Organic molecular aggregates: From aggregation structure to emission property

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Abstract
Organic molecular aggregates have attracted widespread attention over the past decade owing to their unique optoelectronic properties in the aggregate state, which mainly involves the effects of aggregation structure as well as molecular packing mode. Although many examples of H- and J-aggregates defined by molecular exciton model have been found, there are also other types of unconventional aggregates, especially for aggregation-induced emission (AIE) system. In this review, the recent progress of some examples of basic and novel aggregate forms, as well as coassembled forms, presenting distinctive optical features, such as optical waveguide and polarization emission, polymorph-dependent emission and stimuli-responsive luminescence are presented. The systematic insight into the relationship between the aggregation structure and emission property is discussed. Guidelines are therefore anticipated and will direct the future preprogramming molecular design so as to fine-tune the emission feature through a specific aggregation model for developing organic molecular aggregates with desirable optoelectronic properties.

KEYWORDS
molecular stacking, organic crystals, organic luminogens

INTRODUCTION
Organic π-conjugated materials are attracting increasing interest due to their advantages of tunable color, low cost, and easy fabrication. These essential advantages of organic π-conjugated materials ensure their abilities to be used in various fields, such as organic light-emitting diodes (OLEDs),1–6 organic solid state lasers (OSLs),3,4 and organic light-emitting transistors (OLETs).5–7 In such advanced optoelectronic application fields, organic π-conjugated materials are often exhibited as films, crystals, or other solid-state forms. So, the development of organic π-conjugated materials exhibiting high solid-state fluorescence efficiency is in great demand but extremely challenging due to the effect of aggregation-caused quenching (ACQ) in aggregation state. In 2001, the distinctive phenomenon of aggregation-induced emission (AIE) was first found by Ben Zhong Tang in the research of 1-methyl-1,2,3,4,5-pentaphenylsilole molecule.8 Since then, based on the principle of AIE, many efficient fluorescent materials in aggregate forms have been developed.9–13 For the organic π-conjugated materials, the photoluminescent properties in solid state can be largely influenced by the aggregation structures and the molecular stacking models. Early in 1963, Kasha and coworkers in their pioneering work provided the theoretical conception of molecular exciton theory, in which the emission properties are the reflection of interactions between molecular transition dipoles in aggregates.14,15 For example, cofacial, parallel transition dipoles (H-aggregate) usually exhibit blue shift absorption and quenched fluorescence (Figure 1).16 Although H-aggregate is detrimental to fluorescence, it is beneficial for charge transport due to the large π–π overlap. Based on the cofacial packings, the slipping of molecules along the directions of transition dipoles could form staggered J-aggregates, which can exhibit strong fluorescent characters. Later, Spano and coworkers systematically investigated the absorption and emission spectral features of H-aggregates and J-aggregates based on the exciton-vibrational coupling theory.17–19 In 1998, Cornil and coworkers proposed that the strategy to prevent solid-state luminescence quenching is to reduce the exciton interactions.20,21 By rotating the molecules to generate a certain angle between the long axes of the molecules, X-aggregates (or cross-dipole stacking) can be constructed with the reduced exciton interactions due to the reduced π–π interactions between molecular transition dipoles. Although,
possessing a cofacial stacking, X-aggregates can exhibit strong fluorescence.

Organic crystals with well-defined aggregation structures can provide appropriate experimental media to study the structure–property relationship. Additionally, the fast development of X-ray diffraction technology could offer an accurate method to analyze the refined molecular structures and packing patterns in the aggregates. In this review, based on organic luminescent crystals, different aggregation structures and aggregation-dependent luminescent properties are introduced. Then, the experimental examples of regulating solid-state emission properties by manipulating the aggregation structures are summarized. For single-component materials, the polymorphic and the stimuli (stress, heat, light, etc.) induced aggregation-dependent luminescent properties are introduced. For multicomponent materials, cocrystals and the acid protonated crystals are summarized to be the decent strategies of triggering novel luminescent properties. The development of X-ray diffraction technology could offer an accurate method to analyze the refined molecular structures and packing patterns in the aggregates. In this review, based on organic luminescent crystals, different aggregation structures and aggregation-dependent luminescent properties are introduced. Then, the experimental examples of regulating solid-state emission properties by manipulating the aggregation structures are summarized. For single-component materials, the polymorphic and the stimuli (stress, heat, light, etc.) induced aggregation-dependent luminescent properties are introduced. For multicomponent materials, cocrystals and the acid protonated crystals are summarized to be the decent strategies of triggering novel luminescent properties. The deep understanding of the corresponding internal mechanism, especially the relationship between the aggregation structure and luminescent property, can provide important insight in the design of desirable organic luminescent materials.

