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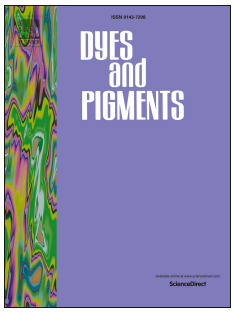

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Graphical Abstract

Synthesis, Characterization and Visible Light Activated Fluorescence of Azo Caged Aggregation-induced Emission Polymers

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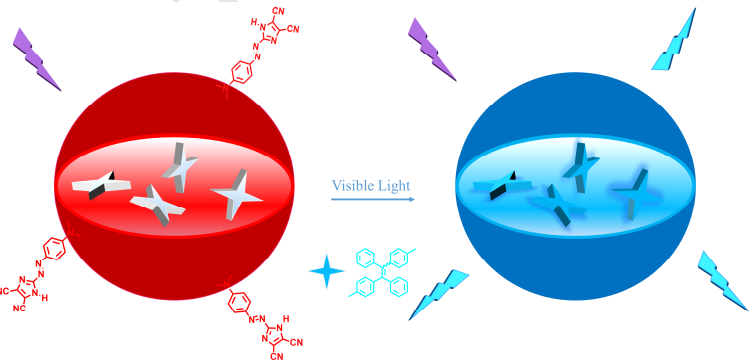
Visible light activated fluorescence of imidazole-type azo caged aggregation-induced emission polymers was reported. The effect of azo contents on fluorescence intensity was studied, which revealed that only a small amount of imidazole-type azo groups could totally cage the strong AIE fluorescence of the polymers. Irradiated with visible light, azo chromophores could be photo bleached, leading to remarkable recovery of the blue fluorescence. Fluorescent patterns have been easily fabricated.



Synthesis, Characterization and Visible Light Activated Fluorescence of Azo Caged Aggregation-induced Emission Polymers

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Abstract

Tetraphenylethylene (TPE) based aggregation-induced emission (AIE) polymers containing different degrees of functionalization of photobleachable azo chromophores were developed and their photophysical properties were explored. The synthesized epoxy monomer derived from TPE core reacted with aniline to give the precursor polymer, which confirmed typical AIE characteristics. Then through a post-polymerization azo-coupling scheme, various contents of 2-phenylazo-4, 5-dicyanoimidazole groups were readily introduced into the TPE based epoxy precusor polymer. Experimental results suggested that only a small amount of such imidazole-type azo component could totally cage the intense AIE fluorescence of the whole polymer due to the fluorescence resonance energy transfer process. By exposure to visible light (450 nm), azo units could be photo bleached notably, thus resulting in dramatic recovery of the blue fluorescence. Depending on this, visible

light induced fluorescent patterns were easily fabricated and erased, indicating that the prepared azo caged AIE Polymers could be promising candidates for anti-counterfeiting and optical information storage.

Keywords: Aggregation-induced emission; Azo caged; Tetraphenylethylene; Visible light; Fluorescent polymer

1 Introduction

In recent years, stimuli-responsive caged fluorescent systems, whose emission is quenched by a quencher and recovers upon cleavage of the quencher under certain stimuli, have attracted considerable attention for their promising prospect in sensors, optical recording devices, etc [1-4]. Anyway, traditional fluorescent compounds generally suffer from the aggregation-caused quenching (ACQ) problem in aggregated or solid state. In 2001, Tang's group proposed aggregation-induced emission (AIE) first to address this thorny issue, leading to new insights into the development of organic luminophores [5-16]. Due to AIEgens' good photostability and high photobleaching resistance in aggregated state, caged AIE materials with stimuli-responsive strategies have been extensively reported, which can be employed in numerous applications ranging from chemical sensing to bioprobes and so on [17-20]. Among diverse stimulus techniques, light is recognized to enjoy plenty of unique advantages. For example, it is exceptionally convenient for light to adjust irradiating position, intensity, beginning and ending time as well as specific wavelengths. However, photoactivatable AIE systems are still rare. Tang et al. have

investigated a new caged fluorophore obtained by connecting a tetraphenylethylene (TPE) derivative and a 2-nitrobenzyl group [21]. The caged compound can be photoactivated and induced to emit strong cyan fluorescence by ultraviolet (UV) exposure. Anyhow, UV light has very high energy, which can be damaging to organisms and result in degradation for scores of macromolecules. To utilize lower energy light resource such as visible light will be a much better choice [22]. In particular, for the caged AIE compound, one fluorescent unit will be often linked with one quencher, thus the fluorescence resonance energy transfer process can take place well. However, one quencher may quench more than one fluorescent group. In terms of this point, the caged AIE polymer may manifest better sensitivity to the stimuli. Furthermore, AIE polymers hold much more advantages in practical applications for their simple fabrication of large area films. Therefore, facile construction of photoactivatable AIE polymers responding to visible light is reasonably important but scarce.

Azo chromophores have been well known for their photoinduced reversible isomerization upon irradiation with light at appropriate wavelength, which promises potential in varying areas such as biological imaging, photoswitching, and many others [23-31]. Besides photochromic behaviours, azo chromophores also have been used as non-fluorescent energy acceptors, which can efficiently quench the fluorescence of the system. We have found that azo groups could be effectively bleached by enzyme or chemical reductant [32-34], causing great changes of both ultraviolet-visible (UV-vis) absorption spectra and fluorescence emission spectra. In

addition to the above biological or chemical method, some kind of azo chromophore has shown photobleachable performance with visible light actually [35]. On the basis of this, a class of visible light triggered AIE-active polymers with various photobleachable azo chromophore contents was synthesized and fully characterized in this work. TPE was implemented as the fluorescent building block in the backbone of epoxy based polymers owing to brief synthesis procedures and easy modifications. Imidazole-type azo chromophores were chosen as photoquenching and photobleaching sites. The photophysical properties of azo caged AIE polymers were sufficiently discussed. Upon irradiation with the light at the wavelength of 450 nm, the absorption band appearing in the visible range (λ_{max} at 466 nm) ascribed to the π–π^* electron transition of azo chromophores decreased noticeably, which was caused by photobleaching without any addition of external reducing agents. Simultaneously, the fluorescent emission of the polymer increased sharply. Furthermore, the fluorescent pattern on the spin-coated film of the prepared azo caged AIE polymer was fabricated and erased by exposure to visible light conveniently, which might be exploited in anti-counterfeiting and optical information storage.

2 Experimental Section

2.1 Materials and characterization

The purification of tetrahydrofuran (THF) was accomplished by distillation with metal sodium and benzophenone under argon atmosphere prior to use. Ultrapure water with resistivity > 18 MΩ·cm was used in the experiments, which was obtained from a Milli-Q water purification system. All other solvents and starting materials

were of analytical grade and purchased from commercial sources, which were directly used without additional purification.

