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PII: S0143-7208(16)00035-8

DOI: 10.1016/j.dyepig.2016.01.024

Reference: DYPI 5077

To appear in: Dyes and Pigments

Received Date: 27 July 2015

Revised Date: 14 December 2015

Accepted Date: 11 January 2016

Please cite this article as: Lu H, Wu S, Zhang C, Qiu L, Wang X, Zhang G, Hu J, Yang J, Photoluminescence intensity and polarization modulation of a light emitting liquid crystal via reversible isomerization of an α -cyanostilbenic derivative, *Dyes and Pigments* (2016), doi: 10.1016/ j.dyepig.2016.01.024.

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Photoluminescence intensity and polarization modulation of a light

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α-cyanostilbenic derivative

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*Corresponding author. Tel:+8613855174354; E-mail address: bozhilu@hfut.edu.cn Abstract

We found reversible photo/thermal isomerization of the α -cyanostilbenic derivative (*Z*)-2-(4-aminophenyl)-3-(4-(dodecyloxy)phenyl)-acrylonitrile, (*Z*)-CN-APHP, which is accompanied by a large decrease in compatibility when mixed with a nematic liquid crystal. Moreover, a novel optical switch using a CN-APHP doped liquid crystal that emits partially linearly polarized light is investigated. By controlling the trans-cis isomerization of CN-APHP, it is possibly to modulate not only photoluminescence intensity but also its polarization. This could open possibilities to design improved optical devices.

1. Introduction

Liquid crystal displays (LCDs) evolved rapidly over the past decades and are currently dominating the flat panel display industry [1,2] due to their advantages such as light weight, thinness and lower power consumption. However, the liquid crystals (LCs) in the displays do not emit light themselves [3] directly and they require an extra light source such as a backlight [4,5], which leads to energy consumption. The emitted light from the conventional backlight is usually unpolarized [2] and correspondingly LCDs require polarizers, which can change the unpolarized light into linearly or circularly polarized light [6]. The dichroic sheet polarizers used in LCDs convert a major fraction of incident light into unwanted thermal energy, which limits the brightness, and energy efficiency of devices with this technology.

Therefore, The polarized light source has great potential to improve the LCD performance. By intrinsically emitting polarized light, polarizing sheets would become unnecessary and also the power consumption could be reduced. Polarized electro- or photo-luminescent light sources have been intensively studied [7,11]. Dyreklev *et al.* demonstrated that an organic electro-luminescence (EL) device emitted polarized light based on aligned conjugated polymers [12]. Sariciftci *et al.* reported that linearly polarized photoluminescence (PL) can be emitted from nematic liquid crystals doped with photoluminescent dyes [13]. Chen *et al.* reported that a cholesteric liquid crystal film doped with fluorescent materials can emit circularly polarized PL [14]. Actually, the emitted light from a single fluorescent molecule is usually polarized, but the light from a macroscopic EL or PL is unpolarized due to disordered molecular distribution. Hence, polarization can be controlled by manipulating the orientation of the fluorescent molecules. Recently, SH Joo *et al.* were able to selectively produce linearly polarized light, circularly polarized light, unpolarized light and partially polarized light from a single photoluminescent cholesteric liquid crystal cell by controlling the molecular orientation electrically [15]. Such a light source with tunable polarization could be useful in many optical devices such as displays or polarization-dependent communication devices [16,17].

Currently, a common problem encountered with dye/LC mixtures is the poor solubility of the organic dye in the liquid crystal. In addition, if the concentration of the dye is too high, the luminescence affected aggregation-caused quenching (ACQ). Fortunately, is by aggregation-induced emission (AIE) was discovered in both silole derivatives [18] and α -cyanostilbenic derivatives [19]. AIE is the exact opposite of ACQ: the luminophors are highly emissive after aggregate formation because intramolecular motion (RIM) is restricted. In order to improve solubility and overcome the typical quenching effect at higher concentration these AIE-active luminescent liquid crystals (LLCs) can be used. LLCs can emit linear or circular polarized light when aligned [3], and have been widely used in information storage devices, polarized organic lasers, anisotropic light-emitting diodes, and one-dimensional semiconductors [20,24].