**H-AGGREGATE SINGLE CRYSTALS**

H-aggregate has the cofacial, parallel molecular stacking with slip angle larger than 54.7° (Figure 1). In H-aggregates, the molecular transition dipoles are oriented “side-by-side,” in which the lower excited state of the two split energy levels generated by dipole interactions is optically forbidden, while the higher one is allowed. There are two significant effects on the optical properties: (a) the main absorption peak is usually blue shifted (“H” for hypsochromic) compared to solution, which corresponds to the optical allowed higher excited states; (b) a low radiative decay rate and suppressed fluorescence are exhibited in H-aggregates due to the optical forbidden lower excited states, which correspond to the emitting state.

Commonly studied H-aggregate chromophores include oligophenylenevinlenes, oligothiophenes, and also perylene diimides. These planer π-conjugated molecules tend to form cofacial, parallel H-aggregates, with the strong π–π interactions between adjacent molecules as the main driving forces. In 2005, Gierschener and coworkers reported the aggregation-related optical properties of distyrylbenzene (DSB) and fluorinated distyrylbenzene (F12DSB) crystals. For DSB crystals, the molecules are organized into H-aggregation with herringbone architectures. The parallel arrangement of the molecular transition dipole moments of DSB molecule induces a strong blue shift of the main absorption peak to 33,900 cm⁻¹ compared with solution state (28,600 cm⁻¹). The decrease of the fluorescence efficiency from ΦF = 0.77 in solution to ΦF = 0.1 in the nanocrystals is induced from the decrease of the radiative decay rate of H-aggregate. For F12DSB single crystals, the fluorescent substituents promote the π–π interactions between the molecules owing to the interactions of the carbon-fluorine dipole moments, hence a side-by-side cofacial arrangement of F12DSB dimers is found. The parallel stacking of the transition dipoles of neighboring molecules causes larger blue shift of the absorption band in F12DSB crystals (35,500 cm⁻¹), indicating stronger intermolecular interactions between F12DSB molecules. The radiative decay rate of F12DSB crystal is two orders of magnitude smaller than that in solution, owing to the optically forbidden transition between the ground state and the lower excited state in crystal.

Although the fluorescence is suppressed in H-aggregates, the cofacial π–π interactions can facilitate the charge transport and increase the charge carrier mobility, which are greatly needed in organic electronic devices. For example, poly(3-hexylthiophene), a widely used material in organic solar cells, has been found to form H-aggregate π-stacks in the spin-coated films. The DSB crystal is a moderate efficient hole transport (p-type) material exhibiting a high charge carrier mobility of 0.024 cm² V⁻¹ s⁻¹, which can be used in organic filed-effect transistors (OFETs).

**J-AGGREGATE SINGLE CRYSTALS**

Increasing the slip angle of the molecules in the cofacial stacking can change the system from H-aggregates to staggered stacked J-aggregates (“J” after Jelley). The “head-to-tail” interactions in J-aggregates also generate energy splitting in excited states, and the lower excited state is optically allowed while the higher one is forbidden. Such intermolecular interactions can affect the photophysical properties of J-aggregates in two ways as follows: (a) J-aggregates often
generate a very moderate red shift in the absorption spectrum compared to the general large blue shift in absorption of H-aggregates; (b) the allowed lower excited states correspond to the emission states, so that J-aggregates often display high radiative decay rates and high fluorescence efficiencies. In 2001, Feast and coworkers reported a 4,4'-bis(2,3,4,5,6-pentafluorostyryl)stilbene molecule, which can form “brickwall” motif J-aggregate by self-assembly based on aryl-fluoroaryl interactions.51

Besides high solid-state luminescence efficiencies, J-aggregates have the potential to exhibit good electronic properties. As the slip angle in J-aggregates is from 0° to 54.7°, partially π–π overlap could be generated between adjacent molecules, which can facilitate the charge transfer between molecules. The realization of integrating highly emissive fluorescence and efficient charge transport properties can promote the potential of J-aggregates to be used in advanced optoelectronic devices.52–66

Liu and coworkers have demonstrated an organic π-conjugated molecule 2,6-diphenylanthracene (DPA) with high mobility and strong emission.52 DPA single crystals were fabricated by physical vapor transport (PVT) technique. The crystal structures show that DPA molecules form herringbone stacking as J-aggregates, which can effectively reduce the ACQ effect of the DPA molecules in solid state. In diluted solution, the 0–0 absorption peak of DPA molecule appears at 398 nm. Compared with solution, DPA nanoparticles exhibit remarkable red shift in absorption and photoluminescence (PL) spectra, with the maximum absorbance at 433 nm and the maximum PL intensity at 441 nm. As shown in Figure 2, DPA crystals exhibit bright blue fluorescence with a photoluminescence quantum yield (PLQY) of 41.2%. Additionally, various strong C–H⋯π intermolecular interactions are generated between neighboring DPA molecules, and can be the driving forces for the molecules to form a two-dimensional network for charge transport. Based on the crystal sheets, OFETs were fabricated to show a rather high mobility of 34 cm² V⁻¹ s⁻¹. It proves that it is accessible to utilize J-aggregates to achieve the goal of obtaining organic semiconductors with high mobility and efficient emission. Moreover, DPA-based OLED arrays could be successfully operated by DPA-based OFET arrays. The demonstration of the successful integrated multifunctional optoelectronic devices using the same semiconducting molecule indicates the great potential of DPA molecule in organic optoelectronic fields, especially in planar integration.

