Synthesis, properties, and applications of poly(ethylene glycol)-decorated tetraphenylethenes†

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Non-charged, water soluble poly(ethylene glycol) (PEG)-decorated tetraphenylethenes (TPEs) with different polymer chain numbers are synthesized in high yields by azide–alkyne cycloaddition. Their aggregation and thermosensitive behaviours are investigated by means of fluorescence spectroscopy, transmission electron microscopy (TEM), zeta potential and dynamic mechanical analyses. All the luminogens are non-emissive in solutions, but emit intensely when aggregated in aqueous solutions, or forming micelles, demonstrating a phenomenon of aggregation-induced emission. The TPE derivative (**1**) carrying one PEG chain forms hydrogels in the THF–water mixture depending on the concentration, water fraction and temperature. All the luminogens are thermosensitive, with their cloud point being tunable by varying the solvent composition and their hydrophilicity. Luminogen **1** is biocompatible and can function as a fluorescent visualizer for intracellular imaging.

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Introduction

Since the observation of the phenomenon of aggregation-induced emission (AIE) in a series of propeller-shaped molecules, more than 100 research groups in the world are now conducting AIE research.^{1–3} AIE luminogens are weakly emissive or non-fluorescent in solutions but are induced to emit efficiently by aggregate formation.¹ Such a characteristic enables them to find potential high-tech applications as chemosensors, bioprobes, immunoassay markers, stimuli-responsive materials and solid-state emitters.^{1–3} Tetraphenylethene (TPE) is a well-known AIE luminogen and enjoys the advantages of facile synthesis, efficient quantum yield in the solid state and high chemical and photo-stabilities. However, its hydrophobic nature greatly limits its biological applications. Physical mixing with water-soluble materials such as bovine serum albumin (BSA) or surfactants help improve its solubility or dispersion in aqueous medium.^{2,3} Whereas this method enjoys the advantage of easy preparation, it tends to reduce the mechanical properties of the dye molecule and is difficult for quantification.

Chemical incorporation of positively and negatively-charged groups is found to be effective to solve this problem. For example, TPE carrying two or four ammonium groups is water-soluble and emits weakly in aqueous solution. Its fluorescence is enhanced dramatically upon binding with calf thymus DNA or bovine serum albumin (BSA), making it to work as a fluorescence “turn-on” sensor for sensitive detection of biomolecules.^{4–6} Electrostatic attraction or hydrophobic interaction of the TPE derivative with DNA and BSA, respectively, restricts the intramolecular rotation of the dye molecule, which blocks the nonradiative relaxation channel and hence enhances the light emission.

The thermal properties of polymers with a lower critical solution temperature (LCST) have been investigated extensively. These polymers possess both hydrophobic and hydrophilic groups and the balance between the two determines their LCST.^{7,8} They are soluble or swell below the LCST in aqueous medium, but precipitate or shrink at temperature above the LCST. This property enables them to find possible applications in tissue engineering and controlled drug delivery. An example is represented by poly(*N*-isopropylacrylamide) (PNIPAM), whose temperature-induced conformational change can be sensitively followed by its functionalization with TPE.⁹ Besides PNIPAM, poly(ethylene glycol) (PEG) is a well-known water-soluble polymer and becomes thermosensitive when melded with hydrophobic moieties.^{10,11} PEG-containing amphiphilic macromolecules, on the other hand, can facilely self-assemble into micelles in aqueous solution. Biocompatible PEG-containing polymers are biomolecules approved by U.S. Food and Drug Administration, and are widely used to enhance the water solubility/dispersibility and biocompatibility of quantum dots, superparamagnetic iron

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oxide nanoparticles and drug carrying polymers for bioimaging and drug delivery.^{12,13} PEG has also been reported to have non-specific interactions with biological substances to avoid immuno response and hence enhance non-specific cellular uptake. These features thus make it useful to improve the hydrophilicity of TPE and meanwhile impart the luminogen with thermosensitivity, self-assembly property and good biocompatibility. However, such a hybrid is rarely reported.¹⁰

In this work, we explored such a possibility and synthesized water soluble, non-charged TPE derivatives with different PEG chain numbers *via* azide-alkyne cycloaddition. We found that TPE carrying one PEG chain (**1**) formed gels in the THF-H₂O mixture, depending on the concentration, water fraction and temperature. All the dye molecules form micelles above the critical micelle concentration (CMC) and are thermosensitive. Luminogen **1** is biocompatible and can selectively image the cytoplasm of living cells.