^{1}H NMR and ^{13}C NMR spectra were conducted with a JEOL JNM-ECA 600 NMR spectrometer by using deuterated chloroform ($CDCl_3$) or deuterated dimethyl sulfoxide (DMSO-d_6) as the solvent and tetramethylsilane as the internal standard. UV-vis absorption spectra were determined by using an Agilent 8453 spectrophotometer. Fourier transform infrared (FTIR) measurements were conducted using an IRTracer-100 spectrometer (Shimadzu). Fluorescence emission spectra were measured on a Hitachi F-7000 fluorescence spectrophotometer. The weight-average molecular weight (M_w), the number-average molecular weight (M_n) and relative molecular mass distribution (MWD) were determined on a gel permeation chromatography (GPC) apparatus with THF as eluent at a flow rate of 1.0 mL·min^{-1}. Equipped with a refractive index detector and fitted with a PL gel 5 mm mixed-D column, the instrument was calibrated by using linear polystyrene (PS) standards. Photoirradiation (450 nm) was performed on a led curing system (IWATA UV-101D) and the formed pattern was observed with a 365 nm UV lamp. The intensity of 450 nm visible light is about 150 and 500 mW·cm^2 for the photobleaching of TPE-IZ-DC with a DF of 2.5% and 38%, respectively. Mass spectra data were recorded on a LCMS-IT/TOF (Shimadzu). Laser light scattering (LLS) measurements were performed on an ALV/DLS/SLS-5022F spectrometer with a multi-τ digital time correlator (ALV/LSE-5003) and a 17 mW solid-state laser (λ = 632 nm) as the light source.

2.2 Synthesis of **TPE-2OH**

To a solution of 4-hydroxybenzophenone (3.97 g, 0.02 mol) in dry THF (80 mL) was added Zn dust (7.85 g, 0.12 mol). The mixture was stirred vigorously for a quarter of an hour to cool to 0 ^{o}C. Into the above mixture was dropwise added titanium tetrachloride (6.6 mL, 0.06 mol) and stirred in an ice water bath for 1 hour. Then it was gradually heated to reflux under argon atmosphere for 24 hours. The reaction was allowed to be cooled to room temperature and quenched with 10% K_2CO_3 aqueous solution and the newly formed precipitate was removed. The residue was extracted three times with 100 ml CH_2Cl_2, dried, filtered. After all of the solvent CH_2Cl_2 has been evaporated under reduced pressure, the target product was further purified by silica-gel column chromatography (300-400 mesh, eluent ethyl acetate / petroleum ether 1:2 vol). White solid in 53% yield. ^{1}H NMR (600 MHz, $CDCl_3$), δ (TMS, ppm): 7.13-6.98 (m, 10H), 6.91-6.85 (m, 4H), 6.59-6.54 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$), δ (TMS, ppm): 154.03, 144.28, 144.17, 139.82, 139.80, 136.79, 136.71, 132.87, 132.85, 131.51, 131.50, 127.82, 127.72, 126.38, 114.79, 114.71. MS(ESI) m/z: $[M-H]^-$ calcd $C_{26}H_{20}O_2$ 363.1391, found 363.1387.

2.3 Synthesis of **TPE-2EP**

A mixture of **TPE-2OH** (1 g, 2.74 mmol), epichlorohydrin (5.07 g, 54.8 mmol) and isopropyl alcohol (35 ml) was sequentially added into 100 mL three-necked round-bottom flask equipped with a magnetic stirrer and refluxed. Then 3.5 ml 20% sodium hydroxide aqueous solution was dropwise added into the mixture over half an hour. The reaction mixture stirred at reflux temperature under argon atmosphere for 5

hours. After cooling to room temperature, the mixture was poured into chloroform and thoroughly washed with ultrapure water till neutrality. The combined organic layer was dried over magnesium sulfate, filtered, and chloroform was removed by rotatory evaporation under reduced pressure. The obtained crude product was further purified by column chromatography over silica gel (300-400 mesh) using ethyl acetate / petroleum ether (1:3 vol) as eluent. Yellow solid in 34% yield. ^{1}H NMR (600 MHz, $CDCl_3$), δ (TMS, ppm): 7.12-7.07 (m, 6H), 7.03-7.01 (m, 4H), 6.92-6.90 (m, 4H), 6.64-6.63 (m, 4H), 4.14-4.11 (m, 2H), 3.89-3.87 (m, 2H), 3.32-3.30 (m, 2H), 2.89-2.87 (t, J = 4.2 Hz, 2H), 2.73-2.71 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$), δ (TMS, ppm): 156.98, 144.22, 139.83, 137.00, 132.69, 131.48, 127.83, 126.39, 113.81, 68.67, 50.21, 44.91. MS(ESI) m/z: [M] calcd $C_{32}H_{28}O_4$ 476.1982, found 476.1928.

2.4 Synthesis of **TPE-AN**

A mixture of **TPE-2EP** (1 g, 2.10 mmol) and phenylamine (0.1955 g, 2.10 mmol) was added into 10 mL Schlenk flask equipped with a magnetic stirrer. After degassing and recharging with argon, the solid was heated to be fused at 150 ^{o}C and kept one hour. Subsequently, the reaction mixture was heated at 110 ^{o}C by stirring for another 24 hours. After the completion of the reaction, the resulting crude product was dissolved into a minimal amount of dimethyformamide (DMF) and then precipitated with excess petroleum ether to remove the unreacted **TPE-2EP** and phenylamine. The product was isolated by filtration, vacuum dried at 65 ^{o}C over 24 hours for the use in further post-polymerization azo-coupling scheme. White powder in 78% yield. ^{1}H NMR (600 MHz, DMSO-d_6), δ (TMS, ppm): 7.12-7.08 (m, 8H), 6.97-6.93 (m, 4H),

6.86-6.82 (m, 4H), 6.71-6.67 (m, 6H), 6.59-6.51 (m, 1H), 5.33 (m, 1H), 5.15 (m, 1H), 4.01 (m, 2H), 3.83 (m, 4H), 3.68-3.66 (m, 1H), 3.55-3.53 (m, 1H), 3.43-3.40 (m, 1H), 3.30-3.27 (m, 1H). GPC: M_n = 13000 g·mol^{-1}; M_w = 25700 g·mol^{-1}; MWD = 1.98.

2.5 Synthesis of typical azo polymers **TPE-IZ-DC**

A series of azo polymers **TPE-IZ-DC** with different degrees of functionalization of azo chromophores were synthesized through a post-polymerization azo-coupling scheme. The brief procedures are as follows. To a solution of 2-amino-4,5-imidazoledicarbonitrile (0.319 g, 2.4 mmol) and 9 mL glacial acetic acid was dropwise added 0.9 mL concentrated sulfuric acid at 0 ^{o}C. Then into the above white mixture was dropwise added sodium nitrite (0.215 g, 3.12 mmol) in 0.9 mL of water to give diazonium salts of 2-amino-4,5-imidazoledicarbonitrile. A mixture of **TPE-AN** (100 mg) and 5 mL DMF was added into 25 mL round-bottom flask equipped with a magnetic stirrer and cooled to 0 ^{o}C. And then, a certain amount of diazonium salts was added dropwise into the above **TPE-AN** solution while the temperature was maintained at 0 ^{o}C. The colourless solution turned to red immediately. After being vigorously stirred overnight, the mixture was poured into excess saturated brine. The pure product **TPE-IZ-DC** with specific azo content was filtered, vacuum dried at 70 ^{o}C for 24 hours.

