AIE/AEE tripodal PEGyl- Mephalan supramolecular and Detection of Trinitrophenol in Water

Zhenghua Zhang[a*], Yonghe Zhang [a], Liyan Cheng [a], Fei Wen [a], Dan Feng,[a] Feng Zhou [a], Yu-Hua Shi[b], Weibing Xu[c*]

[a] Yellow River Basin Ecotope Integration of Industry and Education Research Institute, Lanzhou Resources & Environment Voc-Tech University, Lanzhou 730022, China.

[b] WuWei JinCang Bioscience Co., LTD. Hongshagang Chemical Industrial Park, Wuwei 733000, China

[c] College of Science, Gansu Agricultural University, Lanzhou 730000, China;

Experimental

Materials and Instruments

1, 3, 5-homophenyl chloride, Mephalan, mPEG, dicyclohexyl carbodiimide (DCC), 4-dimethylaminopyridine (DMAP), picric acid and potassium carbonate are analytically pure grades, purchased from Shanghai Aladdin Reagent Co., LTD. Fresh double distilled water was used throughout the experiments. NMR spectra were recorded on Varian Mercury 400 (Mercury-400plus) and Agilent Technologies 600 (Agilent DD2-600 MHz) instruments. Chemical shifts are reported in ppm downfield from tetramethylsilane. The infrared spectra were performed on a Digilab FTS-3000 FTIR spectrophotometer. Mass spectra were performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer. Melting points were measured on an X-4 digital melting-point apparatus and were uncorrected. Photoluminescence spectra were performed on a Shimadzu RF-5301PC fluorescence spectrophotometer. The X-ray diffraction analysis (PXRD) was performed in a transmission mode with a Rigaku RINT2000 diffractometer equipped with graphite monochromated CuKα radiation (λ = 1.54073 Å). Matrix assisted laser desorption ionization time of flight mass spectrometry (Maldi-TOF) analyses were performed by an autoflex speed™ TOF (Bruker Daltonics Inc., Germany) under linear mode with a laser intensity of 2800 and a mass range of 2000 − 200000 amu. The [M+H]+ ions of bovine serum albumin was used to calibrate the spectra.

Synthesis of TA

TA was synthesized according to the method reported in the literature.[1] Mephalan (2.745 g, 9 mmol) was dissolved in 100 mL of anhydrous acetone. Under nitrogen protection, dry potassium carbonate (1.135 g, 8.25 mmol) was added to the

solution, followed by dropwise addition of 1,3,5-triphenylbenzoyl chloride (0.6 g, 2.25 mmol) dissolved in 5 mL of anhydrous acetone to the reaction mixture. The reaction mixture was refluxed for 16 hours, resulting in the formation of a yellow solid. The solid was filtered, washed with a large amount of acetone and 1.0 M hydrochloric acid solution, yielding a white solid product designated as TA with a yield of 92.0%. mp: 147 ℃; ^{1}H NMR (600 MHz, DMSO): δ = 12.76 (s, 1H), 9.18-8.86 (m, 1H), 8.58-8.31 (m, 1H), 7.12 (d, J = 8.4 Hz, 2H), 6.64 (d, J = 8.4 Hz, 2H), 4.53 (dd, J = 49.8, 36.9 Hz, 1H), 3.68 (m, 8H), 3.10-2.93 (m, 2H); 13C NMR (150 MHz, DMSO): δ = 177.67, 166.25, 145.20, 134.90, 130.35, 112.02, 55.33, 52.79, 41.34, 31.04.

Synthesis and characterization of TA-PEGn

TA (0.05 g, 0.047 mmol) and mPEG-n (n: 5k, 2k, 0.75k) were dissolved in 5 mL of dimethyl sulfoxide (DMSO) (with a molar ratio of 3:1 for MPEGn to TA). To this solution, DCC (32 mg, 0.154 mmol) and DMAP (20 mg) were added. The mixture was continuously stirred for 120 hours. Afterward, 20 mL of distilled water was added to the reaction mixture, followed by dialysis for 3 days, resulting in the formation of bright yellow solid materials denoted as TA-PEGn (n is equal to 5, it signifies that the molecular weight of PEG is 5000). TA-PEG5: yield, 75.0%; ^{1}H NMR (600 MHz, DMSO): δ = 8.22 (s, 1H), 7.17-6.88 (m, 2H), 6.79-6.45 (m, 2H), 4.56 (m 1H), 2.94 (d, J = 36.2 Hz, 2H); TA-PEG2: yield: 80.0%; ^{1}H NMR (600 MHz, DMSO): δ = 8.29 (s, 1H), 7.11 (d, J = 29.9 Hz, 2H), 6.62 (d, J = 29.9 Hz, 2H), 4.56 (m, 1H), 2.98 (d, J = 36.0 Hz, 2H); TA-PEG0.75 yield, 78.0%; ^{1}H NMR (600 MHz, DMSO):

δ = 8.31 (m, 1H), 7.25-6.88 (m, 2H), 6.78-6.47 (m, 2H), 5.02 (m, 1H), 3.34 (s, 8H), 2.95 (m, 2H).

[1] E. Fuentes, M. Gerth, J. A. Berrocal, C. Matera, P. Gorostiza, I. K. Voets, S. Pujals*, and L. Albertazzi* J. Am. Chem. Soc. 2020, 142, 22, 10069–10078.

$$\Phi_x = \Phi_s \ \frac{I_x}{A_x} \frac{A_s}{I_s} \frac{\eta_x^2}{\eta_s^2} \qquad\qquad \text{Equation S1}$$

Here, "Φ" represents the quantum yield; "I" denotes the measured fluorescence emission intensity; "A" stands for the optical absorption intensity; "η" represents the refractive index of the solvent; subscripts "s" and "x" respectively refer to quinine sulfate and the sample.

