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1. Introduction

In the past years, stimuli-responsive luminescent materials have gained considerable attention due to their "smart" behavior.^{1–5} Compared with traditional luminescent materials, the luminescence color and intensity of stimuli-responsive luminescent materials change greatly with the application of external stimuli.^{6–11} This unique property endows them with wide applications in mechanochromic materials,^{12–15} temperature sensors,^{16–20} pH detectors,^{21–23} pressure sensors,^{24,25} anti-counterfeiting materials,²⁶ *etc.* A large number of stimuli-responsive luminescent materials have been reported and studied extensively. According to the types of stimuli, stimuli-responsive luminescent materials, pH stimuli-responsive luminescent materials, pH stimuli-responsive luminescent materials, tress stimuli-responsive luminescent materials, tress stimuli-responsive luminescent materials, the stimuli-responsive luminescent materials

The growing demand for smart materials has promoted the development of luminescent materials with dual or multistimuliresponsive behavior. However, the preparation of luminescent

Multistimuli-responsive small-molecule compound with aggregation-induced emission enhancement characteristics: preparation, properties and applications

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A novel multifunction luminescent small-molecule compound with hydrophilic chains was successfully designed and synthesized, which exhibited aggregation-induced emission enhancement (AIEE) characteristics. Even more interesting, it exhibited responsive behavior to temperature, pH and UV irradiation. In aqueous solution, its luminescence intensity showed temperature sensitivity. Initially, its luminescence intensity decreased slightly with an increase in temperature, which was enhanced greatly when the temperature increased to its lower critical solution temperature (LCST). With a further increase in temperature, there was a significant decline in its luminescence intensity. Additionally, it showed different pH and UV irradiation responsive behaviors in water and THF solution. In THF solution, its luminescence intensity was enhanced greatly with the addition of alkali, but it decreased with an increase in UV irradiation time. In aqueous solution, its luminescence intensity was enhanced slightly and its LCST decreased first and then increased with the addition of alkali. However, its luminescence intensity increased with an increase in UV irradiation time. In aqueous solution, its alkali solution used as ink and ordinary paper adsorbed with our prepared small-molecule compound used as rewritable paper.

materials with dual or multistimuli-responsive properties is still a big challenging due to the difficulties of combining different stimuli blocks within one molecule. To date, most of the reported stimuli-responsive luminescent materials only exhibited single stimulus responsive behavior, and only a few reported luminescent materials displayed dual or multistimuli-responsive properties.²⁷⁻²⁹ Zhu and co-workers reported a novel boron-difluoride complex, which was sensitive to mechanical grinding, organic solvent vapours and acid/base vapours.³⁰ Chao and co-workers prepared a novel polyamic acid, which was sensitive to redox species, pH, electrochemical, and pressure stimuli.³¹ Xu and co-workers prepared a novel multistimuli-responsive molecule based on tetraphenylethene.³² The tetraphenylethene derivatives were responsive to grinding, heating, solvent-fuming, and acid and base vapors stimuli. Although some fluorescent materials with multistimuli-responsive properties have been prepared, reports on dual or multistimuli-responsive luminescent materials are still rare owing to the above mentioned problems.

In 2002, Soo Young Park found for the first time that an α -cyanostilbenic derivative exhibited AIEE characteristics.³³ The synthetic α -cyanostilbenic derivative 1-cyano-*trans*-1,2-bis-(4'-methylbiphenyl)-ethylene (CN-MBE) emits weak fluorescence in dilute solution, but its emission intensity is enhanced greatly in the aggregate state. Subsequent studies also suggested that

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 α -cyanostilbenic derivatives show responsive behavior to UV irradiation.^{34,35} With an increase in UV irradiation time, these molecules change from the *trans*-conformation to *cis*-conformation and their luminescence intensity is reduced gradually. Therefore, α -cyanostilbenic derivatives can be used as light stimuli-responsive luminescent materials. After chemical modification, α -cyanostilbenic derivatives can also exhibit temperature stimuli-responsive behavior. Soo Young Park reported two different amphiphilic molecules by incorporating oligo(ethylene glycol) units into dicyanodistyrylbenzene.³⁶ Both molecules exhibited temperature stimuli-responsive behavior and their luminescence wavelength varied with temperature. However, there are no reports on dual or multistimuli-responsive luminescent materials based on α -cyanostilbenic.

Herein, we report a novel multistimuli-responsive luminescent material based on α -cyanostilbenic. To achieve this aim, (*Z*)-2-(4-hydroxyphenyl)-3-(3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)acrylonitrile (**HPTEO3PA**) was synthesized (Scheme 1). To endow the molecule with pH stimuli-responsive properties, the –OH group was introduced, and for temperature stimuli-responsive properties, oligo(ethylene glycol) blocks were introduced. Since α -cyanostilbenic derivatives have their own properties as well as AIEE properties, the synthetic molecule was expected to exhibit AIEE characteristics and show temperature and pH stimuli-responsive properties. The application of our prepared dual-stimuli luminescent compound in temperature sensors, alkali detectors and rewritable materials was also explored.