Motivated by the AIE effect, various new α -cyanostilbenic derivatives have been synthesized [25,26]. Like in ordinary stilbene and azobenzene molecules, the *Z*-*E* isomerization process is accompanied by a strong decrease in structural compatibility with a liquid crystal. In this paper, a new optical switch based on AIE-active luminescent liquid crystals was developed. We find that the fluorescence is partially linearly polarized and the degree of polarization can be continuously controlled via conformational changes of the luminescent liquid crystal. The possibility of photochemical patterning or image recording using these materials has also been demonstrated.

2. Experiment

General Methods

All chemicals were purchased from Sigma Aldrich and used without further purification. The synthetic route for (*Z*)-CN-APHP is described in the supporting information. ¹H NMR spectra were recorded on an Agilent VNMRS600 (600 MHz) spectrometer. UV-vis absorption spectra were recorded with a Shimadzu UV2550 PC spectrometer using samples in solutions. PL spectra were recorded with a HORIBA FluoroMax-4 spectrofluorometer using samples in both solution and a liquid crystal cell. The absolute photoluminescence quantum yields of solid samples were measured with a HORIBA FluoroMax-4 spectrofluorometer with an integrating sphere (HORIBA Scientific, F-3092 integrating sphere). Differential scanning calorimetry (DSC) was performed on a METTLER 82le/400 DSC at a heating and cooling rate of 5 °C min⁻¹. Polarizing optical microscopy was carried out with an E600POL polarizing optical microscope (Nikon, Tokyo, Japan) equipped with a DS-5M CCD camera (Nikon) connected to a DS-L1 control unit (Nikon).

Synthesis of (Z)-2-(4-aminophenyl)-3-(4-hydroxyphenyl)acrylonitrile

This compound was synthesized according to the method described in the literature [27].

Synthesis of (Z)-2-(4-aminophenyl)-3-(4-(dodecyloxy)phenyl)-acrylonitrile ((Z)-CN-APHP)

(*Z*)-2-(4-aminophenyl)-3-(4-hydroxyphenyl)acrylonitrile (500 mg, 2.12 mmol) was dissolved in DMF (10 mL) and NaOH (200 mg, 5 mmol) and stirred for 15 min at RT. Afterwards bromooctane (1.51 g, 7.82 mmol) was added, and the mixture was stirred at 90 °C for 12 h. The mixture was poured into 500 mL water and extracted with ethyl acetate (3×100 mL) three times. After performing silica gel column chromatography (n-hexane : EtOAc = 6:1) the product was recrystallized from ethanol and water to produce a yellow powder (304.11 mg, 0.87 mmol) with a 5

yield of 60.8%.

¹H-NMR (CDCl3, 600 MHz, ppm): δ = 7.80 (d, 2 H, ArH, J = 8.4 Hz), 7.47 (d, 2 H, ArH, J = 8.8 Hz), 7.28 (s, 1 H, =CH), 6.93 (d, 2 H, ArH, J = 8.8 Hz), 6.65 (d, 2 H, ArH, J = 8.4 Hz), 4.00 (t, 2 H, CH₂, J = 6.4 Hz), 3.85(t, 2 H, NH₂, J = 7.4 Hz), 1.77 (m, 2H, CH₂), 1.64 (m, 10H, 5CH2), 0.88 (t, 3 H, CH3, J = 6.0 Hz).

HRMS (MALDI-TOF) m/z [M + H]]+: calcd for C₂₃H₂₈N₂O, 349.2274, found 349.2279.

Preparation of (*E*)-2-(4-aminophenyl)-3-(4-(dodecyloxy)phenyl)-acrylonitrile

((*E*)-CN-APHP)

(Z)-CN-APHP powders (500 mg, 1.44 m mol) were added into DMF (5 mL) and stirred at room temperature for 10 min. Then the solution was irradiated with 440 nm light for 48 h and the (Z)-CN-APHP isomer mostly converted to (*E*)-CN-APHP. (*E*)-CN-APHP was obtained by silica gel column chromatography (n-hexane : EtOAc = 6:1). The product had the appearance of a yellow grease (265.5 mg, 0.76 mmol) with 53.1% yield.