Results and discussion

Synthesis and characterization

The PEG-decorated TPEs (**1–3**) were synthesized according to the synthetic routes shown in Scheme 1. PEG 600 with two hydroxy end groups was mono-tosylated by *p*-toluenesulfonyl chloride to afford **5**, which was further reacted with sodium azide to furnish **6**. Azide-alkyne cycloaddition of **6** with ethynyl-functionalized TPEs **7–9**, respectively, catalyzed by copper(i) bromide in the presence of PMDETA finally gave the desirable products **1–3** in high yields. All the compounds were characterized by standard spectroscopic methods and gave satisfactory analysis data corresponding to their molecular structures. For example, the IR spectrum of **6** shows a strong absorption band associated with the azide stretching vibration at 2107 cm⁻¹, which disappears upon its click reaction with **7** (Fig. 1A). Similarly, the C≡C-H and C≡C stretching vibrations of **7** occur at 3277 and 2108 cm⁻¹, which become invisible in the spectrum of **1**. All these suggest that the PEG chain has been successfully conjugated to the TPE core.

Scheme 1 Synthesis of poly(ethylene glycol)-decorated tetraphenylethenes *via* azide-alkyne cycloaddition.

Fig. 1 IR spectra of (A) **6**, (B) **7** and (C) **1**.

Similar results are obtained from the NMR analyses. The methylene protons (a) next to the azide group of **6** and acetylene proton (e) of **7** resonate at δ 3.28 and 3.02, respectively, which shift to δ 4.59 (a') and 8.32 (e') after the click reaction due to the formation of the triazole ring in **1** (Fig. 2). On the other hand, the spectrum of **1** shows no acetylene carbon resonances of **7** at δ 76.8 and 83.1 (Fig. S1 in the ESI†).¹⁴ New peaks emerge at the aromatic absorption region due to the cyclization of the azide group of **6** with the triple bond of **7** to form triazole rings in **1**.

Aggregation and micellization

Fig. 3A shows the UV spectra of **1–3** in THF solutions. The absorption maximum of **1** is located at 350 nm, which is 50 nm red-shifted from that of unsubstituted TPE due to the electronic

Fig. 2 ¹H NMR spectra of (A) **6** and (B) **7** in CDCl₃, and (C) **1** in (CD₃)₂CO.

Fig. 3 (A) UV spectra of THF solutions of 1–3. Concentration: 0.02 mg mL⁻¹. (B) PL spectra of 1 in THF and THF–H₂O mixtures with different water fractions (*f_w*). Concentration: 0.2 mg mL⁻¹; excitation wavelength: 350 nm. (C) Plot of the relative PL intensity (*I/I₀*) versus the composition of the THF–H₂O mixtures of 1–3. Concentration (mg mL⁻¹): 0.2 (1) and 3 (2 and 3). Excitation wavelength: 360 nm (2) and 370 nm (3). Inset: an enlarged spectrum of 3.

communication between the TPE core and the triazole ring. Increasing the number of triazole ring connected to the TPE core further red-shifts the UV spectrum: the absorption maximum of 2 and 3 occurs at 360 nm and 370 nm, respectively. The dilute THF solution of 1 emits almost no light upon photoexcitation (Fig. 3B). The emission is still weak when less than 70% of water is added into the solution. Afterwards, it rises swiftly. At 95% water content, the PL intensity is 233-fold higher than that in pure THF solution. Since 1 possesses a hydrophobic TPE unit, its molecules should aggregate in aqueous solution with a large amount of water. Clearly, 1 inherits the property of TPE and is AIE-active. A similar phenomenon was also observed in 2 and 3 but the extent of emission enhancement upon aggregate formation is much less than that in 1. For example, even at 100% water content or pure aqueous solution, the PL intensity of 2 and 3 increases only merely

175- and 8.5-fold, respectively. This is understandable as luminogens 2 and 3 contain more hydrophilic PEG chains and hence should possess higher solubility in aqueous solutions. Aggregates are thus less likely to be formed, thus resulting in a weak AIE effect and hence emission.

