Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting information

A perylene monoimide probe based fluorescent micelle sensor for the selective and sensitive detection of picric acid

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Synthesis of PMI-OH

PMI

The mixture of 3,4,9,10-perylenetetracarboxylic dianhydride (2.0 g, 5.0 mmol), 2,5-di-tertbutylaniline (0.56 g, 3.2 mmol), $Zn(OAc)_2 \cdot 2H_2O$ (0.24 g, 1.1 mmol), imidazole (10.0 g, 147.0 mmol) and water (5 mL) was placed in an oven. The mixture was stirred at 190 ºC. After 20 h, the reaction mixture was cooled to RT. The mixture was washed with water (3 x 150 mL) and dried. The crude material was dissolved in CH_2Cl_2 (10 mL) and purified by column using CH_2Cl_2. The product was collected and the solvent evaporated to yield PMI as a bright orange crystalline solid (1.493 g, 62%). The NMR data were consistent with the reported data. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (d, J = 8.0 Hz, 2H), 8.50 (t, J = 8.4 Hz, 4H), 7.95 (d, J = 8.1 Hz, 2H), 7.68 (t, J = 7.8 Hz, 2H), 7.48 (dd, J = 10.9, 4.7 Hz, 1H), 7.35 (d, J = 7.8 Hz, 2H), 2.77 (dt, J = 13.7, 6.8 Hz, 2H), 1.18 (d, J = 6.9 Hz, 12H) (Fig. S1).

PMI-Br

To a stirring solution of **PMI** (0.5 g, 1.04 mmol) in CH_2Cl_2 (50 mL), Br_2 (0.278 mL, 9.73 mmol) was added dropwise. The reaction mixture was stirred at reflux for 2 h. The solution was cooled to room temperature and washed with a concentrated solution of Na_2SO_3 (50 mL, 1 M), then extracted with water (3 x 300 mL). The solution was concentrated in vacuo and passed through a silica column with dichloromethane/ petroleum ether 1 : 1. The **PMI-Br** solution was concentrated in vacuo to afford a red solid that was used without further purifications (425 mg, 73%). Mp: > 300 ºC, ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.60 (d, J = 7.6 Hz, 1H), 9.39 (d, J = 8.4 Hz, 1H), 8.94 (d, J = 5.9 Hz, 1H), 8.70 (t, J = 8.1 Hz, 1H), 8.50 (dd, J = 12.8, 7.8 Hz, 1H), 8.43 (d, J = 6.8 Hz, 1H), 8.26 (d, J = 8.1 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.82 – 7.78 (m, 1H), 7.49 (t, J = 7.8 Hz, 1H), 7.35 (d, J = 7.8 Hz, 2H), 2.76 – 2.70 m, 2H), 1.18 (dd, J = 6.8, 3.2 Hz, 12H) (Fig. S2).

