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Hyperbranched copolymer based photoluminescent vesicular probe conjugated with tetraphenylethene: Synthesis, aggregation-induced emission and explosive detection



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ABSTRACT

A carboxyl functionalized hyperbranched polymer, poly(3-ethyl-3-oxetanemethanol)-*star*-poly(ethylene oxide) (HSP-COOH) was subjected to addition reaction with tetraphenylethene (TPE) containing thioethanol (i.e. 2-((4-(1,2,2 triphenylvinyl)phenethyl)thio)ethanol (TPE-OH) to afford HSP-TPE copolymer with high yields. The TPE grafted hyperbranched copolymer forms homogeneous solution in common organic solvents such as THF. In aqueous solution, the copolymer self-assemble to form aggregates. The aggregates display maximum photoluminescence (PL) in THF/water (3:7 v/v) mixture. The introduction of TPE units into polymer makes it highly sensitive probe for picric acid (PA) with detection limit as low as 20 ppb via aggregation induced emission. The PL was effectively quenched by possible π - π interactions between TPE units of HSP-TPE and hydroxyl containing phenolic acid. The quenching efficiency significantly increased nonlinearly at higher quencher concentration. The present study offers details for design and synthesis of new hyperbranched polymeric fluorescent vesicle probe with high sensitivity.

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1. Introduction

Explosive materials and their detection are one of the pressing concerns in homeland security and global peace during these days. Nitroaromatic compounds (NACs) such as picric acid (PA) and trinitrotoluene (TNT) have been used on a large scale during World War-II [1]. According to the United Nations, there are over 60 regions and countries throughout the world where millions of landmines do exist [2]. Among several explosives, PA has wide-ranging use in military facilities; such as in the dye, leather, pharmaceuticals, rocket fuel production and blasting industries. The PA is highly acidic, readily soluble in water and trace amounts of it can severely effect eyes, skin, liver, kidneys, metabolism, cardiovascular and respiratory systems in both human and wildlife [3–7]. In marine environment, the biotransformation products of PA i.e., picramic acid and 2,4-dinitrophenol are even more toxic than PA [8]. Sensitive and selective detection of PA in aqueous media therefore becomes essential due to its toxicity and investigation of unexploded landmines areas for the global environment and social security. Various methods have been developed for the detection of NACs, for example high pressure liquid chromatography [9,10] electrochemical methods, [11,12] gas chromatography coupled with mass spectrometry [13] and Raman spectroscopy [10,14] in solution phase. However, most of these analytical instruments based detections becomes inappropriate due to expensive, bulky, labor intensive and time-taking operations for practical applications. Therefore, new recognitions approaches for sensitive detection of explosives are desired. Sensors for nitroaromatic explosive materials based on photoluminescence (PL) have attained great attention due to their high sensitivity, stability, selectivity, costeffectiveness and portability [15,16]. Usually, the PL intensity is decreased by an increase in aggregation from fluorophores. This aggregation of fluorophores is caused by the increase in concentration. Contrary to this aggregation-caused quenching (ACQ) aggregation-induced emission (AIE) is another phenomenon which can also be used for the detection of various analytes. Tang et al., have developed variety of TPE fluorophores which show intense/induced fluorescence emission upon aggregation and phenomenon is termed as "aggregation-induced emission (AIE)" effect [17]. TPE along with its derivatives has gained more importance due to its characteristic better photo stability, simple preparation, ease of functionalization and good photoluminescence properties [18-22]. Most of the investigations on TPE as AIE fluorophore were carried out for detection of explosives [23-28] including metal ions [23,29] and biomedical probes [17,20,30-33]. Tang et al. prepared a number of TPE-containing polymers for the detection of explosive materials i.e. PA in aqueous medium [23,24,27,28]. Wang and coworkers used TPE with block copolymers for aqueous detection of Pb^{2+} [29].

