Electronic Supplementary Information

Detection of glutaraldehyde in aqueous environment based on fluorescence quenching of a conjugated polymer with pendant protonated primary amino groups

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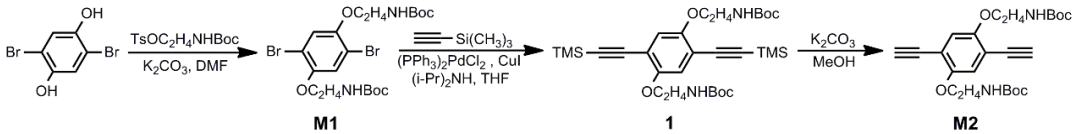
1. Synthesis of Monomers

The monomers were synthesized according to Scheme S1. The experimental details are described below.

Scheme S1. The synthetic route of monomers.



Monomer M1. Under an argon atmosphere, a mixture of 2,5-dibromohydroquinone (0.80 g, 3.00 mmol), tert-Butyl N-[2-(tosyloxy)ethyl]carbamate (2.13 g, 6.75 mmol), and potassium carbonate (4.15 g, 30 mmol) in 15 mL of DMF was refluxed for 24 h at 70 ºC. The reaction mixture was cooled down to room temperature, and stirred for

additional 2 h after adding 200 mL of deionized water. The solid was collected after filtration, and purified by column chromatography with n-hexane/ethyl acetate (2:1, v/v). After removing the solvent, further recrystallization over n-hexane/ethyl acetate to yield a white solid as the product (1.22 g, yield 74%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.46(s, 18H), 3.55(q, 4H), 4.02(t, 4H), 5.05(br, 2H), 7.10(s, 2H). Calcd for $C_{20}H_{30}O_6N_2Br_2$ (%): C, 43.34; H, 5.46; N, 5.05; found: C, 43.21; H, 5.53; N, 4.84.

Compound 1. Monomer M1 (1.12 g, 2.00 mmol) was added to a mixture of CuI (20 mg, 0.10 mmol) and $(PPh_3)_2PdCl_2$ (70 mg, 0.10 mmol) in 10 mL of diisopropylamine and 15 mL of THF, followed by the dropwise addition of trimethylsilylacetylene (0.8 mL, 5.60 mmol) under an argon atmosphere. The mixture was stirred at room temperature for 1 h and refluxed for 12 h at 60 ºC, and then was cooled down to room temperature. The filtrate was collected after the filtration. Crude product was obtained after removing solvent in the filtrate under reduced pressure, which was then purified by flash chromatography on a silica gel column (n-hexane/ethyl acetate, 4:1, v/v). Removing the solvent again and further recrystallization over n-hexane/ethyl acetate yielded a silver powder as the product (0.88 g, yield 75%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.27(s, 18H), 1.45(s, 18H), 3.53(q, 4H), 4.03(t, 4H), 5.11(br, 2H), 6.91(s, 2H).

Monomer M2. A mixture of compound 1 (0.88 g, 1.50 mmol), potassium carbonate (0.10 g, 0.75 mmol), 15 mL of MeOH was stirred for 12 h at room temperature under an argon atmosphere. The resulting mixture was filtered and the filtrate was collected. Crude product was obtained after removing solvent in the filtrate under reduced pressured and then was chromatographed over n-hexane/ethyl acetate (5:2, v/v) on a silica column. Removing the solvent again and further recrystallization over n-hexane/ethyl acetate yielded a light yellow solid as the product (0.53 g, yield 80%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.45(s, 18H), 3.36(s, 2H), 3.54(q, 4H), 4.04(t, 4H), 5.10(br. 2H), 6.97(s, 2H). Calcd for $C_{24}H_{32}O_6N_2$ (%): C, 64.85; H, 7.26; N, 6.30; found: C, 64.54; H, 7.29; N, 6.21.

2. Determining of the Limit of Detection

The limit of detection (DL) of PPE-NH_3^+ to glutaraldehyde (GA) and formaldehyde (FA) was calculated using linear regression theory, [S1] according to the following equations.

$$s_a = \sqrt{\frac{\sum_{i=0}^{n}(x_i - \overline{x})^2}{n-1}} \quad (1)$$

$$\mathbf{S} = \frac{\Delta I}{\Delta c} \quad (2)$$

$$\mathbf{LOD} = \frac{3s_a}{|S|} \quad (3)$$

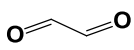
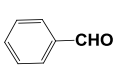
The standard deviation (s_a) regarding the present aqueous solution of PPE-NH_3^+ and the instrument was determined by following procedure. Measure the fluorescence intensities x_i of the solution for more than 10 times, and calculating the corresponding average intensity($\overline{x}$); then the value of the standard deviation (s_a) was calculated according to equation (1).