2. Experimental section

2.1 Materials

Triethylene glycol monomethyl ether, 4-toluene sulfonyl chloride, methyl gallate, lithium aluminum hydride, manganese dioxide, potassium *tert*-butylate, and 4-hydroxybenzyl cyanide were purchased from energy chemical. Tetrahydrofuran, ethanol, acetone, ethyl acetate and other solvents were used as received without further purification.

2.2 Measurements and characterizations

¹H NMR analysis of **HPTEO3PA** was performed on a Bruker ARX400 MHz spectrometer with tetramethylsilane (TMS) as an internal standard. The molecular weight of the synthetic molecules was measured using a Bruker Biflex III MALDI-TOF spectrometer. The absorption spectra of **HPTEO3PA** and its lower critical solution temperature (LCST) were recorded on an Agilent Carry 100 spectrophotometer equipped with a temperature regulating device. Fluorescence spectra of **HPTEO3PA** were recorded on



Scheme 1 Chemical structure of HPTEO3PA.

a PTIQm40 luminescence spectrometer equipped with a temperature regulating device. The UV irradiation test was carried out with a 365 nm ultraviolet lamp (1000 MW). A Zetasizer Nano ZS90 particle size analyzer was applied to measure the size distribution of the **HPTEO3PA** aqueous solution and **HPTEO3PA** THF solution.

2.3 Synthesis of multistimuli-responsive small-molecule compound

The preparation routes for the multistimuli-responsive smallmolecule compound **HPTEO3PA** are shown in Fig. 1. The specific preparation method for **HPTEO3PA** is as follows:

Synthesis of 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate. Triethylene glycol monomethyl ether (30.0 g, 0.183 mol), 5% sodium hydroxide solution (9.96 g, 0.249 mol) and 100 mL THF were added to a 500 mL round-bottom flask. Then the round-bottom flask was placed in an ice bath. 4-Toluene sulfonyl chloride (31.66 g, 0.166 mol) was dissolved in 50 mL THF and then added dropwise to the round-bottom flask. When the THF solution was completely added to the round bottom flask, the reaction mixture was continued with stirring at room temperature for 3 h. Subsequently, the desired product (48.06 g, yield: 82.5%) was obtained through extraction with H₂O and CH₂Cl₂, drying with anhydrous sodium sulfate and desolventizing. ¹HNMR (400 MHz, CDCl₃, δ): 7.76 (d, 2H, Ph-H), 7.32 (d, 2H, Ph-H), 4.18-4.15 (m, 2H, -SO₃CH₂-), 3.70-3.66 (m, 2H, -OCH₂-), 3.62-3.58 (m, 6H, -OCH2-), 3.56-3.50 (m, 2H, -OCH2-), 3.34 (s, 3H, $-OCH_3$, 2.42 (s, 3H, Ph $-CH_3$). Mass spectrometry (MS) (m/z) calcd for C14H22O6S, 318.11; found, 319.10.

Synthesis of methyl 3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy) ethoxy)benzoate. Methyl gallate (5.12 g, 0.0278 mol), anhydrous potassium carbonate (23.11 g, 0.167 mol) and 200 mL 1,4dioxane were added to a 500 mL round-bottom flask and the mixture were stirred at room temperature for 1 h. Subsequently, 2-(2-(2-methoxyethoxy)ethyl)-4-methylbenzenesulfonate (40.0 g, 0.126 mol) was added into the mixture and then the reaction mixture was heated at 110 °C for 36 h. Afterward, the mixture was treated by filtration and the organic phase was collected and the solvent removed with a rotary evaporator to obtain the crude product. The crude product was further purified by column chromatography with ethyl acetate : acetone



Fig. 1 Synthetic routes for the multistimuli-responsive small-molecule compound HPTEO3PA.

(3:1, v/v) as the eluent to give the final product (13.21 g, yield: 80%) as a yellowish liquid. ¹H NMR (δ , ppm, CDCl₃): 7.95 (s, 2H, Ph–H); 4.31–4.27 (t, 6H, –OCH₂–); 3.88 (s, 3H, –COOCH₃); 3.86–3.80 (t, 6H, –OCH₂–); 3.74–3.72 (t, 6H, –OCH₂–); 3.67–3.63 (t, 12H, –OCH₂–); 3.55–3.53 (t, 6H, –OCH₂–); 3.37 (s, 9H, –OCH₃). Mass spectrometry (MS) (*m*/*z*) calcd for C₂₉H₅₀O₁₄, 622.32; found, 623.30.

