

Aggregation-Induced Emission Luminogen-Functionalized Liquid Crystal Elastomer Soft Actuators

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S Supporting Information

ABSTRACT: An aggregation-induced emission (AIE)-active liquid crystal elastomer (LCE) soft actuator is fabricated through chemical incorporation of a four-alkenylarmed tetraphenylethene-core cross-linker into a main-chain LCE matrice by a facile *in situ* two-step acyclic diene metathesis (ADMET) polymerization/cross-linking method. The LCE sample is endowed with the ability to readily tune the photoluminescence property during the fully reversible, thermally induced shape morphing process, which is indeed attributed to the AIE characteristic of tetraphenylethene molecules predominately determined by temperature variation.



INTRODUCTION

Luminescent materials have received considerable scientific attention owing to their fascinating chemical and photophysical properties.^{1–3} Among them, aggregation-induced emission (AIE) has recently emerged as a novel fluorescent phenomenon,⁴ which is in contrast to conventional aggregation-caused quenching (ACQ); the fluorescence emission can be drastically boosted when AIE luminogens (AIEgens) aggregate from isolated molecules.^{5–10} The AIE effect is inherently attributed to the restriction of intramolecular motions,^{11–13} which can activate the radiative transition of AIEgens and consequently tune their fluorescent properties. Such AIE-based materials have been extensively employed in many application fields, ranging from fluorescent chemosensors,¹⁴ fluorescent bioprobes,^{15–17} and gene delivery¹⁸ to organic light-emitting diodes.^{19,20}

In recent years, AIE polymers constructed by incorporation of AIE moieties into macromolecular backbones^{21–24} have brought about many advantages which AIE-active small molecules lacked, such as good processability, ease of functionalization, and diverse application potentials. In particular, stimuli-responsive AIE-based polymeric materials have attracted intensive interest since their luminescent properties can be effectively modulated by many external stimuli including temperature,^{25–28} solvent,^{29–31} mechanical force,^{32,33} swelling degree,³⁴ salt concentration,³⁵ etc. Although many stimuli-responsive fluorescent polymers have been developed, exploration of more AIE-functionalized polymeric materials and more diverse stimuli on triggering AIE function is always a hot topic in this field.

Liquid crystal elastomers (LCEs) as one of the most important representatives of two-way shape memory polymeric materials can undergo reversible shape deformations in response to external stimuli, which intrinsically trigger the LC-to-isotropic phase transitions of LCEs.^{36–41} In a mono-

domain LC state, the macromolecular chains and mesogenic molecules of LCEs are uniaxially oriented. When the temperature jumps into the isotropic phase, the mesogens' anisotropic molecular organization disappears; consequently, the stretched and elongated polymer chains will become relaxed and coiled, and the whole LCE material will perform shape deformation macroscopically. Chemically grafting AIEgens onto LCE networks will provide an interesting stimulusresponsive soft actuator material possessing not only reversible photoluminescence switching behavior but also reversible shape morphing. Here rises an intriguing question in such an AIEgenfunctionalized LCE material: will the intramolecular motions of AIE molecules have a significant variation along with the polymer chain networks transforming from stretched to relaxed during the LC-to-isotropic phase transition? In other words, the objective of this work is to answer the question whether AIEgen-functionalized LCEs have a spontaneous photoluminescence switching in response to the macroscopic shape deformation.

The combination of AIE phenomenon and LCE's reversible actuation can be used to investigate the intrinsic correlation of emission behavior and reversible shape deformation of polymeric materials. It should be mentioned that Wang and Keller recently have fabricated a thermomechanical-responsive photoluminescent nematic LCE composite by physically doping 1,4-bis(α -cyano-4-methoxystyryl)benzene, a classical mechanoresponsive photoluminescence dye, into the polymeric network.^{42,43} However, the physical incorporation of small molecule dyes might limit the real application of this actuator material due to several serious drawbacks, including dye leakage, weak fluorescence, and poor mechanical property

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Figure 1. Chemical composition of an AIE-active LCE film.

associated with increasing content of dopants. Inspired by these pioneering works, herein we report a method to chemically introduce AIEgen units as cross-linkers into main-chain LCE matrices for the first time to construct an AIE-active fluorescent soft actuator with a thermomechanical-induced emission variation function.