PMI-OH

A 125 mL Schlenk flask was filled with **PMI-Br** (100 mg, 0.19 mmol), Cs_2CO_3 (430 mg, 1.32 mmol), H_2O (1 mL), DMF (20 mL), and purged with N_2 for 10 minutes. The PMI-Br may not be dissolved easily until heat was applied. BINAP (10 mg, 0.016 mmol) and [$Pd_2(dba)_3$] (10 mg, 0.011 mmol) were added and the flask was quickly sealed with a greased glass stopper. The solution was heated at 90 ºC for 2 hours after which a green solution was obtained. After cooling, the mixture was diluted with 200 mL of 1 M HCl, which caused a pink/purple precipitate to form. The suspension was filtered with a Buchner funnel and then washed with 500 mL of hot water. The solid was dissolved in a DCM / MeOH (3 : 1) solution and then dried using a rotary evaporator. The compound was then purified on a silica column using DCM : MeOH (3 : 1). The **PMI-OH** solution was concentrated in vacuo to afford a red solid that was used without further purification (58.5 mg, 62%). Mp: > 300 ºC, ^{1}H NMR (500 MHz, DMSO-D_6) δ 11.36 (s, 1H), 8.77 (d, J = 7.7 Hz, 1H), 8.69 (d, J = 8.0 Hz, 1H), 8.61 (d, J = 8.5 Hz, 1H), 8.51 – 8.49 (m, 2H), 8.46 (d, J = 7.8 Hz, 1H), 8.31 (d, J = 8.2 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.46 – 7.42 (m, 1H), 7.32 (d, J = 7.8 Hz, 2H), 7.14 (d, J = 7.8 Hz, 1H), 2.65 –2.62 (m, 2H), 1.06 (d, J = 6.7 Hz, 12H) (Fig. S3). ^{13}C NMR (151 MHz, DMSO-D_6) δ 157.06, 146.56, 138.27, 137.61, 137.42, 137.36, 131.56, 131.22, 129.75, 127.79, 127.60, 127.17, 125.69, 125.49, 125.34, 124.17, 123.77, 123.70, 119.82, 118.85, 118.72, 118.33, 117.89, 116.94, 110.23, 33.68, 30.59, 29.27, 22.86. ESI-MS: m/z calculated for $C_{34}H_{27}NO_3$, 497.2; found: 496.2, $(M)^+$ (Fig. S4). HRMS (ESI): calculated for 497.1991, found: 576.1007 ($(MBr)^-$).

NMR and mass spectra

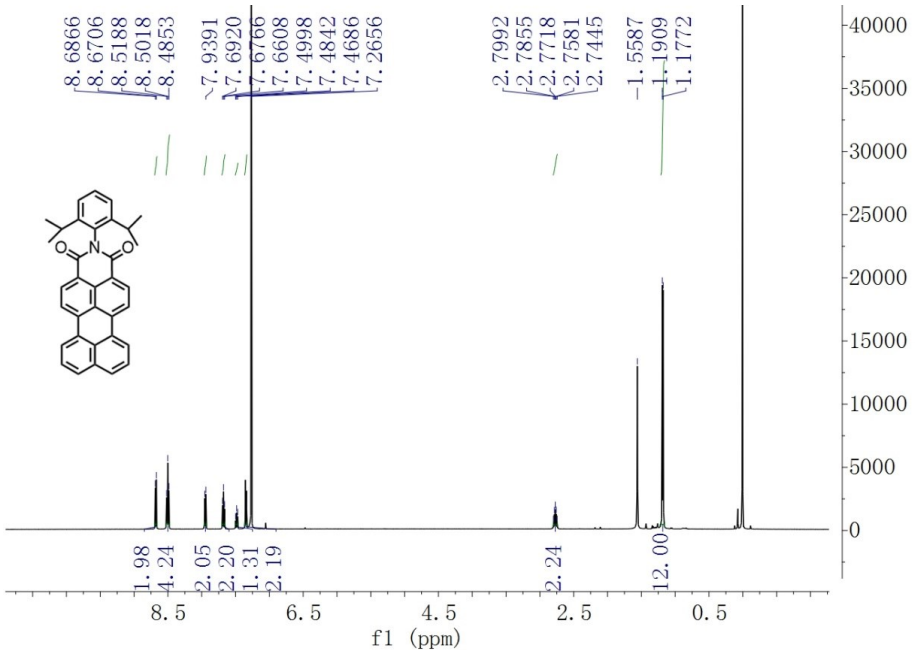

Fig. S1 [1]H-NMR spectrum of **PMI**.

