

Supporting information

Tetraphenylethene decorated with disulfide-functionalized hyperbranched poly(amido amine)s as metal/organic-solvent-free turn-on AIE probes for biothiols determination

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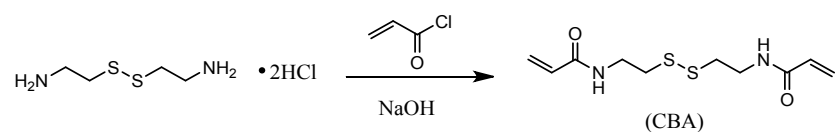
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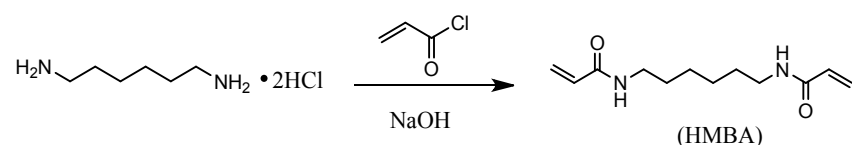
Experimental

The synthesis of CBA



Cystamine dihydrochloride (5.80g, 0.025mol) was added to a four-necked flask equipped with a thermometer, a stirrer and two dropping funnels, then 25mL water was added. After cooling the mixture to 0°C, acryloyl chloride (4.65g, 0.05mol) and an aqueous NaOH solution (0.10mol, 10mL) were added simultaneously and dropwise under stirring in 1 hour, after the addition, the mixture was stirred at room temperature for another 2 hours. Then the white precipitate was collected, and washed with water.

The synthesis of HMBA



1,6-hexanediamine was used to react with acryloyl chloride, the synthesis and purification process are similar with CBA.

Table S1. Normalized Monomers molar feed amount for the synthesis of control samples

Polymer	TPE-epoxide	TAEA	DETA	CBA	HMBA
P1	1	10	--	9	--
P4	1	8	2	9	--
P5	1	5	5	9	--
P6	1	3	7	9	--
P7	1	1	9	9	--
P8	1	10	--	--	9

The synthesis of control samples P4-P8

Set P4 as an example, Firstly, TPE-epoxide (0.40g, 1 mmol) and TAEA (1.20g, 8 mmol) were dissolved in methanol under nitrogen atmosphere, the solution was reflux for about 24 hours until all the epoxy groups were consumed (monitored by TLC). Then the solution was cooled to room temperature. Without further purification, the Michael addition reaction was carried out. CBA (2.34g, 9 mmol) and DETA (0.21g, 2mmol) were added to the solution, and the mixture was stirred at room temperature for 4 days. Subsequently, the pH of the polymerization solution was adjusted to about 2 using 2 M HCl/CH₃OH solution. A large amount of ethyl ether was dropped into the acidified solution under vigorous stirring. The solid product was collected and dried overnight at 40 °C in vacuo.

P5-P7 were synthesized by the same method with P4, and the feed ratio of TAEA and DETA is showing in Table S1, and their ¹H NMR are showing in Figure S11. The signals around 6.65-7.20 ppm are attributed to the TPE groups, and the signals locate at ~3.33 ppm is attributed to the methylene units connected with amide groups of CBA. The signals of TAEA and DETA locate at 2.55-3.25 ppm.

P8 was synthesized by the same method with P1, the only difference was that HMBA, rather than CBA was used to carry out the polymerization. The ¹H NMR is showing in Figure S12. The signals TPE locate at 6.65-7.20 ppm, and the methylene units of HMBA (CONH-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-NHCO) are very and locate at 1.05-1.20ppm. The signals locate at 2.15-3.15 are attributed to TAEA and other methylene groups of HMBA.