Synthesis of (3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)methanol. Aluminum hydride (0.07 g, 0.01748 mol), and 50 mL THF were added to a 250 mL round-bottom flask. Methyl 3,4,5-tris(2-(2-(2-methoxy)ethoxy)ethoxy)benzoate (7.4 g, 0.0119 mol) was dissolved in 40 mL THF and then dropped into the round-bottom flask. Afterward, the reaction mixture was stirred at room temperature for 3 h. When the reaction was completed, dilute hydrochloric acid was added to the above mixture and a clear and transparent solution was obtained. Subsequently, the desired product (6.61 g, yield: 93.5%) was obtained through extraction with H₂O and CH₂Cl₂, drying with anhydrous sodium sulfate and desolventizing. Yield: 93.5%. ¹H NMR (δ , ppm, CDCl₃): 6.62 (s, 2H, Ph–H); 4.58 (s, 2H, Ph– CH₂-O); 4.27-4.00 (t, 6H, -OCH₂-); 3.85-3.76 (t, 6H, -OCH₂-); 3.73-3.71 (t, 6H, -OCH₂-), 3.67-3.63 (t, 12H, -OCH₂-); 3.56-3.53 (t, 6H, -OCH₂-); 3.38 (s, 9H, -OCH₃). Mass spectrometry (MS) (m/z) calcd for C₂₈H₅₀O₁₃, 594.33; found, 595.32.

Synthesis of 2,3,4-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzaldehyde. A mixture of (3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)methanol (6.0 g, 0.01 mol), MnO₂ (17.55 g, 0.202 mol) and 120 mL dry dichloromethane was added to a 250 mL roundbottom flask. The reaction mixture was stirred for 12 h at room temperature. After the reaction was finished, the mixture was treated by filtration and the organic solvent was removed with a rotary evaporator to the obtain crude product, which was further purified by column chromatography with ethyl acetate : acetone (3 : 1, v/v) as the eluent to afford a yellowish liquid product (5.45 g, yield: 92%). ¹H NMR (δ , ppm, CDCl₃): 6.96 (s, 2H, Ph–H); 4.37–4.27 (t, 6H, –OCH₂–); 3.84–3.75 (t, 6H, –OCH₂–); 3.72–3.69 (t, 6H, –OCH₂–), 3.65–3.62 (t, 12H, –OCH₂–); 3.58–3.55 (t, 6H, –OCH₂–); 3.37 (s, 9H, –OCH₃). Mass spectrometry (MS) (*m*/*z*) calcd for C₂₈H₄₈O₁₃, 592.31; found, 593.30.

Synthesis of (Z)-2-(4-hydroxyphenyl)-3-(3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)phenyl)acrylonitrile (HPTEO3PA). A mixture of 2,3,4-tris(2-(2-(2-methoxy)ethoxy)ethoxy)benzaldehyde (5.0 g, 0.0084 mol), 4-hydroxybenzyl cyanide (1.35 g, 0.010 mol), potassium tert-butylate (1.89 g, 0.0169 mol) and 100 mL anhydrous ethanol were added to a 250 mL roundbottom flask. The reaction mixture was heated at 80 °C for 3 h. Subsequently, the crude product was obtained through extraction with H₂O and CH₂Cl₂, drying with anhydrous sodium sulfate and desolventizing. The crude product was further purified by column chromatography with ethyl acetate : acetone (3:1, v/v) as the eluent to obtain the desired product (3.88 g, yield: 65%). ¹H NMR (δ , ppm, CDCl₃): 7.39–7.37 (d, 2H, Ph-H), 7.16 (s, 1H, ==CH-), 7.03 (s, 2H, Ph-H), 6.83-6.81 (d, 2H, Ph-H), 4.24-4.14 (t, 6H, -OCH₂-), 3.88-3.82 (t, 6H, -CH₂O-), 3.77-3.36 (t, 24H, -OCH₂-, -CH₂O-), 3.369 (s, 9H, $-OCH_3$). Mass spectrometry (MS) (m/z) calcd for C₃₆H₅₃NO₁₃, 707.35; found, 708.33.

3. Results and discussion

3.1 Chemical structure characterization of multistimuliresponsive luminescent molecule HPTEO3PA

The multistimuli-responsive luminescent molecule **HPTEO3PA** was successfully synthesized *via* the synthetic routes illustrated in Fig. 1. ¹H NMR and mass spectroscopy were used to investigate the chemical structure of **HPTEO3PA**. Fig. 2a shows the ¹H NMR spectrum of **HPTEO3PA**. As observed, all the peaks in the ¹H NMR spectrum correspond to the hydrogen atoms in the molecule and the integral area of the peaks was in good agreement with the number of hydrogen atoms. This indicated that we obtained pure **HPTEO3PA**. The mass spectrum further confirmed the chemical structure of **HPTEO3PA**. As seen from Fig. 2b, the measured molecular weight was 708.332, 709.350 and 710.372, which was in good agreement with the theoretical molecular weight of **HPTEO3PA** of 707.35, 708.36 and 709.36, respectively.

3.2 AIEE properties of HPTEO3PA

We also investigated the photophysical properties of HPTEO3PA. Fig. 3a shows the UV spectrum of the HPTEO3PA THF solution. As observed, HPTEO3PA exhibited three obvious absorption peaks at about 202 nm, 217 nm and 343 nm. The fluorescence luminescence behavior of HPTEO3PA was also studied and the experimental results indicated that HPTEO3PA also possessed AIEE characteristics. Fig. 3b shows the fluorescence spectra of HPTEO3PA in THF/petroleum ether mixtures. As observed, HPTEO3PA emitted weak fluorescence in pure THF solution. With the addition of non-solvent petroleum ether, the fluorescence intensity remained constant at first and then increased greatly. The maximum luminescence wavelength also remained unchanged and exhibited an obvious red shift when the volume fraction of petroleum ether increased to 95%. The UV absorption spectra changes of HPTEO3PA depending on the petroleum ether fraction in THF were measured. As observed from Fig. 3c, when the volume fraction of petroleum ether was lower than 90%, its UV absorption spectrum was almost unchanged with an increase in petroleum ether. When the volume fraction of petroleum ether was higher than 90%, a new UV absorption band in the range of 400 nm to 500 nm was observed and its intensity increased with an increase in the volume fraction of petroleum ether. The new UV absorption band should be ascribed to the formation of J-aggregates. The new generation of an emission peak at about 480 nm can also be explained by the formation of J-aggregates.