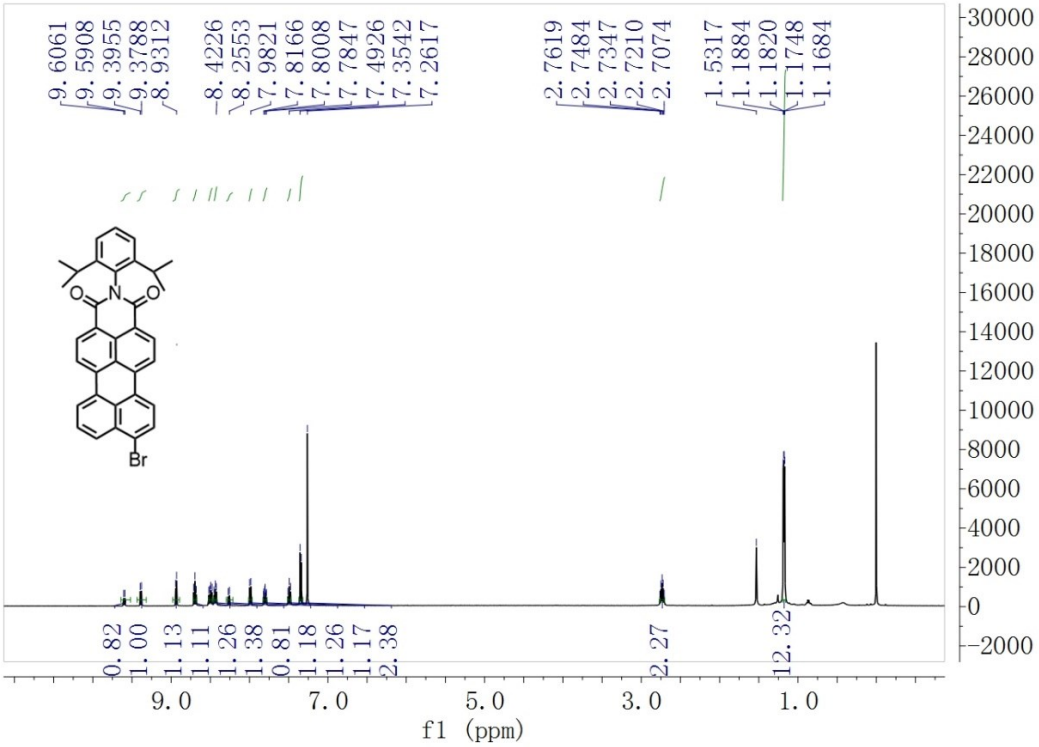

Fig. S2 [1]H-NMR spectrum of **PMI-Br**.