Then, FA or GA of varied concentrations was added into the solution, and the fluorescence emission peak intensity was recorded. The intensity varied linearly with the aldehyde concentration at low concentration as shown in Fig. 4b or Fig. S5b. Therefore, the value of sensitivity (S) in equation (2) was obtained by calculating the slope of the linear part at the lower concertation of aldehydes in the inset of Fig. 4b and Fig. S5b. Finally, the LOD for each analyte was calculated according to equation (3) based on the obtained values for (s_a) and S.

Table S1. The photophysical data for the polymers in different solvents

	$\lambda_{max,\ abs}$ (nm)	$\lambda_{max,\ em}$ (nm)	Φ_f (%)
PPE-NBoc in DMF	431	500	31
PPE-NH_3^+ in DMF	404	472	2.4
PPE-NH_3^+ in H_2O	386	455	0.8

Table S2. The common aldehydes and their applications

Name	**Structure**	**Use**
formaldehyde	HCHO	1) industrial applications (resin, adhesives, textile) 2) disinfectant and biocide (detergent) 3) tissue fixative and embalming agent (food)
acetaldehyde	CH_3CHO	1) precursor to acetic acid 2) essence in beverage and wine
propionaldehyde	CH_3CH_2CHO	1) precursor to trimethylolethane, propanol and propionic acid 2) used as antifreeze, lubricants, dehydrating agent
butyraldehyde	$CH_3(CH_2)_2CHO$	1) important precursor in industrial applications 2) the preparartion of perfume and spices
glutaraldehyde	$CHO(CH_2)_3CHO$	1) disinfectant(medical instruments) 2) crosslinker (biochemistry applications)
glyoxal		crosslinker (coated paper and textile finishes)
benzaldehyde		1) precursor to mandelic acid 2) flavoring agent (baked goods)

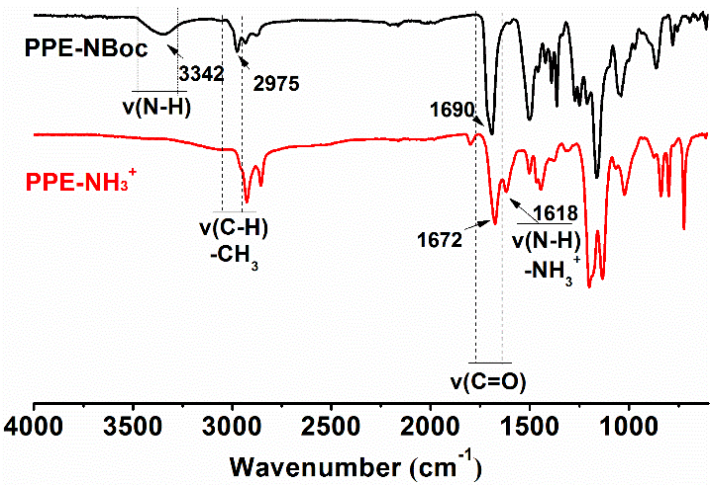


Fig. S1 FTIR spectra of PPE-NBoc and PPE-NH_3^+.

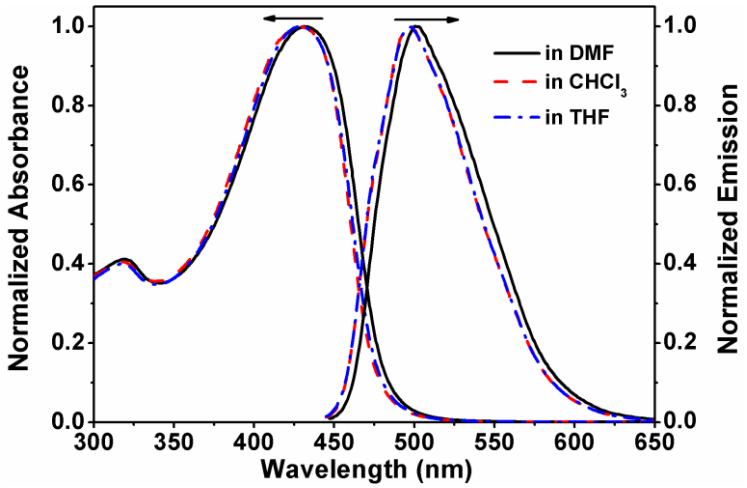


Fig. S2 Absorption and emission spectra of PPE-NBoc in different solvents with concentration of 2×10^{-5} M in repeat unit. The fluorescence was excited at the absorption maximum

