Luminogens

Solid-State Light Emission Controlled by Tuning the Hierarchical Superstructure of Self-Assembled Luminogens

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Solid-state luminescence is an important strategy for color generation via molecular self-assembly. Here, a new luminogen (AT₃EMIS) containing both a rigid chromophore and a flexible dendron is designed and synthesized for multicolor emission. The emission energy of the target material is precisely controlled by adjusting three different columnar arrays through thermal and mechanical stimulation. With well-defined supramolecular organizations in different length scales, the luminescent properties of the light switch can be tuned.

1. Introduction

Luminescence is one of the most useful processes for generating colors from nature to increase species awareness, to attract food, and to defend the attacker.^[1] The luciferase of beetle is a good example of biological materials, which emits a wide range of luminescent colors from green to red depending on the sensitivity to factors as denaturing conditions.^[2] Inspired by nature, material scientists and engineers have tried to develop luminescent materials by utilizing conjugated polymers, inorganic nanoparticles, and alloyed nanobelts.^[3] Among them, organic chromophores are often better suited for practical applications in sensors and displays due to the good processability.^[4] However, conventional luminophores such as thiophene, naphthalene, and pyrene derivatives loss their photophysical properties in the bulk state. They only produce luminescence in a dilute state.^[5] In the recent years, there has been a growing demand for the development of luminescent materials that can convert chemical energy into light energy in the solid state. For example, thin films made from luminogens in the real world are widely used in organic light emitting devices.^[6] Therefore, the development of a luminogen that emits brighter emission by forming an ordered structure in the solid state through a self-assembly process is critical to the next generation of smart material research.

Since the photophysical properties of a material are the result of molecular assemblies that can be influenced by the interaction of subtle factors, it is very difficult to define solidstate luminescence without taking into account the chemical

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structure and the molecular packing structure.^[7] Even a slight chemical modification can have a significant effect on the molecular packing structure and can cause unpredictable properties in the emitted light.^[8] Therefore, to experimentally and theoretically study the molecular self-assembly, the rational and delicate design, and synthesis of new luminogens must precede.^[9] Liquid crystal (LC) phase showing the orientational order and the translational motion observed

in supramolecular luminogens can provide many opportunities to understand the relationship between molecular structure, packing symmetry, and luminescent property in different length scales.^[10] In addition, owing to the dynamic nature of LC molecules, luminogens that reveal the mesomorphic transition behaviors can induce color changes by applying external forces.^[11] Here, we report a novel supramolecular luminogen that exhibits multicolor luminescence which can be switched ON and OFF by thermal and mechanical stimulation.

2. Results and Discussions

2.1. Photophysical Properties and Phase Behaviors of Programmed Luminogens

The target material was newly designed and synthesized starting from a cyano-substituted divinylene arene derivative (**Figure 1**a). The Knoevenagel reaction of the aldehyde derivative and the acetonitrile moiety yielded a luminogen.^[12] AT₃EMIS was obtained by Steglich esterification with 3,4,5-tris-dodecyloxybenzoic acid. Synthetic methods and purification procedures are described in Figures S1–S6 in the Supporting Information. The chemical structure and purity of AT₃EMIS, and its intermediates are confirmed by ¹H and ¹³C nuclear magnetic resonance (NMR) spectra, and matrix assisted laser desorption and ionization time-of-flight (MALDI-ToF) analysis. AT₃EMIS is a rigid chromophore-based compound, but it exhibits high solubility in common organic solvents such as chloroform, hexane, and toluene due to the asymmetrically attached dendron.

Strong solid-state luminescence can be found in AT₃EMIS because of the aggregation induced emission (AIE) characteristics.^[13] The UV–vis absorption spectra of AT₃EMIS are recorded in tetrahydrofuran (THF) solutions (Figure S7, Supporting Information). AT₃EMIS shows two absorption bands at around 320 and 370 nm, corresponding to the benzoate function and the luminogen moiety, respectively.^[14] When the 370 nm UV





Figure 1. Molecular structure a), luminescence property b), and thermal behaviors c) of AT₃EMIS.

light with 1.5 mW cm⁻² intensity is irradiated for exciting the sample, it does not show any emission in the entire visible region. The AT₃EMIS has a drastic change in emission intensity from a nonluminescent solution (SOL) state to a strong luminescent suspension (SUS) state as demonstrated in the Figure 1b. It is widely accepted that the rotational motion of luminogen annihilates the excited state. Note that the cyanosubstituted divinylene arene derivative has a twisted molecular geometry due to the steric factor of the cyanide unit, which allows a nonradiative process.^[15] Addition of a copious amount of methanol (MeOH) as a poor solvent into the SOL state of AT₃EMIS in THF leads the molecular aggregation. Recognition of chemical building blocks through intermolecular interactions can create physical constraints and limit intramolecular rotations.^[16] When the radiation channel is opened, AT₃EMIS emits light. The luminescence quantum yields in the SOL and SUS states are 0.01 and 0.17, respectively, thus demonstrating the concomitant AIE effect of AT₃EMIS.