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Compared to single-molecule probe, sensors based on self-assembly of molecularly imprinted nanoparticles or self-assembled systems are more advantageous due to spatial displayed multivalent chromophores onto the surface of nanoaggregates are easily accessible for the target analyte and leads to higher sensitivity [34-47]. Multivalent probefunctionalized vesicles have also been reported for aqueous detection of different analytes, for example, metal ions, toxins, proteins and biomolecules [35,36,38-43]. For instance, Wang et al., developed fluorescent amphiphilic cellulose nanoaggregates for the detection of 2,4dinitrotoluene (DNT) and PA in aqueous solution [37]. Stevens and coworkers, have reported multivalent nanoparticles prepared form liposomes as enzyme substrate for the detection of phospholipase-A2 [43]. Recently, vesicle-based polymeric chemical sensors for the detection of Hg^{2+} and SO_2 in aqueous medium have been reported [38–40]. Further, the polymeric vesicle-based probe has its higher concentration within a local volume which can definitely increase the sensitivity of detection system [36,41,42].

Benefiting from above advantages, a Polymersome-based sensing system enriched in TPE molecules was developed for sensitive detection PA in aqueous medium as shown in Scheme 1. The solution of HSP-TPE (hyperbranched polymer functionalized with TPE) in THF produced AIE-active HSP-TPE aggregates by introducing various water fractions. These AIE-active HSP-TPE aggregates could detect PA in aqueous solution, with a lower limit of detection (LOD) of 20 ppb and quenching constant of 2.4×10^4 M⁻¹.

2. Experimental section

2.1. Reagents and instrumentation

The HSP sample (degree of polymerization of PEO arms, DParm \approx 10) was prepared according to the method previously reported [48,49] by cationic ring opening polymerization. The characterization of HSPs are provided in the supporting information (Fig. S1–S3). The mole fraction of PEO arm (f_{EO}) was 90.9% and the degree of branching (DB) of the core was 38%. The average number molar mass (M_n) and dispersity (M_w/M_n) of HSP were 9600 Da and 2.5 respectively. The 2,2-Azobis (isobutyronitrile) (AIBN) was procured from Shanghai Reagent Co. China and was recrystallized using ethanol two times before use. Tetran-butylammonium bromide (TBAB), 4-dimethylaminopyridine (DMAP), 4-vinylphenylboronic acid, N,N'-Dicyclohexylcarbodiimide (DCC), (2-bromoethene-1,1,2-triyl)tribenzene (Ph₃Br) and mercaptoethanol were procured from TCI Co., Shanghai, China. Potassium carbonate and

tetrakis-(triphenylphosphine) palladium [Pd(PPh₃)₄] were procured from Alfa Aesar Co. China. All other chemicals and solvents were procured from, Shanghai Chemical & Reagents Co. China, Adamas beta and Aldrich USA. Triethylamine (TEA) and Tetrahydrofuran (THF) were refluxed in CaH₂ before use. The PA stock solution was prepared in deionized water. The GPC of the polymers was determined by HLC-8320GPC (TOSOH, EcoSEC) instrument at 40 °C using DMF as an eluent at 0.6 mL min⁻¹. PerkinElmer LS 55 fluorescence spectrophotometer was used to perform fluorescence experiments. The DSC of the polymer sample was determined via DSC Q2000 (TA Instruments, made of USA) with Thermal Advantage fitted by a cooling system of RCS refrigerator. ¹H and ¹³C NMR spectra were carried on mercury plus 400-MHz (Varian, USA) spectrometer using deuterated solvents (chloroform and DMSO) with TMS (tetramethylsilane, an internal standard). Malvern Zetasizer (Malvern Instruments, Ltd.) was used to perform dynamic light scattering (DLS) experiments in the aqueous medium at 25 °C. A Tecnai G2 Spirit Biotwin instrument was used for transmission electron microscopy (TEM) measurements with 120 kV/voltage. The atomic-force microscopy (AFM) observations were recorded from Multimode Nanoscope-IIIa instrument, USA (Digital Instruments) at 300 kHz using tapping mode. Magnetic stirrer was used during the reactions and silica gel column chromatography was performed to purify the product.