Fabrication of TA-PVA film

The film is prepared using a casting method. The PVA (5g) was dissolved in 60mL deionized water at 80 ℃, and cooled to room temperature for use. PEG5-TA (10mg) was added to 20 ml of PVA solution. The bubbles were removed by ultrasound for 30 minutes, and the solution was poured on a clean glass plate. PVA films containing PEG2-TA and PEG0.75-TA were prepared by the same method.
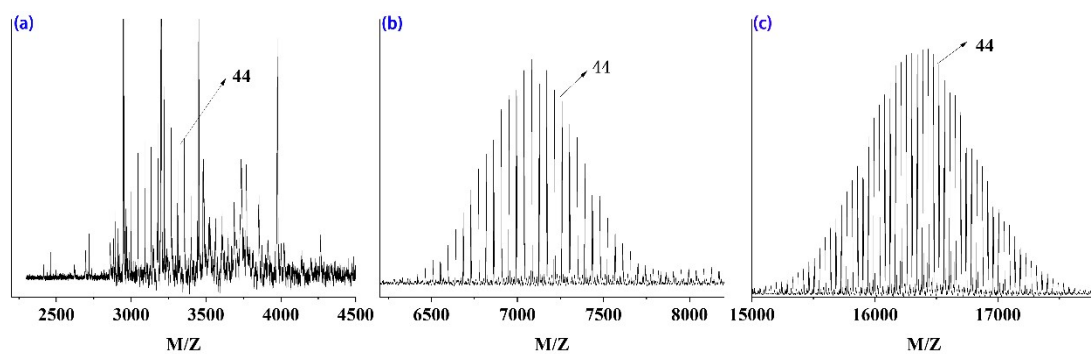
Fig. S1 Typical MALDI-TOF mass spectrum of TA-PEG0.75 (a), 2 (b) and 5 (c).
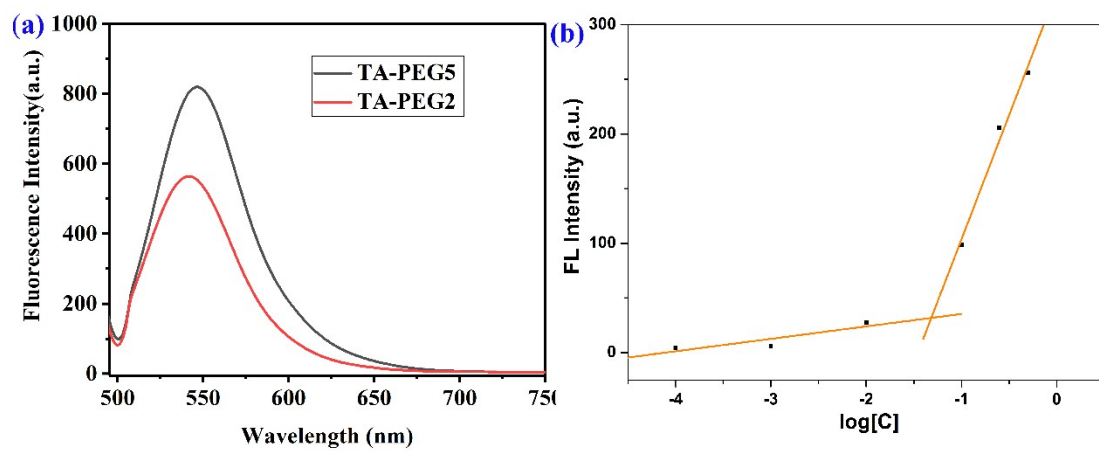
Fig. S2 Fluorescence emission spectra of TA-PEG5 and 2 in pure water (a) and the CAC values of
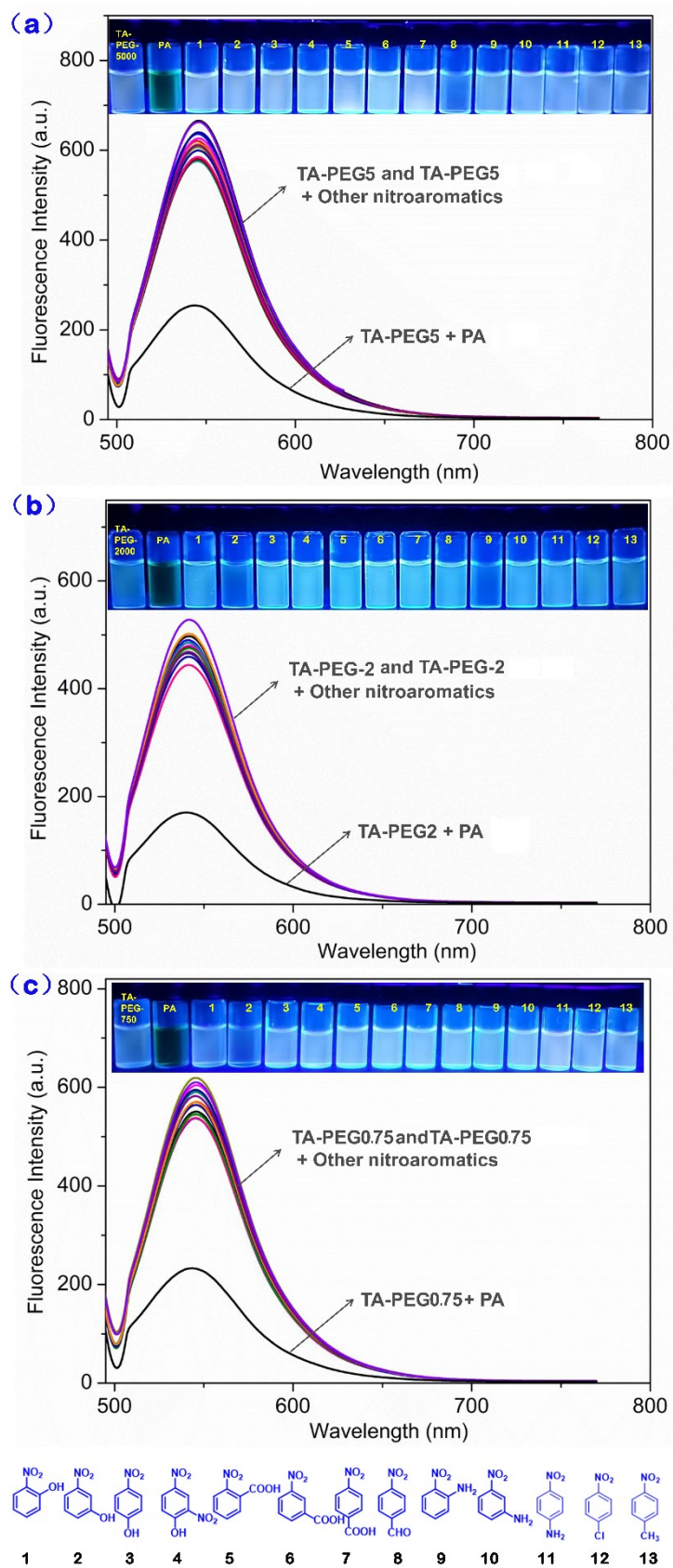
(b)TA-PEG0.75