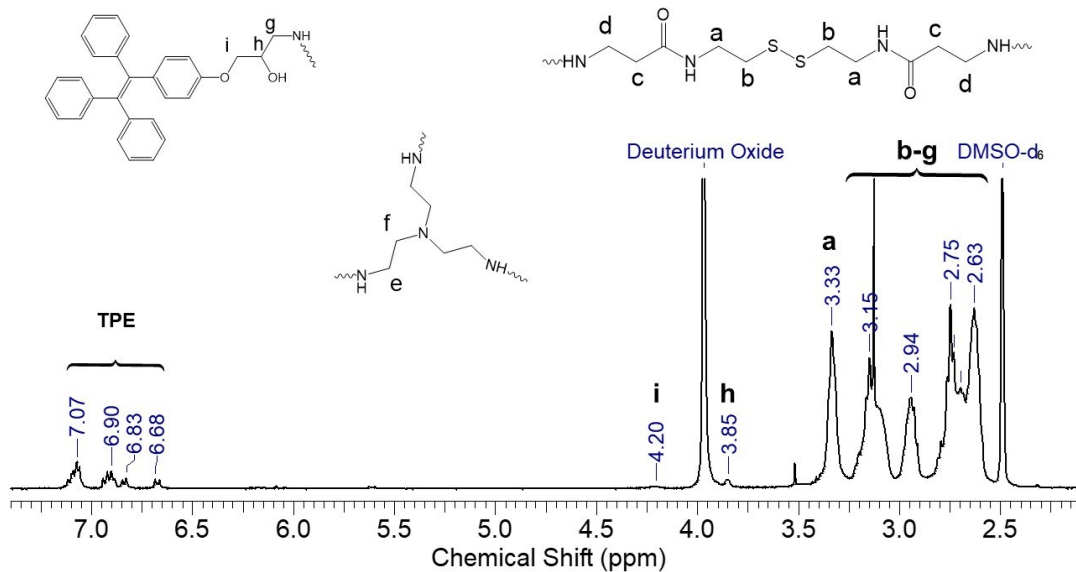


Figure S1. Typical ^1H NMR spectrum of TPE-ssHPA ($\text{DMSO-}d_6$; $\text{D}_2\text{O} = 5 : 1(\text{v/v})$)

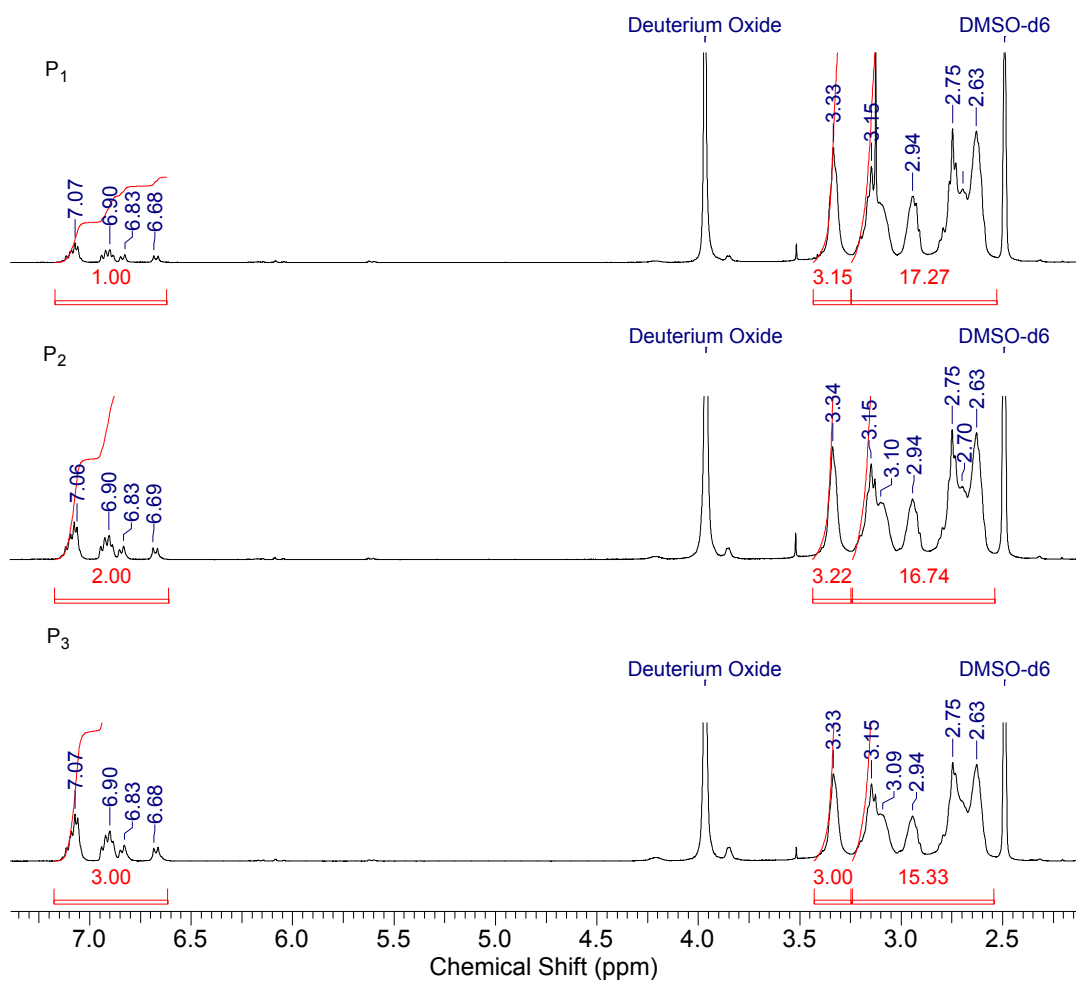


Figure S2. ^1H NMR spectra of P1-P3

Based on Figure S1 and Figure S2, molar ratio of TPE/CBA/TAEA in polymer was calculated according to equation 1:

$$\text{TPE/CBA/TAEA} = (I_{\text{TPE}}/19) : (I_a/4) : [(I_{\text{b-g}} - 3I_a - I_i)/12] \quad (1)$$

Where I_{TPE} denotes the integral of TPE units; I_a denotes the integral of signal a of CBA units; $I_{\text{b-h}}$ denotes the total integral of signals b-h; I_i denotes the integral of signal i.