2.2. Synthesis of (2-(4-vinylphenyl) ethene-1,1,2-triyl) tribenzene (TPE)

The TPE was prepared by the method already reported (Scheme 2) in excellent yield [31]. The 4-vinylphenylboronic acid (2.120 g, 14.32 mmol), Ph₃Br (4 g, 11.94 mmol) were dissolved in toluene (100 mL) in a round bottom flask then TBAB (0.320 g, 0.1 mmol) and K₂CO₃ (aqueous solution, 2 M, 24 mL) were added with stirring followed by addition of Pd(PPh₃)₄ (0.010 g, 8.65×10^{-3} mmol) under nitrogen gas. The reaction lasted for 24 h at 90 °C. After cooled down to room temperature, the toluene was removed via vacuum distillation and then dissolved the product in dichloromethane (DCM, 150 mL). The product was extracted by washing with deionized water (three times) and drying over magnesium sulfate (anhydrous). The obtained crude product was further purified by from silica column chromatography using the mixture of DCM and petroleum ether (4: 1 v/v) and TPE was obtained with excellent yield (88%) after the solvent was evaporated. The ¹H NMR of TPE is given in supporting information (Fig. S4).



Scheme 1. Illustration of self-assembly of the copolymer (HSP-TPE) containing fluorescent TPE probe and sensing behavior of HSP-TPE aggregates towards picric acid (PA). In HSP-TPE the blue, red and grey color present hydrophobic core, hydrophilic arms, and probe molecules resp. The PL intensity of HSP-TPE aggregates is quenched upon addition of picric acid.



Scheme 2. Synthesis of (2-(4-vinylphenyl)ethene-1,1,2-triyl)tribenzene (TPE) and 2-((4-(1,2,2-triphenylvinyl)phenethyl)thio)ethanol (TPE-OH).

2.3. Synthesis of 2-((4-(1,2,2-triphenylvinyl)phenethyl)thio)ethanol (TPE-OH)

The TPE-OH was prepared by reacting TPE and mercapto ethanol in the presence of AIBN as initiator as shown in Scheme 2. To a round bottom flask added TPE (2.255 g, 6.3 mmol), mercapto ethanol (3.938 g, 50.4 mmol), and AIBN (517.3 mg, 3.15 mmol) and toluene (160 mL) and dissolved under nitrogen gas. The reaction flask sealed using rubber stopper after purging (30 min) with nitrogen gas. Then reacted for 24 h at 70 °C. After cooling to room temperature, excess mercapto ethanol and toluene were removed by vacuum distillation. The product TPE-OH was obtained after placing overnight in a vacuum oven at 40 °C (yield 70% approximately). The ¹H NMR of TPE-OH is given in supporting information (Fig. S5).

2.4. Synthesis of HSP-TPE

The HSP-TPE was synthesized in two steps as illustrated in Scheme 3. The prepared HSP sample (degree of polymerization of PEO arms, $DP_{arm} \approx 10$) was used to prepare HSP-COOH in the first step. To a flask (250 mL), added HSP (1.901 g, 3.419 mmol of OH) and dissolved the polymer in THF (70 mL). Then added butanedioic anhydride (683.8 mg, 6.838 mmol) and TEA (0.95 mL, 6.838 mmol and refluxed for 20 h at 70 °C. After cooling the reaction mixture to room temperature the product was precipitated by petroleum ether (three times) at 30–60 °C. The obtained product (HSP-COOH) was dried for 24 h at room temperature by placing in a vacuum oven. The percentage yield of HSP-COOH was about 85%. The HSP-COOH was used in the second step for the preparation of HSP-TPE. To a flask of 100 mL, dissolved HSP-COOH (400 mg, 2.66 mmol of COOH) in dimethylformamide, DMF (40 mL, dried). Then added TPE-OH (1.3 g, 2.98 mmol), 4-Dimethylaminopyridine (DMAP) (25 mg, 0.2 mmol) and DCC (0.823 g, 4 mmol) to the solution and reacted for 24 h at room temperature. The solvent was evaporated from the solution by vacuum distillation and the crude product was obtained. The crude HSP-TPE was then purified by dissolving in THF and precipitating with petroleum ether (three times) and dried for 24 h at 30 °C using vacuum oven to obtain HSP-TPE. The percentage yield of HSP-TPE was about 76%. For further confirmation of HSP, HSP-COOH and HSP-TPE FTIR spectroscopy was carried out (fig. S6 supporting information).