To study the micellization behaviours of the luminogens, the PL of their solutions with different concentrations was investigated at room temperature. Since the solubility of 1 in water is low, study on its micellization and gelation properties is performed in the THF–water mixture. The PL intensity of 1, for example, increases with increasing the solution concentration without causing any spectral change (Fig. 4A). The CMC can be calculated as the intersection point from the plot of relative PL intensity (*I/I₀*) against the logarithm solution concentration (Fig. 4B) and is determined to be 0.1, 0.4, and 0.6 mg mL⁻¹ for 1, 2 and 3, respectively. It is noticeable that the CMC value increases with the number of PEG chains, suggesting that the luminogen becomes more hydrophilic when carrying more PEG chains. Gelation was observed at a concentration of above 5 mg mL⁻¹ in 1, which will be discussed in the next section.

Zeta potential analysis of THF–water mixtures (1 : 9 or 0 : 10 v/v) of 1–3 with a concentration of 1 or 3 mg mL⁻¹ reveals particle sizes of 220.0, 85.7 and 55.6 nm with broad polydispersity of 0.3–0.4, respectively (Fig. 5). On the other hand, the TEM image of 1 shows spherical particles with diameters of ~150 nm (Fig. 6). All these suggest the formation of micelles with an apolar TPE unit inside and hydrophilic PEG chains pointing to the medium. Below CMC, the luminogens are molecularly dissolved in the medium and shows no emission. Increasing the concentration above CMC induces the micelle formation and aggregates the TPE core, thus making the luminogens highly emissive.

Sol-gel transition and thermosensitivity

Supramolecular gels have attracted great interest for their elegant architectures and potential high-tech applications in controlled drug release, template synthesis and biomimetics. To study the complicated gelator–gelator and gelator–solvent interactions, and the sol–gel transition process, various detection techniques such

Fig. 4 (A) PL spectra of 1 in THF–H₂O mixtures (1 : 9 by volume) with different concentrations at room temperature. Inset: photographs of THF–H₂O mixtures (1 : 9 by volume) of 1 with different concentrations taken under 365 nm UV irradiation. (B) Plots of relative intensity (*I/I₀*) versus the logarithm concentration of 1 in the THF–H₂O mixture (1 : 9 by volume) and 2 and 3 in water.

Fig. 5 Particle sizes of aggregates of (A) **1** formed in the THF–H₂O mixture (1 : 9 by volume) and (B) **2** and (C) **3** formed in water. Concentration (mg mL⁻¹): **1** (1) and **3** (2 and 3). Abbreviation: dm = mean diameter, PD = polydispersity.

Fig. 6 TEM micrographs of **1** in the THF–H₂O mixture (1 : 9 v/v) at different magnifications. Concentration: 1 mg mL⁻¹.

as optical observation (transmittance and dropping ball methods) and thermal analysis have been developed. These methods, however, involve the use of bulky machines and measure a general outcome of samples, losing a lot of transition details. Fluorescence-based methods, on the other hand, enjoy the advantage of high sensitivity but are rarely utilized in studying the sol–gel transition, presumably due to the aggregation-induced quenching effect observed in some conventional fluorophores. However, the efficient emission of AIE luminogens in the aggregated state makes them promising for the sol–gel transition study. Herein, we study the sol–gel transition and thermosensitivity of **1–3** using fluorescence spectroscopy.

In the previous section, we found that **1** formed gels at room temperature in the THF–H₂O mixture (1 : 9 by volume) at a concentration of above 5 mg mL⁻¹. This means that below this concentration, the interactions between the gelators as well as gelators and solvent molecules are too weak to form a quasi-solid self-assembly system. The amount of water required for gelation can be lowered by solution thickening. As shown in Fig. 7, the PL from an aqueous solution of **1** with a concentration of 10 mg mL⁻¹ is still weak when the water content is below 75%. After then, the emission becomes stronger accordingly. The aqueous solution starts to emit at 70% water content when doubling the solution concentration to 20 mg mL⁻¹, and a much higher PL enhancement was observed.