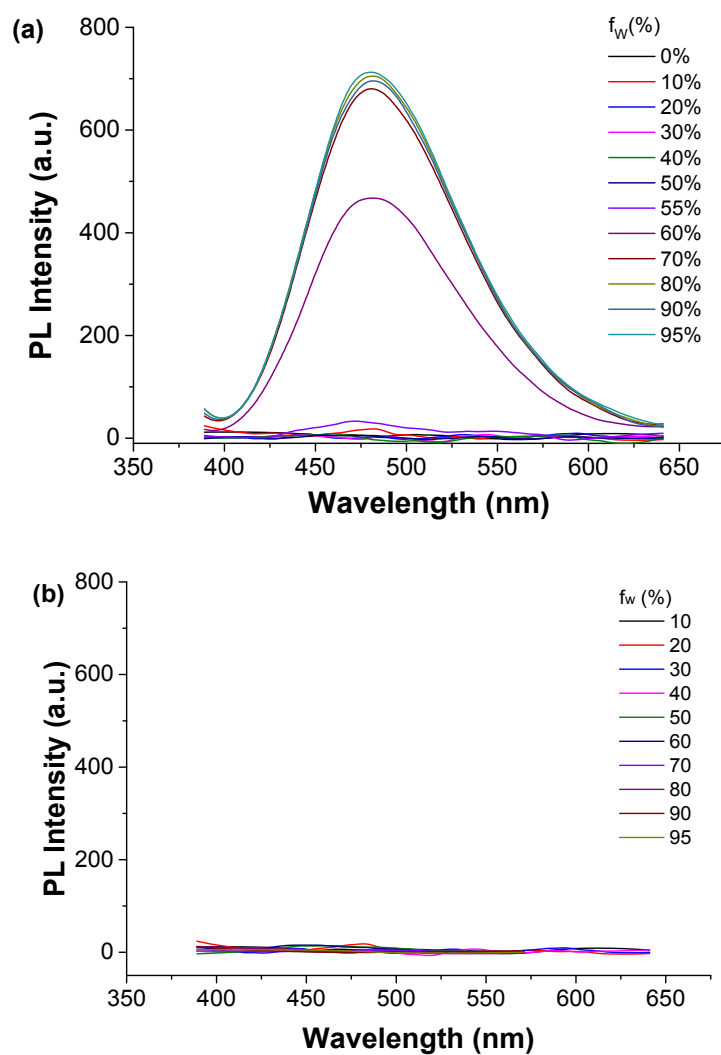


Figure S3. Fluorescence spectra of (a) TPE-epoxide (20 $\mu\text{g}/\text{mL}$) and (b) P1 in water/methanol mixtures (0.2 mg/mL, and concentration of TPE in P1 is $\sim 20 \mu\text{g}/\text{mL}$) with different water fractions. (the pH of the solution was adjusted to 7 by 2M NaOH, $\lambda_{\text{ex}}=360\text{nm}$)

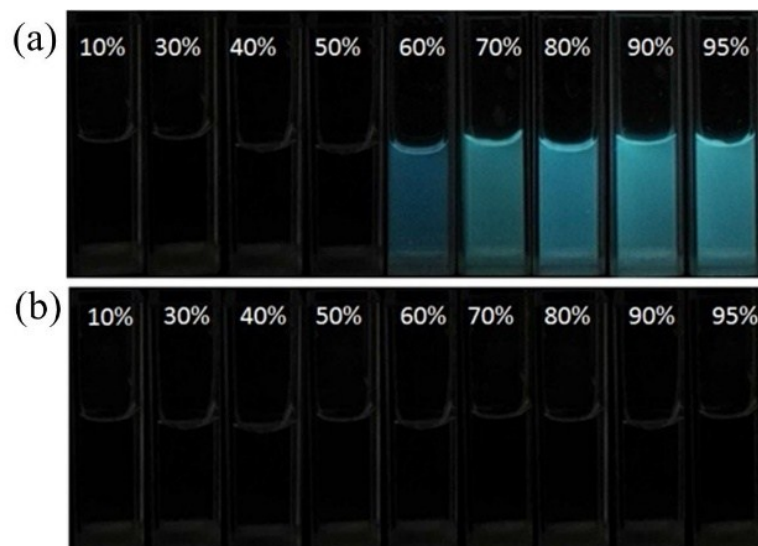


Figure S4. Photographs of (a)TPE-epoxide and (b) P1 in water / methanol mixtures with different fw taken under 365 nm UV illumination. (The concentration for TPE-epoxide and P1 were 20 $\mu\text{g}/\text{mL}$ and 200 $\mu\text{g}/\text{mL}$ respectively, the pH of the solution was set to 7.0 and regulated by 1M NaOH and 1M HCl)