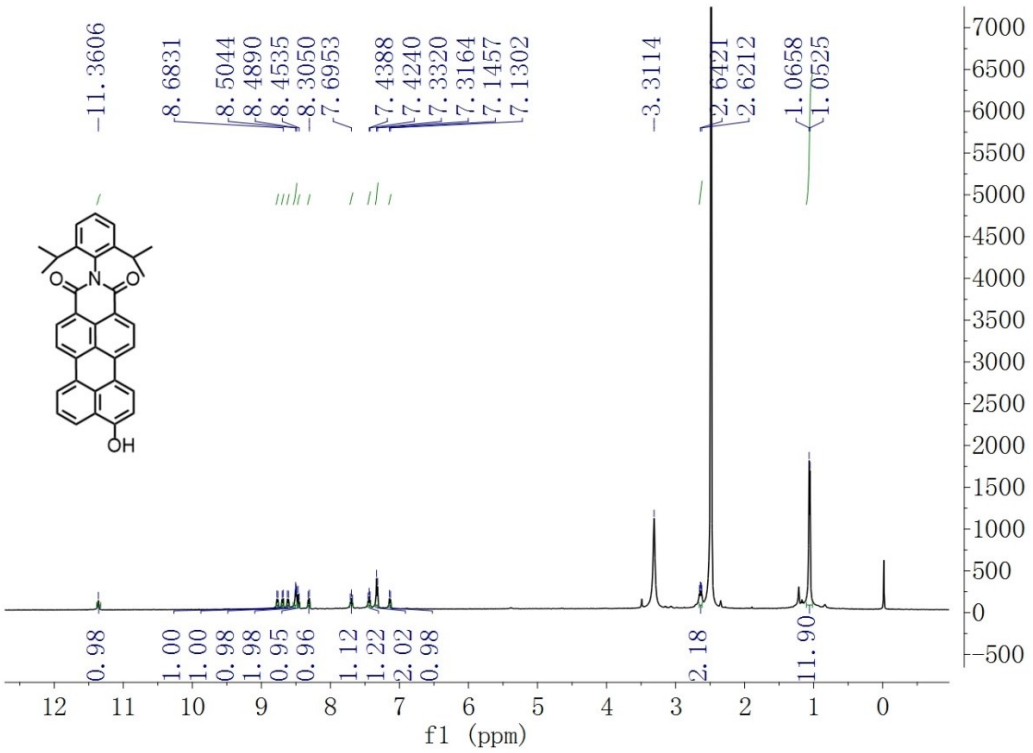

Fig. S3 ^{1}H-NMR spectrum of **PMI-OH**.

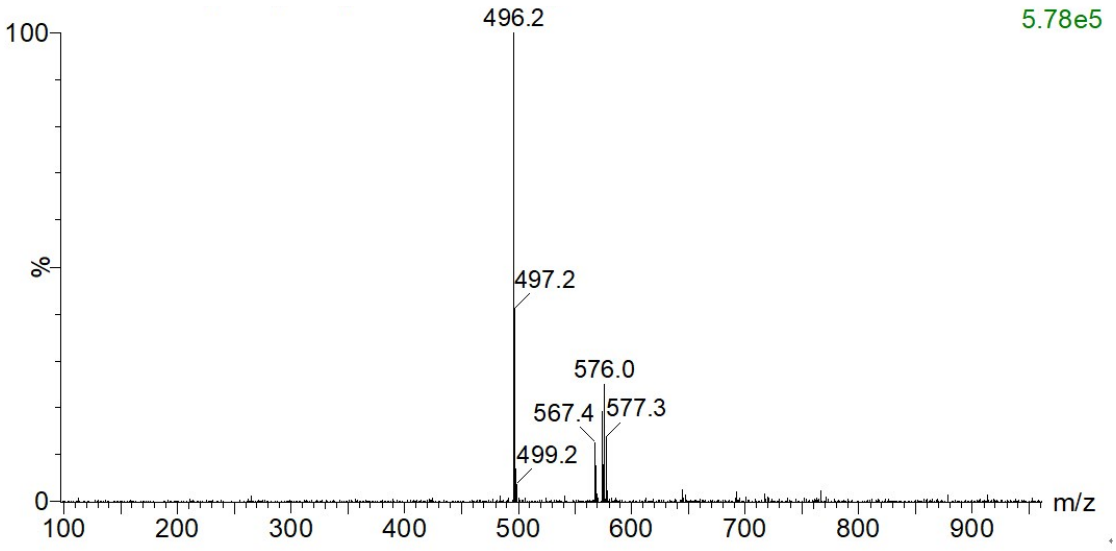

Fig. S4 ESI mass spectrum of **PMI-OH**.

