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Stimuli-Responsive Properties of Aggregation-Induced-Emission Compounds Containing 9,10-Distyrylanthracene Moiety

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Abstract: Two aggregation-induced-emission active luminophores based on 9,10-distyrylanthracene with stimuliresponsive properties are successfully synthesized. A distinct seven- or five-colour luminescence switching built upon a single organic molecule is firstly achieved. These phase transitions can be interconverted by physical stimuli such as grinding by mortar and pestle, heating and exposing to the vapor of organic solvents. Moreover, an applicable strategy for the design of new mechano-responsive materials with π -conjugated luminophores is proposed.

Introduction

Functional materials that change their some properties in response to a single stimulus or multiple stimuli are called smart materials.^[1] Piezochromism refers to a phenomenon that the luminescence properties of materials can change with mechanical force, in which the presence of more than two different pressure-dependent stable or metastable states is essential.^[2-4] Piezochromic luminescent materials have received considerable interest in recent years in view of their potential applications in sensors, memory chips, camouflage. optoelectronic devices, and so forth. [5-8] However, the studies of piezochromic materials remain inadequate due to the absence of an effective mechanism to illustrate the close correlation between the changes of molecular packing and their corresponding luminescence properties. Therefore, the ability to dynamically control the molecular aggregation state and the consequent fluorescence colour and/or intensity is very important to develop new piezochromic luminescent materials.

Many conventional luminophores often experience some

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or partially. In most cases, aggregation-caused emission quenching limits the practical applications of organic materials which often require materials to be solid and films, particularly in optoelectronic devices. ^[1a,1c] Aggregation-induced-emission (AIE) is an intriguing photophysical phenomenon associated with chromophore aggregation.^[9] AIE materials can enhance emission from aggregate or solid state in comparison to their diluted solutions, which have been found in several systems, such as silole, tetraphenylethylene (TPE), triphenylethylene, cyano distyrylbenzene, distyrylanthracene and their derivatives. ^[1,10-12] In the case of 9,10-distyrylanthracene derivatives, the 9,10-divinylanthracene segment can undergo an active rotation process in a diluted solution which quenches the emission from luminophores. But in aggregate state, the intramolecular rotation, in other words, the non-radiative decay channel is blocked which leads to the enhanced emission of molecules. [12-15]

effects of aggregation-caused emission quenching, completely

In fact, a luminescent material sensitive to pressure stimuli with an AIE property was first reported by Park in 2010, which is a CN-substituted distyrylbenzene derivative.^[10] Subsequently, quite a few AIE-based piezochromismic compounds and a relationship between AIE nature and piezochromism were reported by Chi.^[16] AIE compounds with amorphous forms or strong crystallinity are found to be not suitable as piezochromic materials. The proper crystallinity is a prerequisite for AIE-based piezochromism.^[16] As AIE materials can enhance emission in the solid state, it is highly expected to develop high sensitive piezochromic materials based on AIE properties. However, most of AIE-based piezochromismic materials are TPE systems, and moreover, only a dual-color luminescence switching. AIE-based piezochromismic materials with more than two different pressure-dependent stable or metastable states have rarely been reported.[1,16,17]

To obtain multi-colored switching luminophores with enhanced emission in the solid state,^[18-23] we report the design and synthesis of two new 9,10-distyrylanthracene derivatives



Scheme 1. Synthesis of compounds JX01 and JX02.

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denoted as JX01 and JX02 (Scheme 1) and explore their AIE and stimuli-responsive properties. The introduction of planar 3, 6-dimethoxy-carbazole group into JX02 is used to adjust the related properties and for comparison. AIE properties, molecular quantum-chemical packing in crystals, calculations. electrochemical properties, stimuli-responsive properties, thermal stabilities, differential scanning calorimetry (DSC), and X-ray diffraction based on these two compounds were extensively investigated and compared with each other for understanding the structure-property relationships.