To understand the intense light emission of AT₃EMIS in bulk state, we tried to figure out how the molecules self-assembled into an ordered structure. Phase transformation of AT₃EMIS is first identified using differential scanning calorimetry (DSC). The transition temperatures and associated enthalpy values are shown in Figure 1c. The DSC thermogram of AT₃EMIS shows three endothermic peaks during the heating process. The DSC thermogram obtained in the subsequent cooling process is consistent with that attained in the heating process, indicating enantiotropic thermal behaviors.^[17] This compound exhibits a good thermal stability up to 375 °C (Figure S8, Supporting Information).

2.2. Structure Identification of Columnar Superstructure

To gain deeper insight into the self-assembled supramolecular organization, we carefully examined the molecular packing structure of AT₃EMIS in three ordered states using wide-angle X-ray diffraction (WAXD). A macroscopically aligned sample is prepared by the mechanically extruding the AT₃EMIS compound at 155 °C and then quenched to 25 °C. The uniaxially oriented sample is thermally annealed at 105 °C before the 2D WAXD measurement. The direction of the incident X-ray beam is always normal to the extrusion direction (ED). As shown in Figure 2a, the 2D WAXD pattern of AT₃EMIS at 155 °C is obtained with high quality. The diffused ring pattern in the wide-angle region (d = 0.48 nm) indicates that alkyl chains are in the melt state.^[18] In the small-angle region, the reflection at d = 4.52 nm is obviously divided into six spots at an azimuthal angle of 60° (Figure S9, Supporting Information). Due to the lack of higher order diffractions, the ordered phase of AT3EMIS at 155 °C can be considered as a low-ordered LC mesophase.^[19] The vertices of the hexagon corresponding to the (100) reflection indicate that AT₃EMIS forms the columnar hexagonal (Col_{H}) organization with a long-range positional order between the self-assembled columns.^[20] Since the AT₃EMIS luminogen is not disc shaped, it can be deduced that the disc in the column is composed of more than one molecule. The number (*n*) of molecules constituting a single disc of a column can be calculated by the following equation, $n = V \rho N_A M_W^{-1}$, where N_A , M_{W} , V, and ρ is Avogadro number, molecular weight, volume, and density of the unit cell, respectively. Assuming a typical ρ of LC material is about 1.0 g cm⁻³, the unit cell with a thickness







Figure 2. 2D WAXD of uniaxially oriented AT₃EMIS at 155 °C a) and 25 °C c). Schematic illustration of molecular packing model for Col_H b) and Col_R d).

of 0.45 nm contains six molecules.^[21] The discs consisting of AT₃EMIS hexamers are stacked flat with each other without strong π – π stacking.^[22] Therefore, the long axis of disc is aligned along the ED. Note that the rotational isotropy formed by the disordered state of alkyl chains creates the circular columns.^[23] Here, the orientation direction of the column axis (CA) is normal to the ED, and the lattice parameter of Col_H structure is a = b = 5.21 nm and $\gamma = 60^{\circ}$ (Figure 2b).

At 105 °C, many sharp diffraction patterns are appeared in both small- and wide-angle regions (Figure S10, Supporting Information). This means that a highly ordered crystal (K₂) phase appears, forming the intracolumnar disc stacking interactions. Upon decreasing the temperature to 25 °C, diffraction peaks in the wide-angle region are getting narrow and shifting to higher 2 θ -angles, indicating the formation of true crystal (K₁) phase.^[24] Since the structural change of the crystal-to-crystal phase transition requires a tremendous amount of energy, the molecular packing structure in the K₂ phase should resemble the K₁ phase.^[25] As shown in Figure S11 in the Supporting Information, it is realized that the tendency of the diffraction pattern of the uniaxially oriented K₁ sample is not significantly different from that of the K₂ sample.