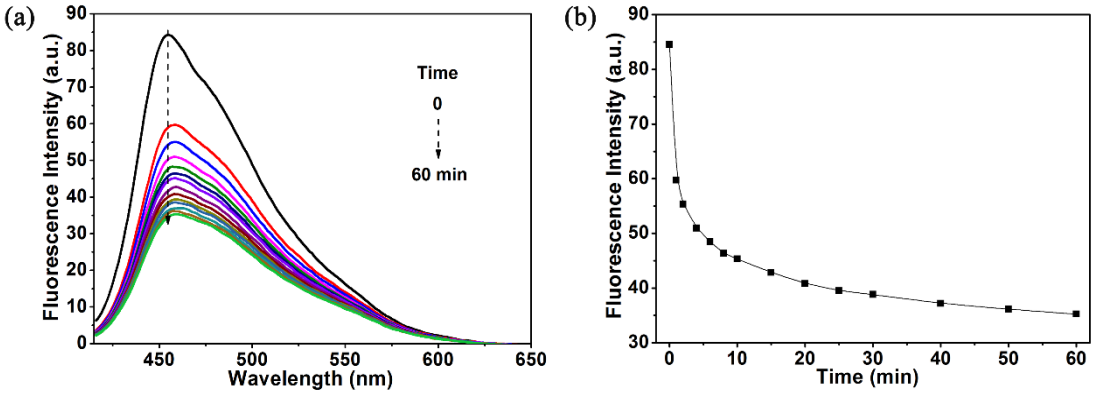


Fig. S3 (a) Emission spectra of PPE-NH_3^+ (2×10^{-5} M in repeat unit) in aqueous solution recorded at different times after adding formaldehyde (FA) (10 mM); (b) The change of the intensity at the emission maximum with the time.

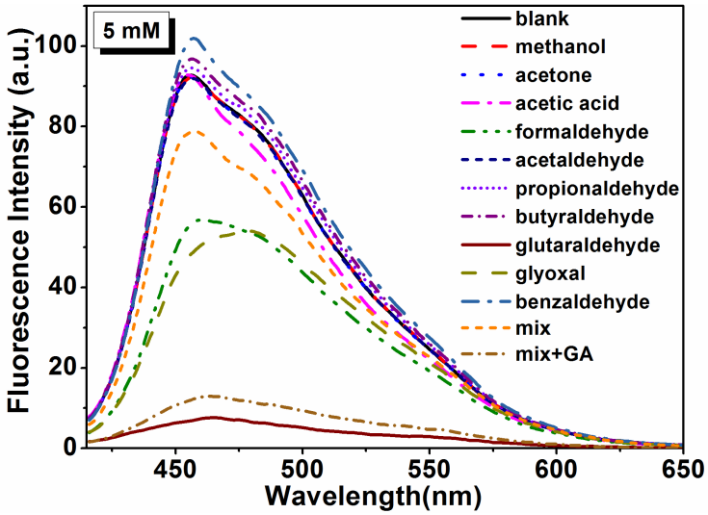


Fig. S4 Emission spectra of PPE-NH_3^+ (2×10^{-5} M in repeat unit) in aqueous solution upon the addition of different analytes (5 mM). The mixture has all the analytes except GA. The excitation was set at 400 nm and response time was 30 min.