PEG is reported to be thermosensitive, showing LCST when attached to poly(ϵ -caprolactone). Similar behaviour was also

Fig. 7 Plot of relative intensity (I/I_0) versus the water fraction in THF–H₂O mixtures of **1** with concentrations of 10 and 20 mg mL⁻¹. Inset: photographs of THF–H₂O mixtures of **1** (10 mg mL⁻¹) with different water fractions taken under 365 nm UV irradiation.

observed in **1–3**, whose process can be followed by the temperature-dependent PL and transmittance analyses. The THF–H₂O mixture (3 : 7 v/v) of **1** with a concentration of 10 mg mL⁻¹ is transparent. Its PL drops progressively with increase in the solution temperature and reaches the minimum intensity at 26 °C. Afterwards, the emission starts to drop again at ~45 °C (Fig. 8A). Thermal agitation generally brings a dissolving effect and dehydration effect on the PL of **1–3**. The dissolving effect

Fig. 8 Plots of (A, C and E) PL intensity and (B, D and F) transmittance against temperature in THF–H₂O mixtures of (A and B) **1**, (C and D) **2** and (E and F) **3** with different water fractions (f_w) and concentrations. Excitation wavelength (nm): 350 (**1**), 355 (**2**) and 360 (**3**).

will enhance the molecular motion, leading to molecular separation and hence a PL drop. The dehydration effect, on the other hand, will promote molecular aggregation, resulting in PL enhancement. The first one seems to be dominated at temperature below 26 °C or before the cloud point, while the first effect becomes more significant from 26 to 45 °C. After then, the effect of molecular motion prevails again and quenches the light emission gradually. The transmittance begins to fall at 29 °C, suggesting that the PEG chain starts to dehydrate. The cloud point determined at 50% transmittance is ~30 °C. A similar PL change was observed in gels of **1** formed in 90% aqueous solution with the same concentration but the cloud point now shifts to 59 °C. The transmittance, on the other hand, rises at 44 °C but drops again at ~60 °C. We believe that the first change is caused by gel to sol transition of the dye molecule, while the second one is caused by the dehydration of the PEG chain. The sol–gel transition is reversible and gelation occurs upon cooling the solution to lower temperatures. The PL of a less concentrated solution with the same composition, on the hand, decreases monotonically due to the predominance of the dissolving effect on the light emission process by heating even the PEG chain dehydrates and aggregates at the cloud point. The cloud point was found to be located at 57 °C from the transmittance measurement. These results show that the solvent composition exerts a stronger effect on the cloud point than the solution concentration. Similar phenomena are observed in **2** and **3**. Since they are more hydrophilic than **1**, their cloud points occur at higher temperatures of 49 °C and 74 °C, respectively. Compared with the transmittance analysis, more information is provided by the fluorescence method. Thus, AIE fluorophores are promising in the phase transition study.

The mechanical properties of **1** are investigated by the rheometric method. As shown in Fig. 9A, the gel with an elastic modulus (G') of 3 Pa and a viscous modulus (G'') of 0.5 Pa is mechanically stable at 25 °C and changes little with time. The G' and G'' increase upon heating and reach their maximum value of 40 Pa and 20 Pa, respectively, at ~50 °C. Afterwards, they drop dramatically due to gel to sol transition and dehydration.

As stated before, **1** forms micelles in aqueous solution at an appropriate concentration. The micelles interpenetrate into each other upon solution thickening and finally gels are

formed. No gels are formed in **2** and **3** even at very high solution concentration, presumably due to their higher hydrophilicity as they possess a larger number of PEG chains. In order to form micelles, their PEG chains have to be bent. This gives rise to a twisted molecular conformation that may hamper gel formation. Thus, both the molecular structure and the balance between hydrophilicity and hydrophobicity of a dye molecule play important roles in its gel formation.