2.6 Preparation of the **TPE-IZ-DC** film

The substrates (quartz glass slides) were ultrasonically cleaned in sodium hydroxide concentrated solution, ultrapure water and acetone, successively. And then they were dried at 70 ^{o}C prior to use. A homogeneous solution of **TPE-IZ-DC** (50 mg) and

DMF (0.5 mL) was filtered with 0.25 μm filter. After that, it was spin-coated onto substrates with a spin speed of 1500 rpm, followed by vacuum drying at 60 ^{o}C for 24 hours.

2.7 Visible light response of the **TPE-IZ-DC** film and fluorescent pattern fabrication

TPE-IZ-DC films were vertically exposed to visible light (450 nm) at room temperature to investigate the visible light response every thirty minutes with UV-vis absorption spectrophotometer and fluorescence emission photometer. Fluorescent patterns on the spin-coating films were fabricated by irradiating with the same light source for 150 minutes through a photomask. Fluorescence images of the above patterns were recorded under a 365 nm UV lamp.

3 Results and Discussion

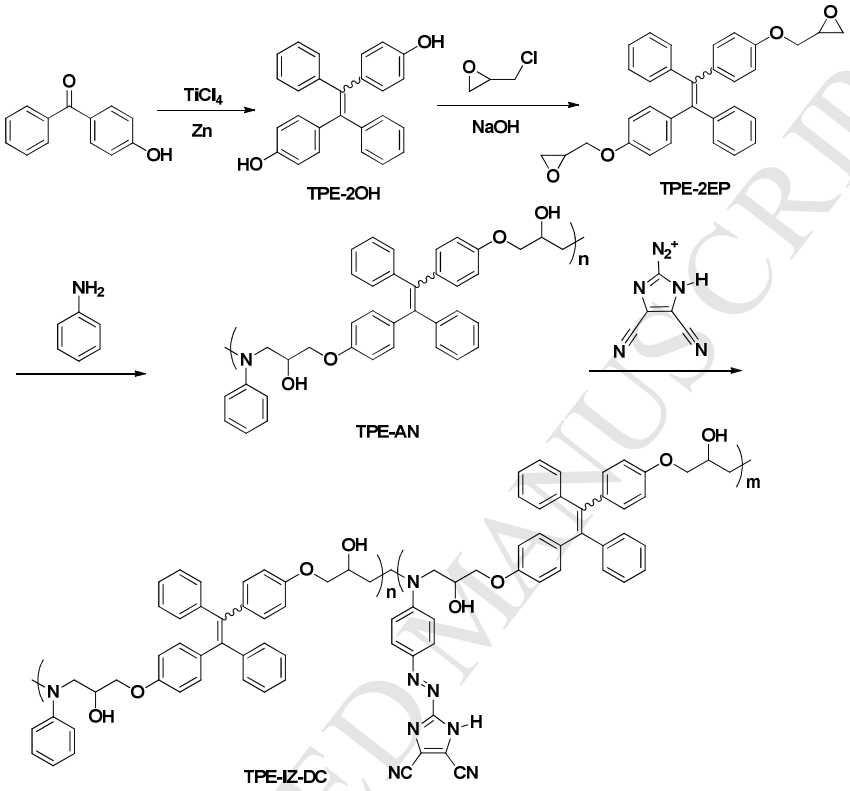
3.1 Synthesis of azo caged AIE polymers **TPE-IZ-DC**

A set of visible light triggered AIE polymers **TPE-IZ-DC** containing different mole fractions of azo groups was achieved and the synthetic route of target polymers **TPE-IZ-DC** was illustrated in Scheme 1. According to the molecular design, synthesis of azo caged polymers **TPE-IZ-DC** was facile with a four-step synthetic approach. 1,2-bis(4-hydroxyphenyl)-1,2-diphenylethene (**TPE-2OH**), an iconic AIEgen, was in a one-step preparation starting from 4-hydroxybenzophenone through a McMurry coupling reaction. The TPE based epoxy compound (**TPE-2EP**) was prepared by incorporating epoxy groups into **TPE-2OH**. Then synthesis of the precursor polymer **TPE-AN** was done by the polycondensation of difunctional

epoxide and phenylamine monomers at relatively low temperature. The molecular weight and molecular weight distribution of the linear polymer **TPE-AN** were determined by GPC method and satisfying results were presented in Fig.S7. The number-average molecular weight and relative molecular mass distribution of the precursor polymer **TPE-AN** were 13000 g·mol^{-1} and 1.98, respectively. Finally, the target polymers **TPE-IZ-DC** were synthesized by the post-polymerization azo-coupling reaction between polymer **TPE-AN** and diazonium salts. The reaction proceeded efficiently as expected and the final products **TPE-IZ-DC** displayed glorious solubility in common organic solvents. Further details could be found in the Experimental Section and Supporting Information.

^{1}H NMR and ^{13}C NMR spectra suggested successful synthesis of all compounds, which were included in the Supporting Information (Fig.S1 - 6). As could be seen from ^{1}H NMR spectra of **TPE-AN** and **TPE-IZ-DC** (Fig.S5 and Fig.S6), the incorporation of 2-phenylazo-4, 5-dicyanoimidazole parts has been identified by combining information as follows. First, peak areas of protons at para-position of anilino groups whose chemical shifts are around 6.55 ppm relatively reduced in the whole low magnetic field corresponding to all aromatic rings. Second, the signal newly appeared at 7.75 ppm was attributed to benzenoid protons at meta positions of amino segments, which was caused by formation of electron-withdrawing azo groups. We defined that degrees of functionalization (DFs) of azo chromophores were molar ratios between 2-phenylazo-4, 5-dicyanoimidazole groups in the final polymer chain and anilino pendants of the precursor polymer **TPE-AN**. Benefiting from efficient azo

coupling reaction, DFs could be controlled by selecting suitable amount of diazonium salts. The DFs have been estimated from ^{1}H NMR by comparing peak areas of protons of azo units and the others in the aromatic region.



Scheme 1. Synthetic route of azo caged AIE polymers **TPE-IZ-DC**.

3.2 AIE effect of the precursor polymer **TPE-AN**

To explore AIE activity of the precursor polymer **TPE-AN**, fluorescence emission spectra were recorded in different ratios of water-DMF mixtures (Fig.1a). DMF was selected as the good solvent because **TPE-AN** could be resolved adequately and soluble with the poor solvent water at any proportion. When a little water was added to the DMF solution of **TPE-AN** (water proportion is lower than 10%), it was not emissive. The two spectra (0% and 10%) seemed to overlap each other. With

increasing the water percentage to 40%, blue fluorescence sharply enhanced, which resulted from vast aggregation formation. After that, the maximum intensity remained the same. The depict changes in fluorescence relative peak intensity (I/I_0) were shown in Fig.1b. The relative intensity ratio (water contents are 90% and 0%, respectively) was as high as 155, thus testifying its AIE nature. In the light of the restriction of intramolecular motion (RIM) mechanism, aggregates of hydrophobic fluorescent materials were increased with increasing poor solvent water. The aggregation of the polymer was confirmed by Tyndall phenomenon and LLS. As water content was 90%, an obvious Tyndall phenomenon emerged (Fig.S8), comparing with that in pure DMF. LLS results also confirmed the formation of **TPE-AN** aggregates (Fig.S9). As water content reach 98%, suspended solids were seen visually. As a result, **TPE-AN** could be highly emissive in the aggregated state with maximum emission wavelength of 472 nm. Similar results were also found in the solid film of **TPE-AN** (Fig.S10). The intense emission of the film also exhibited typical AIE feature. In addition, the blueshift of emission peak position from aggregates to the solid film was about 5 nm.