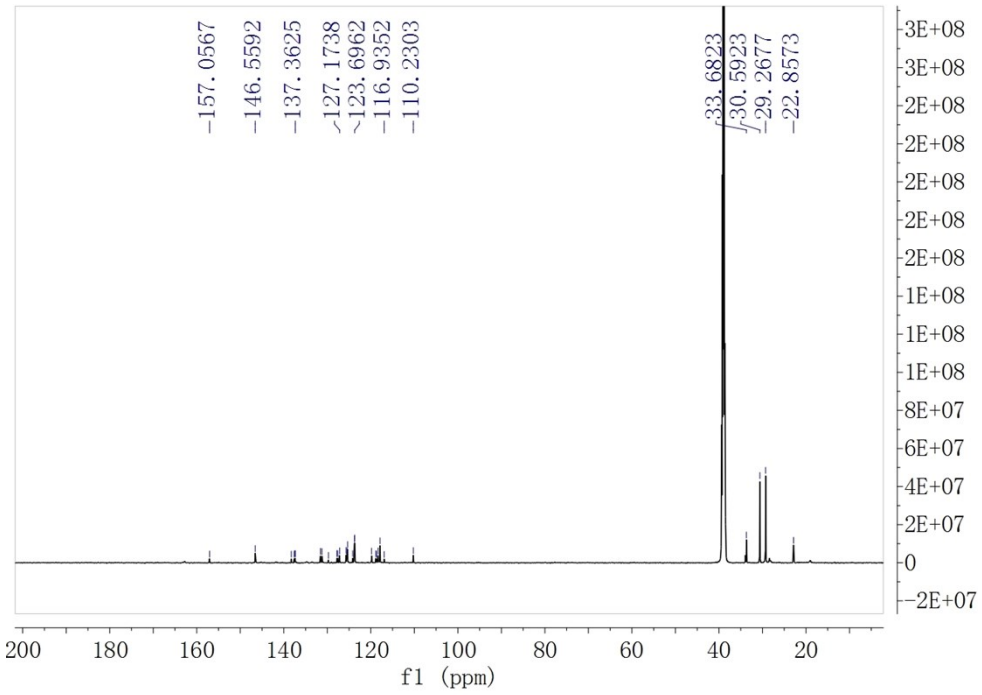

Fig. S5 ^{13}C NMR spectrum of PMI-OH in DMSO-D_6 (600 MHz)

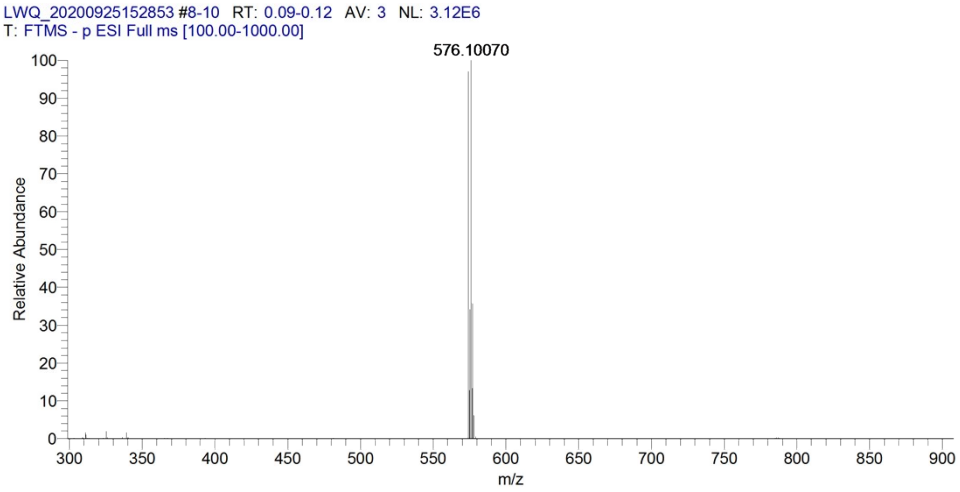

Fig. S6 HRMS (ESI) spectrum of **PMI-OH**.

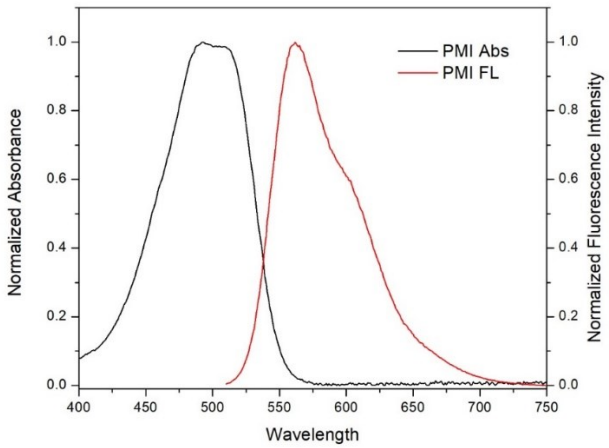

Fig. S7 UV-vis absorption and fluorescence spectra of **PMI** (5 μM) in DMSO.