In vitro cell imaging

Prior to the cell imaging, the cell viability or cytotoxicity of luminogen **1** was evaluated in HeLa cells using an MTT assay. The cells were exposed to varying concentrations (0, 2.5, 5, 7.5, 10 $\mu\text{g mL}^{-1}$) of **1** for 24 h in a CO₂ incubator at 37 °C for cell proliferation (Fig. 10). The result shows that luminogen **1** is generally noncytotoxic at a concentration even up to 10 $\mu\text{g mL}^{-1}$. The efficient PL of AIE dyes in the aggregated state makes them promising as fluorescent visualizers for intracellular imaging. However, they are normally hydrophobic and suffer low solubility in physiological medium. Some water soluble AIE dyes with charged groups have been prepared and can selectively stain the cytoplasm and mitochondrion of living cells. Non-charged water soluble AIE dyes, on the other hand, are seldom reported. Luminogen **1** is amphiphilic and possesses such capability. As shown in Fig. 11, the dye molecule stains the cytoplasmic region of HeLa Cells but not their nucleic parts. The dye molecule may also stain the mitochondria, as some bright filamentous structures are observed. Because of its amphiphilic nature, it is likely

Fig. 10 Effect of **1** on cell proliferation of HeLa cells evaluated by the MTT assay. The cells were exposed to various concentrations of **1** for 24 h.

Fig. 9 Changes in the elastic modulus (G') and viscous modulus (G'') of gels of **1** formed in the THF–H₂O mixture (1 : 9 v/v; 10 mg mL^{-1}) with (A) time at 25 °C, a frequency of 1 Hz and a strain of 5% and (B) temperature at a heating rate of 5 °C min^{-1} .

Fig. 11 (A) Bright-field and (B) fluorescent images of living HeLa cells stained with 5.2 $\mu\text{g mL}^{-1}$ of **1**.

that the aggregates of **1** enter other membrane-bound organelles such as the endoplasmic reticula.

Conclusions

In this work, water soluble AIE luminogens are synthesized in high yields using the technique of azide–alkyne cycloaddition. These luminogens are non-emissive in solutions but emit intensely when aggregated, displaying a novel AIE phenomenon. Under an appropriate concentration, composition and temperature, **1** forms gels in the THF–water mixture. All the luminogens are thermosensitive, with their cloud point being tunable by the solvent composition and their hydrophilicity. Luminogen **1** is cytocompatible and can function as a fluorescent visualizer for intracellular imaging.

Experimental

Materials

1-(4-Ethynylphenyl)-1,2,2-triphenylethene (**7**), 1,2-bis(4-ethynylphenyl)-1,2-diphenylethene (**8**) and 1,1,2,2-tetrakis(4-ethynylphenyl)ethene (**9**) were synthesized according to the literature methods.¹⁴ Poly(ethylene glycol) ($M_n = 600$), *p*-toluenesulfonyl chloride (TsCl), pyridine, sodium azide, copper(i) bromide, pentamethyldiethylenetriamine (PMDETA) and other chemicals and solvents were all purchased from Aldrich and used as received without further purification. Distilled water was used throughout the experiments.

Instruments

¹H and ¹³C NMR spectra were measured on a Bruker ARX 400 NMR spectrometer using CDCl₃ or (CD₃)₂CO as a solvent and TMS as the internal standard. FTIR spectra were recorded on a Bruker spectrophotometer (Tensor 27). The weight-average molecular weight (M_w) and polydispersity indices (PDI or M_w/M_n) of the luminogens were estimated by a Waters Associates gel permeation chromatography (GPC) system equipped with RI, UV and fluorescence detectors using THF as the eluent and polystyrenes as the standard. UV-vis absorption spectra were recorded on a Cary 50 Conc UV visible spectrometer and the transmittance measurements were carried out on a UV/VIS/NIR spectrophotometer (Bruker, Lambda 900) at a wavelength of 550 nm. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer spectrofluorometer LS 55. The temperature control was achieved by placing the sample in a cell compartment connected to the water circulation system. Water from a thermostatted bath was allowed to circulate through the walls of the sample compartment. The final temperature of the sample was measured on a digital thermometer (TES, TES-1310). The particle sizes were measured on a zeta potential analyzer (Brookhaven, ZETAPLUS). To prepare an unstained specimen for transmission electron microscopy (TEM) analysis, a drop of the sample was placed on a carbon-coated copper grid for 2 min. The excess solution was blotted with a filter paper. After drying the grid samples in air, TEM images were taken on a TEM instrument (Japan, JEOL JEM 100CXII) with a camera set at an accelerating voltage of 100 kV.

