Supplementary information for

Selective and Sensitive Detection of Picric Acid Based on a

Water-Soluble Fluorescent Probe

Materials. All chemicals were purchased from Beijing chem. Reagents Co. (Beijing, China), Aladdin, Alfa Aesar, and Sigma-Aldrich and were used as received. Cationic pyrene derivative (PyOEA) was synthesized and purified as follows.

Synthesis of PyOEA
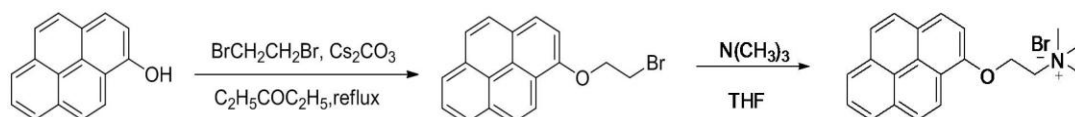
1-(2-bromoethoxy)pyrene (PyOEBr) To an acetone solution (35 mL) of 1-hydroxypyrene (2.18 g, 10.0 mmol), Cs_2CO_3 (6.5 g, 19.9 mmol) and 1,2-dibromoethane (7.48 g, 39.8 mmol) was added and the action was refluxed for 4 hours. The reaction mixture was cooled to room temperature and extracted with dichloromethane. The organic layer was dried ($MgSO_4$), filtered, and evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, petroleum ether/dibromoethane (2:1 v/v)) to give pale yellow solid (3.08 g, 95% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, J = 9.0 Hz, 1H), 8.14-8.05 (m, 4H), 7.99-7.95 (m, 2H), 7.91 (d, J = 9.0 Hz, 1H), 7.49 (d, J = 8.5 Hz, 1H), 4.62 (t, J = 6.0 Hz, 2H), 3.85 (t, J = 6.0 Hz, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 151.99 (s), 131.64 (s), 131.61(s),127.13 (s), 126.73 (s), 126.21 (s), 125.90 (s), 125.86 (s), 125.43 (s), 125.34 (s), 124.82 (s), 124.49 (s), 124.40 (s), 121.09 (s), 120.75 (s), 109.51 (s), 68.97 (s), 29.41 (s). HRMS: calcd [M] for $C_{18}H_{13}BrO$ 324.0150; found, 324.0149.
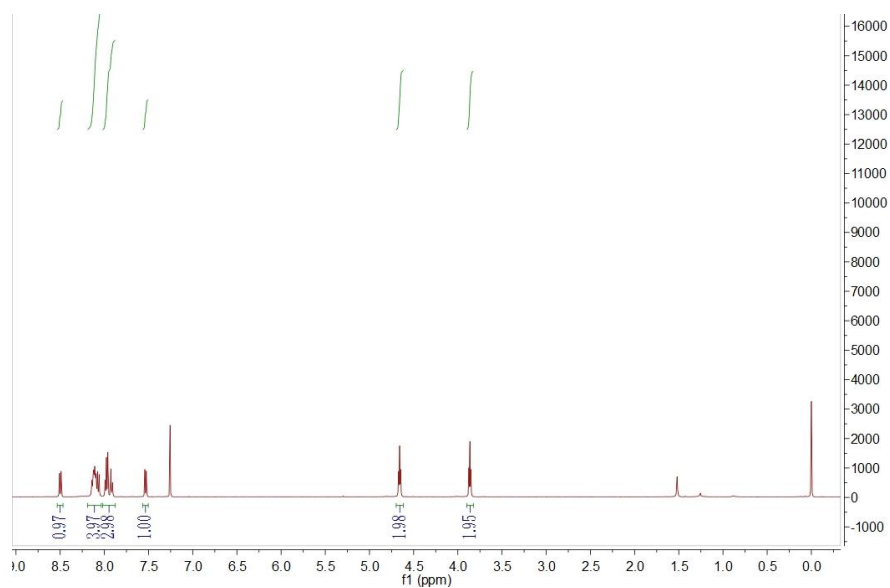
**Fig. S1** ^{1}H NMR spectrum of PyOEBr in CDCl$_3$
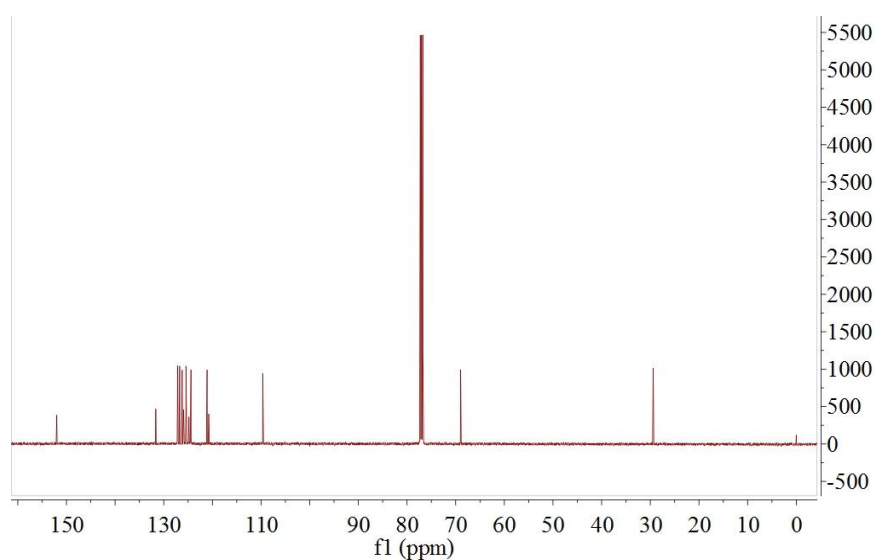