EXPERIMENTAL SECTION

General Considerations. The detailed instrumentation and starting reagents are described in the Supporting Information. The LC monomer **Y1709** was synthesized by following the experimental procedures of previous works.^{44–47}

Synthesis of AIE-Active Cross-Linker TPE-10C. In a 50 mL three-neck round-bottom flask, a solution of potassium carbonate (261 mg, 1.89 mmol) and tetra(4-hydroxyphenyl)ethene (75 mg, 0.19 mmol) in acetonitrile (5.0 mL) was stirred at room temperature under a nitrogen atmosphere for 1.5 h. 10-Bromo-1-decene (591 mg, 2.70 mmol) was slowly added into the above mixture via a syringe, and the resulting solution was refluxed at 87 °C for 24 h. After the solvent was evaporated in vacuo, the residue was diluted with dichloromethane and water. The collected organic fraction was dried over sodium sulfate and concentrated by rotary evaporation. Further purification was conducted by column chromatography (petroleum ether:ethyl acetate = 20/1) to give the final product as a yellowish solid (45 mg, yield 25%). ¹H NMR (600 MHz, CDCl₃, δ): 6.91 (d, J = 8.7 Hz, 8H), 6.63 (d, J = 8.8 Hz, 8H), 5.81 (m, 4H), 5.03–4.90 (m, 8H), 3.87 (t, J = 6.6 Hz, 8H), 2.07-2.00 (m, 9H), 1.78-1.68 (m, 8H), 1.46-1.22 (m, 40H). ¹³C NMR (151 MHz, CDCl₃, δ): 157.33, 139.21, 138.31, 136.82, 132.54, 114.16, 113.53, 67.79, 33.81, 29.51-29.25, 29.07, 28.92, 26.08. HRMS (ESI) *m*/*z* calcd for C₆₆H₉₂O₄ [M]⁺: 948.69901; found 948.69684.

Preparation of AIE-Active LCE Film. As demonstrated in Figure 1, LC monomer Y1709 (82.6 mg, 0.16 mmol), AIE-active cross-linker TPE-10C (14.7 mg, 0.016 mmol), and Hoveyda-Grubbs second catalyst (4.3 mg, 0.007 mmol) were combined in 0.8 mL of odichlorobenzene. The resulting solution was ultrasonicated at room temperature for 5 min to provide a homogeneous solution, which was allowed to be reacted in a nitrogen atmosphere at 58 °C for 3 h to conduct the first partial polymerization/cross-linking process. The resulting polydomain LCE gel was carefully removed from the flask and tailored into a ribbon-shaped sample, which was hung in a nitrogen-filled oven and burdened with a heavy load at 120 °C to achieve uniaxial stretching. The stretched LCE ribbon was fixed on a glass slide by binder clips and kept in the nitrogen-filled oven with the temperature set at 100 °C for 2 days to accomplish the second fullcross-linking step to provide the desired monodomain LCE film ribbon.

RESULTS AND DISCUSSION

The design of the AIE-active LCE system is schematically illustrated in Figure 1. Tetraphenylethene (TPE) was

undoubtedly the most popular AIE molecule⁵ and was chosen as the photoluminescent unit embedded into the LCE matrice. On the basis of the molecular structure of TPE, we built a symmetric four-armed alkene-terminated derivative **TPE-10C**, starting from tetra(4-hydroxyphenyl)ethene. Such a molecule not only possessed AIE characteristics but also played the role of cross-linkers which could be chemically incorporated into α,ω -diene functionalized main-chain liquid crystal polymers through *in situ* acyclic diene metathesis polymerization (ADMET) and simultaneously cross-link the adjacent polymer chains to form a LCE network.