In this circumstance, we focus to figure out the detail molecular packing structure of AT₃EMIS in the K₁ phase. Since the diffraction pattern of the oriented sample matches well with the powder sample, it can be determined that the diffraction at d = 0.45 nm is observed at 58° out of the ED (Figure 2c). These two pairs of peaks explain that the hexamer discotic building block is tilted 58° with respect to the ab-plane. Note that AT₃EMIS forms a conventional head-to-head dimer by the intermolecular hydrogen bond between two hydroxyl groups.^[26] The local dipole moments of the cyanide unit then induce the side-to-side intermolecular coupling of the dimeric building blocks and construct the disc-like arrangement.^[27] However, the series of diffraction arc at $2\theta = 5.25^{\circ}$, 10.5° , and 15.7° is observed on the meridian, which can be assigned as the (001), (002), and (003), respectively. This result supports that three hexameric discs participating in a single column are rotated 90° to the adjacent (ABA stacking) to minimize steric hindrances. The slanted stacking of the hexameric disc in the next stratum of the column is rotated around the CA. Careful structural analysis gives an orthorhombic unit cell with dimensions of a = 5.35 nm, b = 5.52 nm, c = 1.68 nm, and $\alpha = \beta = \gamma = 90^{\circ}$ via the www.advancedsciencenews.com

refinement of the reciprocal lattice, and this phase is close to a columnar rectangular $({\rm Col}_R)$ structure as illustrated in Figure 2d.

2.3. Tunable Luminescence of Light for Multicolor Switch

Based on the structure identification, the molecular packing structures of AT₃EMIS can be manipulated by varying the temperature. As shown in **Figure 3**a, the overall phase transition behaviors are summarized in polarized optical microscopy (POM) images of AT₃EMIS. As expected, the Iso state of AT₃EMIS is confirmed at 185 °C by a complete dark state. The WAXD of AT₃EMIS in the Iso state exhibits only amorphous halos at $2\theta = 2.43^{\circ}$ and $2\theta = 18.8^{\circ}$.^[28] The low-angle halo (d = 3.64 nm) indicates the average periodicity of electron density fluctuations between the nanophase separated rigid

chromophore, while the wide-angle halo (d = 0.47 nm) represents the average distance between the flexible dendrons. At 155 °C, a typical pseudo focal conic texture of LC mesophase is observed.^[29] The K₂ phase at 105 °C shows the defect aggregates across the pseudo focal conic texture. Significant enhancements in birefringence during the K₂-to-K₁ phase transition are due to the close molecular packing of the luminogen cores and the crystallization of aliphatic tails.^[30]

We have found that a simple thermal treatment on the AT₃EMIS compound triggers a change in the luminescence color. Interestingly, AT₃EMIS in the optical cell exhibits the remarkable thermochromic luminescent behaviors in the solid state. Figure 3b shows the luminescence changes of AT₃EMIS measured at different phases during the cooling process from 185 to 25 °C. The thermochromic luminescence behaviors are detected between green and blue, which is easily distinguished



Figure 3. POM images of AT₃EMIS at different temperatures a). Macroscopic images of AT₃EMIS during cooling process under 370 nm UV light irradiation b). Luminescence spectra of AT₃EMIS at each phase c), and the maximum intensity shift behaviors with respect to temperature (inset).



by the naked eye.^[31] The photophysical properties of small molecules with π -electronic conjugation systems depend not only on the individual chemical functions but also on the intermolecular physical bonds, so that it is possible to manipulate the solid-state luminescence of AT₃EMIS through appropriate heat treatment.^[32] In addition, the spectral features of absorbance properties are somewhat different from each phase (Figure S12, Supporting Information). These observations further support that the arrangements of the luminogens in the three ordered structures are changed.^[33]

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At 185 °C, the solid-state of AT₃EMIS does not emit any discernible light because the long-range molecular order is totally disappeared and the intramolecular rotation in the Iso state is activated.^[34] When AT₃EMIS molecules enter the LC mesophase, they emit brilliantly. A broad emission peak with $\lambda_{max} = 490$ nm is detected, as shown in Figure 3c. Considering the molecular packing structure in the LC mesophase, we have found that the restriction of intramolecular motion is useful for preventing nonradiative relaxation. In the LC mesophase, the intramolecular rotational motion of AT₃EMIS is reduced by concomitantly increasing planarity through dimer formation.^[35]

When the temperature is lowered to 105 °C, AT₃EMIS in the K₂ phase emits light at $\lambda_{max} = 520$ nm, which is a 30 nm

bathochromic shift compared to the LC mesophase. The redshift of the emission spectrum for the K₂ phase is the result of increased interactions of the disc and generates the electronic delocalization through the π -conjugation system.^[36] Finally, the K₂ phase is converted to the K₁ phase at room temperature, and the luminescence intensity is remarkably enhanced at $\lambda_{max} = 530$ nm. The redshift in the emission spectrum for the transition from the K₂ phase to the K₁ phase can be explained by the increased interchromophoric interaction, which is evident by another redshift for the transition from the LC mesophase to the K₂ phase.^[37] The additional increase in luminescence intensity should be originated from the complete restriction of AT₃EMIS rotational motion, together with the closer packing of the disc in the self-assembled column.^[38]