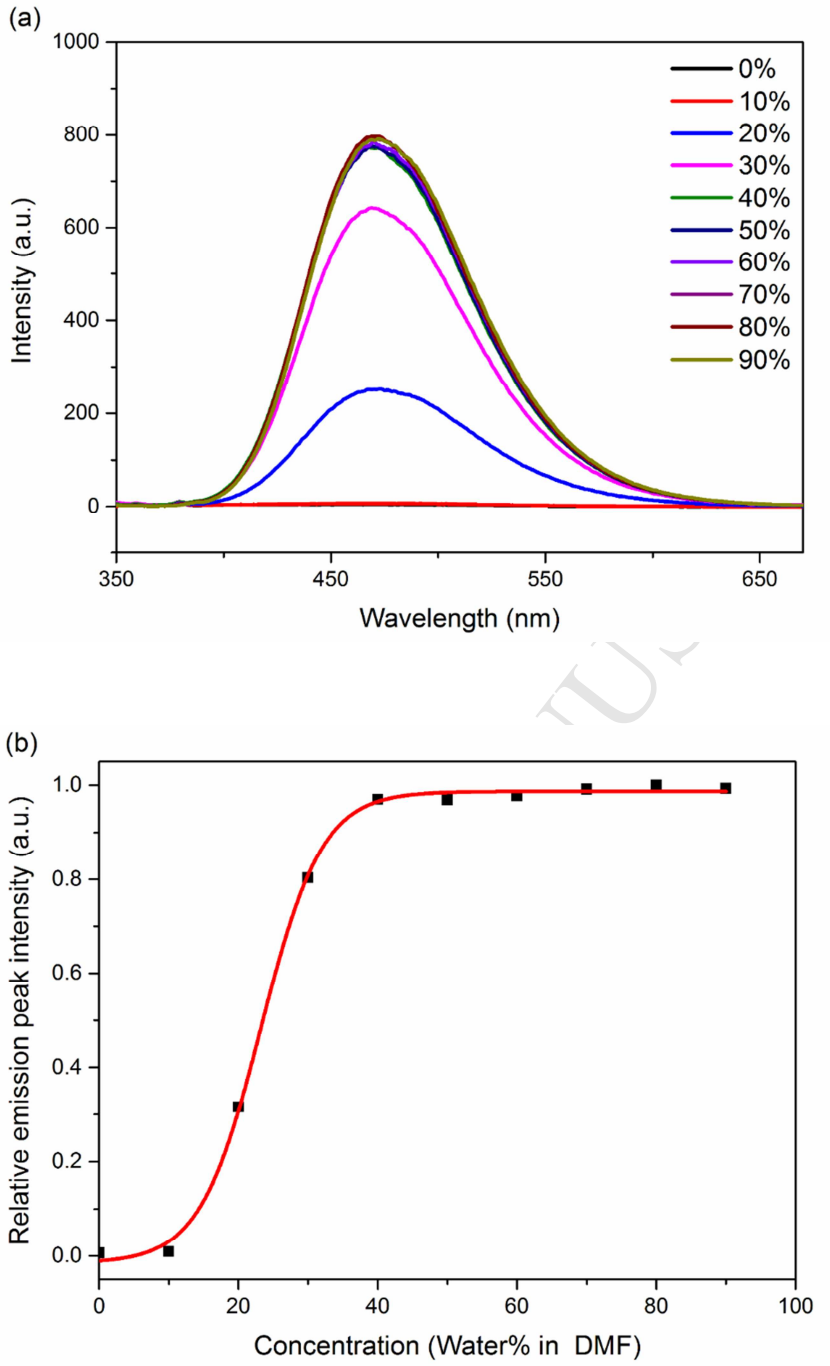
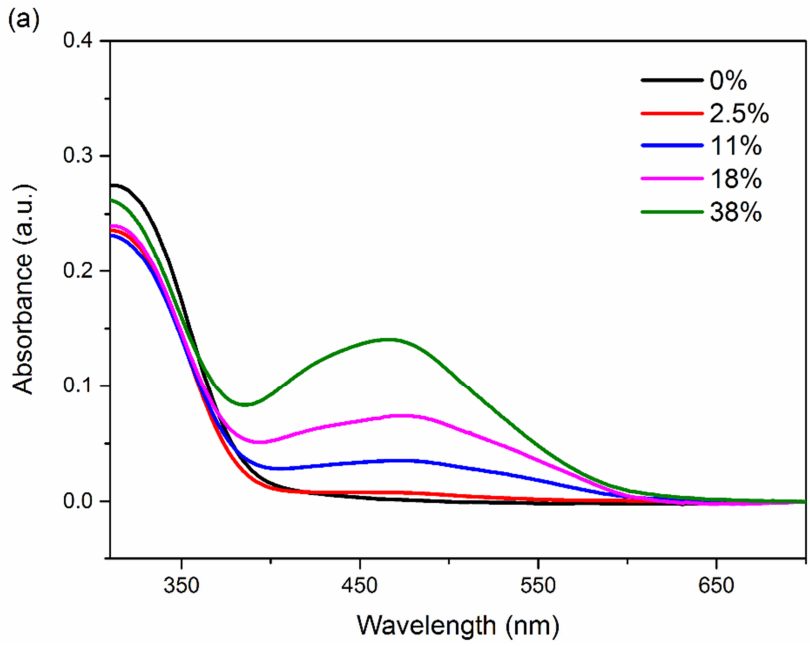


Fig. 1. (a) Changes in fluorescence emission spectra of dilute solutions of **TPE-AN** in water-DMF mixtures with different water fractions. (b) Correlation between the relative emission peak intensity (I/I_0) at 472 nm of **TPE-AN** in water-DMF mixtures and water percentage. Concentration of **TPE-AN**: 0.01 mg/mL; excitation wavelength: 340 nm.

3.3 The relationship between absorption intensity of **TPE-IZ-DC** and

DFs

Besides fluorescence spectrometry, UV-vis absorption spectra of the polymer **TPE-AN** was also recorded to study its optical property, corresponding to **TPE-IZ-DC** with 0% DF, the black line in Fig.2a. No absorption peaks appeared in the visible region for **TPE-AN**. For imidazole-containing polymers **TPE-IZ-DC** with other DFs, they exhibited significant absorption ranging from 370 nm to 600 nm in line with expectations, which also confirmed the introduction of heteroaromatic azo moieties into polymer chains of **TPE-AN** successfully. The absorption maxima appearing at 466 nm resulted from π-π^* electron transition of pseudo-stilbene type azo chromophores. Fig.2b showed that the absorption maxima of **TPE-IZ-DC** in water-DMF mixtures with 90% water fraction increased with the DFs.