Rheological characterization of the gel was performed by using a Rheometric ARES 3 system with 50 mm parallel plate geometry. In order to avoid solvent evaporation, the surface of the sample between two plates was covered with glycerol. The evolution of moduli (G' and G'') versus time was tested at 25 °C with a frequency of 1 Hz and a strain of 5%. The temperature ramp was measured at 1 Hz frequency and a strain of 5% at a heating rate of 5 °C min⁻¹. For cell imaging experiment, HeLa cells were grown overnight on a plasma-treated 25 mm round cover slip mounted onto a 35 mm Petri dish with an observation window. The living cells were stained with **1** (5.2 µg mL⁻¹) for 4 h. The cells were imaged under an inverted fluorescence microscope (Nikon Eclipse TE2000-U) using a combination of excitation and emission filters: $\lambda_{ex} = 330\text{--}380$ nm. The images of the cells were captured using a computer-controlled SPOT charge-coupled device (CCD) camera (SPOT RT SE 18 Mono). HeLa cells were seeded onto a 96-well plate at a density of 8×10^3 per well overnight before being treated with compound **1** in different concentrations. The cell proliferation was measured using an MTT assay according to the manufacturer's instructions. After 24 h incubation in an incubator, the cells were washed three times with $1 \times$ PBS. After that, 10 µL of 3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyltetrazolium bromide (MTT) solution (5 mg mL⁻¹ in phosphate buffer solution) was added into each well. After 4 h of incubation at 37 °C, 100 µL of solubilization solution containing 10% SDS and 0.01 M HCl was added to dissolve the purple crystals. After 8 h of incubation, the optical density readings at 595 nm were taken using a plate reader. Each of the experiments was performed at least 3 times.

Synthesis of PEG 600 mono-tosylate (**5**)

To a pyridine (60 mL) solution of **4** (16.00 mmol) was added TsCl (6.10 g, 32.00 mmol) and the mixture was stirred at room temperature for 2–3 h. The reaction mixture was diluted with dichloromethane (DCM) (200 mL), washed with aqueous 1 M HCl (100 mL), 4% NaHCO₃ solution and brine, and dried over anhydrous Na₂SO₄. After solvent evaporation, the residue was purified on a silica-gel column with the methanol–DCM mixture (1 : 10 v/v) as the eluent. Yield 76%. IR (KBr), ν (cm⁻¹): 3436, 2873, 1664, 1456, 1352, 1296, 1250, 1176, 1110, 923, 820, 777, 665, 554. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.79 (2H, t, $J = 8.0$ Hz, Ts–H), 7.34 (2H, t, $J = 8.0$ Hz, Ts–H), 4.15 (2H, t, $J = 4.8$ Hz, TsOCH₂), 3.77–3.54 (50H, m, OCH₂), 2.43 (3H, d, Ts–CH₃).

Synthesis of PEG 600 mono-azide (**6**)

To an acetonitrile (150 mL) solution of **5** (12.00 mmol) was added sodium azide (1.17 g, 18.00 mmol). After reflux for 32 h and cooling to room temperature, the mixture was diluted with water (200 mL). The aqueous solution was extracted with dichloromethane four times. The combined organic phases were dried over anhydrous Na₂SO₄. After solvent evaporation, the residue was purified on a silica-gel column using methanol–DCM (1 : 10 v/v) as eluent. Yields 95%. IR (KBr), ν (cm⁻¹): 3497, 2873, 2107, 1644, 1455, 1350, 1293, 1251, 1108, 948, 845. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 3.77–3.44 (50H, m, OCH₂), 3.28 (2H, t, $J = 5.0$ Hz, N₃CH₂).