Fig. 2 ¹H NMR spectrum (a) and MS spectrum (b) of HPTEO3PA in CDCl₃.



Fig. 3 (a) UV spectrum of **HPTEO3PA** THF solution, (b) fluorescence spectra and (c) UV spectra of **HPTEO3PA** in THF/petroleum ether mixtures with different petroleum ether fractions (fp). Excitation wavelength: 365 nm and concentration = 5×10^{-5} mol L⁻¹.

The UV spectra and fluorescence spectra of **HPTEO3PA** in THF/ petroleum ether mixtures indicated that **HPTEO3PA** possessed AIEE characteristics and its enhanced fluorescence intensity and obvious red shift can be explained by the formation of J-aggregates and the planarization of the **HPTEO3PA** molecules.³³

3.3 Temperature stimuli-responsive properties and applications of HPTEO3PA

The temperature stimuli-responsive properties of an **HPTEO3PA** aqueous solution was investigated in detail. The experimental results showed that **HPTEO3PA** with longer hydrophilic chain was soluble in water at a lower temperature, while insoluble in water at higher temperature, which indicated that **HPTEO3PA** exhibited temperature stimuli-responsive properties. For example, **HPTEO3PA** could dissolve in water to form a transparent solution (5 mg mL⁻¹) at 25 °C. However, the transparent solution became an opaque turbid fluid when the temperature increased to 50 °C, which is higher than the lower critical solution temperature (LCST) of **HPTEO3PA**. The specific transformation process is shown in Fig. 4.

To further investigate the thermosensitivity of **HPTEO3PA**, an Agilent Carry 100 spectrophotometer equipped with a temperature regulating device was applied to measure the transmittance of **HPTEO3PA** aqueous solutions with different concentrations on heating and cooling. The heating and cooling rate was 1.0 °C min⁻¹. As observed from Fig. 5a, the transmittance of the **HPTEO3PA** aqueous solution indicated obvious thermosensitivity. At lower temperature, **HPTEO3PA** was soluble in water, which resulted in a higher transmittance. The transmittance of the **HPTEO3PA** aqueous solution dramatically decreased when the temperature increased above its LCST, and the transparent aqueous solution turned into an opaque turbid fluid due to the aggregation of **HPTEO3PA**. The concentration of the **HPTEO3PA**



Fig. 4 Photographs illustrating the transmittance change in the **HPTEO3PA** aqueous solution.



Fig. 5 (a) Temperature-transmittance curves of HPTEO3PA aqueous solution, (b) LCST-concentration curves of HPTEO3PA aqueous solution and (c) transmittance curves of HPTEO3PA (5 mg mL⁻¹) upon heating and cooling. Measured wavelength: 600 nm.

aqueous solution has a great influence on its thermosensitivity. The LCST of the **HPTEO3PA** aqueous solution decreased with an increase in concentration (Fig. 5b). As observed from Fig. 5c, the transmittance curves of the **HPTEO3PA** aqueous solution (5 mg mL⁻¹) on heating and cooling basically overlapped, suggesting that the thermosensitivity of the **HPTEO3PA** aqueous solution showed good reversibility.

As mentioned above, when the temperature increased to the LCST, **HPTEO3PA** aggregated. Meanwhile, **HPTEO3PA** is AIEE molecule. Therefore, the aggregation of **HPTEO3PA** caused by heating will improve its luminescence intensity. Specifically, the luminescence intensity will increase with an increase in temperature. To confirm this conjecture, we measured the luminescence intensity of an **HPTEO3PA** aqueous solution (7.5 mg mL⁻¹) at different temperatures. As seen from Fig. 6a, the change in its luminescence intensity can be divided into three stages. Initially, the temperature was lower than LCST, and the luminescence intensity decreased slightly with an increase in temperature. This is because **HPTEO3PA** is more likely to dissipate energy through non-radiation transitions with increasing temperature. In the second stage, the temperature increased to its LCST, and the luminescence intensity was

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Fig. 6 (a) Fluorescence spectra of HPTEO3PA aqueous solution (7.5 mg mL⁻¹) measured at different temperatures and (b) plot of I/I_{25} values versus temperature for HPTEO3PA aqueous solution (7.5 mg mL⁻¹). Excitation wavelength: 365 nm.

enhanced greatly due to the aggregation of **HPTEO3PA**. The luminescence intensity measured at 49 °C was 39.95-fold that measured at 25 °C. In the third stage, further heating led to a slight decrement in emission intensity. This is because the aggregation degree of **HPTEO3PA** was almost unchanged with a further increase in temperature. On the contrary, **HPTEO3PA** is more likely to dissipate energy through non-radiation transitions at higher temperature, leading to a decrement in its emission intensity. The variable temperature fluorescence test indicated that the fluorescence luminescence behavior of **HPTEO3PA** also exhibited temperature stimuli-responsive properties and it can be used as a temperature sensor.