As shown in Figure 1, a classical α,ω -diene molecule, 4undec-10-enyloxybenzoic acid 4-dec-9-enyloxyphenyl ester (Y1709), was chosen as the LC monomer for fabricating main-chain LCE. The synthetic protocols of Y1709 and the four-alkenyl-armed tetraphenylethene-core cross-linker TPE-10C are presented in Scheme 1. 4-Hydroxybenzoic acid (1)

Scheme 1. Synthetic Routes of (a) LC Monomer Y1907, (b) the AIE-Active Cross-Linker TPE-10C, and (c) the AIE-Inactive Cross-Linker TPEA- $10C^{a}$

(a) Synthesis of LC Monomer Y1709:



(b) Synthesis of AIE Active Crosslinker TPE-10C:

$$\begin{array}{c} HO \\ HO \\ HO \\ HO \\ \hline \\ 5 \\ \hline \\ 6 \\ \hline \\ \hline \\ \hline \\ \\ \hline \\ \\ \hline \\ \hline \\ \\ \hline \\ \hline \\ \\ \hline \\ \\ \hline \\ \\ \hline \\ \\ \hline \\ \hline \\ \\ \hline \\ \hline \\ \hline \\ \\ \hline \\ \\ \hline \hline \\ \hline \\ \hline \hline \\ \hline \\ \hline \\ \hline \hline \\ \hline \hline \\ \hline \hline \\ \hline \hline \\ \hline$$

(c) Synthesis of AIE Inactive Crosslinker TPEA-10C:



^{*a*}Reagents and conditions: (i) neat reaction, 260 °C; (ii) 9-decen-1-ol, DEAD, PPh₃, THF, rt; (iii) K_2CO_3 , CH₃CN, 87 °C; (iv) K_2CO_3 , MIBK, 116 °C.

was first esterified with a large quantity of hydroquinone (2) to provide 4-hydroxyphenyl-4-hydroxy benzoate (3) which was further coupled with 9-decen-1-ol through Mitsunobu reaction to give mesogenic monomer Y1709, possessing an enantiotropic smectic A phase as demonstrated in the literature.⁴⁷ The AIE-active cross-linker TPE-10C was obtained through a



Figure 2. (a) UV–vis absorption spectra of **TPE-10C** and **TPEA-10C** dissolved in pure THF and **TPE-10C** in solid state. (b) Fluorescence spectra of dilute solutions of **TPE-10C** dispersed in water/THF mixture with varied water fractions (concentration = 0.21 mM, λ_{exc} = 350 nm). (c) Diagram of the fluorescence peak intensity plotted against the water fraction of **TPE-10C** solution. The inset depicts two emission images of **TPE-10C** solution with 60% and 90% volume percentage of water.



Figure 3. (a) TGA and (b) DSC curves of the AIEgen-functionalized LCE sample. 1D-WAXD patterns of this LCE sample upon (c) heating and (d) cooling processes.

Williamson ether synthesis reaction of tetra(4-hydroxyphenyl)ethene (5) and 10-bromo-1-decene (6). Meanwhile for comparison purposes, we also prepared an AIE-inactive crosslinker TPEA-10C which was synthesized by coupling tetra(4hydroxyphenyl)ethane (8) with 10-bromo-1-decene. The synthetic procedure of TPEA-10C was similar to the one of TPE-10C, although the refluxing solvent was changed to methyl isobutyl ketone (MIBK) due to the poor solubility of compound 8 in acetonitrile.