Fig. S3 Fluorescence emission spectra of (a) TA-PEG5, (b) TA-PEG and (c)TA-PEG0.75 in the presence of various nitroaromatic compounds
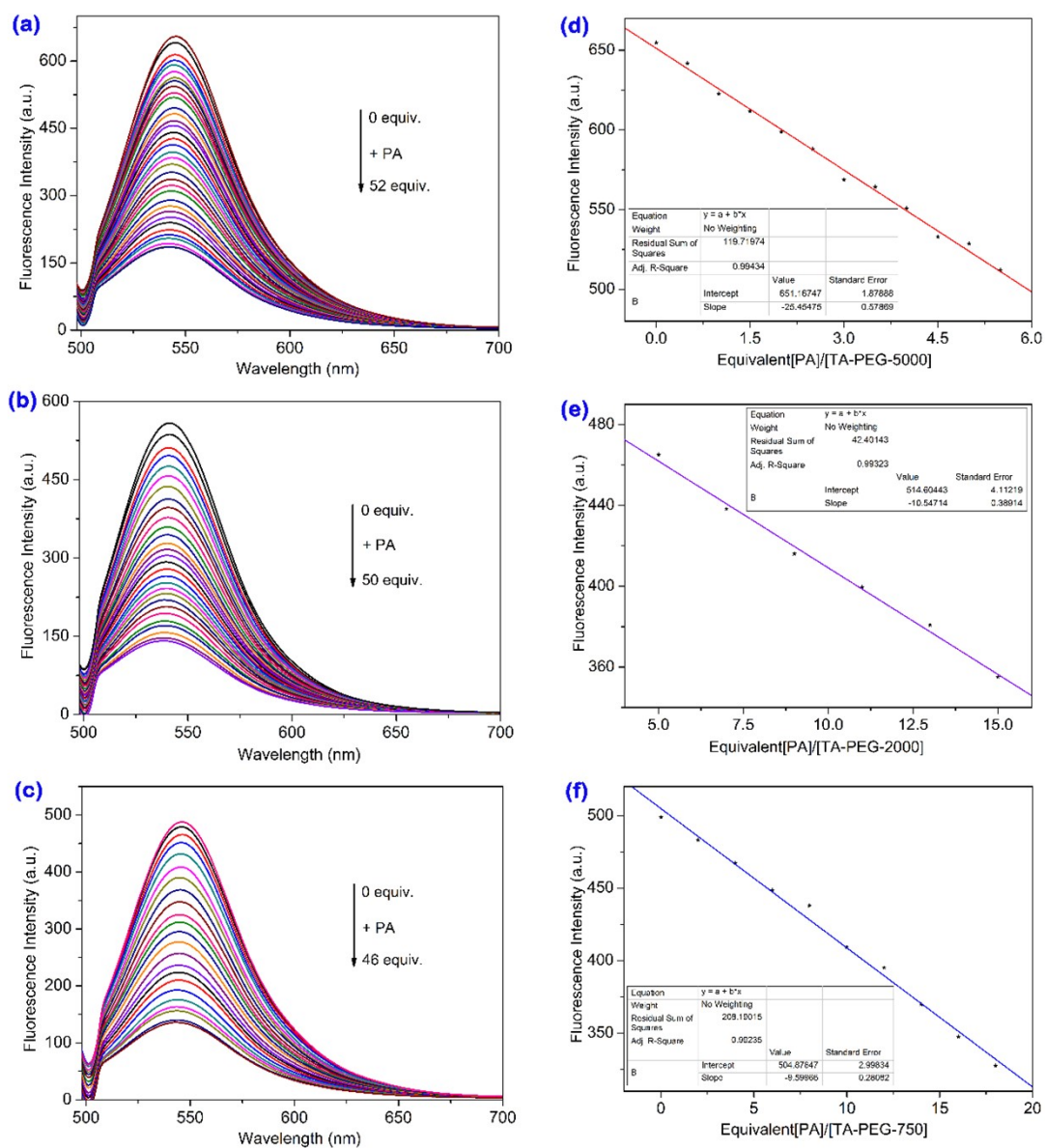
Fig. S4 Fluorescent emission spectra of fluorescence titration of (a) TA-PEG5, (b) TA-PEG2 and (c)TA-PEG0.75 with PA; fluorescent spectra linear fitting for PA by addition of various concentrations of PA to (d) TA-PEG5, (e) TA-PEG2 and (f)TA-PEG0.75