Obtaining the photoluminescence property of new materials at room temperature is very important for practical application of optical devices because it is advantageous for low cost process and high efficiency production.^[39] When gently grinding AT₃EMIS with pestle at room temperature, the green emission by irradiation of 370 nm light instantly changes to intense yellow emission. **Figure 4**a shows the mechanochromic luminescence behaviors. When the yellow powder of crushed AT₃EMIS is fumed directly by dichloromethane, it is completely



Figure 4. Macroscopic photographs a), luminescence spectra b), and diffraction patterns c) of AT₃EMIS at the pristine powder solid, after the mechanical grinding state, and the subsequent dichloromethane fuming process.







Figure 5. Procedures for switching the multicolor luminescence via the thermochromic and mechanochromic behaviors of AT₃EMIS.

restored to green as the original AT₃EMIS. It is evident that the AT₃EMIS powder is divided into two areas: yellow (external ring) and green (center ring). The emission spectra of the initial, ground, and fumed states are summarized in Figure 4b.

To find an answer for the main driving force of the mechanochromic luminescence behaviors, the 1D WAXD patterns are obtained after applying the mechanical force. Figure 4c shows a dramatic reduction in peak intensity with increased peak width for the ground sample. This means that the intermolecular interaction of AT3EMIS in the ground state is weaker than initial state.^[40] However, 1D WAXD pattern of the ground sample still shows a reflection peak at the low-angle region of $2\theta = 2.26^{\circ}$, suggesting the formation of a shear-induced columnar phase (Col_s). The mechanical shear applied to AT₃EMIS reorganizes the molecular arrangement from Col_R to Col_s with the intercolumnar distance of d = 3.94 nm. It is worth mentioning the fact that this kind of grinding process is hard to lead a perfect conversion of the AT₃EMIS packing symmetry because the mechanical force is unevenly applied to the pristine powder in the bulk state.^[41] The residual diffraction peaks corresponding to the Col_R domain are included in the 1D WAXD pattern obtained in the ground sample.

The formation of Col_S results in a bathochromic shift and a broad emission spectra at $\lambda_{max} = 590 \text{ nm.}^{[42]}$ The slippage of the molecular stack by mechanical shear creates a larger π -electron conjugation system.^[43] The partially overlapped luminogens are arranged more linearly. On the other hand, luminogens aligned with the ABA fashion in Col_R show a small portion of the overlap as noted above, so they display emission bands at shorter wavelengths ($\lambda_{max} = 530 \text{ nm}$). The reversibility of mechanochromic luminescence is further investigated. When fumed with dichloromethane, the emission color and diffraction peak are fully recovered to their initial state, indicating the

return from Col_S to Col_R due to partial melting and subsequent recrystallization.

If the emission of AT₃EMIS can be controlled by heat as well as mechanical forces, AT₃EMIS allows us to design a smarter emissive memory system. As shown in Figure 5, the distinctive yellow, green, and blue emissions from the letter "SCI" can be clearly observed in Col_s, Col_R, and Col_H, respectively. The ground AT₃EMIS showing yellow color placed on the glass substrate yields the initial state (i). Upon exposure to dichloromethane vapor at room temperature, the Cols film is converted to the Col_R film (ii) and turns green. When the Col_R film is subsequently placed on a hot stage and heated to form the Col_H phase (iii), AT3EMIS becomes blue. When the film reaches to the Iso state (iv), we cannot find the any emission of light. The multicolor switching protocol is fully reversible, so we can easily turn ON and OFF the luminescence and even adjust the color. For instance, if the luminogen shows a dark color (iv) at 185 °C, the substrate is quenched to 25 °C to generate a green emission (ii). Then we can obtain the yellow emission (i) by shearing the AT₃EMIS film on the glass substrate with a stick. Increasing the temperature directly to 155 °C will emit blue (iii) as expected.