The UV–vis absorption property of **TPE-10C** was measured in pure THF and solid state as shown in Figure 2a. The absorption maximum of **TPE-10C** in solution appeared at ca. 260 nm with a shoulder peak around 325 nm, which was in good agreement with the characteristic of traditional TPE group,³¹ while the absorption maximum of **TPE-10C** in solid state displayed an obvious red-shift to 407 nm, likely due to the *J*-aggregation of TPE units, which arranged TPE molecules in a slipped face-to-face stacking geometry.^{48,49} Figure 2b presented the fluorescence emission spectra of the **TPE-10C** examined in tetrahydrofuran-water cosolvent mixture with different water contents, which clearly exhibited an AIE phenomenon. In this case, THF was used as a good solvent for dissolving TPE-10C while water was selected as a poor solvent for TPE-10C to induce aggregation. The dilute THF solution of TPE-10C was weakly emissive, which was mainly caused by the free intramolecular rotations of phenyl rings of TPE-10C consuming the excited state energy by nonradiative decay.^{4,5} The fluorescence emission peak of TPE-10C solution started to appear at ca. 490 nm and the emission intensity became progressively stronger along with the volume percentage of water increasing from 0% to 90% (Figure 2c), because of the aggregated formation of TPE units, the fluorescence intensity of TPE-10C at 90% water fraction was approximately 83-fold higher than that in the pure THF (the absolute fluorescence quantum yield $\Phi_{\rm F}$ of **TPE-10C** dispersed in THF with 0% and 90% water fractions was estimated as 0.09 and 7.51, respectively).



Figure 4. 2D-WAXD patterns of LCE sample recorded at (a) 20 °C, (b) 70 °C, and (c) 100 °C; the X-ray incident beam was parallel to the film normal direction. (d) Schematic illustration of TPE molecule aligned along the film stretching direction. (e, f) POM images of LCE film measured at room temperature.

With the monomer Y1709 and the cross-linker TPE-10C in hand, we adopted a two-step in situ ADMET polymerization/ cross-linking protocol to prepare the designed AIEgenfunctionalized uniaxial-aligned LCE soft actuator materials. As described in the Experimental Section, a mixture composed of LC monomer Y1709, AIE-cross-linker TPE-10C, and olefin metathesis catalysts with a molar ratio of 91.1/8.9/3.9 was dissolved in a small amount of o-dichlorobenzene and further heated to 58 °C under a nitrogen atmosphere for 3 h to fulfill the first in situ ADMET polymerization/cross-linking approach to give a partial-cross-linked polydomain LCE gel. After several experimental trials, we found that Hoveyda-Grubbs second generation catalyst could efficiently play the catalysis role in this in situ ADMET system while the reactions using Grubbs first/ second generation catalysts failed in providing good-quality LCE gels. Before performing the second in situ ADMET polymerization/cross-linking protocol, we sliced the obtained polydomain LCE gel into film ribbons and stretched the ribbons uniaxially to force the LC mesogens to transform from polydomain state to monodomain manner. The stretched monodomain LCE sample was kept at 100 °C, which was in the range of its LC phase to preserve its monodomain anisotropic order for 2 days, to achieve the second full-cross-linking purpose to provide the desired AIEgen-functionalized uniaxialaligned LCE ribbon actuator. Here the longitudinal stretch ratio, l, was defined as the longitudinal length ratio of the stretched sample to the initial polydomain LCE ribbon; the corresponding LCE ribbon was named as LCE-l. Meanwhile, a referenced LCE film containing monomer Y1709 and AIEinactive cross-linker TPEA-10C was also prepared by using the similar fabrication protocol of AIEgen-functionalized LCE film.

The thermal property of this AIEgen-functionalized LCE material was investigated by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and one-dimensional wide-angle X-ray diffraction (1D-WAXD). As illustrated in Figure 3a and Figure S14a, the thermal decomposition temperatures of the AIEgen-functionalized LCE sample and the referenced LCE sample under a nitrogen atmosphere with 5% weight loss were estimated as 332 and 335 °C, which demonstrated that both the AIEgen-functionalized LCE film

and the referenced LCE film had good thermal stability and could fulfill most of the application requirements. Two nearly identical DSC curves as shown in Figure 3b and Figure S14b presented two distinct peaks on both heating and cooling cycles, and there were no obvious glass phase transition above the room temperature, which indicated that both the AIEgenfunctionalized LCE sample and the referenced LCE sample might have two enantiotropic LC phases in the range from room temperature to the isotropic state (above 110 °C). Figure 3c,d depicts the one-dimensional WAXD patterns of AIEgenfunctionalized LCE sample obtained in both the heating and cooling processes. At low temperature, there were two intense diffraction peaks, one each located in the low-angle region and the wide-angle region, which gradually became more and more diffusive as the temperature increased. Combining the DSC data and 1D-WAXD result, we could imagine that this AIEgenfunctionalized LCE sample might have a smectic layer structure at low temperature and a nematic phase at high temperature.