Fig. S2 ^{13}C NMR spectrum of PyOEBr in CDCl$_3$

***N,N,N*-trimethyl-2-(pyren-1-yloxy)ethanaminium bromide (PyOEA).** To a solution of PyOEBr (1.62 g, 5.0 mmol) in THF, trimethylamine dissolved in EtOH (1.8 mL) was added and the mixture was stirred at 40 ℃ for 4 hours. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The crude product was poured into THF and filtered. After washing with THF, white solid of PyOEA was obtained (1.72g, 90% yield). ^{1}H NMR (500 MHz, DMSO) δ 8.42 (d, *J* = 9.0 Hz, 1H), 8.31 (d, *J* = 8.5 Hz, 1H), 8.25-8.21 (m, 2H), 8.18 (d, *J* =

9.5 Hz, 1H), 8.11 (d, J = 9.0 Hz, 1H), 8.0 (m, 2H), 7.85 (d, J = 8.5 Hz, 1H), 4.87 (m, 2H), 4.06 (t, J = 4.5 Hz, 2H) 3.33 (s, 9H). ^{13}C NMR (125 MHz, DMSO) δ 151.50 (s), 131.67 (s), 131.49 (s), 127.74 (s), 127.13 (s), 127.02 (s), 126.34 (s), 125.57 (s), 125.54 (s), 125.38 (s), 125.10 (s), 124.85 (s), 124.50 (s),121.28 (s), 119.78 (s), 110.41 (s), 65.07 (s), 62.98 (s), 53.66 (s). HRMS: calcd [M-Br] for $C_{21}H_{22}NO$, 304.17; found, 304.1698.
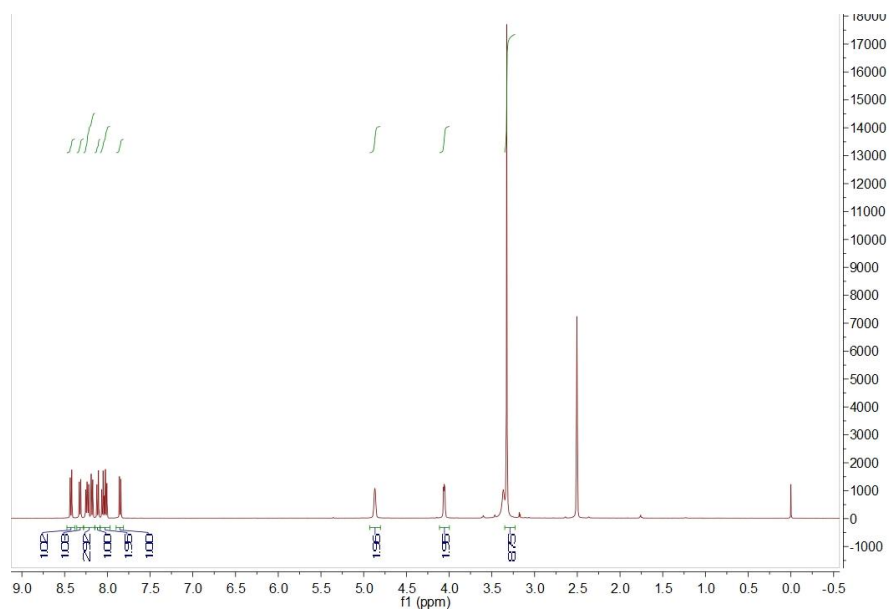