Results and Discussion

Synthesis

The synthetic procedures of two fluorescent compounds (**JX01** and **JX02**) are shown in Scheme 1. The detailed synthetic procedures of key intermediates (**2**, **4** and **7**) were described in SI, which were prepared according to the reported methods.^[8,24-26] The double bonds were introduced by Wittig-Horner reaction. The reaction of aldehyde (**4** or **7**) with stabilized phosphorus ylide led to olefin with excellent *E*-selectivity. The molecular structures of new compounds (**JX01** and **JX02**) were characterized by ¹H/¹³CNMR spectroscopy (Figure S5, S6 and S8, SI), high-resolution mass spectrometry (HRMS) (Figures S7 and S9, SI), and X-ray diffraction (Figures 1 and 2; Figures S10–S13, SI). All these analytical data are consistent with the proposed structures.

AIE properties

The fluorescence behavior of JX01 and JX02 was studied in diluted solutions of H₂O/THF with different H₂O fractions (Figure Figures S15, S17 and S18, SI). The 9,10-3: divinylanthracene segment can undergo an active rotation process in pure THF solution that deactivates the corresponding excited states, thus making them nonemissive in solution. As H_2O is non-solvent for JX01 and JX02, these organic molecules have to aggregate when a large amount of H₂O is added. When the volume fraction of H₂O exceeds a critical value (60% for JX01 and 50% for JX02), the intramolecular rotations of aryl rotors are greatly restricted owing to the physical constraint. This restriction of intramolecular rotations blocks the non-radiative pathway and opens up the radiative channel. As a result, these organic molecules become emissive in the aggregate state.^[12-14] Plot of photoluminescence intensity versus different H₂O fractions in H₂O/THF mixtures shows the fluorescence behavior of JX01 and JX02 while changing the H₂O portion (Figure 3; Figure S15, SI). Notably, the fluorescence intensity of JX02 decreases in H₂O/THF mixtures containing 80% of H₂O, which is often observed in some AIE compounds, but its intrinsic mechanism still remains enigmatic.^[13] Just as expected, quantum yields of JX01 and JX02 in pure THF are very low (0.018 and 0.093, respectively). When the volume fraction of H₂O exceeds a critical value (60% for JX01 and 50% for JX02), they both exhibit higher quantum yields. As the planar carbazole group of JX02 can induce an enhanced π-



Figure 1. Six π - π stacking molecules of JX01. (Hydrogen atoms were omitted for clarity.)



Figure 2. Nine stacking molecules of JX02.

conjugation effect, in the same H_2O contents, **JX02** shows remarkably higher quantum yields than **JX01** (Table S2, SI).

Their UV-vis absorption spectra and the corresponding molar absorption coefficients in the mixed solvents (H₂O/THF, 1.0×10^{-5} mol/L) were reported. For **JX01** and **JX02**, the spectra profiles almost remain unchanged with H₂O contents below 60% and 50%, respectively. The spectral region starts to increase at a H₂O content of 70% or 60%, which could be attributed to the light-scattering or Mie effect of nano-aggregate suspension in solvent mixtures, as the organic molecules begin to aggregate in this solvent composition.^[27] (Figures S14 and S16, Table S3, SI). Both fluorescence and UV-vis absorption spectra confirm that **JX01** and **JX02** have a significant AIE effect caused by molecular aggregates with an addition of H₂O to H₂O/THF mixtures.



Figure 3. Fluorescence spectra of **JX01** (10.0 μ M) in H₂O/THF mixtures with different H₂O contents at 25 °C. Inset (a): Plot of fluorescence peak intensity versus different H₂O fractions. Inset (b): Fluorescence emission in different H₂O fractions under UV-light (365 nm).





Figure 4. Calculated frontier molecular orbitals of JX01 and JX02.

Compound	λ_{onset}	ΔE_{g}	HOMO	
	(1111)	(ev)	(ev)	(ev)
JX01 ^[a]	-	2.67	-4.38	-1.71
JX01 ^[b]	515	2.40	-5.45	-3.05
JX02 ^[a]	-	2.69	-4.75	-2.06
JX02 ^[b]	483	2.56	-5.73	-3.17

[a] Obtained from calculation. [b] Obtained from CV. [c] Estimated according to the onset wavelength of UV absorption. [d] LUMO = ΔE_g + HOMO.