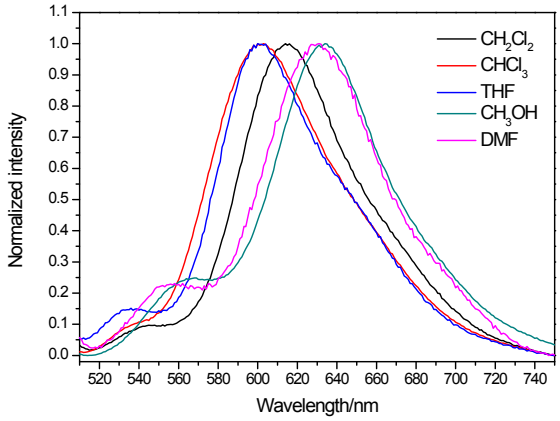

Fig. S8 Fluorescence spectra of **PMI-OH** (5 μM) in CH_2Cl_2, $CHCl_3$, THF, CH_3OH and DMF.

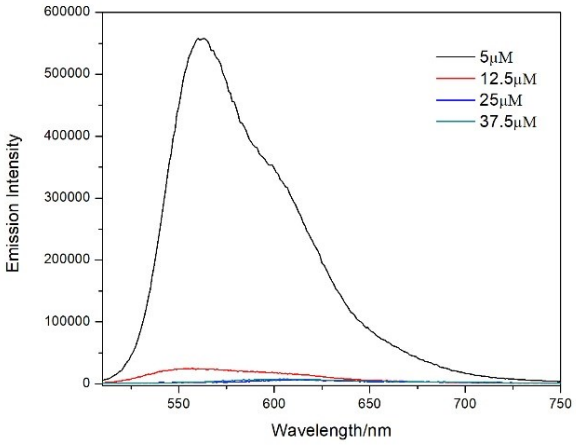

Fig. S9 The fluorescence spectra of **PMI** at 5, 12.5, 25, and 37.5 μM in DMSO.

Table S1 Degree of quenching of **PMI-OH** (5 μM) excimer fluorescence in the presence of different percentage of H_2O in H_2O - DMSO solvent mixtures

Water fraction (v/v, %)	10	20	30	40	50	60	70	80	90
Quenching %	3.92	30.11	51.59	64.23	81.39	96.24	99.02	99.65	99.84

Table S2 Comparison of selectivity, K_{sv} and detection limit towards PA in comparison with previous literatures

Publications	Selectivity	$K_{sv}(M^{-1})$	Detection limit(M)	Response with PA
This work	moderate	1.85×10^5	5.0×10^{-7}	Turn-off
J. Org. Chem. 2013, 78, 1306.	moderate	3.80×10^6	1.5×10^{-6}	Turn-off
J. Mater. Chem. C, 2020, 8, 8257.	high	1.54×10^5	6.1×10^{-8}	Turn-off
Talanta., 2020, 208, 120372.	high	3.22×10^4	1.2×10^{-7}	Turn-off
J. Org. Chem., 2015, 80, 4064.	moderate	5.72×10^6	2.26×10^{-8}	Turn-off
RSC Adv., 2020, 10, 6497.	moderate	/	5.8×10^{-8}	Turn-off
J. Photoch. Photobio. A., 2020, 388, 112201.	high	/	2.4×10^{-7}	Turn-off