Fig. S3 ^{1}H NMR spectrum of PyOEA in DMSO-d6
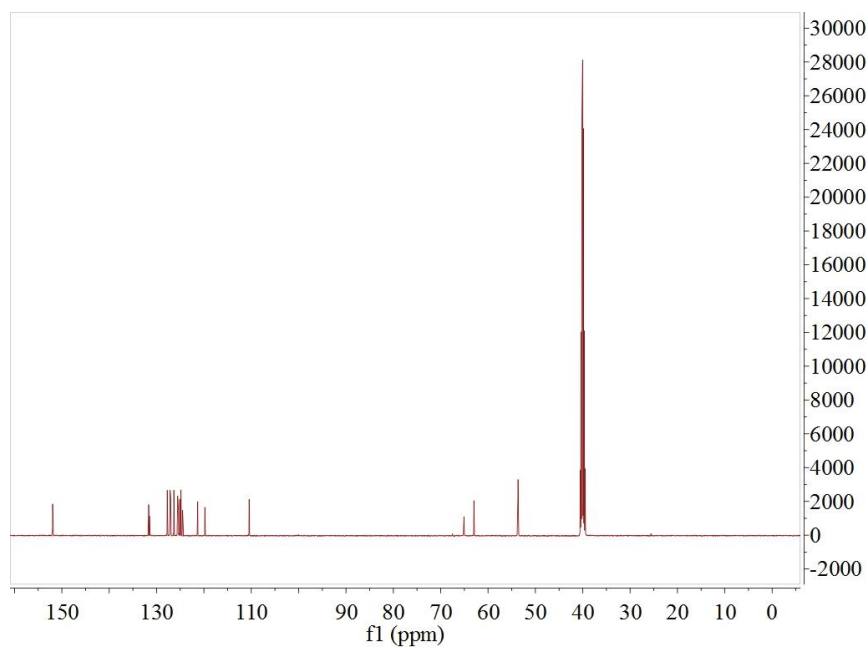
Fig. S4 ^{13}C NMR spectrum of PyOEA in DMSO-d6

Sample preparation. The stock solution of PyOEA and PA were prepared in pure water. The stock solutions of other organic interferents were initially dissolved in DMSO with a relatively high concentration. Stock solutions of PyOEA and PA were mixed directly to give the desired concentration and then measured with fluorescence spectrometer immediately.