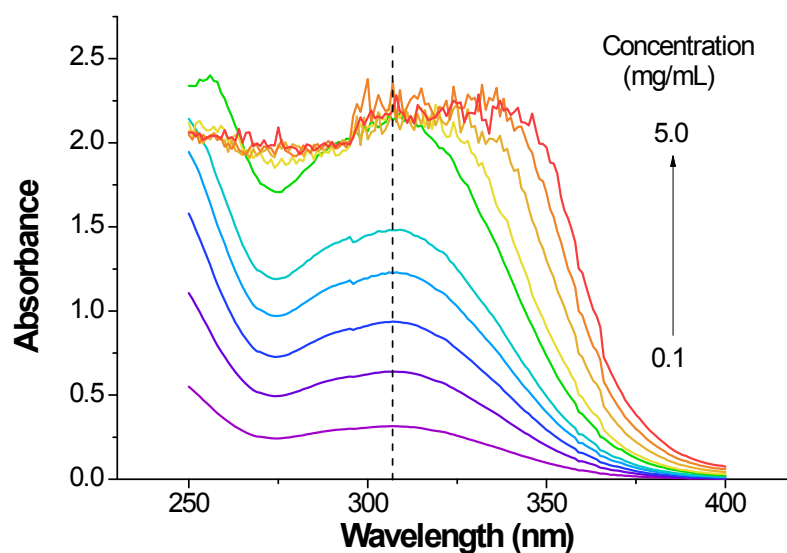


Figure S5. UV-vis spectra of P1 aqueous solution with different concentration.