¹H-NMR (CDCl3, 600 MHz, ppm): δ = 7.26 (d, 2 H, ArH, *J* = 8.4 Hz), 7.16 (d, 2 H, ArH, *J* = 8.8 Hz), 7.13 (s, 1 H, =CH), 6.72 (d, 2 H, ArH, *J* = 8.8 Hz), 6.65 (d, 2 H, ArH, *J* = 8.4 Hz), 4.00 (t, 2 H, CH₂, *J* = 6.4 Hz), 3.85(t, 2 H, NH₂, *J* = 7.4 Hz), 1.77 (m, 2H, CH₂), 1.64 (m, 10H, 5CH₂), 0.88 (t, 3 H, CH₃, *J* = 6.0 Hz).

Device preparation

The nematic liquid crystal (E7) was purchased from Jiangsu Hecheng Display Technology. The material used in this work consists of E7 (87%) and CN-APHP (13%). The mixture was stirred in the isotropic phase (95 °C) for 1 hour to ensure complete dissolution. It was then injected into an empty cell with anti-parallel rubbed polyimide alignment layers by capillary action. The cell gap was controlled by a dispersion of 7 μ m spacer.

3. Result and discussion

In order to clarify the thermodynamic, optical and photo-physical properties of the *Z*- and *E*-isomers, CN-APHP with pure *Z*- and pure *E*-isomers were prepared separately. Fig. 1(b) shows the images of (*Z*)- and (*E*)-CN-APHP under room and UV-light. Pure (*Z*)- and (*E*)-CN-APHP can readily be distinguished as the PL intensity differs clearly. (*Z*)-CN-APHP emits bright bluish green light with high PL quantum yields ($\Phi_f = 0.67$). While, (*E*)-CN-APHP is barely fluorescent (PL quantum yield is only 0.01) when excited with 365 nm UV light.

The mesomorphic properties of CN-APHP were characterized by both differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The phase-transition temperatures are revealed in the DSC traces. Fig. 1(d) shows the POM photograph of (Z)-CN-APHP at 78 °C during the heating process. When (Z)-CN-APHP was heated above 73 °C, anisotropic mesomorphic textures became clearly visible. Mesomorphic textures could also be observed during cooling of (Z)-CN-APHP which suggests that the liquid crystal is enantiotropic. The DSC spectra of (Z)-CN-APHP are shown in Fig. 1(c), the result agrees with the POM observation very well. The liquid crystal phases appear in the temperature range from 73 to 86 °C during heating (Z)-CN-APHP at a rate of 5 °C per minute. However, no liquid crystal phase can be observed during heating of (E)-CN-APHP, as shown in Fig. S2. (E)-CN-APHP converts from the solid to the liquid state directly at 70 °C during the heating cycle. According to the calculation results based on the density functional theory, the optimized molecular structure of the Z-isomer is coplanar and rod-like which can be seen in Fig. S3(a). This is very beneficial if compact molecular stacking is to be achieved. This is probably the reason why the Z-isomer exhibits liquid crystal phases. Since the two rings of the *E*-isomers are significantly twisted, the optimized geometrical structure is expected to be bent as shown in Fig. S3(b), which prevents effective molecular planarization and stacking in the aggregation state. In addition, the observed decrease of PL when transitioning from the *Z*-isomer to *E*-isomer is attributed to the bent structure of the *E*-isomer. Such a structure generally leads to reduced restriction of intramolecular motions (RIM).

The quite different geometry of the π -conjugated backbone significantly affects the absorption and emission properties of (*Z*)- and (*E*)-CN-APHP. Fig. 2(a) shows that the absorption peak (λ_{max}) of (*Z*)-CN-APHP in DMF solution (2×10⁻⁵ mol·L⁻¹) is at 379 nm with a molar extinction coefficient (ε) of 30950 cm⁻¹·M⁻¹. In contrast, (*E*)-CN-APHP has λ_{max} at 364 nm with ε = 12550 cm⁻¹·M⁻¹. Both the hypsochromic shift (15 nm) and the decrease of the molar extinction coefficient at λ_{max} when transitioning from the *Z*-isomer to *E*-isomer are attributed to the bent structure of the *E*-isomer. This generally causes the effective conjugation length to decrease. Fig. 2(b) shows the PL spectra of a CN-APHP solution excited at 365 nm. The PL intensity of the *Z*-isomer solution is much higher than the one of the *E*-isomer solution.