3.4 pH stimuli-responsive properties and applications of HPTEO3PA

The introduction of the –OH group endows **HPTEO3PA** with pH stimuli-responsive properties. Thus, we initially studied the influence of pH on the LCST of an **HPTEO3PA** aqueous solution. Fig. 7a shows the temperature–transmittance curves of **HPTEO3PA** aqueous solutions (5 mg mL⁻¹) with different mole fraction of NaOH. As observed, the mole fraction of NaOH had a great influence on the thermosensitivity of the **HPTEO3PA** aqueous solution. Fig. 7b shows the LCST curves of **HPTEO3PA** aqueous solution. With an increment in NaOH mole fraction, the LCST of **HPTEO3PA** decreased firstly and then increased. When the mole ratio of NaOH to **HPTEO3PA** was over 1:1, the LCST remained unchanged even with an enhanced mole fraction of NaOH. The addition of NaOH destroyed the hydrogen bonding between water and **HPTEO3PA**,³⁷ and therefore the hydrophilicity



Fig. 7 (a) Temperature–transmittance curves of **HPTEO3PA** aqueous solution (5 mg mL⁻¹) with different mole fractions of NaOH and (b) LCST curve of **HPTEO3PA** aqueous solution (5 mg mL⁻¹) with different mole fractions of NaOH. Measured wavelength: 600 nm.

of **HPTEO3PA** was weakened, resulting in a decline in its LCST. As the mole fraction of NaOH continued to increase, the –OH groups reacted with NaOH to yield –ONa, leading to an increase in the hydrophilicity of the whole molecule. Therefore, the LCST increased with increasing mole fraction of NaOH. When the mole ratio of NaOH to **HPTEO3PA** was greater than 1:1, all the –OH groups were translated into –ONa, and the LCST was approximately independent of the NaOH mole fraction.

We also studied the relationship between pH and the photophysical properties of the **HPTEO3PA** aqueous solution. Fig. 8a shows the UV spectra of **HPTEO3PA** aqueous solutions with different mole fractions of NaOH. As observed, the absorption peak shifted to a shorter wavelength firstly and then shifted to a longer wavelength with the addition of NaOH. As mentioned above, the addition of NaOH would weaken the hydrophilicity of **HPTEO3PA**, and therefore **HPTEO3PA** will aggregate to form a more twisted conformation, resulting in a blue-shift in its absorption peak. As the mole fraction of NaOH continue to increase, the hydrophilicity of **HPTEO3PA** was enhanced to form a more planar conformation, resulting in a red-shift in its absorption peak. Fig. 8b shows the fluorescence spectra of **HPTEO3PA** aqueous solutions with different mole fractions of NaOH. The fluorescence intensity increased due to aggregation.

In THF solution, the photophysical properties of **HPTEO3PA** changed greatly when alkali was added. Fig. 9(a) shows the normalized fluorescence spectra of **HPTEO3PA** THF solutions with addition of different alkalis. As observed, the maximum luminescence wavelength shifted to a longer wavelength and



Fig. 8 UV spectrum (a) and fluorescence spectrum (b) of HPTEO3PA aqueous solution with different mole fractions of NaOH. Excitation wavelength: 365 nm and concentration = 5×10^{-5} mol L⁻¹.



Fig. 9 (a) Normalized fluorescence spectra of HPTEO3PA THF solution with the addition of different alkalis and (b) fluorescence spectra of HPTEO3PA THF solution alone and with the addition of octylamine. Excitation wavelength: 365 nm for HPTEO3PA and 440 nm for HPTEO3PA with added alkaline substance. Concentration = 5×10^{-5} mol L⁻¹.

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Fig. 10 Pictures of HPTEO3PA THF solution and HPTEO3PA THF solution with the addition of octylamine under 365 nm UV light. Concentration = 5×10^{-5} mol L⁻¹.

the higher the alkalinity, the greater its red shift. The maximum luminescence wavelength of the HPTEO3PA THF solution was 429 nm, while it shifted to 537 nm when solid NaOH or solid KOH was added. Considering this interesting property, HPTEO3PA can be used as a detector for alkali. The luminescence intensity of HPTEO3PA THF solution enhanced greatly with the addition of alkaline substances. The luminescence intensity was enhanced 255-fold when octylamine was added (Fig. 9b). The luminescence color also changed from blue to yellowish green upon the addition of octylamine (Fig. 10). The luminescence intensity and the obvious red-shift should be attributed to the intramolecular charge transfer effect (ICT). With the addition of alkali, the -OH groups interacted with the alkali, resulting in oxygen atoms with a negative charge. Therefore, the electron donating ability of the oxygen atoms was enhanced greatly. Since -CN is an electron-withdrawing group, the HPTEO3PA molecules have a strong ICT effect with the addition of alkali. Meanwhile, the higher the alkalinity, the stronger the electron-donating ability of the oxygen atom, resulting in a longer wavelength fluorescence emission peak.