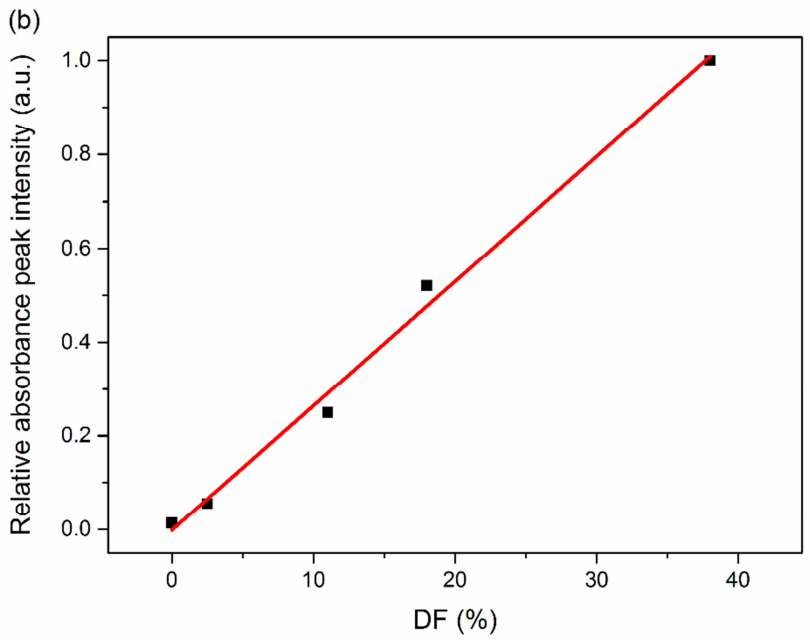


Fig. 2. (a) Changes in UV-vis absorption spectra of dilute solutions of **TPE-IZ-DC** with different DFs in water-DMF mixtures (90% water fraction). (b) Correlation between the relative absorption peak intensity (I/I_0) at 466 nm of **TPE-IZ-DC** and DFs in water-DMF mixtures (90% water fraction). Concentration of **TPE-IZ-DC**: 0.01 mg/mL.

3.4 Fluorescence quenching effect of **TPE-IZ-DC**

Since the absorption band of azo units almost covered all of emission region of TPE components proved in Fig.S11, fluorescence resonance energy transfer process would work and fluorescence of the polymers **TPE-IZ-DC** would be faded (Fig.3a). To verify the quenching efficiency, the influence of azo contents on fluorescence intensity was investigated. Fig.3b gives the curve of relative emission peak intensity at 472 nm of azo-containing polymers **TPE-IZ-DC** in water-DMF mixtures with 90% water fraction vs. DFs. It turned out as expected that the maximum value of emission intensity apparently decreased almost one order of magnitude by only 2.5% azo contents, implying excellent quenching efficiency of fluorescence.

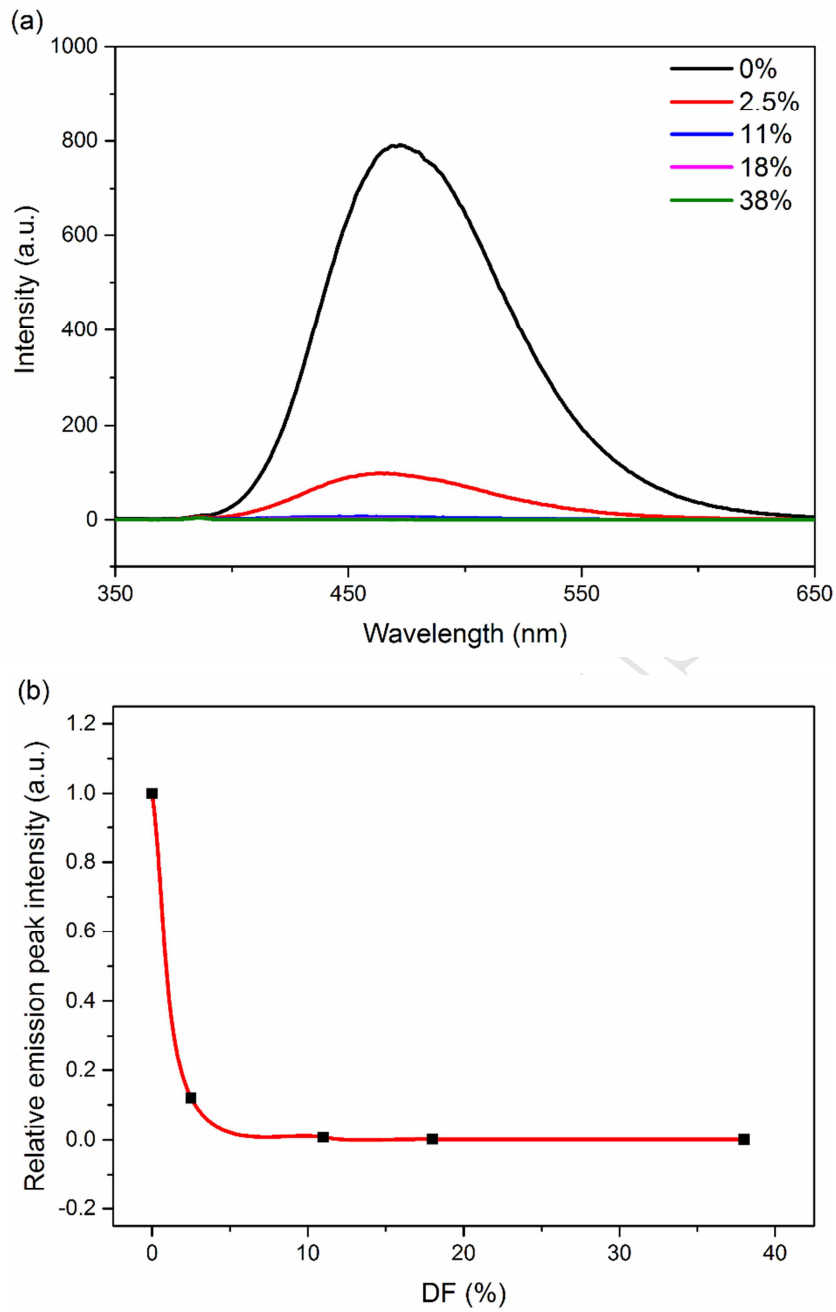


Fig. 3. (a) Changes in fluorescence emission spectra of dilute solutions of **TPE-IZ-DC** with different DFs in water-DMF mixtures (90% water fraction). (b) Correlation between the relative emission peak intensity (I/I_0) at 472 nm of **TPE-IZ-DC** in water-DMF mixtures (90% water fraction) and DF. Concentration of **TPE-IZ-DC**: 0.01 mg/mL; excitation wavelength: 340 nm.