Another J-aggregate crystal with integrated high fluorescence efficiency and good charge transport property is demonstrated by Ma and coworkers.67 As shown in Figure 3, a butterfly-like π-conjugated molecule 5,5'-bis(2,2-diphenylvinyl)-bithiophene (BDPV2T) is presented to integrate efficient solid-state fluorescence and charge transport properties. Due to the steric hindrance and strong intermolecular C–C and C–H⋯π interactions induced by the substituted phenyls, the BDPV2T molecules in single-crystal structures adopt staggered stacking with slip angle of 31° and perpendicular distance of 3.939 Å. As expected, BDPV2T crystals with such J-aggregate structure was also proved to show integrated optical and electronic properties. For example, BDPV2T crystals exhibit a high solid-state PLQY of 30%, ultra-low amplified spontaneous emission (ASE) threshold of 8 kW cm⁻², high optical gain up to 70 cm⁻¹, and high hole mobility up to 1 cm² V⁻¹ s⁻¹. The outstanding optoelectronic characteristics of BDPV2T crystal ensure its potential application for photodetectors, field-effect transistors, and light-emitting transistors. Additionally, Tao and coworkers have reported two organic π-conjugated molecules containing large terminal triphenylamine groups, 1,6-distriphenylamineethynylpyrene (1,6-DTEP) and 2,7-distriphenylamineethynlypyrene (2,7-DTEP), which showed J-aggregate structure in solid-state and ultra-high UV detectivity of 10¹⁸, indicating the great potential of 1,6-DTEP and 2,7-DTEP molecules to be used as phototransistors for UV-photodetecting applications.68

The integration of high mobility and efficient luminescence is aiming to realize electrically pumped laser, which remains great challenge. Recently, Liu and coworkers have reported a great example of high mobility organic laser
The fascinating X-aggregation was first observed in the work of Bartholomew et al. on the crystal packing modes of distyrylbenzene derivatives in 2000. Among them, the benzene rings of adjacent molecules in the 1,4-bis(2,2-diphenylethenyl)benzene crystal forms an edge-to-face stacking mode, which indicates that the C–H⋯π interactions contribute to form a cross-stacking mode. Later, Xie and coworkers demonstrated that 2,5-diphenyl-1,4-distyrylbenzene (DPDSB) crystal based on cross-dipole stacking mode exhibited high fluorescence efficiency. The crystal structure analysis revealed that there was no face-to-face π⋯π interactions between adjacent molecules due to the long distance (4.1 Å) between the central rings. Each cross-stacking dimer contained two crystallographically independent conformational molecules, which acted as proton donors and acceptors to form two different types of C–H⋯π hydrogen bonds.

By manipulating the molecular stacking structure, Zhang and coworkers reported a twisted butterfly-like 9,10-bis (2,2-diphenylvinyl) anthracene (BDPVA), which exhibited high fluorescence efficiency based on the cross-dipole stacking mode. Due to the steric hindrance caused by the peripheral phenyl groups, the butterfly wings help to maintain the twisted structure of the molecule to a certain extent. As shown in Figure 5, BDPVA molecules with two independent crystallographic conformations form a 1D molecular column along the b-axis in a cross-stacking mode (rotation angle ca. 67°). There are C–H⋯π interactions (3.192 Å, 145.9° and 3.193 Å, 133.2°) between adjacent molecules of each stacked column, indicating that the C–H⋯π interactions are the main driving forces for the construction of the cross-dipole aggregation mode of BDPVA molecules. The twisted butterfly-like structure and the large phenyl groups protect the center divinylanthracene to avoid the formation of aggregation structures (such as H-aggregate) that are not conducive to fluorescence. Fascinatingly, based on the cross-dipole aggregation structure, BDPVA exhibits high solid-state fluorescence efficiency.
FIGURE 4 (A) Chemical structure of LD-1 molecule and fluorescence image of LD-1 single crystals. (B) High-resolution lasing spectra of LD-1 crystal at 390 and 410 nm under different pump densities, and the corresponding pump density-dependent emission intensities. (C) Color-coded image, (D) schematic, and typical optoelectronic characteristics of LD-1-based OLET devices. Copyright 2020, American Chemical Society

FIGURE 5 Crystal image of BDPVA under 365 nm UV light and two conformational structures (conformation 1 is drawn in blue and 2 in red) of BDPVA in the crystal. Copyright 2013, John Wiley and Sons

low threshold ASE and high-efficiency electroluminescence performance, and is expected to become a competitive alternative material for organic lasers and OLEDs.