To further understand the influence of alkali on the photophysical properties of **HPTEO3PA** in different solvents, we measured the UV spectra of **HPTEO3PA** aqueous solution, **HPTEO3PA** aqueous solution with added NaOH, and **HPTEO3PA** THF solution with solid NaOH (Fig. 11). In aqueous solution, the B absorption peak showed an obvious blue-shift with the addition of NaOH. In THF solution, the B absorption peak was almost



Fig. 12 Fluorescence spectra of HPTEO3PA in CH₂Cl₂ and methanol solutions with the addition of NaOH. Excitation wavelength: 365 nm and concentration (c) = 5×10^{-5} mol L⁻¹.

unchanged; however, a new absorption peak was observed at 450 nm, which was derived from the intramolecular charge-transfer. We also measured the fluorescence spectra of **HPTEO3PA** in CH_2Cl_2 and methanol solutions with the addition of NaOH. As observed from Fig. 12, the **HPTEO3PA** CH_2Cl_2 solutions showed one obvious emission at about 408 nm and an obvious emission band ranging from 510 nm to 610 nm. These two emission peaks powerfully prove the existence of the ICT process. In methanol solution, **HPTEO3PA** only showed one obvious emission at about 520 nm. This is because strong polar methanol is conducive to the stability of ICT state and therefore enhanced the ICT process greatly.

We also developed a rewritable material based on **HPTEO3PA**. Solid alkali or alkali solution was applied as ink and ordinary paper adsorbed with **HPTEO3PA** was used as rewritable paper. As shown in Fig. 13a, the ordinary paper adsorbed with **HPTEO3PA** emitted blue fluorescence under 365 nm UV light. We then wrote "XTU" on this paper using solid NaOH as the ink. The three letters "XTU" emitted stronger yellow-green fluorescent light under 365 nm UV light and the other unwritten area still emitted blue fluorescence, showing stronger visual contrast (Fig. 13b). Furthermore, the written word could be easily removed. As seen from Fig. 13c, when the paper was fumigated with hydrochloric acid, the three letters "XTU" were removed quickly and the whole paper reverted to its original state, showing blue fluorescence





Fig. 11 UV spectra of HPTEO3PA aqueous solution (blue line), HPTEO3PA aqueous solution with the addition of NaOH (red line), and HPTEO3PA THF solution with the addition of solid NaOH. Concentration (c) = 5×10^{-5} mol L⁻¹.

Fig. 13 (a) Picture of ordinary paper adsorbed with **HPTEO3PA**, (b) picture of ordinary paper adsorbed with **HPTEO3PA** written with NaOH, (c) picture of ordinary paper fumigated with hydrochloric acid and (d) picture of ordinary paper adsorbed with **HPTEO3PA** rewritten with NaOH. All pictures were taken under 365 nm UV light.

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under 365 nm UV light. Thus, the paper could be reused. When wrote "XTU" on this paper again, the letters "XTU" still emitted yellow-green fluorescence and showed stronger visual contrast (Fig. 13d). Thus, the test results indicated that **HPTEO3PA** can be used as a rewritable material.

3.5 UV irradiation stimuli-responsive properties of HPTEO3PA

UV irradiation also affected the properties of HPTEO3PA. Thus, we initially studied the influence of UV irradiation on the LCST of HPTEO3PA. Fig. 14(a) shows the temperature-transmittance curves of the HPTEO3PA aqueous solution treated with 365 nm UV irradiation for 2 h. HPTEO3PA also exhibited temperature stimuli-responsive properties even under UV irradiation and its LCST was enhanced obviously. As observed from Fig. 14(b), the LCST of all the HPTEO3PA aqueous solutions was enhanced by 1-2 °C after UV irradiation. The enhanced LCST can be explained as follows: on the one hand, HPTEO3PA changed from the trans-conformation to cis-conformation with a greater dipole moment, resulting in an enhancement in its hydrophilicity. On the other hand, HPTEO3PA can self-assemble into a core-shell structure with a hydrophilic oligo(ethylene glycol) shell and hydrophobic α -cyanostilbenic core. After UV irradiation, the α -cyanostilbenic changed from the *trans*-conformation into *cis*conformation, resulting in a smaller size of α -cyanostilbenic. Therefore, the thickness of the hydrophobic core became smaller. Due to the synergism of these two aspects, the LCST of the HPTEO3PA aqueous solution was enhanced obviously. A schematic of this mechanism is shown in Fig. 15.