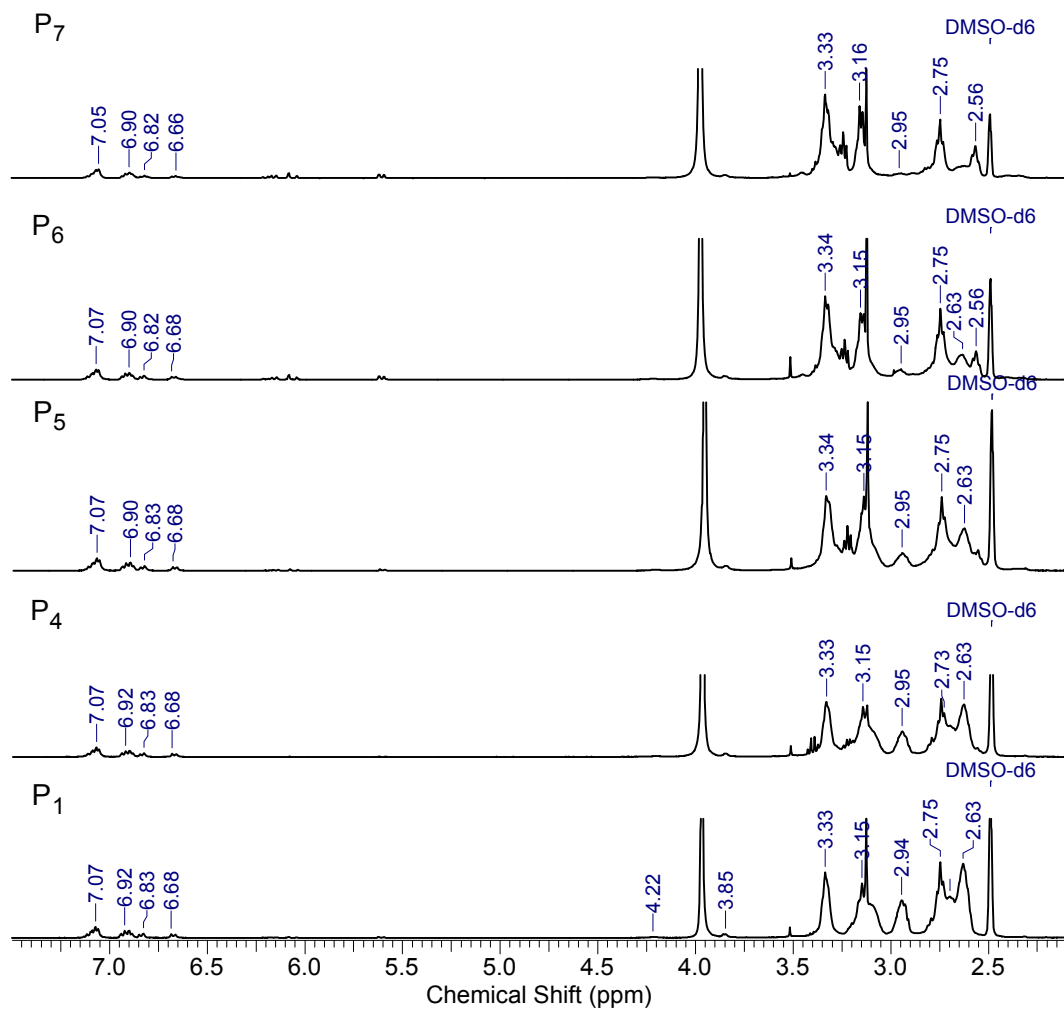


Figure S6. ^1H NMR spectra of P₁ and P₄-P₇.

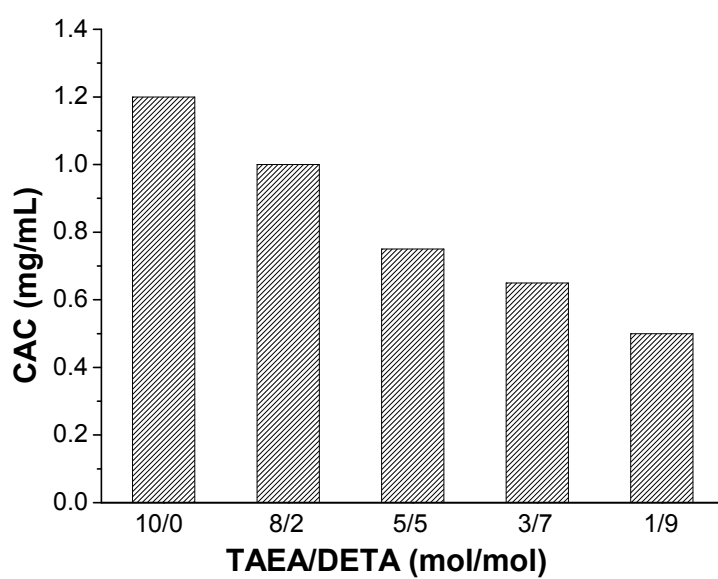


Figure S7. The effect of feed ratio of TAEA/DETA of TPE-HPA on its CAC (pH=7)

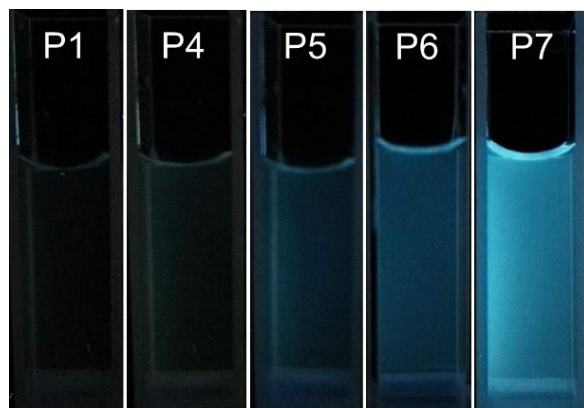


Figure S8. Photographs of P1, P4-P7 aqueous solution under a UV lamp (polymer concentration: 1 mg/mL, pH = 7)

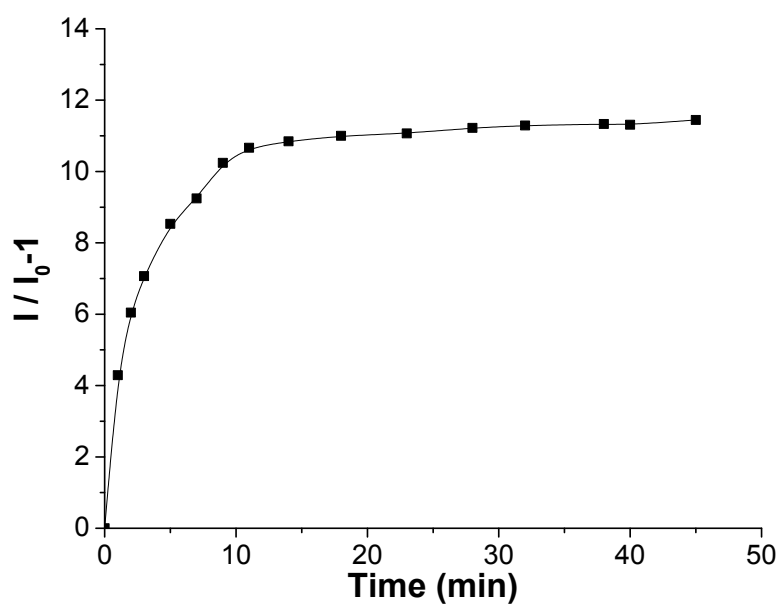


Figure S9. The plot of the changes in PL intensity at 475nm versus GSH incubate time. (P1: 200 $\mu\text{g/mL}$; borate buffer: 0.05M, pH = 7.4; GSH: 0.1mM; $\lambda_{\text{ex}} = 360\text{nm}$)