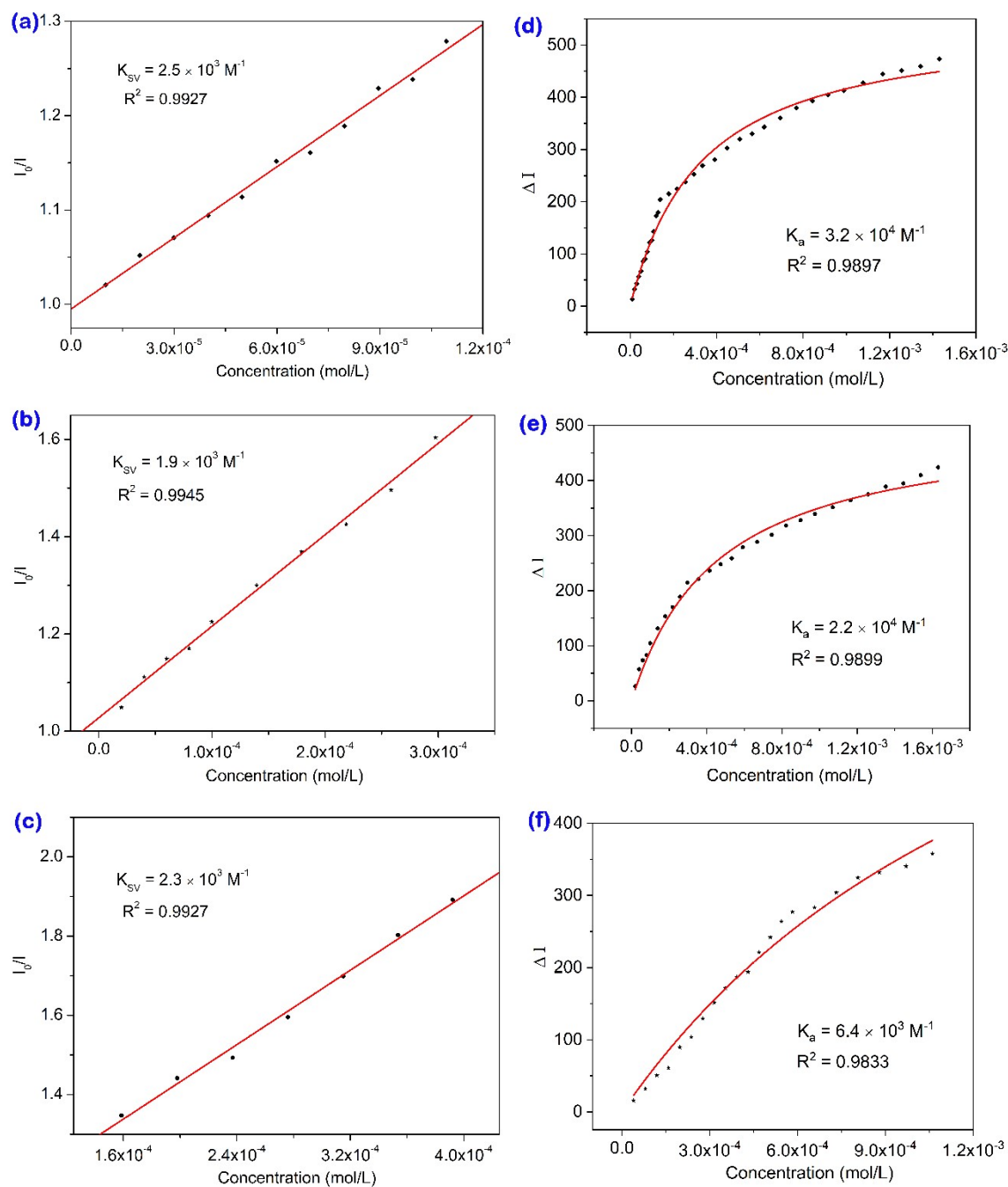
Fig. S5 Quenching efficiencies of (a) TA-PEG5, (b) TA-PEG2 and (c)TA-PEG0.75 in the presence of different concentrations of PA; fluorescent spectra nonlinear curve fitting by addition of various concentrations of PA to (d) TA-PEG5, (e) TA-PEG2 and (f)TA-PEG0.75
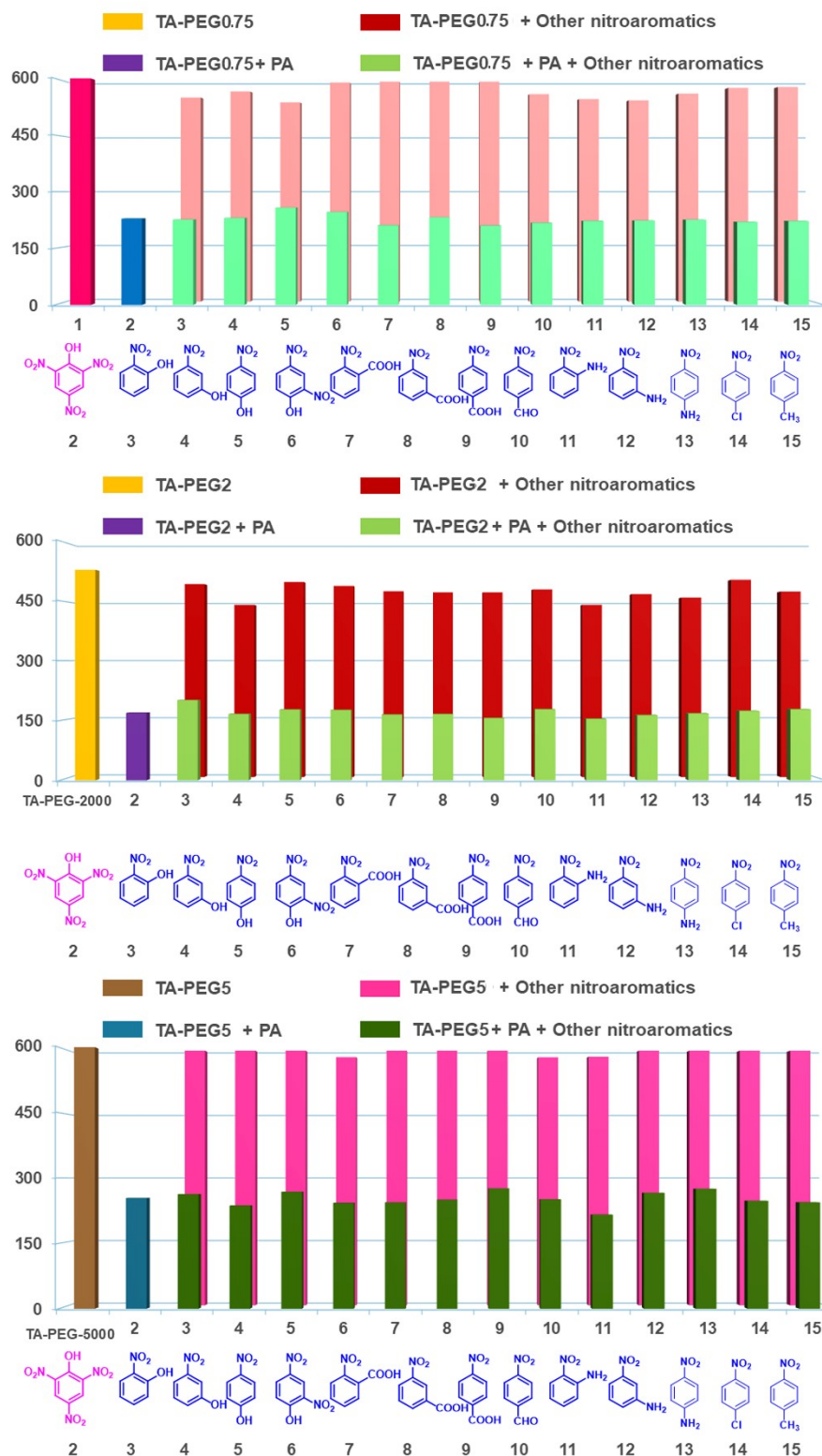
Fig. S6 Fluorescence intensity of (a) TA-PEG5, (b) TA-PEG2 and (c) TA-PEG0.75 to PA in