3.5 Visible light response of the **TPE-IZ-DC** film

The epoxy based polymers **TPE-IZ-DC** had satisfactory thermal stability, good

transparence and favourable film-forming property. On the grounds of these, **TPE-IZ-DC** films were obtained using the spin-coating method and visible light response over different durations of light irradiation was measured by UV-vis absorption spectra at first, as described in Fig.4. Given the convenience of photobleaching, azo amount in the polymer was set at 2.5%. It has been demonstrated that absorption maxima at 469 nm of the **TPE-IZ-DC** film reduced prominently under continuous irradiation at the wavelength of 450 nm. Within only 30 minutes, absorption intensity of residual azo functional groups was rapidly lost approximately 50%. After illumination for 150 minutes, it was only ninth of the originally state, indicating a sensitive response to visible light as well as a high signal-to-noise ratio.

For pseudo-stilbene type azo chromophores, cis state is unstable and will rapidly relax to the trans form. As shown in Fig.5, the absorption intensity at 469 nm from **TPE-IZ-DC** decreased with the increase of irradiation time and the absorption peak of **TPE-IZ-DC** upon irradiation was not recoverable at all even though we left the film in the dark for a long time or heated. Besides, the irreversible color change of the film was easily seen from red to almost colorless with the naked eye. It should be considered that azo chromophores ultimately disappeared by photobleaching instead of photoisomerization. FTIR spectra were also used to prove this photobleaching process. As presented in Fig.S12, several characteristic peaks in FTIR spectra assigned to absorption bands of **TPE-IZ-DC** (DF = 38%) decreased apparently, which could be also postulated the photobleaching of azo chromophores after exposure to 450 nm light.

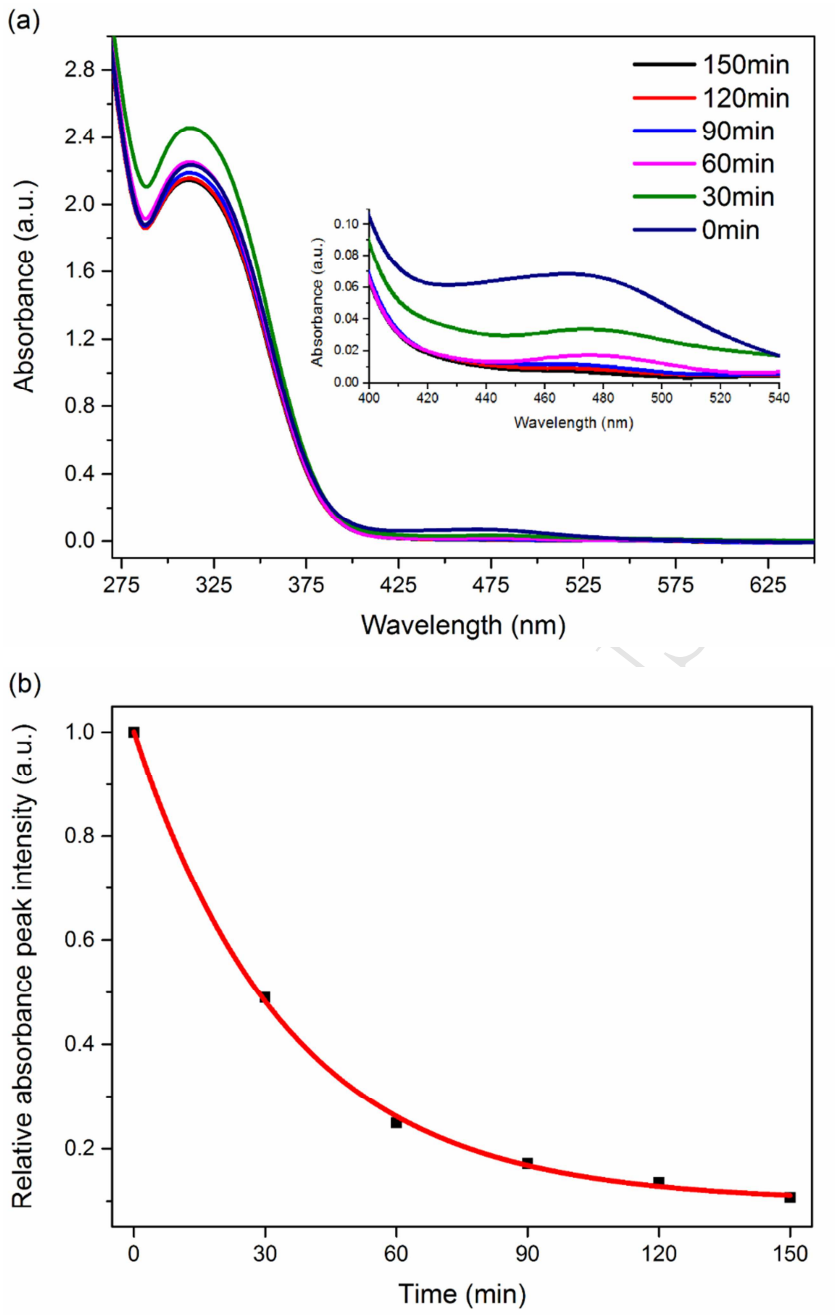
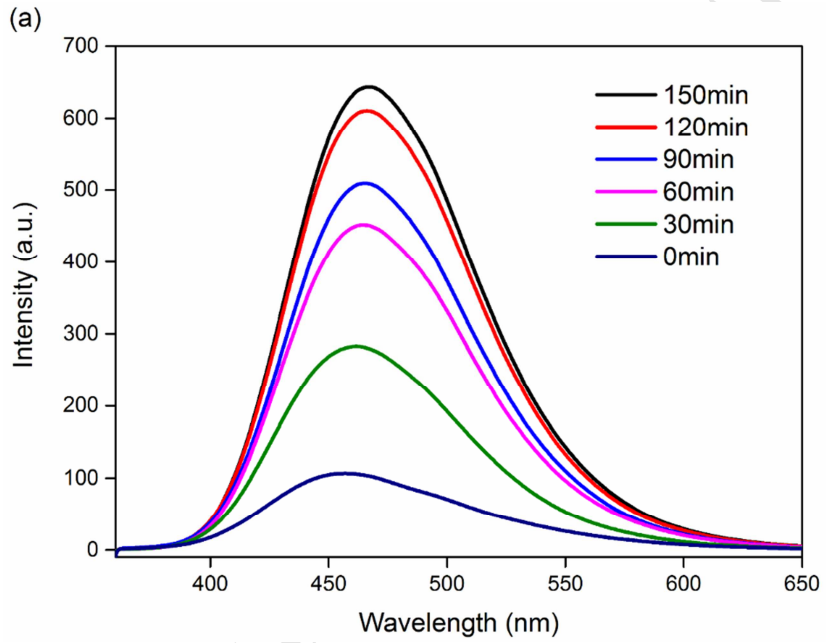


Fig. 4. (a) Time dependent absorption changes of the **TPE-IZ-DC** film irradiating with visible light at the wavelength of 450 nm. (b) Correlation between the relative absorption peak intensity (I/I_0) at 469 nm of the **TPE-IZ-DC** film and exposure time.