To further elucidate the mesomorphic properties of these two LC phases and meanwhile investigate the homogeneous alignment effect of this AIEgen-functionalized LCE material, two-dimensional wide-angle X-ray diffraction (2D-WAXD) experiments were applied to examine a LCE-3.5 sample with the X-ray incident beam parallel to the film normal direction. As presented in Figure 4a,b, a pair of crescents in the high-angle region were situated in the direction perpendicular to the film stretching direction, which implied that mesogens were uniaxially aligned along the external stretching direction. In the low-angle region, four diffraction arcs were located at 2θ = 3.7° (*d*-spacing = 2.38 nm), which implied a highly ordered smectic C (SmC) phase existing at low temperature. Interestingly, there was a pair of low-intensity diffraction arcs appearing along the meridian direction ($2\theta = 10.2^{\circ}$, d-spacing = 0.87 nm), which might derive from some "frozen", orderly packed TPE units (Figure 4d). When the temperature was raised to 100 °C, which was in the second LC phase range, the four low-angle arcs became much more diffusive as shown in Figure 4c, which implied a nematic phase with SmC fluctuation⁵⁰ existing at high temperature. Meanwhile, the diffraction signal along the meridian direction vanished because

increasing temperature would revive the intramolecular rotations of TPE units. Eventually, the mesomorphic property of this AIEgen-functionalized LCE material was concluded as SmC-89 °C-N-110 °C-Isotropic (on heating) and Isotropic-103 °C-N-82 °C-SmC (on cooling).

The order parameter (*S*) was calculated from the WAXD patterns to evaluate the orientation extent of mesogens with respect to the external stretching direction. The calculation was defined based on eq $1:^{51,52}$

$$S = \frac{1}{2} (3\langle \cos^2 \alpha \rangle - 1)$$
$$\langle \cos^2 \alpha \rangle = \frac{\int_0^{\pi} I(\alpha) |\sin \alpha| \cos^2 \alpha \, d\alpha}{\int_0^{\pi} I(\alpha) |\sin \alpha| \, d\alpha}$$
(1)

Here, the intensity profiles $I(\alpha)$ data as a function of azimuthal angle α were integrated based on WAXD patterns. The order parameter value of a perfect uniaxial-aligned sample would be S = 1, and the value of a completely random sample was S = 0. As a result, the orientation parameter S of the AIEgen-functionalized LCE sample showed high values of 0.96, 0.95, and 0.93 at 20, 70, and 100 °C, respectively. From a macroscopic perspective, these results indicated that the LCE sample had a highly ordered orientation along the film stretching direction. Polarized optical microscope (POM) observation further verified this conclusion. As presented in Figure 4e,f, a full birefringence extinction could be observed when the polarizer was perpendicular or parallel to the film's longitudinal direction which was also the external stretching direction. In contrast, the highest transmittance could be found after rotating the film of 45° with respect to the crossed analyzer, which was the characteristic of a perfect alignment of mesogenic groups. Such a LCE film demonstrated a high quality homogeneous alignment effect.

The mechanical property of the AIEgen-functionalized LCE material was investigated by a dynamic mechanical analyzer (DMA Q800, TA Instruments) with a tension clamp at varied temperatures. The static stress—strain measures of the LCE films were conducted along the film stretching direction respectively at 30, 60, 95, 105, and 120 °C. The measurements were performed on LCE-3.5 ribbons with 0.1 mN preload force at a strain rate of 0.1 N/min. The relevant mechanical properties of the LCE samples are summarized in Table 1 and

 Table 1. Mechanical Properties of AIE-Active LCE Sample (LCE-3.5)

temp (°C)	Young's modulus (MPa)	max tensile strength (MPa)	elongation at break (%)
30	60.06	7.40	20.33
60	32.53	6.44	30.43
95	9.57	4.03	51.91
105	2.50	1.15	53.79
120	1.27	1.06	60.61