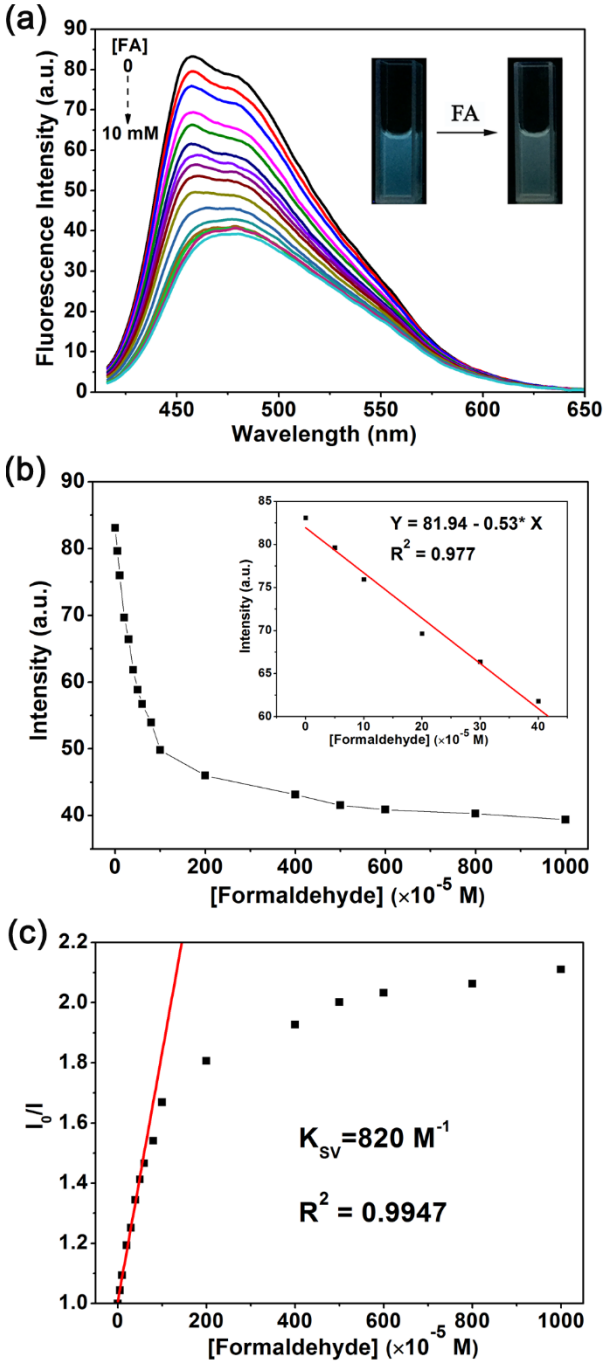


Fig. S5 Emission spectra （excited at 400 nm）of PPE-NH_3^+ (2×10^{-5} M in repeat unit) in aqueous solution for formaldehyde (FA) in different concentrations (recorded 30 min after adding FA); insert showing the photos of the polymer solution under 365 nm UV lamp before and after adding 1 mM FA. (b) The intensities at the emission maxima after adding FA in various concentrations; Inset showing the enlarged plot for the FA concentration from 0 to 40×10^{-5} M and the linear fit for calculating the limit of detection (LOD). (c) the Stern-Volmer plot for the quenching of PPE-NH_3^+ by FA.

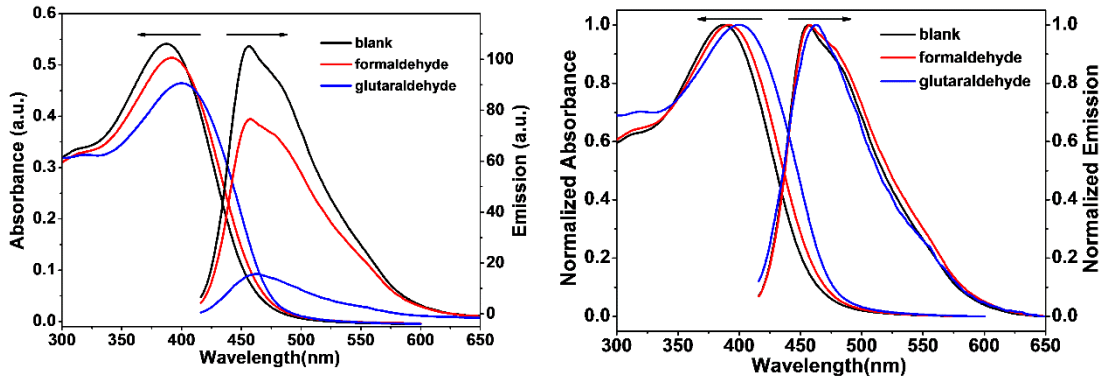


Fig. S6 Absorption spectra and emission spectra （excited at 400 nm） of PPE-NH_3^+ (2×10^{-5} M in repeat unit) in aqueous solution upon adding water, formaldehyde (FA) (1mM) and glutaraldehyde (GA) (1 mM) without (left) and with (right) normalization.