In order to better understand the relationship between the photoluminescent properties of organic molecular aggregates and corresponding stacking structures in crystals, Ma and coworkers have proposed an ideal model based on 9,10-bis-(2,2-di(4-fluorophenyl)vinyl)anthracene (BDFVA) polymorphisms to understand the optical properties of X-aggregation and J-aggregation. As shown in Figure 6, the green emitting G-phase crystals are stacked in J-aggregation with pitch angle of 25.9°, and the PLQY of the crystal is 43%. Crystallographic analysis shows that there are two different C–H⋯F interactions and π–π interaction (d = 3.8 Å) between...
adjacent molecules, which can induce the molecules arranged in J-aggregation pattern. In contrast, two adjacent molecules of different conformations in the blue emitting B-phase crystal form as X-aggregation with a crossing angle of $73.5^\circ$, and the PLQY of the crystal is 60%. Different from J-aggregation mode, multistrong intermolecular interactions (five different C–H···F and one kind of C–H···π interactions) exist in X-aggregation of B-phase, which can rigidify the intramolecular vibrations and rotations to promote a higher solid-state PLQY. Different twist degree of molecular conformations and the difference in interactions are the causes of polymorphism. The more conformationally twisted B-phase molecules and C–H···π interactions help to form X-aggregation, while various C–H···F interactions contribute to stabilize the aggregation structure. Compared with J-aggregation, the more abundant interactions in X-aggregation can further reduce the fluorescence quenching effect. Moreover, in X-aggregation, all the split states are optical transition allowed energy levels due to the small energy splitting. Impressively, the X-aggregate crystals of B-phase exhibit better ASE performance, such as lower threshold (198 μJ cm$^{-2}$), narrower bandwidth, and higher gain (103.1 cm$^{-1}$), which are expected to have potential applications in solid-state lasers.

AGGREGATION-INDUCED EMISSION (AIE)

AIE describes the phenomenon that organic π-conjugated molecules show dim or no emission in dilute solution but much enhanced emission in aggregates or solid states.\textsuperscript{5–13} AIE molecules often exhibit twisted chemical structures. In 2001, Liu and coworkers first proposed the concept of AIE when they investigated the fluorescent properties of rotor-rich methyl-pentaphenylsilole.\textsuperscript{5} Later in 2003, they found that the quenched emission in solution state of such twisted molecules was induced by the intramolecular rotations, which could accelerate the nonradiative decay.\textsuperscript{75} The formation of aggregation state of these molecules can restrict the intramolecular motions, thus to reduce the nonradiative decay and enhance the emission. Therefore, the mechanism of AIE is proposed to be the restriction of intramolecular motions.

Recently, Gu and coworkers discovered a natural Berberine (BBR) chloride as an AIE molecule, which exhibited bright emission in solid state.\textsuperscript{76} The PLQY of this molecule in water solution is 0.2%, while BBR chloride crystals show enhanced emission with PLQY of 15%. Single-crystal structures indicate that the adjacent BBR molecules are stacked with large intermolecular distances exceeding the typical π–π stacking distance that quenches the photoluminescence. Additionally, various intermolecular C–H···C, C–H···O, O···O, and C···O interactions are the main driving forces to fix the molecular conformations and make the chromophore highly emissive in the crystalline state. The development of highly emissive red dyes in solid state is a challenging task. Most recently, Zheng and coworkers demonstrated organic nanocrystals with bright near-infrared (NIR) emission centered at 704 nm based on an AIE luminogen (DCCN).\textsuperscript{77} The PLQY of DCCN nanocrystals was determined to be 12%, which was rather high among solid-state NIR emitters. Moreover, the nanocrystals with strong NIR emission were successfully applied for third harmonic generation microscopy to reconstruct the 3D vasculature of the mouse cerebral vasculature. The nanocrystals can realize ultradeep imaging of 800 μm and high spatial resolution of small vessels with diameters of 2.7 μm.
MANIPULATING AGGREGATION STRUCTURE

Single component

In a single-component system, the aggregation structures can be manipulated in two ways. One is the formation of crystalline polymorphs in crystal systems, and the other is applying the external stimuli on solid-state fluorescent materials.

Polymorphs

Because the intermolecular interactions are easily affected by the external environment, it is possible to provide polymorphic crystals from particular chromophores. The fluorescent properties can be regulated with the help of crystalline polymorphs with different aggregation structures (including molecular conformation, intermolecular interaction, and stacking mode). In 2012, Dong and coworkers reported three crystalline polymorphs of 9,10-bis((E)-2-(pyrid-2-yl)vinyl)anthracene (BP2VA). As shown in Figure 7A, J-type aggregation is presented in C1, while C2 adopts H-type aggregation. In particular, dimers stacked face-to-face are formed in C3. The enhanced π–π interactions between adjacent anthracene planes lead to a change in luminescence color from green of C1 to red of C3. In addition to the stacking modes, the enhancement of exciton coupling and orbital overlap between adjacent molecules are also important factors leading to a red shift of emission. Taking advantage of the characterization of the three crystalline polymorphs, it is clarified that the red shift of emission of BP2VA powder under grinding or external pressure is due to the change in the aggregation structures (Figure 7B). The property of piezochromic luminescence of BP2VA could have wide applications in pressure-sensitive devices and optical recording materials.