2.5. Self-assembly of HSPs in water

Self-assembly of HSPs was achieved according to previously reported method [48,49] by slowly introducing 10 mL of deionized water into a 50 mL flask containing 10 mg of the polymer while stirring. The polymer solution was kept on stirring at room temperature for 30 min resulting HSPs vesicles (concentration = 1 mg/mL).

2.6. Self-assembly of HSP-TPEs probe in THF/water mixture

For self-assembly of HSP-TPEs, the polymer was first dissolved in THF and then deionized water was introduced dropwise into its THF solution while vigorous stirring. The THF solution of the polymer was prepared with concentration = $5 \ \mu g \times mL^{-1}$. Aggregates of HSP-TPE were prepared with the increasing amount of water content from 0 to 90% in THF solution.

2.7. Limit of detection for picric acid (PA)

Limit of detection (LOD) for PA was determined by reported method [50,51] via fluorescence titration of PA aliquots and HSP-TPE (concentration = 5 μ g × mL⁻¹) aggregates mixture with 70% water content in THF solution. The fluorescence titration was then plotted in order to obtain corresponding PA concentration (C_T) where fluorescence intensity changed sharply. The product of C_T and C_L (the HSP-TPE concentration) gave LOD as shown by the equation below:

$$LOD = C_L \times C_T$$



Scheme 3. The synthesis of HSP-TPE by esterification reaction from TPE-OH and HSP-COOH produced from carboxylation of HSP.

2.8. Determination of Stern-Volmer constant

Another useful information regarding the sensitivity of the probe for PA was obtained by plotting Stern-Volmer plot and determining the Stern-Volmer constant (K_{SV}) [28,50,51]. The plot is obtained as a function of [PA] using the following relationship:

$$Io/I = 1 + K_{SV} \times [PA]$$

where 'I_o' is the initial fluorescence intensity when [PA] is zero and 'I' is the fluorescence intensity at any point.

3. Results and discussion

3.1. Characterization of HSPs and HSP-TPEs

The synthetic route for the HSP-TPE copolymer is given in Scheme 3. The monomers TPE (i.e., 2-(4-vinylphenyl)ethene-1,1,2-triyl) tribenzene) was prepared by using Suzuki coupling reaction employing catalyst (i.e., tetrakis-(triphenylphosphine) palladium) [31] whereas TPE-OH was prepared by simple addition reaction using AIBN as an initiator. The TPE-OH was successfully grafted to carboxylic acid terminated poly(ethylene oxide) (PEO) arms of HSP-COOH by esterification. The ¹H NMR spectrum of HSP is given in Fig. S2 in supporting information. When compared, ¹H NMR peaks signals of the samples HSP-COOH $(DP_{arm} \approx 10)$, TPE-OH and HSP-TPE in Fig. 1, spectral signals *A-E* and *f-k* were from HBPO core and PEO arms respectively. The ¹H NMR spectra for HSP-COOH (Fig. 1) displayed new signals at δ 12.3 ppm from – COOH, protons **a**, δ 4.39 ppm from protons **f** and δ 2.43 ppm from CH_2 - (butanedioic anhydride) protons **b**, **b'** when compared to ¹H NMR for HSP (Fig. S2) confirmed successful conversion of -OH (end group) of HSP to -COOH groups [52,53]. The conversion percentage of -OH groups to -COOH was calculated to be approximately 77% by integral peaks comparison from **A** and **b**, **b'** using the relation $(S_{\mathbf{b},\mathbf{b}'}/4)/(S_{\mathbf{A}'})$ 3) or $(3S_{b, b'}/4S_A)$ '. The ¹H NMR spectra of HSP-TPE when compared with HSP-COOH, new signals peaks are observed at δ 7.08 to 6.93 ppm are assigned to protons from TPE. Moreover, signals at δ 4.03 (proton c), 2.75 (proton d, d') and 2.67 (proton e) ppm are resultant of ester linkage formation. Also the protons **b**, **b**' in HSP-COOH are shifted to



Fig. 1. ¹H NMR spectra of (a) HSP-COOH, (b) TPE-OH and (c) HSP-TPE in chloroform-d.