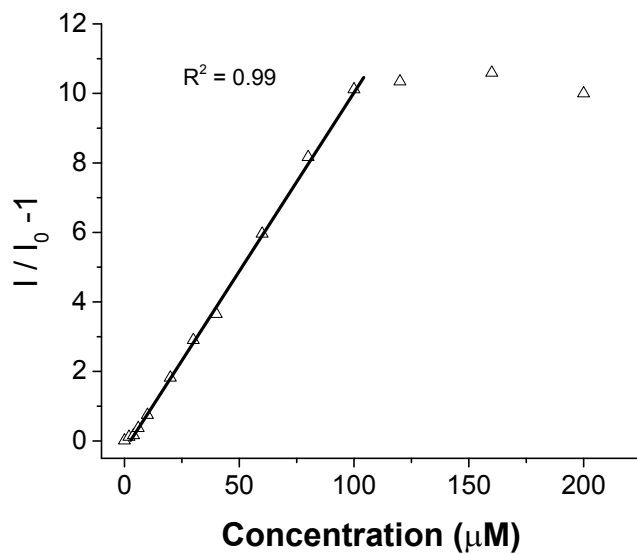


Figure S10. Plot of relative emission intensity enhancement at 475 nm versus Cys concentration. (P1: 200 μg/mL; borate buffer: 0.05M, pH = 7.4; GSH: 0.1mM; $\lambda_{\text{ex}} = 360\text{nm}$)

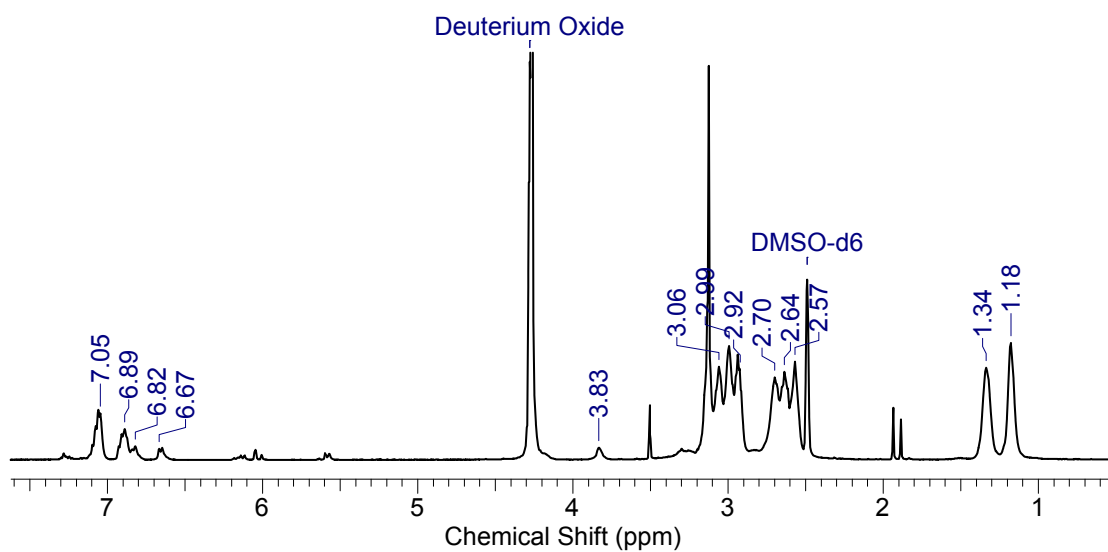


Figure S11. ¹H NMR spectrum of P8

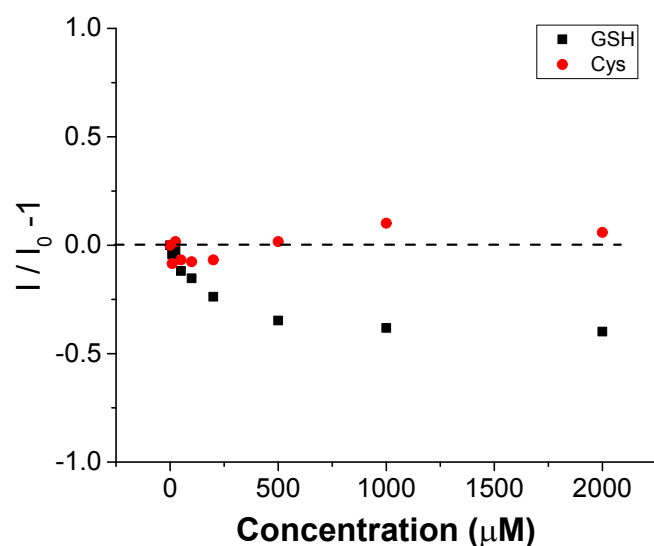


Figure S12. The PL intensity change of P8 aqueous solution with incubating in different concentration of GHS or Cys. (P8: 0.2 mg/mL, 0.05 M borate buffer, pH = 7.4, P4 was incubated with GSH or Cys for 1 hour before measurement)