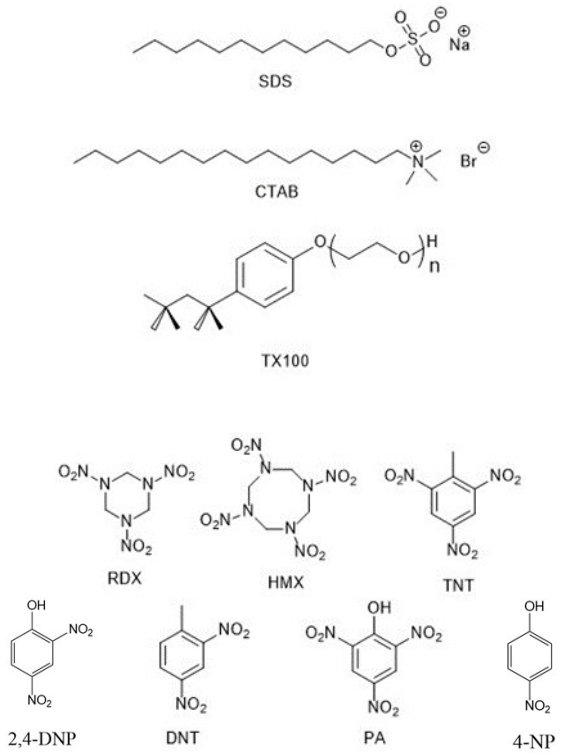

Fig. S10 Chemical structures of the three surfactants and the explosives used in the present study.

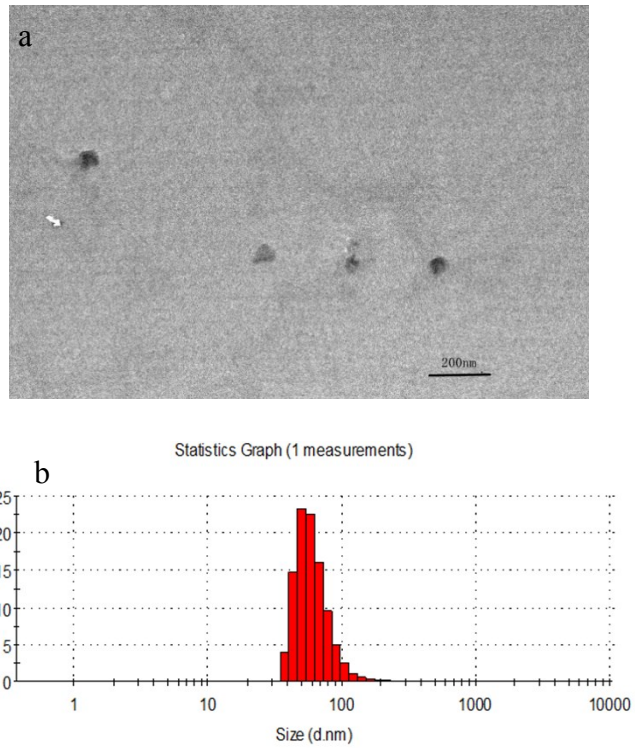

Fig. S11 TEM (a) and DLS (b) of the PMI-OH@TX100 micelles in H_2O / DMSO (9 : 1, v / v) solution.

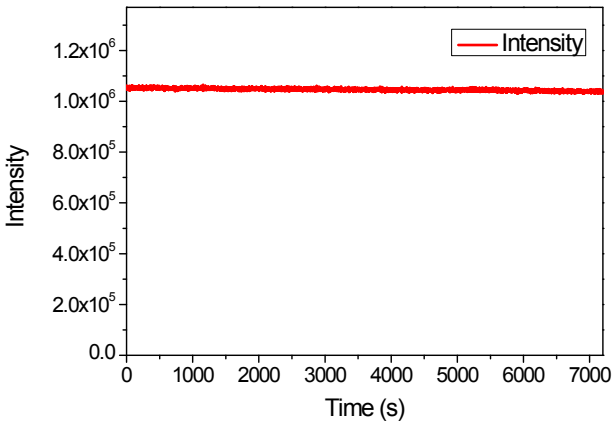

Fig. S12 PMI-OH@TX100 micelles photostability in H_2O / DMSO (9 : 1, v / v) assay solution. **PMI-OH**, 5 μM.

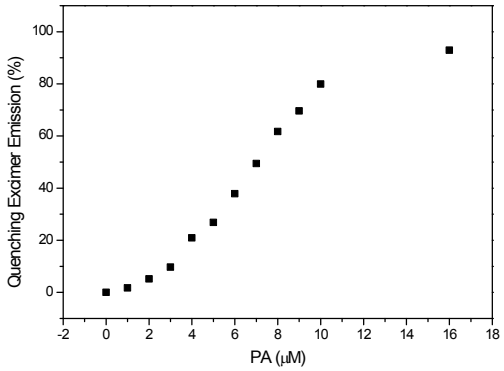

Fig. S13 The fluorescence quenching efficiency at 630 nm with PA concentration. Assay solution, H2O / DMSO (9 : 1, v /v); PMI-OH, 5 μM.