Different aggregation structures will lead to different excited states and thus induce different luminescent properties in polymorphic crystal systems. Using the aggregation structures of the two different polymorphs of 1,10-[2-(4-acridonophenyl)-2-phenylethenylidene]bis[4-methoxybenzene] (APMOB) as a research platform, Jiang and coworkers explored the fluorescence switching responses of APMOB molecules under external stimuli (mechanical grinding and thermal stimuli). Experiments reveal that C1 with loose packing structure is transformed into C2 with tight packing structure after grinding followed by thermal stimuli. During the phase transition, the excited state forms a transition from the locally excited (LE) state to the intramolecular charge transfer (ICT) state, which causes the fluorescence to switch. This work has guiding significance for the understanding of the relationship between molecular arrangement/conformation and photophysical properties of the polymorphs. Similarly, Shao and coworkers reported remarkable luminescence switching of the two polymorphs (G-phase and O-phase) of the 9,10-bis-(E)-
4-(pyridin-3-yl)styril)anthracene (BP3SA) upon grinding force, hydrostatic pressure, and acid/alkali treatments. The green emission is shown in the G-phase with J-type aggregation (Figure 8A), while the orange emission is shown in the O-phase with H-type aggregation (Figure 8B). The experiment revealed that a structural transition from the O-phase to the G-phase occurred by grinding and heating processes. The different structures of the two crystal phases result in different sensitivity of luminescence switching to hydrostatic pressure, and acid/alkali vapor. The O-phase has fewer intermolecular interactions compared with the G-phase, thus it is more sensitive to hydrostatic pressure. The G-phase has strong C–H⋅⋅⋅N bonds, which can be destroyed or reconstructed under acid or alkali stimuli. Therefore, the luminescent switching of G-phase is more distinct than that of O-phase during the protonation–deprotonation process.

Wang et al. constructed a polycrystalline system based on a novel boron-containing molecule named 1,3-diaryl-β-diketone and fluorobis(pentafluorophenyl)borane. One of the crystal phases (1OC) can switch fluorescence under compressing (isotropic pressure), grinding (anisotropic pressure), and smashing (tensile force). The emission spectrum of 1OC has an obvious blue shift under smashing. Because under the action of tensile force, the intermolecular interactions are weakened and the molecular aggregates are loosened on the fracture surfaces. The fragmental crystal converts into amorphous powders and exhibit red-shift fluorescence upon grinding. The distance between π-planes in 1OC is shortened under compressing, therefore the crystals show significantly red-shifted emission. The emission spectrum of the ground or decompressed samples are almost the same as 1RC, which indicates that the phase transformation may occur under external stresses. In a word, the crystal phase transformation is induced and the aggregation structures undergo different changes under different mechanical forces, which has different effects on the fluorescence emission of crystals. The aggregation structures not only affect the emission color, but also affect the fluorescence efficiency. In 2020, Ma and coworkers reported two crystal polymorphisms of BDFVA (Figure 8C). Due to crystallization-induced emission enhancement, the fluorescence efficiency of the crystals is significantly improved compared with the corresponding dilute solution. In addition, B-phase adopts X-aggregation, in which the split excited states are all optically allowed. Therefore, B-phase exhibits a higher fluorescence efficiency, compared to G-phase with J-aggregation. Experiments show that the two polymorphs exhibit excellent ASE, and therefore the materials can be applied to organic solid-state lasers.
Solid-state luminescent materials

The above-mentioned AIE luminogens, which are different from the traditional fluorescent molecules with large $\pi$-conjugated planes, can generate fluorescence because the twisted structure suppresses non-radiative transitions in the aggregated state. Luminescent materials in solid state (a kind of aggregation form), have received widespread attention. The light/heat/pH/solvent/force active unit in solid-state luminescent materials will change under external stimulation. Successively, the aggregation structures will be reorganized, and the fluorescent properties will be regulated. For example, Qi and coworkers presented a donor–acceptor (D–A) molecule, acridonyl-tetraphenylethene (AD-TPE).\textsuperscript{82} Under mechanical grinding and hydrostatic compression, the molecular stacking converts from a crystalline phase to an amorphous phase, exhibiting outstanding turn-on and color-tuned luminescence. Through crystal structure analysis and computational studies, the effect of transformation of aggregation structures on luminescence has been explored in detail. Under the mechanical stimuli, the intramolecular geometrical conformation changes, which causes the switching of excited state characteristics (from LE state to ICT state). This further leads to the change of luminescence from very weak emission to bright blue-green emission (Figure 9A,B).