Synthesis of TPE derivatives 1–3

Luminogen **1** was synthesized with the reagent feed ratio [6]/[7]/[CuBr]/[PMDETA] of 1/1.1/1.1/1.1. While for **2** and **3**, a feed ratio [6]/[8]/[9] of 1.1/1/1 was used instead. The click reaction between **6** (469 mg, 0.75 mmol) and **7** (294 mg, 0.825 mmol) was conducted at 35 °C in a 50 mL Schlenk flask with 30 mL of DMF, CuBr (118.4 mg, 0.825 mmol) and 3.65 mL PMDETA (0.825 mmol). After stirring for 36 h, the reaction mixtures were diluted with water (300 mL) and the aqueous solution was extracted with dichloromethane four times. The combined organic phases were further washed with brine six times and dried over Na₂SO₄. After solvent evaporation, the residue was purified on a silica-gel column using DCM as eluent to give the corresponding product in a yield of 92%. For **2** and **3**, the filtrates were condensed to 10 mL and then precipitated in ethyl ether three times. All the products were purified and characterized by GPC and FTIR, ¹H NMR and ¹³C NMR spectroscopies.

Luminogen 1. Yield 92%. *M_w* 1100; *M_w/M_n* 1.3. IR (KBr), ν (cm⁻¹): 3484, 3055, 2871, 1950, 1752, 1598, 1493, 1446, 1351, 1298, 1251, 1112, 1045, 947, 855, 825, 756, 703, 666, 627, 585. ¹H NMR (400 MHz, (CD₃)₂CO), δ (ppm): 8.32 (1H, s, triazole-H), 7.66 (2H, d, *J* = 7.6 Hz, triazole-Ar-H), 7.14–7.02 (17H, m, Ar-H), 4.59 (2H, t, *J* = 4.8 Hz, CH₂-triazole), 3.92 (2H, t, *J* = 4.8 Hz, OCH₂CH₂-triazole), 3.60–3.51 (48H, m, OCH₂). ¹³C NMR (100 MHz, (CD₃)₂CO), δ (ppm): 147.42, 144.62, 144.02, 142.13, 141.66, 132.44, 132.03, 130.60, 128.65, 127.46, 125.59, 122.22, 73.58, 71.18, 70.12, 62.00, 50.89.

Luminogen 2. Yield 85%. *M_w* 2100; *M_w/M_n* 1.3. IR (KBr), ν (cm⁻¹): 3418, 3020, 2866, 2111, 1645, 1469, 1392, 1351, 1300, 1249, 1118, 971, 926, 844, 805. ¹H NMR (400 MHz, (CD₃)₂CO), δ (ppm): 8.33 (2H, s, triazole-H), 7.68 (4H, t, *J* = 7.4 Hz, triazole-Ar-H), 7.13–7.05 (14H, m, Ar-H), 4.59 (4H, t, *J* = 4.8 Hz, CH₂-triazole), 3.91 (4H, t, *J* = 4.8 Hz, OCH₂CH₂-triazole), 3.60–3.51 (96H, m, OCH₂). ¹³C NMR (100 MHz, (CD₃)₂CO), δ (ppm): 147.43, 144.54, 144.09, 141.83, 132.51, 132.09, 130.09, 128.80, 127.61, 125.71, 122.38, 73.62, 71.27, 70.11, 61.97, 51.43, 50.90.

Luminogen 3. Yield 82%. *M_w* 3600; *M_w/M_n* 1.3. IR (KBr), ν (cm⁻¹): 3428, 3136, 2869, 2105, 1645, 1459, 1350, 1297, 1250, 1109, 972, 946, 843, 807. ¹H NMR (400 MHz, (CD₃)₂CO), δ (ppm): 8.33 (4H, s, triazole-H), 7.70 (8H, d, *J* = 7.2 Hz, triazole-Ar-H), 7.17 (14H, *J* = 7.2 Hz, d, Ar-H), 4.57 (8H, s, CH₂-triazole), 3.89 (8H, s, OCH₂CH₂-triazole), 3.60–3.40 (192H, m, OCH₂). ¹³C NMR (100 MHz, (CD₃)₂CO), δ (ppm): 147.43, 144.01, 141.67, 132.67, 130.78, 125.81, 122.51, 73.61, 70.72, 70.11, 61.95, 51.43, 50.92.