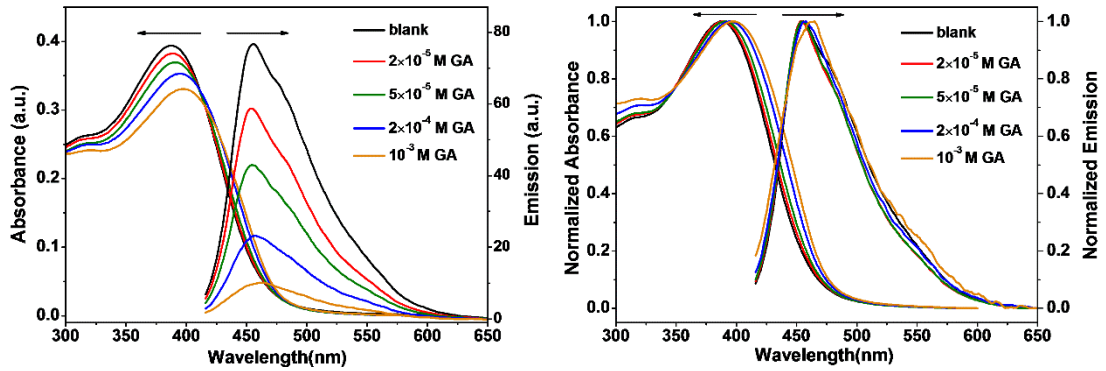


Fig. S7 Absorption spectra and emission spectra （excited at 400 nm） of PPE-NH_3^+ (2×10^{-5} M in repeat unit) in aqueous solution upon adding water, and glutaraldehyde (GA) in different concentration without (left) and with (right) normalization.

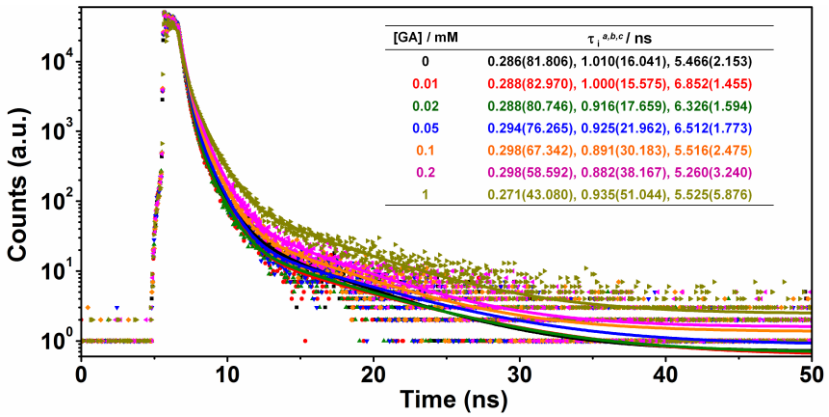


Fig. S8 Time-resolved fluorescence decays of PPE-NH_3^+ (2×10^{-5} M in repeat unit) in aqueous with and without GA in different concentration. Inset showing the lifetime and weight fractions (excited at 406 nm, detected at 458 nm, measured at room temperature).

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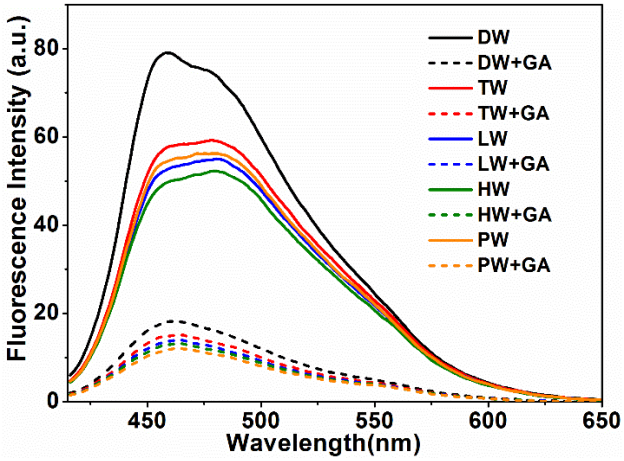

Fig. S9 Emission spectra of PPE-NH_3^+ (2×10^{-5} M in repeat unit) in aqueous solution upon adding different water samples (with/without 1 mM of GA). The excitation was set at 400 nm and the response time was 30 min.

Reference

(S1) Q. Sun, Y. Lu, L. Liu, K. Liu, R. Miao, Y. Fang, *ACS Appl. Mater. Interfaces* 2016, **8**, 29128.