_2$Cl$_2$, the amorphous powder could resume the original crystals. Moreover, different treatments on the amorphous **PDPP** powder could result in other polymorphs. Heating could lead to a red-emissive crystalline powder (λ_{max} = 646 nm) while fuming with the CH$_2$Cl$_2$ vapor would produce an orange-emissive crystalline powder with a peak at 596 nm. Single-crystal X-ray diffraction analysis and theoretical calculations revealed that the conformational flexibility of the two phenothiazine moieties should account for the multi-color emissive transformations.

Molecular stacking alteration commonly involves the interchanges of H- and J-aggregation (sometimes X-aggregation may be involved). For instance, Peng Chong Xue and co-workers reported that the original crystal of a benzothiazole derivative with phenothiazine moiety (**CBVP**) displayed yellow emission at 560 nm.[79] After being ground, the emission 596 nm *H*-aggregates. The original emission could be recovered by fuming, exhibiting a reversible luminescence color change from yellow to orange-red with a spectral shift of 36 nm under mechanical force stimuli (**Figure 5d**). UV absorption and single crystal analysis confirmed that the reversible mechanochromism is due to the transition of H-aggregates to J-aggregates after grinding.

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3. Conclusion and Outlook

In the two decades since the discovery of AIE, research in this field has grown exponentially, with over 2000 AIEgens being recorded in the universal database for aggregate science.[85] As the focus shifts from investigating individual AIE to exploring aggregate science, controlling the molecular aggregation process has emerged as a key challenge. In addition to synthesizing new AIEgens, understanding and regulating molecular aggregation has emerged as a pivotal objective on the path to understanding the "aggregate science."

Controllable molecular aggregation bridges the gap between solutions and solids. Broadly, it enables polymorph control, an aim pursued throughout physical chemistry but achieved thus far mainly by trial and error.[86] Most reported polymorphs differ only in molecular packing.[87-88] Conformational polymorphs are rarer and more challenging to control, as molecules must overcome energy barriers to adopt different conformations in the solid state.[89] Conformational AIEgen polymorphs are especially interesting, as different conformers can possess distinct electronic properties, essentially behaving as different molecules. Advancing this field requires deep knowledge of physical chemistry principles.

Overall, progress in controllable molecular aggregation will greatly expand material availability and processability, not just for aggregate science but for organic materials broadly. Developing strategies to manipulate AIEgen aggregation actively is thus an important goal worthy of pursuit.

Here, we summarized three general methodologies for controlling molecular aggregation, which can help guide the development of new functional aggregate materials. The first strategy is molecular modification before aggregation, where properties like size, shape, and substituents are altered to influence intermolecular interactions during aggregation. The second involves manipulating the aggregation process through solvent induction, temperature control, and kinetics vs thermodynamics. The third uses post-processing methods like photo- and mechano-induction to modify the properties of the final aggregate material. Due to the experimental easiness, the first and third have gradually been discovered and investigated. On the other hand, the second is the most challenging, although

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generalizable, as dynamic processes are naturally more complex to perceive and control.

Each strategy has been demonstrated through examples to modulate properties like emission color, crystallinity, and molecular orientation. Looking forward, there is still much room to expand on these strategies and discover new techniques for precise, controllable aggregation. For instance, machine learning and AI methods could also help predict optimal molecular design and processing conditions. Overall, advancing our ability to control molecular aggregation will open vast possibilities for creating functional materials with emergent properties targeted for real-world applications.

The future of aggregate science is full of exciting possibilities. Developing strategies to control molecular aggregation precisely will significantly enhance material availability and processability in aggregate science and, more broadly, across organic materials research. Aggregate science stands at the forefront of materials research, poised to make substantial contributions to diverse fields like healthcare, technology, and sustainable materials by discovering novel materials with unique optical properties. Realizing the full potential of aggregate science requires persisting in foundational research to uncover the fundamental principles governing molecular aggregation. Researchers worldwide are constantly developing new ways to understand aggregation mechanisms and dynamics, which means that the field of aggregate science is continually evolving. With precise control over molecular aggregation, the future looks bright for developing novel multifunctional materials, breakthrough characterization techniques, integration with cutting-edge technologies, and considering sustainability and environmental impact. The aggregate science field offers various opportunities to make a transformative impact across a range of fields.

ACKNOWLEDGEMENTS

AUTHOR DECLARATIONS

Conflict of Interest

The authors declare no competing interests.

DATA AVAILABILITY

Data sharing does not apply to this article as no new data were created or analyzed in this study.

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