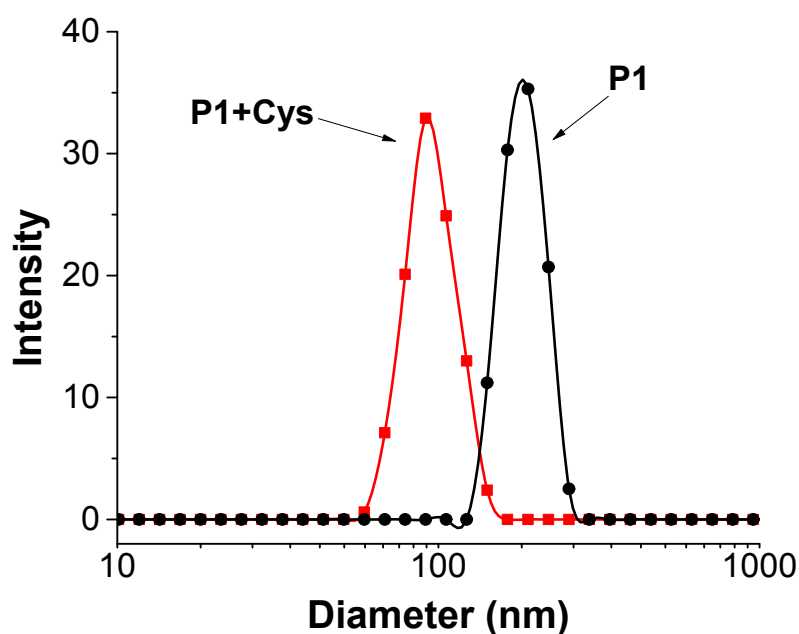


Figure S13. DLS of P1 aqueous solution before and after the adding of Cys (P1: 0.2mg/ML; borate buffer: 0.05M, pH 7.4; Cys: 0.1 mM)

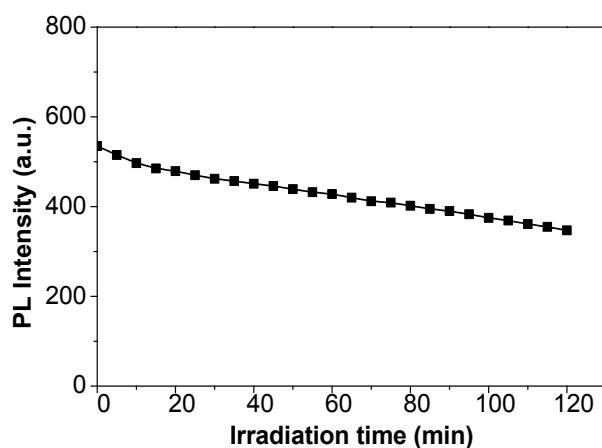


Figure S14. Photostability of P1 aqueous solution (4 mg/mL) under UV light irradiation (light intensity is $\sim 60 \text{ mW/cm}^2$)

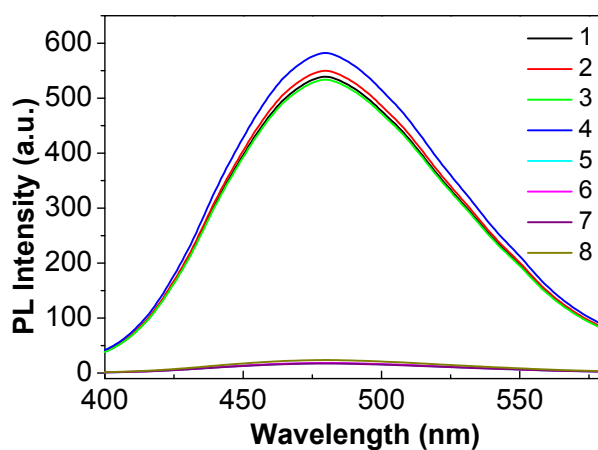


Figure S15. Influence of H_2O_2 and hydroxyl radicals generated from the mixture of H_2O_2 and Fe^{2+} on the PL intensity of P1 aqueous solution: (1) 4 mg/mL TPE-ssHPA; (2) 4 mg/mL TPE-ssHPA+100 μM H_2O_2 ; (3) 4 mg/mL TPE-ssHPA+500 μM H_2O_2 ; (4) 4 mg/mL TPE-ssHPA+100 μM H_2O_2 +100 μM Fe^{2+} ; (5) 0.3 mg/mL TPE-ssHPA; (6) 0.3 mg/mL TPE-ssHPA+100 μM H_2O_2 ; (7) 0.3 mg/mL TPE-ssHPA+500 μM H_2O_2 ; (8) 0.3 mg/mL TPE-ssHPA+100 μM H_2O_2 +100 μM Fe^{2+}