the presence of various nitroaromatic compounds; (d) molecular structures of different nitroaromatic compounds
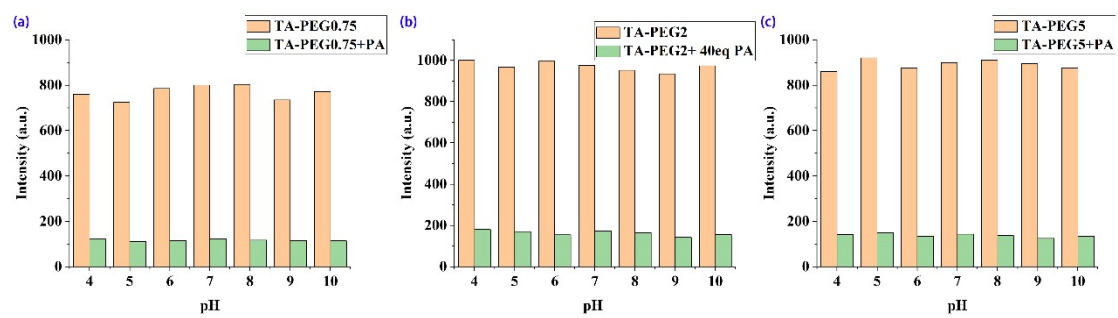
Fig. S7 Fluorescence intensity of TA-PEGn solution (1.0 X 10 $^{-4}$ mol L^{-1}) with and without PA solution (40 eq) in different pH values.
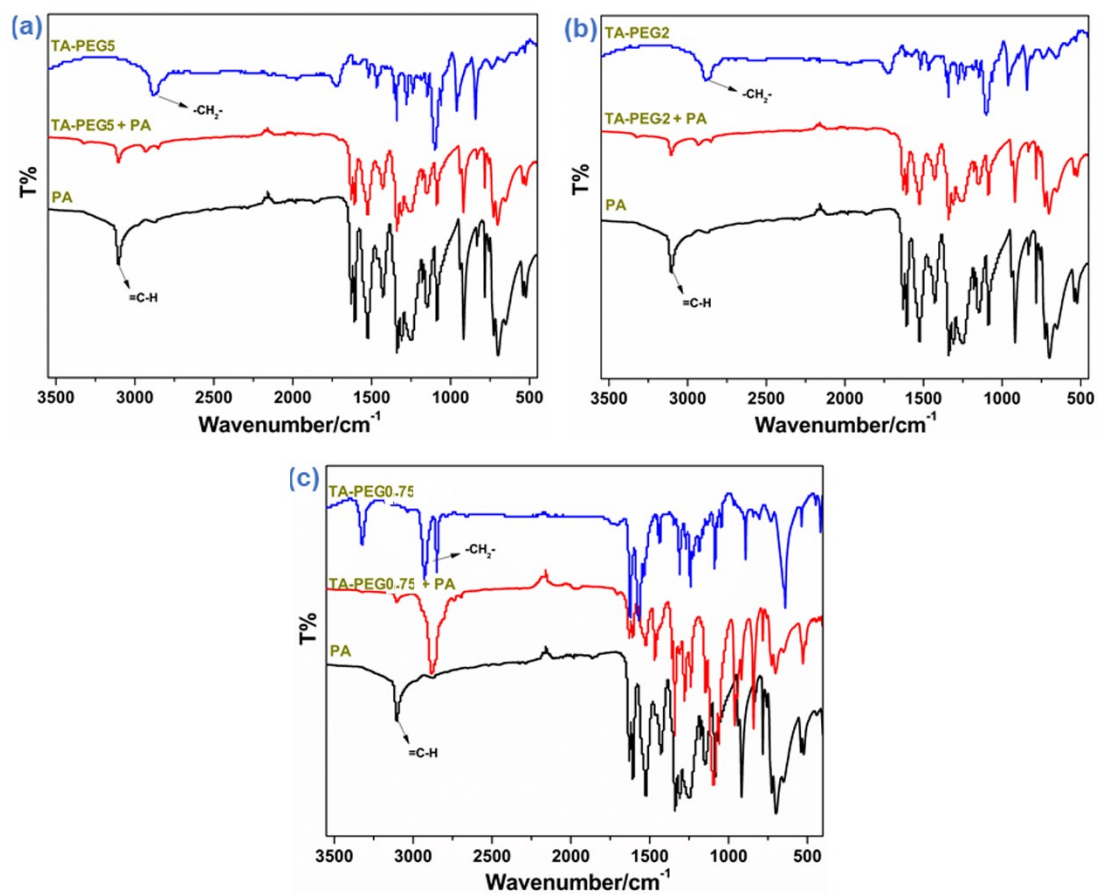
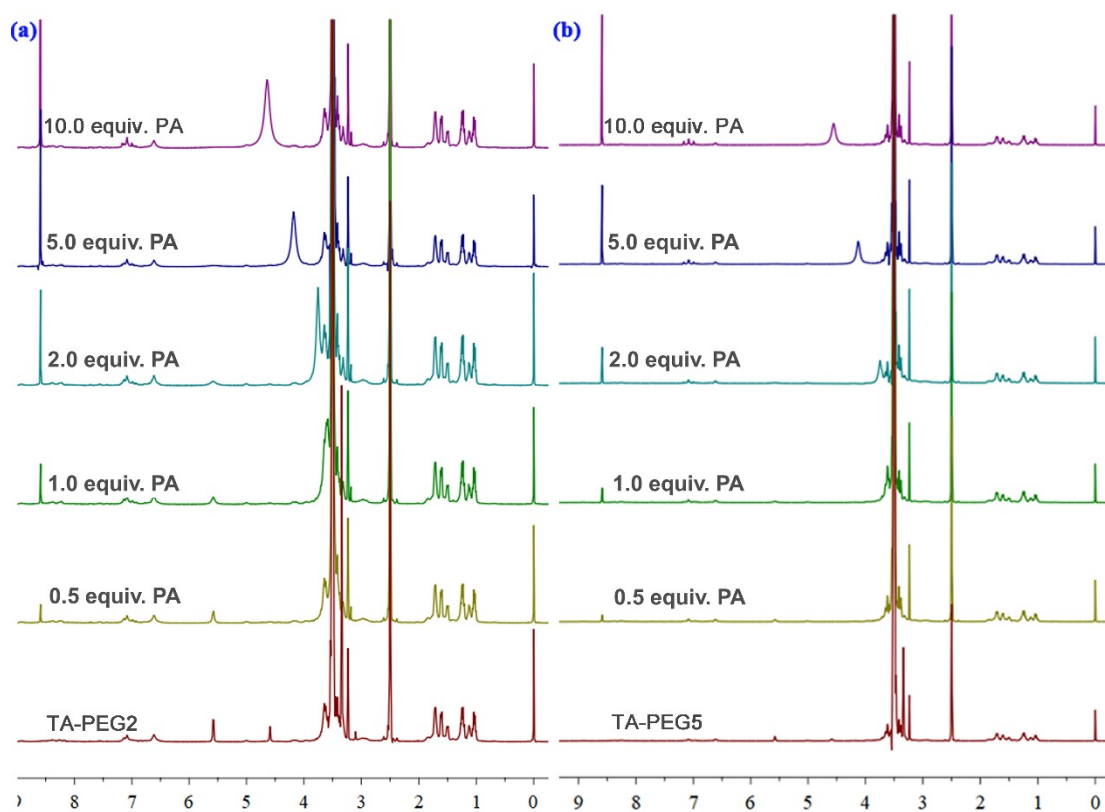Fig. S8 IR spectra of TA-PEGn, TA-PEGn + PA and PA