The morphology of aggregated molecules in H_2O/THF mixtures with different H_2O fractions was observed by ultra-high resolution scanning electron microscope (SEM). The SEM images evidently show their different aggregated forms: nanostructure units (Figures S19 and S20, SI).

Crystal structure elucidations

As shown in Figures 1, 2 and Figures S10-S13, SI, X-ray diffraction analyses unambiguously clarify the molecular structures of JX01 and JX02, revealing that all molecules adopt highly twisted conformations in the crystal state. Such twist stress is believed to be released when triggered by external pressure or heating, which leads to the planarization of molecular conformation resulting in a red shift of fluorescence spectra. For triarylamine-based JX01, the central nitrogen atom is bounded with three carbon atoms via sp^2 -hybridization (planar configuration), and the three phenyl groups assume a propellerlike structure relative to the plane defined by three C-N bonds. In crystal, there is a strong intermolecular interaction between the benzene ring of triphenyl amine and the benzene ring of anthracene through π - π stacking interactions. Due to the nonplanar structure of triarylamine, the molecular configuration of JX01 is beneficial to restrain complex intermolecular aggregation (Figure 1; Figure S11, SI).^[28] For JX02, the planar carbazole group can induce a stronger intermolecular interaction and the two adjacent molecules are bound together by hydrogen bonds (C-H···O) to form molecular layers (ca. 2.46 and 2.60 Å, Figure S13, SI). Furthermore, there are many multiple hydrogen bonds (C-H···O) between molecular layer with a distance of ca. 2.66 Å (Figure 2), which help to rigidify the molecular conformation, so that these molecular layers become clearly evident and distinct in crystal (Video S1, SI). As a result, the close-stacked arrangements of JX02 molecules should be much more robust. Of course, the interfaces are easy to be destroyed through slip deformation by external stimuli.

Calculation

To gain insight into the molecular structure and electron distribution, the optimized geometries of JX01 and JX02 were calculated by using density functional theory (DFT) at B3LYP/6-31G (d, p) level based on a Gaussian09 software package with the isodensity surface values fixed at 0.02 (Figure 4). For JX01 and JX02, the distribution of frontier molecular orbitals is similar and both LUMOs are mainly located on the 9,10-divinylanthracene segment. In contrast, their HOMOs delocalize throughout the entire molecules and the HOMO distribution of JX02 is more uniform due to the introduction of planar carbazole groups. The results indicate that the electrons could transfer from triphenyl amine or carbazole group to 9,10divinylanthracene core in excited state. The calculated energy levels of molecular orbital are displayed in Table 1, which show that the molecular conformations affect the HOMO and LUMO energy levels. The HOMO levels of JX01 and JX02 are -4.38 and -4.75 eV, respectively. Although the HOMO of JX01 is 0.37 eV higher than that of JX02, the values of excitation transition energy (ΔE_g) are very close.

Cyclic voltammetry (CV)

CV was recorded to determine the ground-state oxidation potential (Figures S21–S23, SI). On the basis of the reported HOMO level of spiro-OMeTAD (–5.22 eV),^[29] the HOMO levels of **JX01** and **JX02** are –5.45 and –5.73 eV, respectively. ΔE_g was calculated from the onset wavelength of UV absorption (515 nm, 2.40 eV for **JX01** and 483 nm, 2.56 eV for **JX02**; Figures S24 and S25, SI).^[30] LUMO energy levels were obtained from HOMO energy and ΔE_g and calculated to be –3.05 and –3.17 eV, respectively (Table 1). Both calculation and experiment results suggest that the HOMO and LUMO levels of **JX01** are up-shifted. Thus, the introduction of triphenyl amine group on primary ligand can increase the HOMO energy because of its stronger electron-donating effect.



Figure 5. Seven phase transition sequences for compound JX01.

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Figure 6. Five phase transition sequences for compound JX02.