solution, the absorption and emission changes of both pure (Z)-CN-APHP and (E)-CN-APHP molecules in dilute DMF solution (2×10^{-5} mol·L⁻¹) were monitored during excitation at 440 and 254 nm for the $Z \rightarrow E$ and the $E \rightarrow Z$ photoisomerization process, respectively. The absorption peak of (Z)-CN-APHP shifts from 379 nm to 366 nm (photostationary state, PSS_{440 nm}) accompanied by a gradual decrease in absorbance as a function of exposure time at 440 nm excitation as shown in Fig. S5(a). The time-dependent PL spectra of the CN-APHP solution were measured at 365 nm excitation wavelength. As seen from Fig. 3(b), the PL in solution decreased considerably when 440 nm excitation was used. In contrast, λ_{max} of (E)-CN-APHP gradually red-shifted and its absorbance increases until the PSS_{254 nm} when excited with 254 nm light as shown in Fig. S5(a). Fig. S5(b) shows the intensity of the photoluminescence emission increasing with exposure time. These results demonstrate that both *Z* to *E* and *E* to *Z*-isomerization in solution are reversible between the $PSS_{440 nm}$ and $PSS_{254 nm}$ as seen from Fig. 3 (c) and (d). On the basis of the conversion equation using the absorbance values of *Z*- and *E*-isomers, it was calculated that the resulting *Z/E* conversion ratio of (*Z*)- and (*E*)-CN-APHP was approximately 25/75 (PSS_{440 nm}), and 50/50 (PSS_{254 nm}), respectively. Since the protons in vinylene and phenyl-rings are placed in very different chemical environments, the photoisomerization process of (*Z*)-CN-APHP could also be clearly monitored by taking ¹H NMR spectra as shown in Fig. S4(a). With prolonged excitation time, the amount of the *E*-isomer increased gradually with a simultaneous decrease of the *Z*-isomer until a photostationary state was reached. According to the proton peaks of vinylene in the *Z* and *E*-isomers in ¹H NMR spectra, Fig. S4(b) shows that the *Z/E* conversion ratio of CN-APHP is 25/75 at the photo-stationary state. The results are consistent with the conversion ratio obtained with the absorbance value.

For better understanding of the isomerization process of the CN-APHP molecules and because the *Z*-*E* isomerization may also be triggered thermally, we also investigated the thermal behavior of the CN-APHP solution. As presented in Fig.4, the cyanostilbene unit adopts a *Z*-form (black line) in initial state. The *Z*-to-*E* photoisomerization occurs when the solution is exposed to 440 nm light and reaches equilibrium after 20 min exposure time (blue line). Most of the *E*-isomer molecules can be converted back to the *Z*-form by heating at 160 °C (red line). The resulting *Z*/*E* conversion ratio at PSS_{160 °C} was approximately 90/10, which is higher than that at PSS_{254 nm}.

The peculiar $Z \leftrightarrow E$ isomerization process of CN-APHP molecules is very interesting for potential use in optical memory devices. The isomerization of CN-APHP in positive liquid crystals 87 % E7 and a 13 % (*Z*)-CN-APHP mixture was investigated. As seen from Fig. S6, the phase-transition temperatures of the host LC and doped E7 are revealed in the DSC trace at a heating/cooling rate of 5 $^{\circ}$ C per minute and there is only one phase-transition whose temperature changes from 58.2 $^{\circ}$ C to 63.3 $^{\circ}$ C. It means that (*Z*)-CN-APHP is structurally compatible with E7. When the mixture of (*Z*)-CN-APHP and E7 is filled into the anti-parallel rubbed cell, *Z*-isomer molecules are oriented within the template of liquid crystals due to the rod-like structure as displayed in Fig. 5(a). During the photo-excitation at 440 nm, *Z*-isomers gradually convert into *E*-isomers and show phase separation as a result of the poor compatibility between the *E*-isomers and the E7 liquid crystals. A large number of liquid crystal domains appear within the surrounding *E*-isomer matrix, forming so-called fluorescent-molecule-dispersed liquid crystals (FMDLC) as seen from Fig. 5(b). The photoluminescence intensity of FMDLC can be switched repeatedly with an electric field [27]. After the cell was heated above 160 $^{\circ}$ C for 50 h, most of the *E*-isomer molecules can be converted back to the *Z*-form. This increase the compatibility and liquid crystalline domains disappear and convert back to the uniform planar phase as displayed in Fig. 5(c).