Fig. S9 The partial ^{1}H NMR spectra of the TA-PEG2 (a) and (b) 5 in the presence of varying amounts of PA
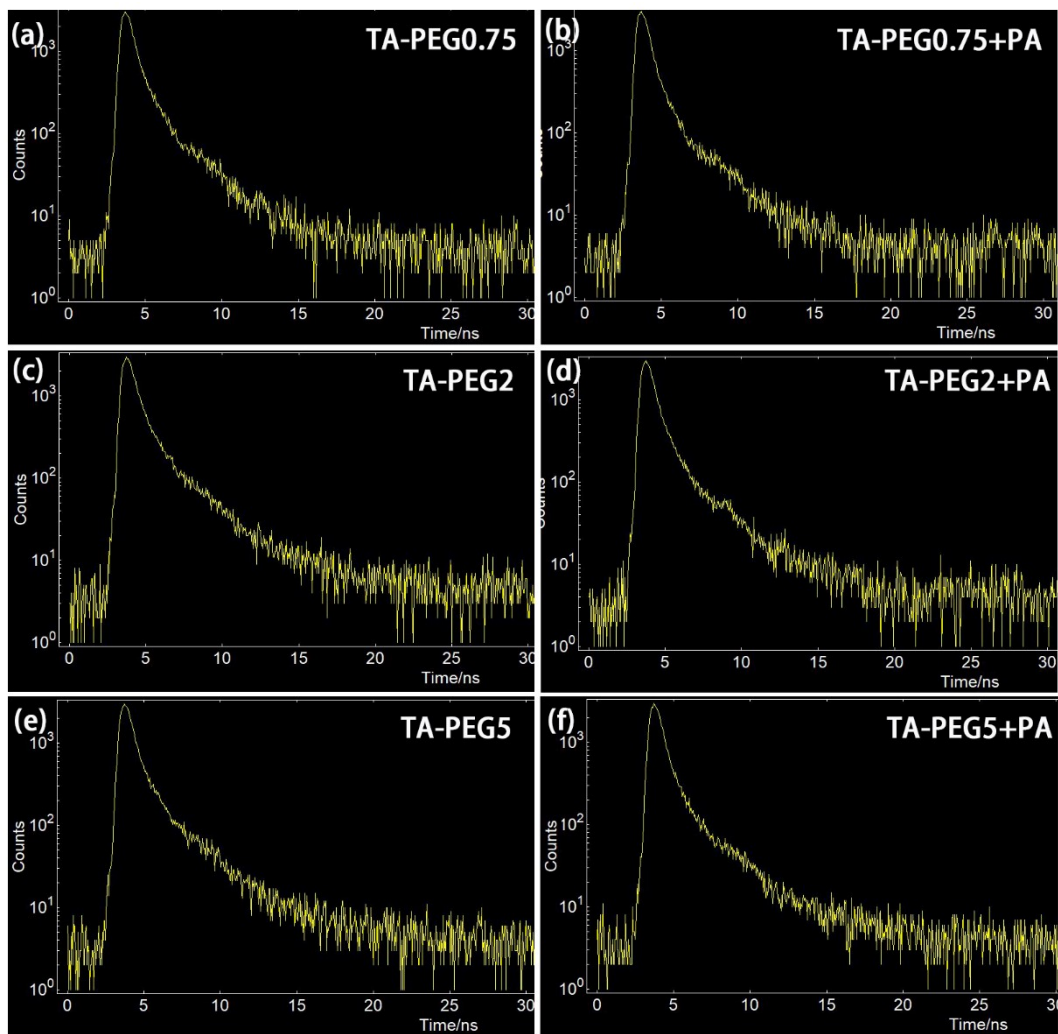
Fig.S10 the fluorescence lifetime of pure TA-PEGn solution without and with 40eq PA solution
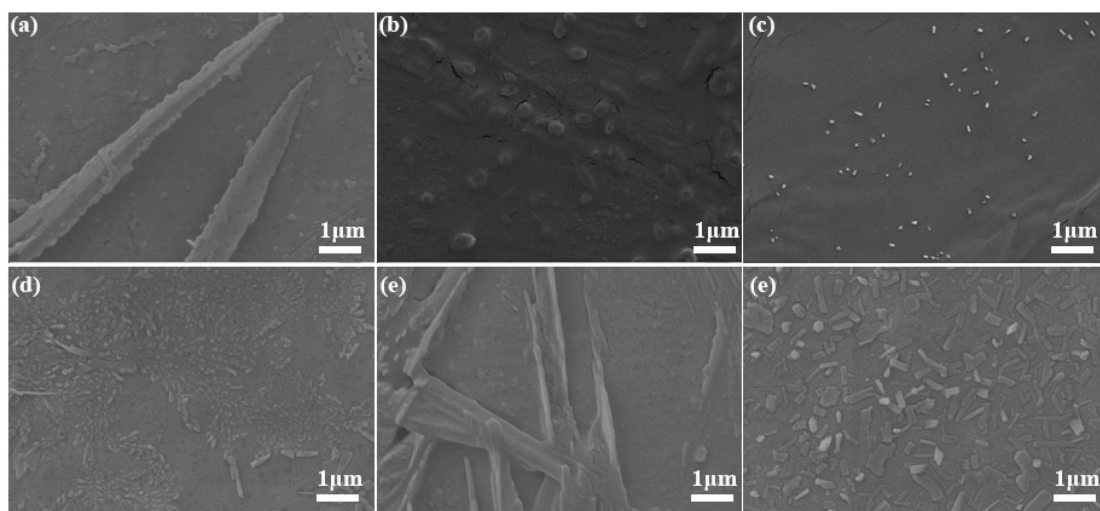
Fig. S11 SEM images of free TA-PEG0.75(a) + PA(d), (b) TA-PEG2 (b) + PA (e) and (c) TA-PEG5 (c) + PA (f).
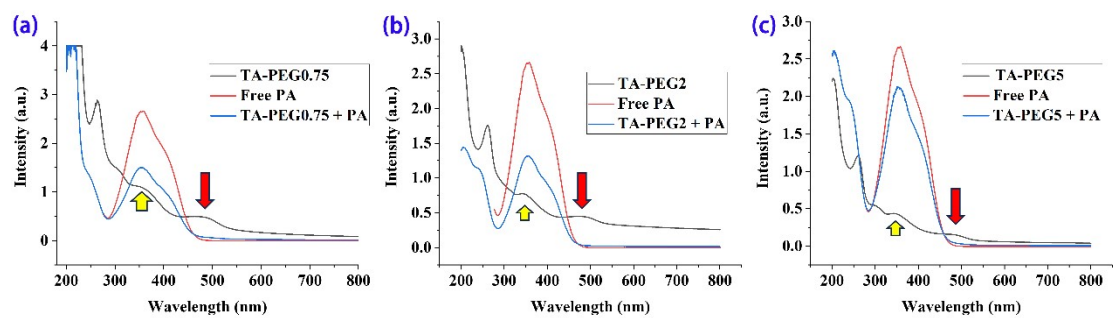