Figure S12; the longitudinal Young's moduli (E) of these LCE samples were 60.06, 32.53, 9.57, 2.50, and 1.27 MPa. Most importantly, the Young's modulus could be preserved at 1.27 MPa even when the temperature jumped over its clearing point, which was attributed to the advantage of main-chain end-on mesogenic network. The increase of the temperature would gradually decrease the Young's modulus and the maximum

tensile strength, while the elongations at break contrarily increased from 20.3% to 60.6%. Overall, this LCE material had good mechanical property; it behaved like a strong rubber at room temperature and could also preserve sufficient elastic property and mechanical strength in the isotropic phase.

The UV-vis absorption properties of the AIEgen-functionalized LCE film and the AIE-inactive LCE film were measured directly on the film. As shown in Figure 5a, two intense absorption peaks of AIEgen-functionalized LCE film appeared at ca. 260 and 410 nm, which was similar to the characteristic absorption of the AIE unit TPE-10C in the solid state. One intense absorption peak of AIE-inactive LCE film appeared at ca. 265 nm. The fluorescence emission behavior of the LCE film was however very similar to the one of TPE-10C, which emitted maximally at 485 nm when excited at 350 nm. The LCE sample presented very sensitive fluorescence responses against various organic solvents. The relative fluorescence intensities of LCE samples dispersed in tetrahydrofuran, hexanes, chloroform, and methanol were plotted against the swelling time As shown in Figure 5b,c, when this LCE material was immersed in THF or chloroform, the fluorescence of this LCE sample was quickly quenched, and the relative fluorescence intensity dramatically declined to ca. 0.03 times the original value of the dry state in 5 min and remained almost consistent even after the swelling time was further lengthened to 60 min. On the contrary, employing hexanes or methanol as the solvent would significantly retard the fluorescence decreasing rate of the LCE sample. In the first 5 min, the relative fluorescence intensity of the LCE sample immersed in methanol dropped to 48% and could steadily preserve more than 42% in the next 55 min, while the relative fluorescence intensity of the LCE sample immersed in hexanes had a sharp drop to 35% in the first 10 min and gradually decreased to ca. 14% of the original value in 60 min. This solvent-responsive fluorescence variation was indeed derived from the swelling capabilities of the AIEgen-functionalized LCE sample in various organic solvents. The swelling degree (Q) of LCE samples against swelling time is plotted in Figure 5d; the swelling degree (Q) was defined based on the following equation: $Q = (W_{wet} - W_{wet})$ $(W_{\rm dry})/(W_{\rm dry})^{31}$ where $W_{\rm wet}$ was the weight of LCE sample at any given time and W_{dry} was the weight of LCE sample at its dry state. Compared with hexanes and methanol, THF and chloroform were much better swelling solvents, could effectively penetrate through the LCE matrice, activate the intramolecular rotations of the phenyl rings of TPE crosslinkers, and consequently diminish the fluorescent emission of the TPE units.

In order to investigate the thermal-responsive property of this AIEgen-functionalized LCE material, one LCE-3.5 ribbon was placed on a Mettler PF82HT hot stage and heated/cooled with a constant heating/cooling rate of 5 °C/min. As presented in Figure 6 as well as Movie S1 and Movie S2, the LCE-3.5 ribbon remained almost motionless in a temperature range from 30 to 100 °C, which was in its LC phase, and drastically shrank along the longitudinal direction when further heated to above its LC-to-isotropic phase transition and reached its maximum contraction when the temperature approached to 125 °C. After cooling back to room temperature, this LCE film could fully expand to its original shape. In order to have a better observation of the LCE molecular orientation at different temperatures, POM images of the AIEgen-functionalized LCE film were taken at 30, 50, 70, 90, 110, and 130 °C. As presented in Figure S13, the transmittance of AIEgen-functionalized LCE



Figure 5. (a) UV–vis absorption spectra (solid line) and fluorescence spectra (dotted line) of LCE samples measured directly on the film at 20 °C (λ_{exc} = 350 nm). (b) Photograph of LCE samples dispersed in various solvents for 5 min under irradiation of a UV 365 nm lamp (scale bar = 1 cm). Time-course (c) fluorescence intensity and (d) swelling degree of AIEgen-functionalized LCE sample dispersed in tetrahydrofuran, hexanes, chloroform, and methanol (λ_{exc} = 350 nm).