Fig. 5 (d) shows the emission spectra (λ_{ex} =365 nm) of the cell in three states. At this excitation wavelength, no photoluminescence from the host LC is observed and the cell emits blue light at the maximum located between 470 - 478 nm. The cell in the initial state emits relatively strong blue light while the peak maximum of the cell is red-shifted to 478 nm compared to the cell in PSS_{440 nm} (470 nm) and PSS_{160 °C} (477 nm). This is likely due to the bent structure of the *E*-isomer. Even though the PL of (*E*)-CN-APHP is inferior to (*Z*)-CN-APHP, the PL at PSS_{440 nm} shows enhanced blue emission compared to PSS_{160 °C}. FMDLC is a highly inhomogeneous state with a large number of randomly oriented LC domains, which strongly scatters the incident light. Photons of the incident light entering the cell have to undergo

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multiple refraction before leaving the cell. This maximizes the chances to interact with fluorescence molecules and thereby increases fluorescence emission. Moreover, as shown in Fig. 5e and Fig. S7, the PL intensity can be switched repeatedly between $PSS_{440 nm}$ and $PSS_{160 \,^{\circ}C}$ and modulated by controlling the exposure time to 440 nm light. As presented in Fig. 5(f), the CN-APHP doped LC is suitable for recording of images. The $PSS_{160 \,^{\circ}C}$ was set as background and the letters "HFUT" appear as PSS_{440nm} optical features.

In addition to the controllability of PL intensity based on the isomerization of CN-APHP, the degree of polarization of PL from CN-APHP can also be switched and operated in memory mode. Since (*Z*)-CN-APHP is a luminogen with liquid crystalline properties, we suspected that anisotropic emission could be accomplished with it. Polarized PL spectra were recorded and a rotatable polarizer (0 ° - 360 °) was placed between the sample and the detector. Fig. S8 describes the plots of the polarized intensity of photoluminescence light parallel and perpendicular to the rubbing direction of the liquid crystal cell versus exposure time of 440 nm light. Fig. S9(a) shows a polar diagram of the PL intensity of the (*Z*)-CN-APHP doped liquid crystal cell. The cell reveals a PL maximum for the directions of 0 ° and 180 ° - which is the rubbing direction, and a minimum value at the directions of 90 ° and 270 ° - which is perpendicular to the rubbing direction.

Based on the above results, the dichroic ratios of polarized PL spectra of the CN-APHP doped LC cell at $PSS_{160 \ ^{\circ}C}$ and $PSS_{440 \ nm}$ were studied. At $PSS_{160 \ ^{\circ}C}$, the orientation of the LC mixture was parallel to the alignment layer. The dichroic ratio is about 2.0. As shown in Fig.6(b), the anisotropic emission almost disappeared at $PSS_{440 \ nm}$ and the dichroic ratio is only 1.2. In addition, the dichroic ratio can change continuously by increasing the exposure time to 440 nm light as ploted in Fig. S10.

More interesting, the PL intensity parallel to the liquid crystal direction at PSS_{160 °C} is similar

to that at $PSS_{440 nm}$. The PL intensity normal to the liquid crystal direction at $PSS_{440 nm}$ is larger than that at $PSS_{160 °C}$. Based on these results, a novel pattern-recording method was demonstrated. A UV lamp was used as light source to illuminate the mixture and a polarizer was used to analyze the change in PL efficiency. In Fig. 6(c), we can clearly see the letters "HFUT" when the polarizer is oriented *vertically* to the rubbing direction of the cell. When rotating the polarizer *parallel* to the rubbing direction, the letters "HFUT" disappear.

4. Conclusions

In summary, we have synthesized an AIE-active luminescent liquid crystal, (*Z*)-CN-APHP, which can be converted into *E*-isomers via 440 nm photoexcitation with a simultaneous decrease in structural compatibility with a nematic liquid crystal. A new optical switching effect based on the CN-APHP doped liquid crystals has been demonstrated. It emits partially linearly polarized light. By controlling the reversible photo/thermal *Z*/*E* isomerization process, not only PL intensity but also the PL polarization can be switched or modulated. Moreover, the possibility of photochemical patterning or image recording with these materials has been demonstrated. Our results may help create a new modulating technique for future light-switchable photonic devices and displays.