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Notes and references

- (a) J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu and B. Z. Tang, *Chem. Commun.*, 2001, 1740; (b) B. Z. Tang, X. Zhan, G. Yu, P. P. S. Lee, Y. Liu and D. Zhu, *J. Mater. Chem.*, 2001, **11**, 2974; (c) Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Commun.*, 2009, 4332; (d) Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2011, **40**, 5361; (e) D. Ding, K. Li, B. Liu and B. Z. Tang, *Acc. Chem. Res.*, 2013, **46**, 2441; (f) S. J. Yoon, J. H. Kim, K. S. Kim, J. W. Chung, B. Heinrich, F. Mathevet, P. Kim, B. Donnio, A. J. Attias, D. Kim and S. Y. Park, *Adv. Funct. Mater.*, 2012, **22**, 61; (g) N. B. Shustova, A. F. Cozzolino, S. Reineke, M. Baldo and M. Dincă, *J. Am. Chem. Soc.*, 2013, **135**, 13326; (h) J. Huang, X. Yang, J. Wang, C. Zhong, L. Wang, J. Qin and Z. Li, *J. Mater. Chem.*, 2012, **22**, 2478.
- W. Qin, D. Ding, J. Z. Liu, W. Z. Yuan, Y. Hu, B. Liu and B. Z. Tang, *Adv. Funct. Mater.*, 2012, **22**, 771.
- (a) K. Li, Y. H. Jiang, D. Ding, X. Zhang, Y. T. Liu, J. L. Hua, S. S. Feng and B. Liu, *Chem. Commun.*, 2011, **47**, 7323; (b) D. Ding, K. Li, W. Qin, R. Y. Zhan, Y. Hu, J. Z. Liu, B. Z. Tang and B. Liu, *Adv. Healthcare Mater.*, 2013, **2**, 500.
- H. Tong, Y. Hong, Y. Q. Dong, M. Haussler, J. W. Y. Lam, Z. Li, Z. F. Guo, Z. H. Guo and B. Z. Tang, *Chem. Commun.*, 2006, 3705.
- Y. Hong, M. Haussler, J. W. Y. Lam, Z. Li, K. K. Sin, Y. Q. Dong, H. Tong, J. Z. Liu, A. J. Qin, R. Renneberg and B. Z. Tang, *Chem.-Eur. J.*, 2008, **14**, 6428.
- H. Tong, Y. Hong, Y. Q. Dong, M. Haussler, Z. Li, J. W. Y. Lam, Y. P. Dong, H. H. Y. Sung, I. D. Williams and B. Z. Tang, *J. Phys. Chem. B*, 2007, **111**, 11817.
- (a) N. A. Platé, T. L. Lebedeva and L. I. Valuev, *Polym. J.*, 1999, **31**, 21; (b) H. Y. Liu and X. X. Zhu, *Polymer*, 1999, **40**, 6985; (c) Y. Chen, J. E. Gautrot and X. X. Zhu, *Langmuir*, 2007, **23**, 1047.
- K. Iwai, Y. Matsumura, S. Uchiyama and A. P. Silva, *J. Mater. Chem.*, 2005, **15**, 2796.
- L. Tang, J. K. Jin, A. Qin, W. Z. Yuan, Y. Mao, J. Mei, J. Z. Sun and B. Z. Tang, *Chem. Commun.*, 2009, 4974.
- (a) C. Y. Gong, S. Shi, P. W. Dong, B. Kan, M. L. Gou, X. H. Wang, X. Y. Li, F. Luo, X. Zhao, Y. Q. Wei and Z. Y. Qian, *Int. J. Pharm.*, 2009, **365**, 89; (b) X. Yin, F. Meng and L. Wang, *J. Mater. Chem. C*, 2013, **1**, 6767.
- (a) A. J. Dong, Y. L. Zhai, L. Xiao, H. Y. Qi, Q. Tian, L. D. Deng and R. W. Guo, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 503; (b) L. N. Goswami, Z. H. Houston, S. J. Sarma, S. S. Jalisatgi and M. F. Hawthorne, *Org. Biomol. Chem.*, 2013, **11**, 1116.
- A. C. Albertsson and I. K. Varma, *Biomacromolecules*, 2003, **4**, 146.
- F. Couet, N. Rajan and D. Mantovani, *Macromol. Biosci.*, 2007, **7**, 701.
- R. R. Hu, J. W. Y. Lam, J. Z. Liu, H. H. Y. Sung, I. D. Williams, Z. N. Yue, K. S. Wong, M. M. F. Yuen and B. Z. Tang, *Polym. Chem.*, 2012, **3**, 1481.