Figure 6. Photo images of thermally induced actuation behaviors of one LCE-3.5 ribbon sample exposed to (a) UV 365 nm radiation and (b) ambient light (scale bar = 5 mm). The reversible shape deformations of two LCE-3.5 films with (c) AIE-active cross-linkers **TPE-10C** and (d) AIE-inactive cross-linkers **TPEA-10C** during heating–cooling cycles. Movies S1-S4 show the thermally induced actuation scenarios.

film remained almost unchanged in a temperature range from 30 to 90 $^{\circ}$ C, which implied the morphology of the LCE sample almost remained unaffected, while a distinct birefringence

fading phenomenon could be observed when the temperature approached its LC-to-isotropic phase transition temperature (110 and 130 $^{\circ}$ C), which demonstrated the LCE material



Figure 7. (a) Fluorescence spectra of the LCE-3.5 sample at different temperatures ($\lambda_{exc} = 350$ nm). (b) Fluorescence (orange line) and the longitudinal shape deformation (L/L_{iso}) (blue line) of the LCE-3.5 ribbon versus temperature. (c) Correlation of longitudinal stretch ratio l and fluorescence intensity ($\lambda_{exc} = 350$ nm) of LCE samples measured at different temperatures.

experienced an anisotropic-to-isotropic molecular director variation. The longitudinal deformations (L/L_{iso}) of the LCE-3.5 sample against heating—cooling cycle numbers are plotted in Figure 6c,d, where L_{iso} is the minimum length of the LCE-3.5 ribbon in its isotropic state and L is the length of the LCE-3.5 ribbon at any given temperature. Both the AIEgen-functionalized LCE ribbon and the AIE-inactive LCE ribbon could repeatedly execute such reversible contraction/expansion during continuous heating—cooling cycles as demonstrated in Movie S3 and Movie S4, which implied that these LCE materials as a thermal actuator had good fatigue durability. Overall, through all these above comparison experiments, we could conclude that the introduction of AIEgens would not affect the thermal response, stability, actuation, and repeatability of LCE materials.

Interestingly, the longitudinal length ratio of the LCE-3.5 ribbon appearing at 30 °C to the same ribbon at 125 °C was roughly 2.20, which indicated that the longitudinal length of the fully cross-linked isotropic-phase LCE sample was not equal to but much smaller (ca. 63%) than the one of the partially cross-linked unstretched polydomain LCE sample. Meanwhile, the fluorescence emission intensity of the LCE-3.5 ribbon gradually decreased along with temperature rising and the shape shrinkage of the ribbon, as shown in Figure 6a and Movie S1.

We further quantitatively conducted the fluorescence response experiments of the LCE-3.5 ribbon along with the variation of temperature. The fluorescence emission spectrum of this LCE sample was recorded with an excitation wavelength of 350 nm in a temperature range from 35 to 135 °C. As presented in Figure 7a, the maximal fluorescence emission peak of the LCE-3.5 film appeared at ca. 485 nm, and the emission intensity gradually declined during the heating process. Apparently, the increase of temperature would activate the intramolecular rotation and vibration of phenyl rings of TPE units^{53,54} and further weaken the AIE effect. In addition, a progressive bathochromic shift of the maximum emission wavelength was observed as temperature increased, possibly due to the conformation variations of TPE units.^{31,55} At low temperature, the "frozen" LCE matrix might force TPE-10C to have a twisted conformation packed in a very limited small space, while at high temperature the increased mobility of macromolecules would allow TPE-10C to have more relaxed conformations, which could be supported by the XRD results (Figure 4a-d).