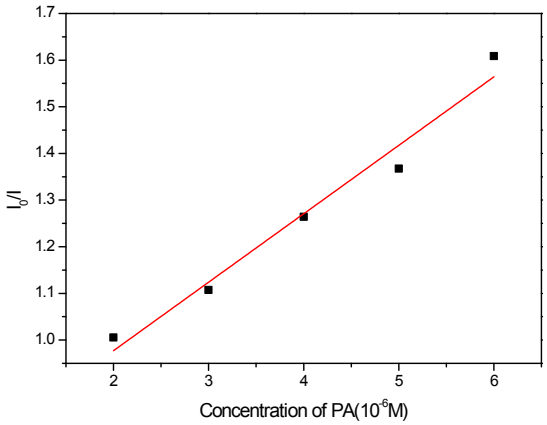

Fig. S14 The Stern-Volmer plots of **PMI-OH**.

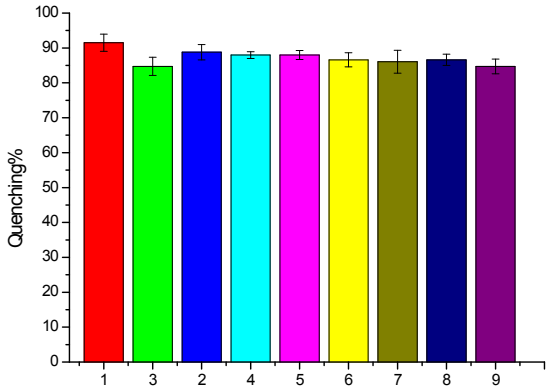

Fig. S15 The fluorescence quenching efficiency of PMI-OH@TX100 micelles with PA in the presence of anions and cations, 1) No ions; 2) $PbNO_3$; 3) $ZnNO_3$; 4) $NiCl_2$; 5) Na_2SO_3; 6) KCl; 7) NaH_2PO_4, 8) $MnCl_2$; 9) NaBr. Ion concentration, 1 mM.

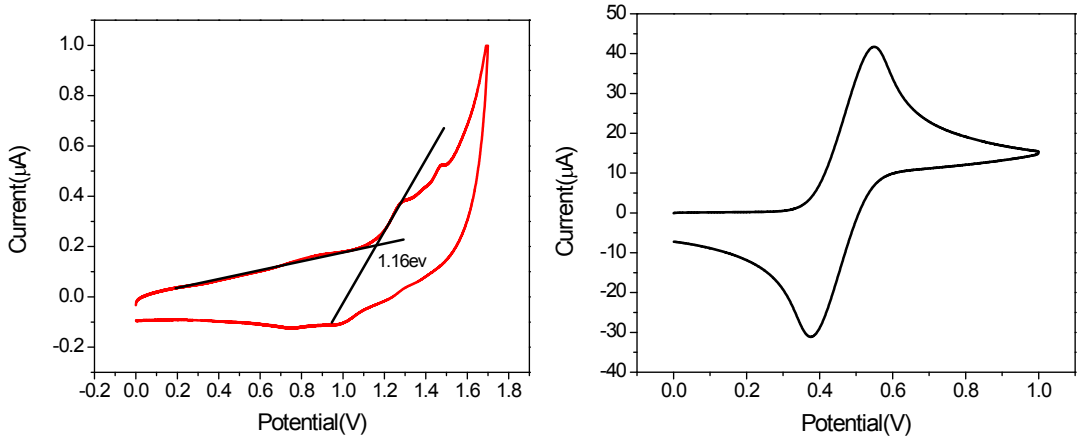

Fig. S16 The cyclic voltammograms of **PMI-OH** (left) and ferrocene (right), scan rate = 50 mVs^{-1}.