The photophysical properties of **HPTEO3PA** showed different UV irradiation responsive behaviors in water and in THF solution. In aqueous solution, the luminescence intensity increased first and remained almost unchanged with an increase in the 365 nm UV irradiation time (Fig. 16a). With the irradiation of UV light, the luminescent wavelength of **HPTEO3PA** shifted to a shorter wavelength, while its luminescence intensity increased. After irradiation for 50 min, the luminescent wavelength and the luminescence intensity was independent of irradiation time. At this moment, the maximum luminescence intensity was enhanced 46.4-fold than before (Fig. 16b). Even more interesting is that a new emission peak located at a longer wavelength was observed



Fig. 14 (a) Temperature-transmittance curves of HPTEO3PA aqueous solution treated with 365 nm UV irradiation for 2 h and (b) LCST of HPTEO3PA aqueous solution before and after UV irradiation. Measured wavelength: 600 nm.



Fig. 15 Schematic illustration of the conformation transformation of the HPTEO3PA aqueous solution treated with 365 nm UV irradiation.

when irradiated for 20 min. The emission intensity of this new peak increased and it shifted to a longer wavelength with an increase in UV irradiation time until 90 min. The maximum luminescence wavelength of the new emission peak shifted from 491 nm to 512 nm and the luminescence intensity was enhanced 4.83-fold when the UV irradiation time increased from 20 min to 90 min (Fig. 16c). The blue-shift of the emission peak located at a shorter wavelength indicated that the *trans*conformation turned into the *cis*-conformation with an increase in irradiation time. The enhanced emission intensity of the peak located at a shorter wavelength may have resulted from the aggregation of the *cis*-conformation. The formation of the new emission peak located at a longer wavelength also evidenced the aggregation of the *cis*-conformation and the new emission peak should be the excimer emission. Some references have been



Fig. 16 (a) Fluorescence spectra of HPTEO3PA aqueous solution with different UV irradiation times, (b) plots of I/I_0 values and the maximum luminescence wavelength (emission peak located at a shorter wavelength) versus UV irradiation time for HPTEO3PA aqueous solution and (c) plots of I/I_{20} values and the maximum luminescence wavelength (emission peak located at a longer wavelength) versus 365 nm UV irradiation time for HPTEO3PA aqueous solution. Excitation wavelength: 365 nm and concentration = 5 mg mL⁻¹.



Fig. 17 Pictures of HPTEO3PA aqueous solution with different UV irradiation times taken under a 365 nm UV light.

reported that the excimer emission can enhance luminescence intensity.^{38,39} However, we first reported UV irradiation-induced fluorescence enhancement *via* the production of excimers.

Fig. 17 shows the change in the fluorescence luminescence behavior of the **HPTEO3PA** aqueous solution (5 mg mL⁻¹) with different 365 nm UV irradiation times. The **HPTEO3PA** aqueous solution emitted weak blue fluorescence. After irradiation for 20 min, its fluorescence intensity was enhanced, and the luminescence wavelength shifted to shorter wavelength. After irradiation for 2 h, the fluorescence intensity enhanced greatly, and the wavelength shifted to longer wavelength. Then, the luminescence color of the **HPTEO3PA** aqueous solution turned green. This change is in good agreement with the fluorescence test results.

The reversibility of the emission behavior of the HPTEO3PA aqueous solution was also characterized. The test results are shown in Fig. 18. As observed from Fig. 18a, the emission peak located at a longer wavelength had a blue shift and the emission intensity decreased with irradiation of 256 nm UV light. After irradiation for 50 min, the maximum luminescence wavelength shifted from 512 nm to 487 nm and the luminescence intensity decreased to 3% (Fig. 18c). The emission peak located at a shorter wavelength had a red shift and the emission intensity decreased with 256 nm UV irradiation time (Fig. 18a). After irradiation for 110 min, the maximum luminescence wavelength shifted from 417 nm to 442 nm and the luminescence intensity decreased to 2.8% (Fig. 18b). This decrease in intensity can be explained by the configuration transformation of HPTEO3PA. HPTEO3PA changed from the cis-conformation to the trans-conformation when irradiated with 256 nm UV light. It is worth noting that after 256 nm UV irradiation for 110 min, the emission intensity and the maximum luminescence wavelength of the HPTEO3PAHPTEO3PA aqueous solution reverted to their original state completely when no 365 nm UV light was applied. The test results indicated that the trans-conformation is reversible and the emission behavior is also reversible. The reversible emission behavior also excluded the possibility of photochemical reaction and photochemical products.

The fluorescence luminescence behavior of the **HPTEO3PA** THF solution also changed with UV irradiation time. As observed from Fig. 19, the luminescence intensity of the **HPTEO3PA** THF solution decreased with an increase in UV irradiation time.



Fig. 18 (a) Fluorescence spectra of **HPTEO3PA** aqueous solution with different 256 nm UV irradiation times, (b) plots of I/I_0 values and the maximum luminescence wavelength (emission peak located at a shorter wavelength) *versus* 256 nm UV irradiation time for **HPTEO3PA** aqueous solution and (c) plots of I/I_0 values and the maximum luminescence wavelength (emission peak located at a longer wavelength) *versus* 256 nm UV irradiation time for the **HPTEO3PA** aqueous solution. Excitation wavelength: 365 nm and concentration = 5 mg mL⁻¹.



Fig. 19 Fluorescence spectra of HPTEO3PA THF solution (5 mg mL⁻¹) with different UV irradiation times. Excitation wavelength: 365 nm.