Fig. S12 the UV intensity of TA-PEGn solution (1.0 X 10 $^{-5}$ mol L^{-1}), free PA (1.0 X 10 $^{-3}$ mol L^{-1}) and mixture of TA-PEGn and PA slution (40 eq PA).
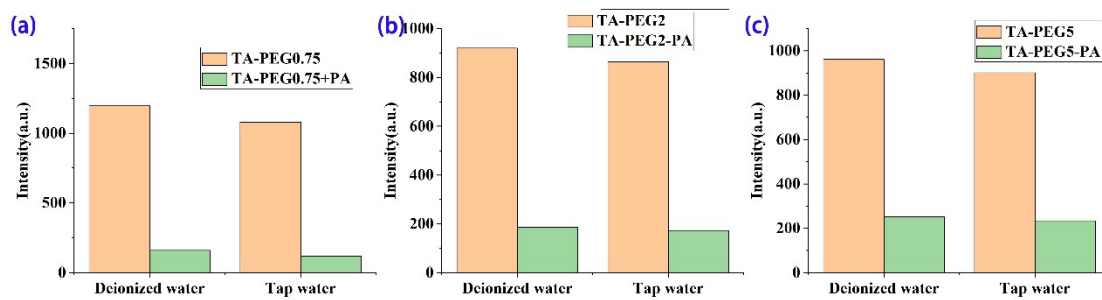
Fig. S13 Fluorescence intensity of TA-PEGn solution (1.0 X 10 $^{-4}$ mol L^{-1}) with and without PA solution (40 eq) in deionized water and tap water.
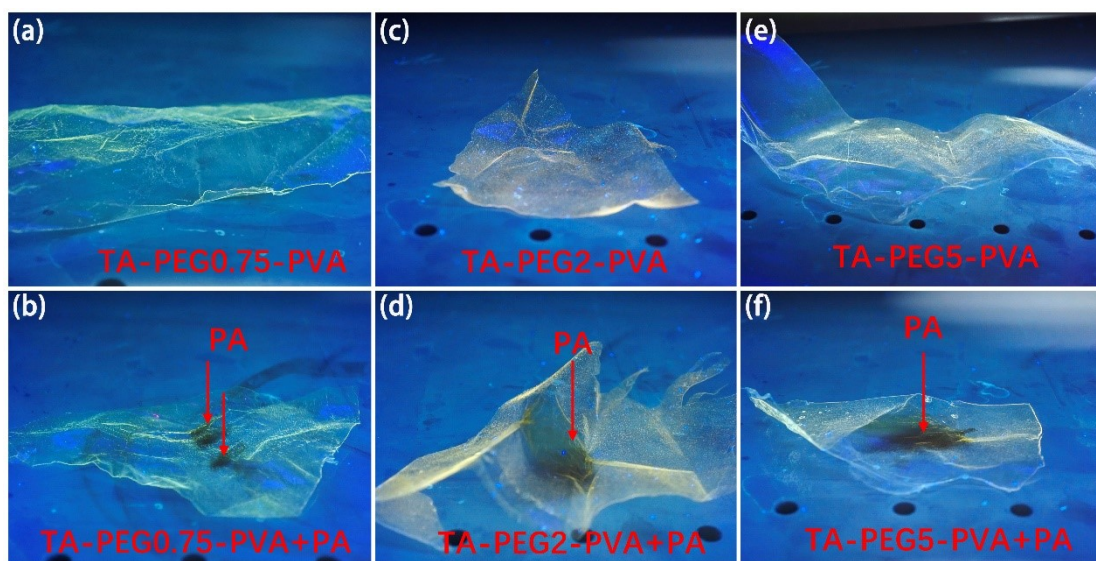
Fig. S14 Fluorescence images of TA-PEGn-PVA film without and with PA solution under 365 nm lamp