The relative fluorescence emission intensities (I/I_{35}) and longitudinal deformations (L/L_{iso}) of the LCE-3.5 sample against temperature are plotted in Figure 7b, where I_{35} is the fluorescent intensity of the LCE-3.5 ribbon measured at 35 °C and *I* is the fluorescent intensity of the LCE-3.5 ribbon measured at any given temperature. As illustrated in Figure 7b, the normalized fluorescence intensity was inversely proportional to temperature and experienced a ca. 59% decrease from 35 to 135 °C, while the longitudinal deformations $(L/L_{\rm iso})$ of the LCE-3.5 sample did not exhibit a linear correlation with temperature variation but presented a jump change around the LC-to-isotropic phase transition temperature (110 °C). In this case, we can conclude that the fluorescence emission intensity variation of AIEgen-functionalized LCE material was mainly determined by the temperature effect instead of the macroscopic shape deformation.

In order to examine the correlation between LCE film's macroscopic shape deformation and fluorescence intensity, we synthesized a series of AIEgen-functionalized LCE ribbons (LCE-1.0, LCE-1.5, LCE-2.0, LCE-2.75, and LCE-3.5) with different stretching ratios, measured the fluorescence emissions of all these LCE samples at various temperatures (50, 75, 95, 105, 115, 125, and 135 °C), and plotted their maximal fluorescence intensities at 485 nm against their longitudinal stretch ratio l in Figure 7c. As clearly demonstrated in Figure 7c, at any specific temperature, the fluorescence emission intensity always showed a declining trend along with the increase of stretching extent of LCE sample, which implied that the intramolecular motions of AIE molecules did not become restricted during the stretching process; on the contrary, when the polymer chain networks transformed from relaxed to stretched, the TPE units might experience a transformation from the aggregation state to deaggregation state, which would diminish the fluorescence emission. Another interesting phenomenon was that an obvious fluorescence intensity transition point appeared when the longitudinal stretch ratio lreached to 2.0, particularly at low temperatures, which implied that the aggregation degree of TPE moieties might have a threshold value when the LCE films were stretched to twice their original lengths. Inside this range (1.0 < l < 2.0), a small stretching force could cause a sharp decrease of the aggregation degree of TPE moieties, and the fluorescent emission intensity would present a dramatic decrease correspondingly; while beyond this stretch ratio (l > 2.0), TPE molecules had already been separated from each other to some extent that further deaggregation would not induce a big change of the fluorescent emission intensity.

CONCLUSION

In summary, we reported the first example of AIEgen-bonded LCE material prepared by a facile two-step *in situ* ADMET polymerization/cross-linking protocol. Such an AIEgen-func-

tionalized LCE actuator could perform fully reversible, thermally induced shape morphing and meanwhile have a spontaneous photoluminescence switching in response to the thermomechanical shape deformation. In a typical heating process, temperature rising would provide activation energy for intramolecular motions of AIE molecules and weaken the fluorescence emission; contrarily, the simultaneous relaxation of the polymer chain networks would induce the aggregation of AIE units and enhance the AIE effect. In conclusion, the photoluminescence variation was predominately determined by the temperature effect, while the macroscopic shape deformation of LCE, although playing an antagonist role, was almost negligible. We hope that the investigation of this AIE-active LCE material will open up a new horizon for thermomechanically controllable fluorescent soft actuators.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.8b00677.

Instrumentation information; syntheses and characterizations of **Y1709**, **TPE-10C**, and the AIEgen-functionalized LCE film (PDF)

Movie S1: thermally induced reversible contraction/ elongation of AIEgen-functionalized LCE film exposed to UV 365 nm radiation (AVI)

Movie S2: thermally induced reversible contraction/ elongation of AIEgen-functionalized LCE film exposed to ambient light (AVI)

Movie S3: repeatability test of AIEgen-functionalized LCE film exposed to UV 365 nm radiation (AVI)

Movie S4: repeatability test of the referenced AIEinactive LCE film exposed to ambient light (AVI)

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The authors declare no competing financial interest.

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