Stimuli-responsive properties

Interestingly, in the solid state, multi-colored switching luminophores which were different in molecular packing mode under an external stimulus were observed (Figures 5 and 6, seven colors for JX01 and five colors for JX02). When compound JX01 was subjected to reprecipitation or recrystallization, two different forms were obtained: yellow powder (JX01-1, λ_{em} = 569 nm) by reprecipitation from CH₂Cl₂ with a slow addition of hexane and orange crystal (JX01-2, λ_{em} = 592 nm) by recrystallization from CH₂Cl₂/hexane mixtures (Figure 5). When JX01-1 and JX01-2 were ground with a mortar and pestle, they were transformed to a red powder bearing an amorphous form (**JX01-3**, λ_{em} = 643 nm, Figures S26–S30, SI). The 74 nm red shift of fluorescence emission upon grinding $(JX01-1 \rightarrow JX01-3)$ is a very significant pizeochromica effect.^[6] After heating at 160 °C for 60 s, the red ground powder (JX01-3) turned into an orange amorphous form (JX01-5, λ_{em} = 600 nm, Figures S31 and S32, SI). Moreover, when JX01-3 was put into a sealed beaker containing a small amount of CH2Cl2 at 25 °C for 30 s, the color changed from red to orange due to the morphological transition from amorphous phase to crystalline (JX01-4, $\lambda_{em} = 615$ nm, Figures S35, S36 and Video S2, SI). This material with a fast response speed can be applied for in situ measuring device. Similarly, after being ground with a mortar and pestle, JX01-4 and JX01-5 can also be transformed into a red powder (JX01-3, Figures S33, S34, S37 and S38, SI). Moreover, the switching processes between JX01-3 and JX01-4 could be repeated several times without any fatigue (Figure S39, SI). These reversible emission spectra without any obvious reduction of emission intensity make JX-01 a promising candidate for pressure or solvent detector. At last, when JX01-1and JX01-2 were placed on a thin glass plate and heated by a hot plate at 160 °C for 60 s, two similar orange powder states (JX01-6, λ_{em} = 602 nm, and JX01-7, λ_{em} = 606 nm, Figures S40-S43, SI) were observed, respectively. Although JX01-6 exhibits an emission spectrum similar to that of JX01-7, their X-ray diffraction (XRD) patterns are different (Figures S52 and S53, SI). Further, the DSC analysis of JX01-1 and JX01-2 indicates the morphological difference between JX01-6 and JX01-7, and more details about this difference will be discussed in the subsequent DSC thermograms.

Similarly, when compound **JX02** was subjected to reprecipitation or recrystallization, two different forms were obtained: green powder (**JX02-1**, $\lambda_{em} = 537$ nm) by reprecipitation from CH₂Cl₂ with a slow addition of hexane and yellow-green crystal (**JX02-2**, $\lambda_{em} = 574$ nm) by recrystallization

from CH_2Cl_2 /hexane mixtures (Figure 6). When JX02-1, JX02-2, JX02-4 and JX02-5 were ground with a mortar and pestle, they were all transformed to an orange powder bearing an amorphous form (**JX02-3**, λ_{em} = 604 nm, Figures S54–S57, S62, S63, S68 and S69, SI). The 67 nm red shift of fluorescence emission upon grinding (JX02-1→JX02-3) is a very significant pizeochromica effect.^[6] When JX02-3 on a glass plate was exposed to CH₂Cl₂ vapor at 25 °C, the color also quickly (ca. 30 s) changed from orange to yellow-green (**JX02-5**, λ_{em} = 565 nm, Figures S66 and S67, SI). As these stimuli were nondestructive in chemical structure, JX02-3 and JX02-5 could be interconverted by application of grinding-fuming process for many times without fatigue (Figure S70, SI). After heating at 160 °C for 60 s, the orange ground powder (JX02-3) turned into a yellow-green form (**JX02-2**, λ_{em} = 569 nm, Figures S58 and S59, SI). When JX02-2 and JX02-3 were heated at 260 °C for 3 min, they were both transformed into a green powder (JX02-4, λ_{em} = 534 nm, Figures S60, S61, S64 and S65, SI).