In addition to the above-mentioned piezochromic luminescent materials, photochromic materials have attracted extensive research interests due to the potential applications in the advanced functional photonic fields, such as optical storage\textsuperscript{83,84} and high-resolution imaging.\textsuperscript{85,86} In 2017, Qi and coworkers reported a highly efficient photochromic molecule, named DSA-2SP (9,10-distyrylanthrance [DSA], spiropyran [SP]).\textsuperscript{87} Under alternating UV light, visible light, and heat treatment, DSA-2SP underwent reversible color changes in absorption and fluorescence. Under 365 nm UV light irradiation, SP is isomerized to form merocyanine (MC), which promotes transformation of aggregation structure, hence the switch in absorption and fluorescence are realized. The structural isomerization and fluorescence change before and after UV irradiation are shown in Figure 9C. They demonstrate that the DSA-2SP molecule with reversible luminescence modulation property can be used in anti-counterfeiting
inks and super-resolution imaging agents. Similarly, Yang and coworkers presented two unique examples of photore sponsive materials (TPEA-SP and TPEB-SP) with reversible dual fluorescence switches in solid states.88 SP can perform reversible photoisomerization between the closed state and the MC open form under the stimuli of UV and visible irradiation. The experimental and theoretical calculation results show that under UV light, the intramolecular energy transfer from TPE to MC moiety can take place, which leads to the transformation of the fluorescence between bright cyan and red. The molecular dynamics simulation shows that TPEA-MC exhibits a looser stacked structure compared with TPEA-SP, which promotes reversible isomerization.

**Multicomponent**

**Cocrystals**

Besides the single-component aggregates introduced above, similarly, multicomponent aggregation structure tends to combine the advantages of each component, which has synergistic and collective effects.89 More interestingly, the addition of multiple components makes the whole material produce unexpected effects in terms of luminescent properties. Among them, the organic cocrystal is particularly regarded as a unique and novel crystalline form, which is obtained by connecting different molecules through a variety of non-covalent interactions, including hydrogen bonds, halogen bonds, charge-transfer (CT) interactions, and so on.90 Cocrystals have clear and unique structures and packing modes. At the same time, the structure is long-range ordered and defect-free, which can facilitate us to better reveal the relationship between structure and luminescent performance from the perspective of adjusting the aggregation structure.

Focusing on these characteristics, in 2018, Liu and coworkers reported a D–A CT cocrystal, CT-R.91 1,4-Bis-p-cyanostyrylbenzene (CNDSB) was selected as donor (D) and 1,2,4,5-tetracyanobenzene (TCNB) molecule with strong electron-withdrawing ability as acceptor (A). Red CT-R cocrystals with block-like shape exhibit obvious hypochromatic and bathochromatic shifts upon anisotropic grinding and isotropic compression, respectively (Figure 10A). Upon grinding, the molecular arrangement of CT-R cocrystals changes to its polymorphic form CT-O. As shown in Figure 10B, CT-R exhibits the segregated stacking mode with moderate π–π and CT interactions. It is completely different that CT-O cocrystals possess the mixed stacking mode driven by two types of intermolecular C–H···N interactions, and the D–A molecules form unique mixed alternative molecular columns. Therefore, under the action of the grinding force, slippage and rearrangement process happened, and the π–π interactions and the D–A interactions between CNDSB and TCNB molecules were weakened, which led to enhanced and blue-shifted fluorescence emission. On the other hand, the packing modes in the crystal is basically unchanged during the pressurization process. Through theoretical simulation and calculation, it is found that as the static pressure increases, the length of the three crystal axes are shortened. The isotropic static pressure stimulation leads to a tighter packing structure in CT-R, as shown in Figure 10B, and it also leads to the enhancement of π–π and CT interactions. As a result, the fluorescence spectrum of the CT-R cocrystal is red shifted and the fluorescence quantum efficiency is significantly reduced.

Inspired by the above cocrystal strategy to obtain luminescent materials with different stimulus responses,92 Tian and coworkers further explored the influence of external stimuli on the molecular structure at the molecular level, as well as the corresponding mechanism that led to the fluorescence response, and then realized the regulation of the luminescence performance. In 2020, a cocrystal system with reversible phase transformation between yellow-emitting polymorph I and green-emitting polymorph II triggered by...
tetrahydrofuran (THF) fuming, heating, or grinding was reported. The cocystal system was designed based on a luminescent molecule, 9,10-bis((E)-2-(pyridin-4-yl)vinyl)anthracene (BP4VA, Figure 11A) and a halogenated conformer, 1,3,5-trifluoro-2,4,6-triiodobenzene (FIB). Through a slow solvent evaporation process, two polycrystalline-phase crystals with different luminescence characteristics were obtained. The various forms of medium-strength intermolecular hydrogen bonds and halogen bonds in crystal I (Figure 11B) could act as the driving forces for self-assembly, allowing molecules to aggregate and expand into layered structure. However, in crystal II, there are $\pi-\pi$ interactions between each BP4VA molecule and four adjacent FIB molecules, forming local coplanar H-aggregates. During the heating process, as the temperature increased, the vibration and rotation of the BP4VA molecules would gradually increase, which may change the molecular conformation, and the directional non-covalent bonds in crystal I were easily weakened or even destroyed. The change of molecular orientation promoted the formation of nondirectional $\pi-\pi$ interactions, which in turn would promote the rearrangement of specific molecules in the BP4VA-FIB system and cause the transformation from crystal I to crystal II.