As expected, changes of absorption intensity of the **TPE-IZ-DC** film greatly affected its fluorescence performance. Fig.5 clarified the blue fluorescence recovery after photobleaching by the same process of irradiation with visible light monitored by

fluorescence emission spectra. It could be found that characteristic emission definitely increased as exposure time increased, in accordance with the UV-vis absorption spectra. After irradiating the film with the same light source for 150 minutes, photobleaching caused an increase in maximum emission intensity at 467 nm by more than six times since fluorescence resonance energy transfer process did not work anymore.



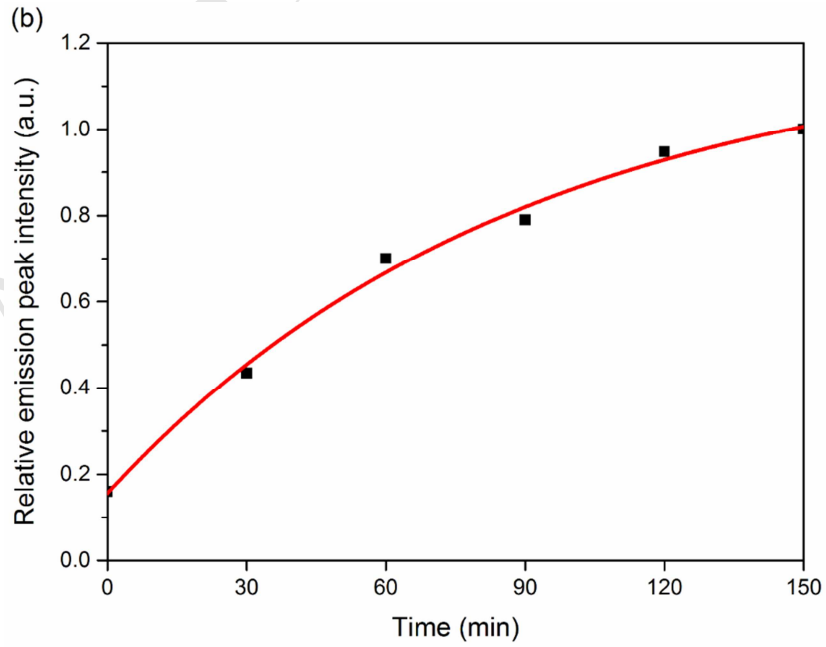


Fig. 5. (a) Time dependent fluorescence intensity changes of the **TPE-IZ-DC** film irradiating with visible light at the wavelength of 450 nm. (b) Correlation between emission peak intensity (I/I_0) at 467 nm of the **TPE-IZ-DC** film and exposure time.

3.6 The fluorescent pattern fabrication

The above results that visible light possessed the ability to efficiently blench azo chromophores and fluorescent emission was enhanced concomitantly impelled us to make an attempt at fabricating fluorescent patterns by the mask method. These observed patterns on the basis of photobleaching were transcribed from designed photomasks. The feasibility and simplicity of the valid and powerful technique were proved with an example. The mask was positioned onto the **TPE-IZ-DC** film, and then the film was exposed to visible light using 450 nm light source for 150 minutes. It was satisfying that the fluorescence of illumination field was brighter than its surroundings. The letter pattern "FL" as a representative emerged as displayed in Fig.6. After further irradiation, the pattern was almost completely erased. Due to this successful demonstration, large-area or/and complicated patterns would be easily tailored when films of the desired size and corresponding masks were applied, making **TPE-IZ-DC** potentially suitable for optical information storage materials, antifake materials and other application areas.

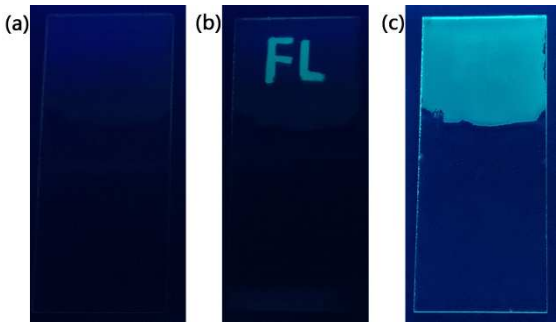


Fig. 6. The photographs of a piece of untreated film (a), the fluorescent pattern fabricated on exposed areas by visible light irradiation process (b) and the pattern erasure after removing the mask under continuous irradiation (c) taken under a 365 nm UV lamp.

4 Conclusions

Azo caged aggregation-induced emission polymers were synthesized and their fluorescence performance activated by visible light was fully characterized. The effect of azo contents on fluorescence intensity was studied, which revealed that only a small amount of imidazole-type azo groups could totally cage the strong AIE fluorescence of the polymers due to the fluorescence resonance energy transfer process. Irradiated with visible light, azo chromophores could be photo bleached, leading to remarkable recovery of the blue fluorescence. Visible light induced fluorescent patterns have been fabricated and erased, which indicated that the prepared azo caged AIE Polymers could especially competitive in the material design of anti-counterfeiting and optical information storage.

Declaration of Interest

The authors declare no competing financial interest.

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References

[1] Bae J, McNamara LE, Nael MA, Mahdi F, Doerksen RJ, Bidwell III GL, et al.

Nitroreductase-triggered activation of a novel caged fluorescent probe obtained from methylene blue. Chem. Commun. 2015;51(64):12787-90.

[2] Wei P, Li B, de Leon A, Pentzer E. Beyond binary: optical data storage with 0, 1, 2, and 3 in polymer films. J. Mater. Chem. C. 2017;5(23):5780-6.

[3] Belov VN, Wurm CA, Boyarskiy VP, Jakobs S, Hell SW. Rhodamines NN: A Novel Class of Caged Fluorescent Dyes. Angew. Chem. Int. Ed. 2010;49(20):3520-3.

[4] Chen S, Bian Q, Wang P, Zheng X, Lv L, Dang Z, et al. Photo, pH and redox multi-responsive nanogels for drug delivery and fluorescence cell imaging. Polym. Chem. 2017;8(39):6150-7.

[5] Luo J, Xie Z, Lam JWY, Cheng L, Chen H, Qiu C, et al. Aggregation-induced emission of 1-methyl-1,2,3,4,5-pentaphenylsilole. Chem. Commun. 2001(18):1740-1.

[6] Mei J, Leung NL, Kwok RT, Lam JW, Tang BZ. Aggregation-induced emission: together we shine, united we soar! Chem. Rev. 2015;115(21):11718-940.

[7] Wu Z, Pan K, Mo S, Wang B, Zhao X, Yin M. Tetraphenylethene-Induced Free Volumes for the Isomerization of Spiropyran toward Multifunctional Materials in the Solid State. ACS Appl. Mater. Interfaces. 2018;10(36):30879-86.

[8] Yang B, Zhang X, Zhang X, Huang Z, Wei Y, Tao L. Fabrication of aggregation-induced emission based fluorescent nanoparticles and their biological imaging application: recent progress and perspectives. Mater. Today. 2016;19(5):284-91.

[9] Mei J, Huang Y, Tian H. Progress and Trends in AIE-Based Bioprobes: A Brief Overview. ACS Appl. Mater. Interfaces. 2018;10(15):12217-61.