2.87 ppm (**l**, **l**') in HSP-TPE. Further signal peak at δ 12.3 ppm (proton **a**) due to –COOH, has become almost negligible. These results confirmed the synthesis of HSP-TPE. The percentage of TPE grafted to HSP was calculated by comparing the integral peaks of protons (**A**) of –CH₃ groups of HSP core and integral peaks of the protons of TPE using the relation '(S_{TPE}/19)/(S_A/3) or (3S_{TPE}/19S_A)' and it was about 31%. The differential scanning calorimetry (DSC) was conducted of HSP-TPE copolymer and glass transition (T_g) was observed at temperature = 29.37 °C from DSC curve given in Fig. S7 (supporting information).

3.2. Self-assembly and morphology of HSP-TPE aggregates

The self-assembled aggregates of HSPs (concentration = 1 mg/mL) obtained by direct hydration [48,49] were subjected to TEM, DLS and AFM spectroscopy which confirmed the vesicle configuration (Fig. S8 supporting information). The HSP-TPE self-assemble into vesicles (Fig. 2) when water is introduced to their THF solution (5 μ g × mL⁻¹). The TEM image of HSP-TPE (3:7 THF/Water v/v) (Fig. 2a) displays a vesicular morphology with a clear dark boundary outside compared to the internal pool. The average size of the spherical vesicles measured by DLS is Ca. 712 nm with PDI of 0.38 (Fig. 2b). The AFM image (Fig. 2c) shows spherical morphology of the HSP-TPE vesicles. The height profile (Fig. 2d) shows an average diameter and height of HSP-TPE vesicles is 704 nm and 3.6 nm, respectively (diameter to height ratio is 1:196). One reason for the large size vesicles is due to aggregation from direct hydration method. Another possible reason is the increase in the hydrophobic character by the introduction of TPE molecules in the amphiphilic hyperbranched HSPs which further increased hydrophobic interaction between large-sized TPE molecules inside the vesicle.

3.3. Photoluminescence of HSP-TPE aggregates

TPE molecules with multiple aryl groups are soluble in good solvents where the aryl groups can rotate freely around the central stator linked through single bonds are virtually non-luminescent. These intramolecular free rotations are responsible for the conversion of photonic energy into heat thus deactivates the excited states non-radioactively. However, in a poor solvent (i.e. water), it forms aggregates and becomes AIE active due to restriction in intramolecular free rotation. In the current case, aggregates of HSP-TPE at concentration = 5 μ g \times mL^{-1} were obtained by introducing water into their THF solution while vigorous stirring. The electronic absorption from UV spectra and fluorescence emission intensity from emission spectra of HSP-TPE aggregates in THF/ water (3:7 v/v) mixture is observed at peaks ~333 nm and 390 nm respectively (Fig. S9 in supporting information).

Representatively, as shown in Fig. 3a, the HSP-TPE in solution form show a weak PL at excitation wavelength $\lambda = 333$ nm, whereas, HSP-TPE solutions in THF become photoluminescent when water in different concentrations is used as precipitant. As the amount of water is increased up to 70% in the THF solution, the value of PL is also increased and an intense PL peak is recorded at ~390 nm under similar measurement conditions. TPE unit in HSP-TPE polymer is hydrophobic in nature therefore, the polymer must show aggregation in THF/water mixtures. Consequently, HSP-TPE polymer is induced to turn on light by aggregation and is AIE active under high water content. The restricted intramolecular rotation of TPE in HSP-TPE aggregates resulted in excimers formation and become emissive by blockage of non-radiative channels. By adding water more than 70% in THF solution of HSP-TPE, decreased the PL intensity, this was caused by the low solubility of the polymer. Another reason for this behavior is the decrease in the number of AIEactive molecules per unit volume [1]. The PL intensity of the THF/ water aggregates with different amount of water is shown in Fig. 3b and shows maximum PL intensity at 3:7 (ν/ν) of THF/water mixture.