Similarly, great contribution has been made by Bolla and coworkers in the development of ASE cocrystals. They adopted cocystal strategy to achieve controllable molecular packing motifs (DPYA-BrFB and DPYA-IFB, 2,6-diprydyl anthracene [DPYA], 1,4-dibromotetrafluorobenzene [BrFB], 1,4-diodotetrafluorobenzene [IFB], Figure 12A) by subtly modulating halogen bonds from C–Br$\cdots$N to C–I$\cdots$N, which led to a significant increase in the radiation decay rate up to 10 times, larger ASE radiative decay selectivity to four times, and decreased ASE threshold from 223 to 22 $\mu$J cm$^{-2}$. This study revealed the cocystal method to tailor the stacking structures and intermolecular interactions of luminescent materials, giving a promising future for the development of organic ASE or laser materials by fine-tuning a variety of radiation-decay pathways. On the other hand, Fan and Yan fabricated multicomponent molecular hybrids by supramolecular cocystallization using different small molecules with DPA. Based on rational design and the regulation of molecular orientation, orderly D–A stacking were formed with highly enhanced electrochemiluminescence (ECL) signals (Figure 12B). Interesting work has been done by Wang and coworkers by introducing a volatile third party THF to obtain a reconfigurable molecular assembly in a ternary solvated cocystal (NDI-Cornene)-THF. Due to the weakened intermolecular interactions, as shown in Figure 12C, the loosely stacked modes can be deliberately adjusted by external stimuli (heating, grinding, or solvent), accompanied by obvious changes in photophysical properties. It is not difficult to conclude from the above examples that cocystal strategy is an effective method to control luminescent performance.

### Acid protonated crystals

In the field of multicomponent aggregates, apart from the self-assembled cocrystal, there is also a common way to combine luminescent materials, especially the AIEgens, with acid (such as HCl, H$_2$SO$_4$). After protonation, the change of the structure leads to alteration of the electron-withdrawing ability, the frontier orbitals, and the corresponding transition energy. Finally, the effect on the emission properties is realized. In order to clarify the internal relationship between aggregated molecules and the changes of fluorescence under this protonation effect, Zhang and coworkers selected 9,10-bis((E)-2-(pyridin-3-yl)vinyl)anthracene (BP3VA) and fumigated its powder by HCl vapor. As time increased, the fluorescence was gradually red shifted from 525 to 586 nm (Figure 13A). Then, the protonated powder was placed in a trimethylamine (TEA) atmosphere and the luminescence returned to green fluorescence. Two crystals of BP3VA and...
**FIGURE 12**  (A) Fluorescence images of DPYA, DPYA-BrFB, and DPYA-IFB microcrystals, power-dependent PL intensities, and band-width of DPYA-BrFB crystal and DPYA-IFB crystal.94 Copyright 2020, John Wiley and Sons. (B) Chemical structure of conformers and the corresponding stacking fashions based on molecular hybrids in different cocrystals.95 Copyright 2016, John Wiley and Sons. (C) Diagram of the transformation of molecular packing in the lattice based on ternary cocrystal (NDI-Cornene)-THF under multistimuli.96 Copyright 2020, John Wiley and Sons

**FIGURE 13**  (A) PL spectra and stacking structure of BP3VA and BP3VA-HCl crystals.99 Copyright 2013, Royal Society of Chemistry. (B) Fluorescence images, molecular structures, and the calculated frontier orbital contributions of BP4VA molecule and the protonated form.100 Copyright 2013, Royal Society of Chemistry. (C) Fluorescence images and molecular structures of BP4VA, BP4VA-1H, and BP4VA-2H crystals.102 Copyright 2017, American Chemical Society
BP3VA-HCl were obtained. In BP3VA crystals, as shown in Figure 13A, a packing mode similar to J-type aggregation along the b-axis was observed, with C–H⋯π interactions formed between adjacent molecules. Obviously, Cl− joined in the stacking of BP3VA-HCl crystals and the two pyridines of the BP3VA molecule are both protonated. The molecules in BP3VA-HCl crystals are arranged in a uniaxial orientation. Plenty of C–H⋯π interactions and multiple X–H⋯Cl− (X = C, N) interactions exist in BP3VA-HCl crystals. The twisted structure caused by internal steric hindrance prevents the molecules from forming cofacial aggregates. Meanwhile, the protonation of pyridines changes the distribution of the electron cloud in molecules, causing the variation of energy levels of the frontier orbitals. These changes will eventually be displayed on the shift of the emission spectrum. Dong and coworkers also reported a similar novel switch phenomenon that can be tuned between green and red in the emission by different acidic/basic atmospheres in BP4VA (Figure 13B). Through theoretical calculations, it is found that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are mainly distributed on the divinylanthracene group and partially located on the entire molecule in a BP4VA molecule, respectively. However, after the BP4VA molecule is protonated, the electron cloud is spread over the whole molecule and its density increases on pyridine in LUMO. In this way, the excited molecule can be stabilized at a lower bandgap owing to the delocalized LUMO, which results in a red shift of absorption and emission. At the same time, some new supermolecular interactions are formed during the protonation process, leading to a fire-new aggregation structure and a variation in the emission. In 2014, Chen and coworkers reported a proton-triggered hypsochromic luminescence molecule, 1,1′-(2,5-distryl-1,4-phenylene) dipiperidine (DPD). They demonstrated that the process of protonation/deprotonation could result in different stacking modes of DPD, which may lead to the blue-shifted luminescence. The study of DPD is beneficial to the design and synthesis of novel functional fluorescent materials, which can be applied to stimuli-response luminescence.