[10] Gao H, Zhang X, Chen C, Li K, Ding D. Unity Makes Strength: How Aggregation-Induced Emission Luminogens Advance the Biomedical Field. Adv. Biosys. 2018;2(9):1800074.

[11] Zhao Q, Chen Y, Liu Y. A polysaccharide/tetraphenylethylene-mediated blue-light emissive and injectable supramolecular hydrogel. Chin. Chem. Lett. 2018;29(1):84-6.

[12] Yang Z, Chi Z, Mao Z, Zhang Y, Liu S, Zhao J, et al. Recent advances in mechano-responsive luminescence of tetraphenylethylene derivatives with aggregation-induced emission properties. Mater. Chem. Front. 2018;2(5):861-90.

[13] Wang J, Mei J, Hu R, Sun JZ, Qin A, Tang BZ. Click Synthesis, Aggregation-Induced Emission, E/Z Isomerization, Self-Organization, and Multiple Chromisms of Pure Stereoisomers of a Tetraphenylethene-Cored Luminogen. J. Am. Chem. Soc. 2012;134(24):9956-66.

[14] Wu W, Ye S, Huang L, Xiao L, Fu Y, Huang Q, et al. A conjugated hyperbranched polymer constructed from carbazole and tetraphenylethylene moieties: convenient synthesis through one-pot "A2 + B4" Suzuki polymerization, aggregation-induced enhanced emission, and application as explosive chemosensors and PLEDs. J. Mater. Chem. 2012;22(13):6374-82.

[15] Luo Q, Cao F, Xiong C, Dou Q, Qu D-H. Hybrid cis/trans Tetra-arylethenes with Switchable Aggregation-Induced Emission (AIE) and Reversible Photochromism in the Solution, PMMA Film, Solid Powder, and Single Crystal. J. Org. Chem. 2017;82(20):10960-7.

[16] Ozturk S, Atilgan S. A tetraphenylethene based polarity dependent turn-on fluorescence strategy for selective and sensitive detection of Hg2+ in aqueous medium and in living cells. Tetrahedron Lett. 2014;55(1):70-3.

[17] Yuan Y, Zhang R, Cheng X, Xu S, Liu B. A FRET probe with AIEgen as the energy quencher: dual signal turn-on for self-validated caspase detection. Chem. Sci. 2016;7(7):4245-50.

[18] Gu K, Qiu W, Guo Z, Yan C, Zhu S, Yao D, et al. An enzyme-activatable probe liberating AIEgens: on-site sensing and long-term tracking of β-galactosidase in ovarian cancer cells. Chem.

Sci. 2019;10(2):398-405.

[19] Peng L, Zheng Y, Wang X, Tong A, Xiang Y. Photoactivatable Aggregation-Induced Emission Fluorophores with Multiple-Color Fluorescence and Wavelength-Selective Activation. Chem. - Eur. J. 2015;21(11):4326-32.

[20] Wang L, Li Y, You X, Xu K, Feng Q, Wang J, et al. An erasable photo-patterning material based on a specially designed 4-(1,2,2-triphenylvinyl)aniline salicylaldehyde hydrazone aggregation-induced emission (AIE) molecule. J. Mater. Chem. C. 2017;5(1):65-72.

[21] Yu CYY, Kwok RTK, Mei J, Hong Y, Chen S, Lam JWY, et al. A tetraphenylethene-based caged compound: synthesis, properties and applications. Chem. Commun. 2014;50(60):8134-6.

[22] Wu B, Xue T, Wang W, Li S, Shen J, He Y. Visible light triggered aggregation-induced emission switching with a donor–acceptor Stenhouse adduct. J. Mater. Chem. C. 2018;6(31):8538-45.

[23] Chevalier A, Renard P-Y, Romieu A. Azo-Based Fluorogenic Probes for Biosensing and Bioimaging: Recent Advances and Upcoming Challenges. Chem. - Asian J. 2017;12(16):2008-28.

[24] Zhang J, Hu T, Liu Y, Ma Y, Dong J, Xu L, et al. Photoswitched Protein Adsorption on Electrostatically Self-Assembled Azobenzene Films. ChemPhysChem. 2012;13(11):2671-5.

[25] Wang D, Wang X. Amphiphilic azo polymers: Molecular engineering, self-assembly and photoresponsive properties. Prog. Polym. Sci. 2013;38(2):271-301.

[26] Ren H, Chen D, Shi Y, Yu H, Fu Z, Yang W. Charged End-Group Terminated Poly(N-isopropylacrylamide)-b-poly(carboxylic azo) with Unusual Thermoresponsive Behaviors. Macromolecules. 2018;51(9):3290-8.

[27] Wang G, Zhao XL, Zhao Y. Synthesis of azobenzene-containing liquid crystalline gelator for

use in liquid crystal gels. Chin. Chem. Lett. 2008;19(5):521-4.

[28] Lv J-a, Liu Y, Wei J, Chen E, Qin L, Yu Y. Photocontrol of fluid slugs in liquid crystal polymer microactuators. Nature. 2016;537:179.

[29] Wang J, Wang S, Zhou Y, Wang X, He Y. Fast Photoinduced Large Deformation of Colloidal Spheres from a Novel 4-arm Azobenzene Compound. ACS Appl. Mater. Interfaces. 2015;7(30):16889-95.

[30] Wang J, Wu B, Li S, Sinawang G, Wang X, He Y. Synthesis and Characterization of Photoprocessable Lignin-Based Azo Polymer. ACS Sustainable Chem. Eng. 2016;4(7):4036-42.

[31] Yu X, Chen H, Shi X, Albouy P-A, Guo J, Hu J, et al. Liquid crystal gelators with photo-responsive and AIE properties. Mater. Chem. Front. 2018;2(12):2245-53.

[32] Wang J, Wu B, Li S, He Y. NIR light and enzyme dual stimuli-responsive amphiphilic diblock copolymer assemblies. J. Polym. Sci., Part A: Polym. Chem. 2017;55(15):2450-7.

[33] Li S, Wang J, Shen J, Wu B, He Y. Azo Coupling Reaction Induced Macromolecular Self-Assembly in Aqueous Solution. ACS Macro Lett. 2018;7(4):437-41.

[34] Wu B, Wang W, Wang J, Li S, He Y. Redox triggered aggregation induced emission (AIE) polymers with azobenzene pendants. Dyes and Pigments. 2018;157:290-7.

[35] Ye G, Qu X, Wang X, Bai Y, He Y, Wu B, et al. Epoxy-based Polymer Containing Imidazole-type Azo Chromophores for Integrated Waveguide Applications. J. Macromol. Sci., Part A: Pure Appl.Chem. 2010;47(12):1167-71.

Highlights

1. Imidazole-type azo caged aggregation-induced emission polymers were synthesized.

2. Only a small amount of imidazole-type azo groups could totally cage the strong AIE fluorescence of the polymers.

3. Imidazole-type azo chromophores of the polymers could be photo bleached with visible light, leading to activating their fluorescence performance.

4. Visible light induced fluorescent patterns have been easily fabricated and erased.