3. Conclusion

We introduced a new luminogen (AT₃EMIS) that can switch the luminescent color by applying thermal as well as mechanical stimulation. Our experimental results indicated that understanding the self-assembled hierarchical superstructures is one of the easiest and most important ways to predict and adjust the emission energy of the target material. By precisely controlling three different columnar structures (Col_R , Col_H , and Col_S) of AT₃EMIS, the solid-state luminescence can be reversibly switched

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from green to blue, and yellow. Due to straightforward synthesis and precise structure manipulation, AT₃EMIS can be a good candidate for next generation luminescent materials that can be applied to memory devices, security inks, and medical diagnoses.

4. Experimental Section

Materials and Characterization: All reagents were commercially obtained and used without further purification. Column chromatography was performed using the silica gel 60 (Merck). NMR spectra were recorded on a spectrometer (Varian Oxford As500). MALDI-ToF mass (Voyager-DE STR Workstation) experiment was conducted to identify the chemical structure and purity. The thermal behaviors were monitored by using the DSC (Perkin Elmer PYRIS) and POM (Nikon Eclipse). The WAXD measurements were used by CuK_{α} X-ray (Rigaku). Thermal stability was determined by thermogravimetric analysis (TGA) (TA Q50). The molecular simulation program (Accelrys Cerius) was utilized to calculate the energy minimized geometry. Absorption spectra were detected by a spectrophotometer (Scinco S3100). Emission spectra were taken by a spectrofluorometer (Shimadzu RF6000).

Synthesis of Cyano-Substituted Divinylene Arene: 4-Hydroxybenzaldehyde (16.4 mmol) and 1,4-phenylenediacetonitrile (6.6 mmol) were dissolved in 1-propanol (18 mL) and acetic acid (0.79 mL). The solution was heated at reflux under nitrogen atmosphere and piperidine (0.97 mL) was carefully added. After 24 h the reaction mixture was cooled to room temperature, and the yellow solid was filtered, and washed with methanol (yield: 83%). ¹H NMR (400 MHz, dimethyl sulfoxide (DMSO)-*d*): δ = 8.01 (s, 2H), 7.85 (m, 4H), 7.76 (m, 4H), 6.95 (m, 4H) ppm.

Synthesis of 3,4,5-Trisdodecyloxybenzoic Acid: 1-Bromododecane (217.0 mmol) was slowly added, after K₂CO₃ (330.0 mmol) was added into the solution of methyl 3,4,5-trihydroxybenzoate (54.0 mmol) in dried dimethylformamide (100 mL). The mixture was additionally stirred for 12 h at 100 °C. The gummy solid obtained by filtration and evaporation was dissolved in chloroform. The resulting mixture was washed with distilled water and dried over MgSO₄. The crude product was refluxed in the NaOH (30.0 mmol) solution with ethanol (100 mL) for 6 h. After cooling the mixture to room temperature, 1000 mL of distilled water was added. The resulting mixture was acidified with HCl. The precipitate was then filtered, washed with deionized water, and dried under vacuum to give a white solid (yield: 94%). ¹H NMR (400 MHz, CDCl₃): δ = 7.24 (s, 2H), 3.96 (m, 6H), 1.81 (m, 6H), 1.46 (m, 6H), 1.39 (m, 48H), 0.86 (m, 9H) ppm.

Synthesis of AT₃EMIS: A solution of cyano-substituted divinylene arene (1.19 mmol) in dried dimethylformamide (50 mL) was added to a solution of 3,4,5-trisdodecyloxybenzoic acid (0.29 mmol), N-(3dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (1.48 mmol), and 4-(dimethylamino)pyridine (1.48 mmol) in dried chloroform (20 mL). After stirring the mixture for 72 h at room temperature, the product was extracted with chloroform and water. The combined organic layer was dried over MgSO₄. The crude product was purified by column chromatography with silica gel using ethyl acetate:methylene chloride = 1:3 to yield a pale yellow powder (yield: 68%). ¹H NMR (400 MHz, CDCl₃): δ = 7.95 (d, 2H), 7.84 (d, 2H), 7.66 (m, 4H), 7.51 (s, 1H), 7.49 (s, 1H), 7.43 (d, 2H), 7.32 (d, 2H), 6.89 (d, 2H), 5.67 (s, 1H), 4.08 (m, 6H), 1.85 (m, 6H), 1.38 (m, 54H), 0.83 (t, 9H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 156.5, 158.2, 152.7, 143.8, 142.7, 141.4, 136.7, 135.4, 132.4, 131.3, 126.9, 122.8, 117.9, 116.2, 110.5, 109.5, 108.1, 73.8, 69.7, 31.9, 29.8, 25.7, 24.1, 13.5 ppm; MS (MALDI-ToF) m/z calcd: 1021.46 [M+Na]+; found: 1043.96.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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