The fluorescence quantum yields (Φ_F) of HSP-TPE aggregates (concentration = 5 µg × mL⁻¹) were estimated in order to determine the



Fig. 2. Morphology of HSP-TPE self-assemblies with THF/water (3:7 v/v) mixture. (a) TEM image (b) DLS curve (c) AFM image and (d) vesicle height profile.

quantitative picture of the HSP-TPE using standard conditions. The Φ_F values for 0 to 20% water content were almost same (~0.1) and increased gradually up to a maximum of 7% Φ_F (approximately) for 70% of water

content (Fig. 3c) which is about 70 fold greater than Φ_F in THF solution alone. The optical microscopic image of the aggregates of HSP-TPE under bright and fluorescent light have already been discussed in Fig. 3d.



Fig. 3. Photoluminescence (PL) spectra of (a) HSP-TPE in THF/water mixtures using different water percentage with an excitation wavelength of $\lambda = 333$ nm, (b) PL intensity and (c) quantum yields (Φ_F) of HSP-TPE with the increasing amount of water content (polymer concentration: 5 μ g × mL⁻¹) and (d) optical microscopic image of vesicular aggregates under bright light and fluorescent micrographs under blue light (inset figure).

3.4. Sensing ability of HSP-TPE aggregates

The sensing ability of the HSP-TPE aggregates was investigated in terms of quenching efficiency (by reduction in fluorescence emission) of the probe (with 5 μ g × mL⁻¹ in water/THF; 7:3 v/v dispersion) upon addition of 10 equiv. of picric acid (PA), nitrobenzene (NB), catechol, benzoic acid (BA), toluene, p-nitrophenol (p-NP) and metal ions $(Fe^{2+}, Fe^{3+}, K^+, Hg^{2+}, Cu^{2+}, Cr^{3+}, Ba^{2+} and Ni^{2+})$. Among interfering organic compounds, PA has shown most effective quenching response towards HSP-TPE polymers with quenching efficiency of 98% as shown in Fig. 4. The considerable high quenching efficiency from PA was due to donor-acceptor intermolecular photoinduced mechanism of electron rich fluorophore and electron deficient nitroaromatic [54]. Other NACs (NB and p-NP) also have shown some quenching compared to toluene since it possess no electron withdrawing group and consequently show no quenching response. For practical applications aspect, there could be presence of metal ions as impurities in environmental samples. Therefore, fluorescence quenching response of HSP-TPE probe was further analyzed against different metal ions. Form the Fig. 4 it can be concluded that metal ions have no fluorescence quenching impact for HSP-TPE probe.

3.5. Sensitive detection of picric acid (PA) by HSP-TPE

The NACs, for example, 2,4,6-trinitrotoluene (TNT), 2,4dinitrotoluene (DNT) and PA are used as explosive materials in warfare. Their sensitive detection is of anti-terrorism and homeland-safety implications. Due to commercially unavailability of TNT and DNT, the PA was used as a model explosive compound in the present study. The PL properties of HSP-TPE aggregates in THF/water mixtures can be employed as a probe for sensitive detection of PA. Upon PA addition to HSP-TPE (concentration = $5 \ \mu g \times mL^{-1}$) aggregates with 3:7 (ν/ν) of THF/water mixture, HSP-TPE shows PL at same wavelength but with decreasing intensity sensitively as shown in Fig. 5. Clearly discerned from the PL spectrum data that PL intensity is quenched significantly by introducing even a very small concentration of PA and is fully quenched with PA concentration of 40 $\mu g \times mL^{-1}$ or 40 ppm.

3.6. Calculation of limit of detection (LOD) for picric acid (PA)

Limit of detection (LOD) for PA by HSP-TPE was measured as reported in the literature [50,51] by plotting PL intensity from HSP-TPE aggregates with 3:7 (v/v) of THF/water mixture against PA concentration in equivalents as shown in Fig. 6. Taking the datum value as $C_T = 0.004$ equiv., LOD for PA can be determined by using the equation as given below:

 $LOD = CL \times CT.$



Fig. 4. Extent of fluorescence quenching efficiency of HSP-TPE ($5 \ \mu g \times mL^{-1}$ in water/THF; 7:3 v/v dispersion) by adding 10 equiv. of picric acid (PA), nitrobenzene (NB), catechol, benzoic acid (BA), toluene, p-nitrophenol, Fe²⁺, Fe³⁺, K⁺, Hg²⁺, Cu²⁺, Cr³⁺, Ba²⁺ and Ni²⁺.