To gain further insight into the mechanofluorochromism, the influence of different applied pressure on luminescence of compounds JX01 and JX02 was investigated. The powder (JX01-1 or JX02-1) was placed in a hole (diameter: 7 mm) of a steel mould and the hydrostatic pressure was controlled by a display meter of press (Figure S81c, SI). During the compression process, the fluorescence maximum of pellets (JX01-1) gradually red-shifted to 619 nm (orange) at 0.1 GPa and eventually to 645 nm (red) at 0.5 GPa (Figure 7). The fluorescence spectrum ($\lambda_{em} = 645$ nm) under a pressure of 0.5 GPa is very similar to that of the ground powder (JX01-3). Similarly, for JX02-1 sample, the fluorescence maximum of pellets gradually red-shifted to 574 nm (yellow-green) at 0.1 GPa and eventually to 601 nm (orange) at 0.5 GPa (Figure S81, SI). The fluorescence spectrum (λ_{em} = 601 nm) under a pressure of 0.5 GPa is also very similar to that of the ground powder (JX02-3). As the applied pressure increased, the fluorescence emission of pellets (JX01-1 or JX02-1) showed a gradual red shift. For JX01 and JX02, multiple phenyl peripheries are linked to 9,10-divinylanthracene core via a rotatable carboncarbon single bond to form an AIE moiety. The steric effects among these phenyl rings force the molecules to adopt a highly twisted conformation. The twisted conformations, weak $\pi-\pi$ stacking interactions and/or hydrogen bonds make molecular packing relatively loose and generate many cavities with a low lattice energy. These loose molecular packing and labile cavities render the crystal to be easily destroyed by conformational planarization or slip deformation under external stimuli, which might be responsible the dramatic color change for of luminescence.[12-14]

Thermogravimetric analysis (TGA) and DSC thermograms

TGA measurements show that **JX01-1** and **JX02-1** have high decomposition temperatures (415 and 420 °C, respectively) (Figures S82 and S83, SI). The three forms (**JX01-1**, **JX01-2** and **JX01-3**) of **JX01** were analyzed by DSC from 25 to 280 °C (Figures S84–S89, SI). An obvious

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Figure 7. (a) Fluorescence spectra of **JX01-1** powder under external pressure. (b) The observed color changes from light yellow ($\lambda_{em} = 569 \text{ nm}$) to red ($\lambda_{em} = 645 \text{ nm}$) due to different applied pressure.

endothermic peak is observed at 162 °C in the first heating DSC profile of JX01-1 (Figure S84, SI), which means that heating could convert the thermodynamically stable crystalline sample into a metastable state via an endothermic process at about 162 °C. This result is consistent with the transformation of JX01-1 into JX01-6 at 160 °C (Figures S40 and S41, SI). For JX01-2, there are three endothermic peaks in the first heating DSC profile (167, 218 and 240 °C, Figure S86, SI). Although the first endothermic peaks of JX01-1 and JX01-2 are close (162 vs. 167 °C), their melting points have a big difference (218 vs. 240 °C). This result further proves the morphological difference between JX01-6 and JX01-7. In the DSC profile of JX01-2, the peak at 218 °C may originate from JX01-1. A possible reason is that a small amount of JX01-1 was also formed when the orange crystal (JX01-2) was recrystallized from CH₂Cl₂/hexane mixtures. In the DSC profile of JX01-3, a broad exothermic peak is observed at 162 °C in the first run, which coincides with the conversion processes from JX01-3 to JX01-5 (Figures S31, S32 and S88, SI). This result demonstrates that the amorphous ground sample (JX01-3) can undergo an exothermic recrystallization process at about 162 °C, and JX01-5 is thermodynamically more stable than JX01-3.