Furthermore, in 2017, Ma and coworkers focused on the effects of different types of acids, and planned to start with the degree of protonation to study the luminescent properties of the aggregated states. The symmetrical and asymmetrical protonation states were realized via combining BP4VA with H2SO4 or HCl (Figure 13C). Compared with neutral crystal, the fluorescence of the crystal protonated by H2SO4 (BP4VA-2H) has a significant red shift at 605 nm with orange-red emission. Adjacent molecules are arranged in a dislocation-slip H-aggregation mode, which contains a large number of non-covalent interactions. The fluorescence of the crystal protonated by HCl (BP4VA-1H) exhibits further bathochromic-shift emission to 640 nm. The asymmetric structure of BP4VA-1H makes the molecules closely arrange in a head-to-tail manner. Combined with theoretical calculations, it is found that the neutral BP4VA has the largest energy gap of 3.39 eV. The delocalized electron cloud density of BP4VA-2H and BP4VA-1H molecules can effectively stabilize the molecules in the excited states and result in a reduced energy gap. Coupled with the enhancement of excitonic coupling between the transition dipoles of adjacent molecules, the fluorescence spectra of the protonated crystals are red shifted compared to the neutral crystal, and BP4VA-1H is more red shifted than BP4VA-2H. All these works have demonstrated the close relationship between the luminescent performances and the aggregation structures of multicomponent luminescent materials. Furthermore, it will be possible to control the aggregation structures to obtain desired smart materials.

**SUMMARY AND PERSPECTIVES**

Crystal structure analysis of organic luminescence materials, combined with optical spectroscopy and quantum-chemical calculation, provides a unique opportunity to study the structure–property relationships and to identify the structural intramolecular factors that drive the molecules packing into a particular architecture and generating specific optoelectronic properties. From the examples discussed in this review, it can be summarized that planar, linear π-conjugated molecules, such as oligophenylenevinylene and oligothiophenes, tend to stack into H-aggregates, with strong π–π interactions between adjacent molecules as the driving forces to stabilize the architecture. Introducing small rotating terminal substituents, such as phenyl and diphenyl, to the planar, linear molecules could increase the terminal steric hindrance, which can drive the molecules slipping along the molecular axes to form J-aggregate structures. Twisted AIE molecules, such as DSA derivatives and DSB derivatives, with short π-plane center cores and twisted π-conjugated terminal groups, are likely to stack in a crossed construction with a rotation angle, which is so-called X-aggregate. In J- and X-aggregates, π–π interactions scarcely existed, instead, multiple H-bonds, such as C–H⋯π, C–H⋯F, C–H⋯O interactions, are generated from terminal substituents and are acting as the driving forces to connect the molecular networks. As for the potential applications of these aggregates, it mainly depends on the optical and electronic properties, which are in turn closely related to their aggregation structures. For example, H-aggregate single crystals grown by PVT method (up to cm2-sized plate-like or needle-like shapes) are good candidates as the active materials in OFET devices, owing to their high charge carrier mobilities induced from the strong π–π interactions. X-aggregate single crystals with ribbon-like or needle-like shapes (length up to ~1 cm) are suitable to show optical waveguiding and light amplification, which have the potential applications in the field of solid-state laser devices. As for J-aggregate single crystals (size up to several mm2 by PVT), which have been proved to successfully integrate high mobility and efficient fluorescence, the crystals are great candidates for OLED devices and are most promising candidates for electrically pumped lasing devices. Additionally, AIE nanocrystals with red/NIR emission and μm-sized dimensions have potential applications in the field of bioimaging.

The understanding of the structure–property relationships can provide important insight into the rational design of desirable organic π-conjugated materials. Analyzing the structures and properties of structurally well-defined organic single crystals is indeed an efficient way to reveal the related disciplines. Additionally, polymorphism of single crystals has presented an excellent strategy for deeper investigation of structure–property relationships and the internal mechanism.
of emission changes upon external stimuli. More importantly, the structurally well-defined crystals are not only an ideal model for basic research but are also promising candidates for the application in OLEDs, solid-state lasers, sensors, or optical recording, due to their unique merits against film samples, such as drastically reduced defects and good thermostability. In the future, cocryystals with multiple components would be the research emphases as they can generate multiple functionalities from different parts of ingredients. But the selection of materials, the proper conditions for cocrystal growth, and the mechanism of multicomponent-induced properties are still challenging and need to be deeply investigated.

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