Table S1 The LOD, K_a and K_{sv} of TMs with PA

Compounds	TA-PEG0.75	TA-PEG2	TA-PEG5
MW of PEG	750	2000	5000
Φ（%）	34.7	76.9	81.1
LOD（M）	1.8×10^{-6}	1.1×10^{-6}	5.7×10^{-7}
K_a（M^{-1}）	6.4×10^3	2.2×10^4	3.2×10^4
K_{sv}（M^{-1}）	2.3×10^3	1.9×10^3	2.5×10^3

Table S2 Comparative study of the Ksv and the detection limit (LOD) achieved in material used for the detection of PA.

Materials	LOD	Ksv	Mechanism	Medium	Ref
9-Anthraldehyde AIE	8.1×10^{-6}	1.9×10^{5}	Static	Water	1
vanillin-based AIE	7.2×10^{-8}	7.0×10^{3}	-	Water	2
Antipyrine Schiff AIE	1.2×10^{-5}	1.9×10^{5}	-	Water	3
Zn(II) MOF	7.0×10^{-4}	7.0×10^{4}	IFE and Static	Water	4
Cd(II) Framework	1.6×10^{-6}	9.3×10^{4}	-	Water	5
Naphthalimide AIE	4.7×10^{-8}	7.4×10^{4}	Dynamic	Methanol	6
Carbon quantum dots	4.1×10^{-5}	-	IFE	Water	7
Carbon quantum dots	5.0×10^{-6}	-	DQ	Water	8
Carbon quantum dots	1.8×10^{-3}	-	FRET	Water	9
Polymer microspheres	8.5×10^{-5}	1.5×10^{4}	FRET	Methanol	10
Triphenylaminebased SOF	8.2×10^{-5}	-	ET	Water	11

1. Das D, MaityA, Shyamal M, Maity S, Mudi N, Misra A. Aggregation induced emission of 9-Anthraldehyde microstructures and its selective sensing behavior towards picric acid. J Mol Liq 2018;262:446–55.

2. Shyamal M, Das D, GiriS PK, Misra MA. Aggregation-induced emission-based highly selective 'turn-off' fluorogenic chemosensor for robust quantification of explosive picric acid in aqueous and solid states. Mater Today Che 2019;14:100193.

3. Maity S, Shyamal M, Das D, Mazumdar P, Sahoo GP, Misra Ajay. Aggregation induced emission enhancement from antipyrine-based schiff base and its selective sensing towards picric acid. Sensor Actuator B Chem 2017;248:223–33.

4. Hu YJ, Li YM, Zheng K, Zhang WH, Liu YL, Yang H. Construction of a Zn(II)-containing MOF for highly selective detection of picric acid and inhibition of human glioma cell growth. J Mol Struct 2020:1202.

5. Senthilkumar S, Goswami R, Smith VJ, Bajaj HC, Neogi S. Pore wall-functionalized luminescent Cd(II) framework for selective CO$_2$ adsorption, highly specific 2,4,6- Trinitrophenol

detection, and colorimetric sensing of Cu2þ ions. ACS Sustainable Chem Eng 2018;6(8):10295–306.

6. Dyes and Pigments 181 (2020) 108563

7. Hydrothermal synthesis of carbon quantum dots as fluorescent probes for sensitive and rapid detection of picric acid

8. S. F. Chen, Y. Song, F. P. Shi, Y. L. Liu and Q. Ma, *Sens. Actuators, B*, 2016, **231**, 634.

9. F. L. Cheng, X. Q. An, C. Zheng and S. S. Cao, *RSC Adv.*, **5**, 93360.

10. Highly cross-linked fluorescent poly(cyclotriphosphazene-co-curcumin) microspheres for the selective detection of picric acid in solution phase

11. Fluorescence enhancement through the formation of a single-layer two-dimensional supramolecular organic framework and its application in highly selective recognition of picric acid