The decreased luminescence intensity can also be explained by the conformation transformation of HPTEO3PA. The fluorescence luminescence of HPTEO3PA behaved differently in THF solution and in aqueous solution. This is because the cis-conformation HPTEO3PA molecules resulted from UV irradiation could be dissolved completely in THF and there was no aggregation for the cis-conformation HPTEO3PA molecules. However, HPTEO3PA could self-assemble into core-shell structures in aqueous solution. When irradiated with UV light, the trans-conformation HPTEO3PA molecules turned into cis-conformation HPTEO3PA molecules. Therefore, the hydrophobic α -cyanostilbenic with the *cis*conformation aggregated (Fig. 15). On the one hand, the aggregation will induce an enhancement in the fluorescence of the cisconformation HPTEO3PA molecules. On the other hand, the aggregation will lead to the formation of excimers, which will produce a new emission peak and the emission intensity will enhance with an increase in UV irradiation time.

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Fig. 20 Size distributions of (a) HPTEO3PA aqueous solution and (b) HPTEO3PA THF solution with different 365 nm UV light irradiation times. Concentration = 5 mg mL⁻¹.

To confirm the above explanation, the size distributions of the HPTEO3PA aqueous solution and HPTEO3PA THF solution with different UV irradiation times were also studied. As observed from Fig. 20a, the diameter of the HPTEO3PA aqueous micelle solution was about 120 nm, which increased greatly with UV irradiation time.40 When exposed to 365 nm UV light for 120 min, the diameter increased to about 192 nm. The test results indicated that HPTEO3PA could self-assemble into micelles and the diameter of the micelles increased with UV irradiation time. While in THF solution, the diameter of HPTEO3PA was only about 2.32 nm. After UV irradiation for 20 min, the diameter of HPTEO3PA decreased to 1.74 nm (Fig. 20b). These results suggested that HPTEO3PA cannot form aggregates in THF solution and the molecular size of HPTEO3PA decreased when HPTEO3PA changed from the trans-conformation to the cisconformation under the effect of UV irradiation. The difference in the diameter change between the HPTEO3PA aqueous solution and HPTEO3PA THF solution treated with different UV irradiation times indicated that the enhanced emission intensity by UV irradiation originates from the formation of aggregates.

The UV absorption spectra of **HPTEO3PA** with different UV irradiation times in aqueous solution and in THF solution were characterized. As observed from Fig. 21, the maximum UV absorption peak of the **HPTEO3PA** THF solution and **HPTEO3PA** aqueous solution shifted to a shorter wavelength and its absorption intensity decreased after treatment with 365 nm UV irradiation. The blue-shift of the maximum UV absorption peak should be attributed to conformation transformation of **HPTEO3PA**. When irradiated with UV light, the *trans*-conformation changed to the *cis*-conformation, resulting in a more twisted conformation. Therefore, the conjugation degree of the whole molecule decreased and the maximum



Fig. 21 UV spectra of **HPTEO3PA** THF solution (a) and **HPTEO3PA** aqueous solution (b) with different UV irradiation times. Concentration = 5×10^{-5} mol L⁻¹.

absorption peak shifted to a shorter wavelength. We also observed that a new absorption peak appeared at about 250 nm after UV irradiation. Additionally, the absorption intensity of the new peak was enhanced with an increase in UV irradiation time. The new absorption peak should be ascribed to the formation of the *cis*conformation. The test results of the UV absorption spectra of **HPTEO3PA** with different UV irradiation times suggested that 365 nm UV irradiation can lead to a conformational transformation in **HPTEO3PA** in both THF and aqueous solution.

4. Conclusions

Herein, we prepared a novel α -cyanostilbenic-based fluorophore. The synthetic compound HPTEO3PA exhibited obvious AIEE properties, which emitted weak fluorescence in a good solvent while its emission intensity was enhanced greatly in the aggregate state. HPTEO3PA also showed stimulus-responsive behavior to temperature, pH and UV irradiation. Firstly, it showed thermosensitivity. HPTEO3PA was soluble in water at a lower temperature, while insoluble at a higher temperature. The luminescence behavior of HPTEO3PA also showed temperature sensitivity and its luminescence intensity showed the trend of declining-rising-declining with an increase in temperature. Secondly, HPTEO3PA showed pH sensitivity. In aqueous solution, the LCST of HPTEO3PA decreased first and then increased with the addition of alkali. The luminescence intensity increased slightly with the addition of alkali. While in THF solution, the luminescence intensity was enhanced greatly with the addition of alkali and the maximum luminescence wavelength exhibited different degrees of red-shifting with the addition of different alkalis, which could be used as probe for alkali. HPTEO3PA could also be used as a rewritable material. Lastly, HPTEO3PA showed UV irradiation sensitivity. In THF solution, its luminescence intensity decreased with an increase in UV irradiation time. In aqueous solution, its luminescence intensity increased with an increase in UV irradiation time. Its luminescence color changed from blue to green after irradiation for 2 h. This study offers a new method to prepare AIEE-active multistimuli-responsive fluorescent materials.

Conflicts of interest

There are no conflicts to declare.

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