Acknowledgments

This research was supported by Basic Research Program of China (Grant No. 2012CB723406), National Natural Science Foundation of China (Grand No. 61107014, 51203039, 2120417, 21174036, 51103034), Program for New Century Excellent Talents in University (Grant No. NCET-12-0839), National National High Technology Research and Development Program of China (Grant No. 2012AA011901).

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Fig. 1 (a) Molecular structure of (Z)-CN-APHP and (E)-CN-APHP. (b) Images of (Z)- (above) and (E)-CN-APHP (below) under room and UV light. (c) DSC curves of (Z)-CN-APHP at a heating/cooling rate of 5 °C per minute. (d) POM photograph of (Z)-CN-APHP at 78 °C during heating process.



Fig. 2 Absorption (a) and photoluminescence spectra (b) of (Z)- and (E)-CN-APHP in DMF solution (2×10-5 mol· L-1).



Fig. 3 UV-vis absorption (a) and photoluminescence spectra of (Z)- and (E)-CN-APHP in DMF after increasing the photoexcitation time of 440 and 254 nm light, respectively. Absorbance at 365 nm (c) and photoluminescence intensity at 505 nm (d) appear modulated during alternating excitation at 440 nm (black circle, for 5 min) and 254 nm (red circle, for 20 min) because of the reversible isomerization process.



Fig. 4 (a) UV-vis absorption spectra of CN-APHP in DMF solution (2×10-5 mol· L-1) in different states.



Fig. 5 Schematic illustration of the molecular arrangement and POM of the CN-APHP doped liquid crystal cell at different states. (a) initial state (pure Z-isomer), (b) PSS_{440 nm} and (c) PSS_{160 °C}, (d) Photoluminescence spectra of the cell at the three states, (e) Repeated switching of PL intensity between PSS_{440 nm} and PSS_{160 °C}, (f) Recorded pattern by the optical switch using two stable states: PSS_{440 nm} ("HFUT") and PSS_{160 °C} (background).



Fig. 6 Polarized photoluminescence spectra of the CN-APHP doped liquid crystal cell at $PSS_{160 \ ^{\circ}C}$ (a) and $PSS_{440 \ nm}$ (b). The recorded pattern of CN-APHP doped LC cell under the polarizer with the optic axis perpendicular (c) and parallel (d) to the rubbing direction of the liquid crystal cell: $PSS_{440 \ nm}$ ("HFUT") and $PSS_{160 \ ^{\circ}C}$ (background).

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Fig. S2 DSC curves of (E)-CN-APHP at a heating/cooling rate of 5 °C per minute.



Fig. S3 Geometry optimization of (Z)-CN-APHP (a) and (E)-CN-APHP (b) by quantum chemical calculations based on density functional theory.



Fig. S4 (a) 1H NMR spectra of CN-APHP in DMF solution after various irradiation time under
440 nm light (protons in the vinylene of Z-isomer form (▼) and E-isomer form (△). (b) Changes of Z-to-E conversion ratio as a function of UV irradiation time.



Fig. S5 The gradual changing of the absorption (a) and photoluminescence intensity (b) from all-Z-isomer to the PSS440 nm by prolonging the illumination time of 440 nm (black square)and all-E-isomer to the PSS254 nm by increasing the illumination time of 254 nm (red circle), respectively.



Fig. S6 DSC curves of host E7 and (Z)-CN-APHP doped E7 at a heating/cooling rate of 5 °C per minute.



Fig. S7 The changing tendency of photoluminescence intensity of CN-APHP doped liquid crystal cell by increasing exposure time of 440 nm light.



Fig. S8 The plots of the polarized intensity of photoluminescence light parallel (red line) and perpendicular (black line) to the rubbing direction of the liquid crystal cell versus exposure time of 440 nm light.



Fig. S9 The polar photoluminescence intensity of the CN-APHP doped liquid crystal cell at initial state (pure Z-isomer) (a), PSS440 nm (b) and PSS160 °C (c).



Fig. S10 The changing tendency of fluorescence dichroic ratio through increasing the illumination time.

- A new optical switch based on AIE-active luminescent liquid crystals was developed.
- The mixture material can emit partially linearly polarized light.
- It is possibly to modulate photoluminescence intensity and its polarization.
- It has the potential to be used in improved optical devices.

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