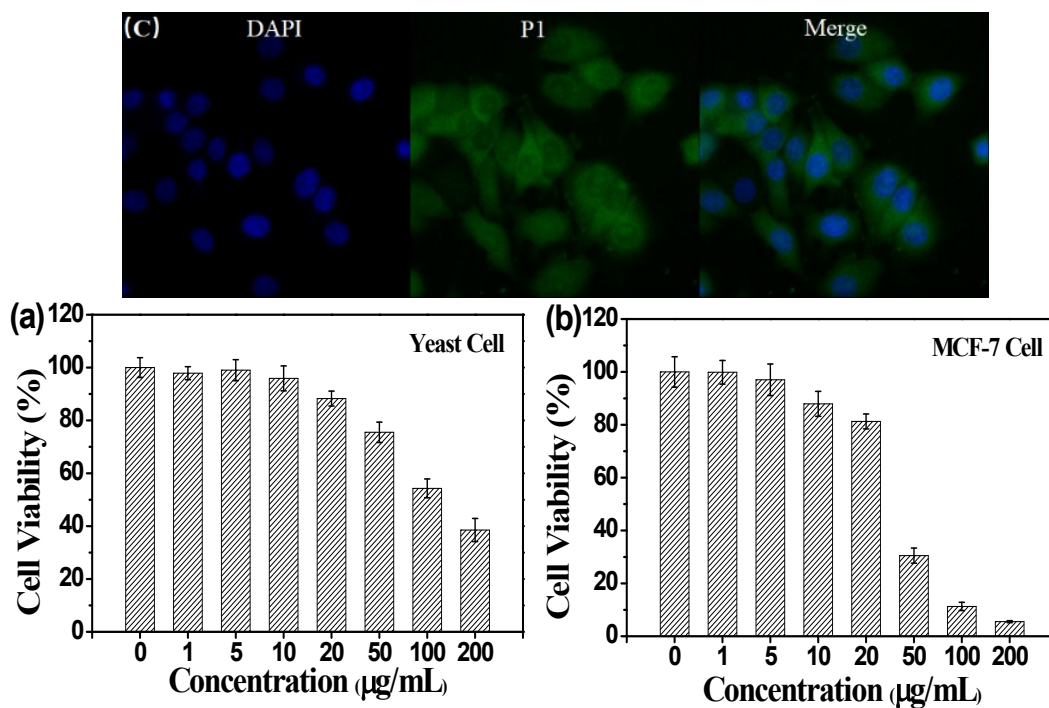


Figure S16. (a) Cellular toxicity of P1 on Yeast cell viability, (b) Cellular toxicity of P1 on MCF-7 cell viability, (c) Fluorescent field images of MCF-7 cells treated with nucleus label dye DAPI (10 $\mu\text{g/mL}$) and P1 (10 $\mu\text{g/mL}$)

AIE probe	solvent	Biothiol detection	LOD	Ref
DMTPS-mDCV	DMSO/ Water: 3/2(v/v)	Turn-on	0.50 μ M	[1]
TPENNO ₂	DMSO/Water: (DMSO, 2.5 %, v/v)	Turn-on	0.18 μ M	[2]
TPE-DPP	THF/Water: 2/3(v/v)	Turn-on	0.05 μ M	[3]
Zincke's saltsubstituted TPE	DMSO/Water: (DMSO, 0.5 %, v/v)	Turn-on	0.04 μ M	[4]
TPE-SS-Peptide	DMSO/Water: (DMSO, 0.5 %, v/v)	Turn-on	4.26 μ M	[5]
TPE-naphthalimide	DMSO/Water: 1/9(v/v)	Turn-on	1.90 μ M	[6]
TPE- cyclic RGD (cRGD) peptide	DMSO/Water: (DMSO, 0.5 %, v/v)	Turn-on	1.00 μ M	[7]
TPE-Py	Acetonitrile/Water: 1/4(v/v)	Ratiometric	0.35 μ M	[8]
TPE-poly(amido-amine)	Water	Turn-on	0.34μM	This work

Table S2 Comparison of AIE probes for the detection of biothiols

Refs:

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aggregation-induced emission characteristics for distinguishing homocysteine over cysteine and glutathione, *J. Mater. Chem. C*, 2015, 3, 8397-8402.