The three forms (JX02-1, JX02-2 and JX02-3) of JX02 were analyzed by DSC from 50 to 350 °C (Figures S90–S95, SI). In the DSC profile of JX02-2, a short and broad peak at 259 °C is observed in the first run, which is consistent with the transformation of JX02-2 into JX02-4 at 260 °C (Figures S60, S61 and S92, SI). For JX02-3, there are three peaks in the first heating DSC profile (162, 235 and 336 °C, Figure S94, SI). The exothermic peak at 162 °C coincides with the transformation of **JX02-3** into **JX02-2** at 160 °C (Figures S58 and S59, SI). Similarly, the amorphous ground sample (**JX02-3**) undergoes an exothermic recrystallization process at about 160 °C, and **JX02-2** is thermodynamically more stable than **JX02-3**. The second peak at 235 °C means when the heating temperature is further increased, **JX02-3** can be further transformed, which substantiates the phase transition sequences: **JX02-3**→**JX02-2** \rightarrow **JX02-4** (Figure 6).

Wide-angle X-ray diffraction (WAXD) spectra

WAXD spectra unequivocally reveal stimuli-induced changes between different forms (Figures S44–S53 and S71–S80, SI). Sharp and intense reflections of **JX01-1**, **JX01-2**, **JX01-4**, **JX01-6** and **JX01-7** can be observed, indicating their crystalline structures. After being ground, the XRD pattern of **JX01-3** (Figures S46–S48, SI) indicates a phase conversion of crystal to amorphousness (**JX01-1**, **JX01-2** and **JX01-4** to **JX01-3**). When **JX01-3** was fuming with CH₂Cl₂ vapor for 30 s, an amorphous form to a crystalline phase transition occurred (**JX01-3**→**JX01-4**), and some reflection peaks were observed (Figures S35, S36 and S50, SI). In contrast, when **JX01-3** was heated at 160 °C for 60 s, the amorphous form remained intact during phase conversion (**JX01-3** to **JX01-5**, Figures S31, S32 and S51, SI).

Similarly, the XRD patterns of JX02-3 (Figures S74–S77, SI) reveal that JX02-1, JX02-2, JX02-4 and JX02-5 are all transformed into an amorphous form with grinding. But, when JX02-3 was fuming with CH_2Cl_2 vapor, the amorphous form remained intact during phase conversion (JX02-3 to JX02-5, Figures S66, S67 and S80, SI). In contrast, when JX02-3 was heated at 160 °C for 60 s, an amorphous form to a crystalline phase transition occurred (JX02-3 to JX02-2, Figures S58, S59 and S73, SI). The above results suggest that the compounds (JX01 and JX02) under investigation represent enantiotropic systems and their metastable states can readily be influenced by crystallization conditions or external stimuli.

pH response

JX01-1 can exhibit a prominent Lewis base character because of the electron-donating triphenyl amine group, which can undergo repeatable protonation and deprotonation. The evaluation of pH responsiveness was conducted in the solid state. Trifluoroacetic acid (TFA) and aqueous ammonia (NH₃) vapor were employed as stimuli. **JX01-1** on a glass plate appears orange in daylight and emits bright yellow light under UV illumination. Its color visually changed from orange to jasper when exposed to TFA gas. After fumed with NH₃ vapor, its original color was recovered. The orange-jasper color switching process is reversible and repeatable (Figure 8). This pH-



Figure 8. Color changes of a TFA or NH₃ fumed sample (JX01-1).

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responsive behavior is attributed to the protonation of triphenyl amine group, which effectively eliminates the intrinsic intramolecular charge transfer (ICT) effect of donor–acceptor molecules.^[1,31] But such pH-induced fluorescence switching cannot be reproduced by using the following acids: HCI, HNO₃, HCOOH, CH₃COOH, H₃PO₄, HCIO₄ and H₂SO₄. For **JX02-1**, its pH-responsive color change is indistinct, which might be ascribable to the weak basicity of carbazole group (Figure S96, SI).