Fig. 5. Fluorescent spectra of (a) HSP-TPE in THF/water (3:7 v/v) mixture with varied amount of picric acid (PA) at an excitation wavelength of $\lambda = 333$ nm.

 C_L = Concentration of HSP-TPE, C_T = Concentration of PA at which change is observed.

$$LOD = 5 \ \mu g \times mL^{-1} \times 0.004 \ equiv.$$

 $= 20 \times 10^{-3} \,\mu g \times m L^{-1}$.

$$= 20 \text{ ppb.}$$

The result shows that HSP-TPE probe is more sensitive towards PA compared to most of the PA detection probes [50,51,55].

3.7. Stern-Volmer plot and Stern-Volmer constant (K_{SV})

The relative PL intensities quenched by PA concentrations was plotted in the Stern-Volmer plot as shown in Fig. 7. The quenching constant or Stern-Volmer constant (K_{SV}) was determined according to the method reported in the literature [28,50,51] and corresponded to 2.4 × 10⁴ M⁻¹ which is among the best values [28,55]. The Stern-Volmer plot shows a linear quenching trend by PA below 20 µg × mL⁻¹ of PA concentration as shown in Fig. 7 with a correlation factor equal to 0.995. The Stern-Volmer plot deviated from linearity towards upside at PA concentration above 20 µg × mL⁻¹ (Fig. 7). The deviation from linearity was due to the higher amount of PA which caused "super quenching" by self-absorption along with energy transfer [55,56]. Other possible reason could be an interaction between PA and TPE domains (Lewis acid-base type) [27].

3.8. Visual detection of PA under UV Light

From practical applicability point of view, visual detection of PA in aqueous solution with high sensitivity is important. Test paper strips (*dia* 2 cm²) prepared by immersing into HSP-TPE solution (5 μ g × mL⁻¹) could suffice the desired task. Different concentrations of PA (10, 0.1, 0.01 and 0 μ M) were introduced to HSP-TPE test paper strips



Fig. 6. Plot of fluorescence intensity of HSP-TPE at an excitation wavelength of $\lambda = 333$ nm versus PA concentration.



Fig. 7. A Stern-Volmer plot of relative PL intensity of HSP-TPE ($I_o/I-1$) vs. PA concentration where I_0 is PL intensity at [PA] = 0 and I is the PL intensity at a specific concentration with HSP-TPE in THF/water mixture.

and were observer under UV-light as shown in Fig. 8. The PA with 0.01 μ M produced visually detectable lowest dark spot whereas the 10 μ M produced highest dark sport on the test paper strip. It can therefore be concluded that the visual detection of PA form test paper strips of HSP-TPE can be used for infield environmental applications.

4. Conclusions

The photoluminescent hyperbranched poly(3-ethyl-3oxetanemethanol)-*star*-poly(ethylene oxide) (HSP) copolymers containing (2-(4-vinylphenyl)ethene-1,1,2-triyl)tribenzene (TPE) were successfully synthesized. The amphiphilic hyperbranched copolymer is self-assembled in aqueous solutions forming aggregates. The aggregation induced emissions of the photoluminescent hyperbranched copolymer have been studied. The results indicate that the as prepared vesicular probe can be used for the sensitive and selective detection of PA among miscellanous analytes. Additionally, the limit of detection HSP-TPE based sensor was calculated as low as 20 ppb. Further, the real time application was carried out by using the test paper strips. The results reveals excellent detection under UV light.

CRediT authorship contribution statement

Faran Nabeel: Conceptualization, Methodology, Software, Data curation, Writing - original draft, Visualization, Investigation. Tahir Rasheed: Conceptualization, Methodology, Software, Data curation, Writing - original draft, Supervision, Writing - review & editing. Muhammad Farhan Mahmood: Software, Validation. Salah Ud-Din Khan: Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



Fig. 8. Response of HSP-TPE test papers for different concentrations of picric acid under UV light.

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Appendix A. Supplementary data

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