Conclusions

In summary, AIE-based piezochromism with a reversible seven- or five-color luminescence switching built upon a single organic molecule has been firstly achieved. The fluorescence switching process can be smoothly triggered through disrupting the ordered molecular packing (mechanical grinding) and repacking (heating or solvent annealing). These phase transitions were confirmed by color changes, fluorescence spectra, WAXD patterns and DSC thermograms. The loose molecular packing and labile cavities in crystal might be responsible for the dramatic color change of luminescence. In addition, a pH-responsive AIE system (JX-01) displays a reversible fluorescent "ON/OFF" response when fumed with volatile TFA/NH₃ vapors. These design principles appear to be readily applicable to new mechano-responsive materials with πconjugated luminophores. Further investigation / of distyrylanthracene derivatives with expanded π systems and their applications for organic devices are underway.

Experimental Section

Synthesis of compound JX01. Under an Ar atmosphere, a two-necked flask equipped with a magnetic stirrer was charged with compound 2 (182 mg, 0.38 mmol, 1.0 equiv.), compound 4 (280 mg, 0.84 mmol, 2.2 equiv.), NaH (500 mg, 20.8 mmol, 54.8 equiv.) and THF (6 mL). The reaction mixture was heated at 40 °C for 48.0 h and cooled to room temperature. The reaction was quenched with H₂O and extracted with ethyl acetate five times. The extract was then dried over magnesium sulfate and filtered. After evaporation at a reduced pressure, the residue was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1, V/V), affording compound JX01 as solids (200 mg, 62.9%). The product was further purified by recrystallization (hexane/dichloromethane) for property measurements. ¹H NMR (400 MHz, CDCl₃) δ (TMS, ppm): 8.41– 8.39 (m, 4H), 7.76 (d, J = 16.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 4H), 7.46–7.43 (m, 4H), 7.12 (d, J = 8.0 Hz, 8H), 7.00 (d, J = 8.0 Hz, 4H), 6.87-6.82 (m, 10H), 3.81 (s, 12H). ¹³C NMR (100 MHz, CDCl₃) δ (TMS, ppm):155.99, 148.66, 140.79, 137.00, 132.85, 129.66, 127.29, 126.73, 126.65, 126.58, 125.02, 122.35, 120.64, 114.77, 55.53. HRMS (ESI/Q-TOF) m/z: [M]+ Calcd for $C_{58}H_{48}N_2O_4$ 836.3609; Found 836.3631.

Synthesis of compound JX02. Under an Ar atmosphere, a two-necked flask equipped with a magnetic stirrer was charged

with compound 2 (492 mg, 1.03 mmol, 1.0 equiv.), compound 7 (663 mg, 2.00 mmol, 1.94 equiv.), NaH (1.0 g, 41.7 mmol, 40.4 equiv.) and THF (15 mL). The reaction mixture was heated at 45 °C for 24.0 h and cooled to room temperature. The reaction was quenched with H₂O and extracted with ethyl acetate five times. The extract was then dried over magnesium sulfate and filtered. After evaporation at a reduced pressure, the residue was subjected to column chromatography on silica gel (petroleum ether/dichloromethane = 1/1, V/V), affording compound JX02 as solids (630 mg, 73.5%). The product was further purified by (hexane/dichloromethane) recrystallization for property measurements. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.49-8.47 (m, 4H), 8.05 (d, J = 16.0 Hz, 2H), 7.91 (d, J = 8.0 Hz, 4H), 7.66 (d, J = 8.0 Hz, 4H), 7.59 (d, 4.0 Hz, 4H), 7.56-7.52 (m, 4H), 7.45 (d, J = 8.0 Hz, 4H), 7.11-7.00 (m, 6H), 3.98 (s, 12H). HRMS (ESI/Q-TOF) m/z: $[M]^+$ Calcd for $C_{58}H_{44}N_2O_4$: 832.3296; Found:832.3314.

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Conflict of interest

The authors declare no conflict of interest.

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AIE-based piezochromism with a distinct seven-color luminescence switching built upon a single organic molecule is firstly achieved.



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Stimuli-Responsive Properties of Aggregation-Induced-Emission Compounds Containing 9,10-Distyrylanthracene Moiety