Spectral measurements. Absorption and emission spectra were collected by using a HITACHI U-3900 UV-VIS spectrophotometer and a HORIBA Scientific Fluorolog®-3 spectrofluorometer, respectively. ^{1}H NMR and ^{13}C NMR spectra were carried out on a Bruker Avance III 500 spectrometer.
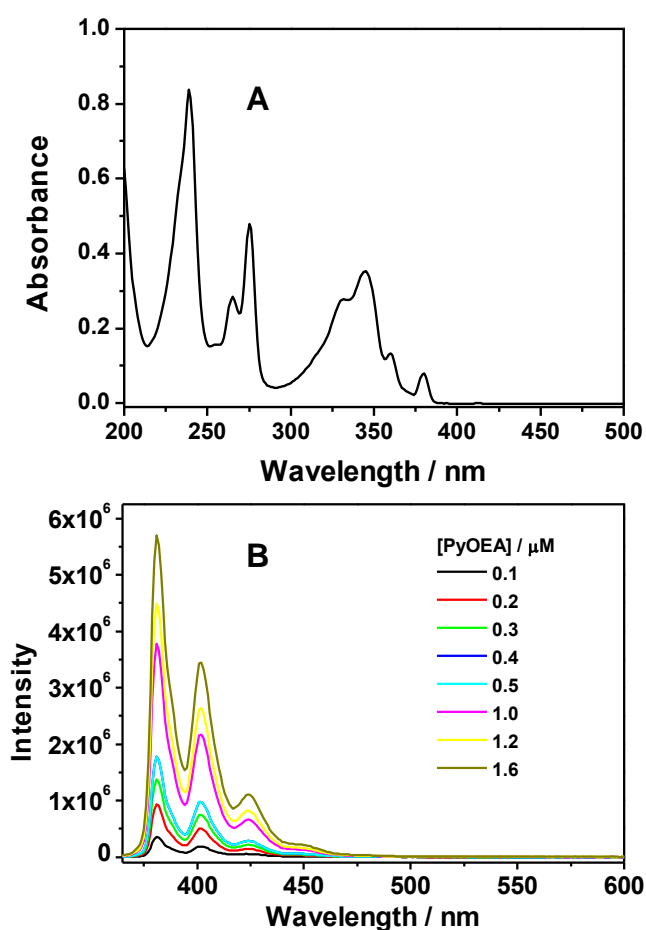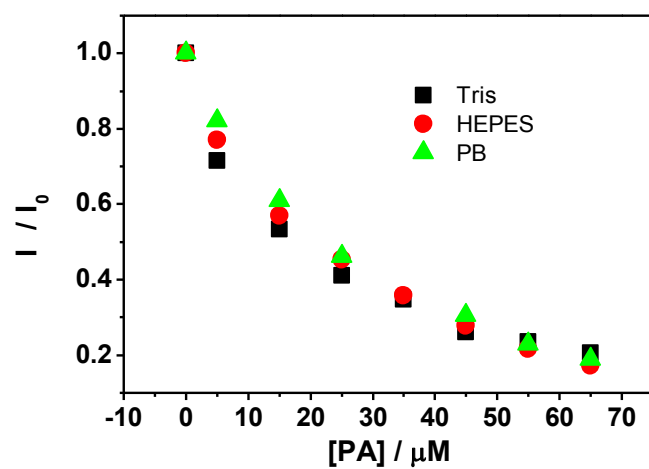
Fig. S5 Absorption (A) and emission (B) spectra of PyOEA in 10 mM HEPES buffer (pH 7.4); λ_{ex} = 345 nm.
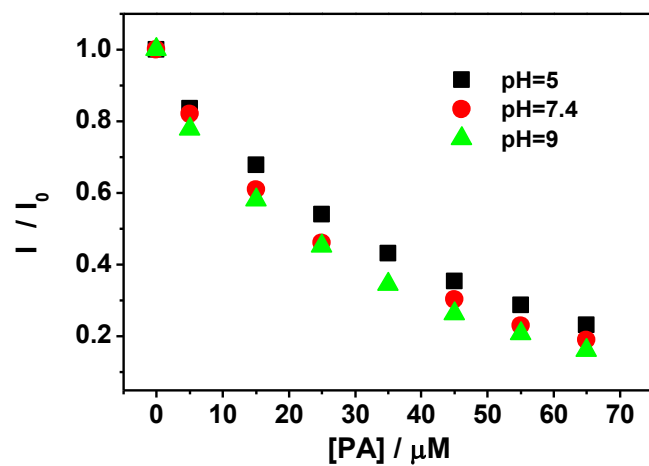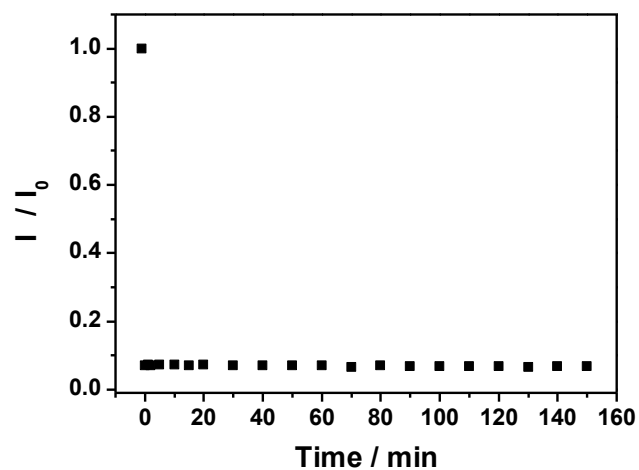
Fig. S6 Plots of I / I_0 vs [PA] in aqueous solution with different pH values as indicated.
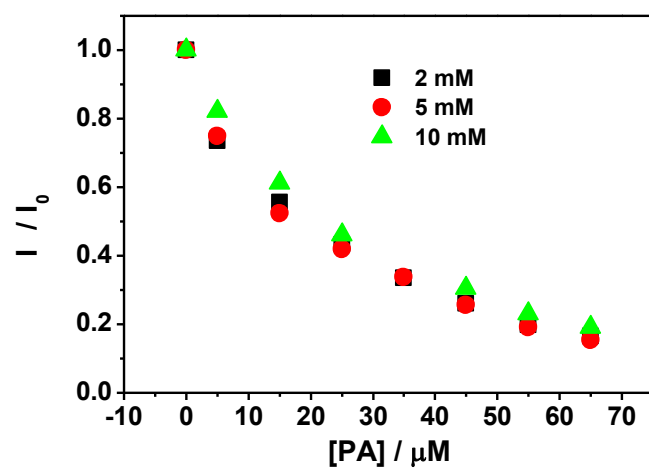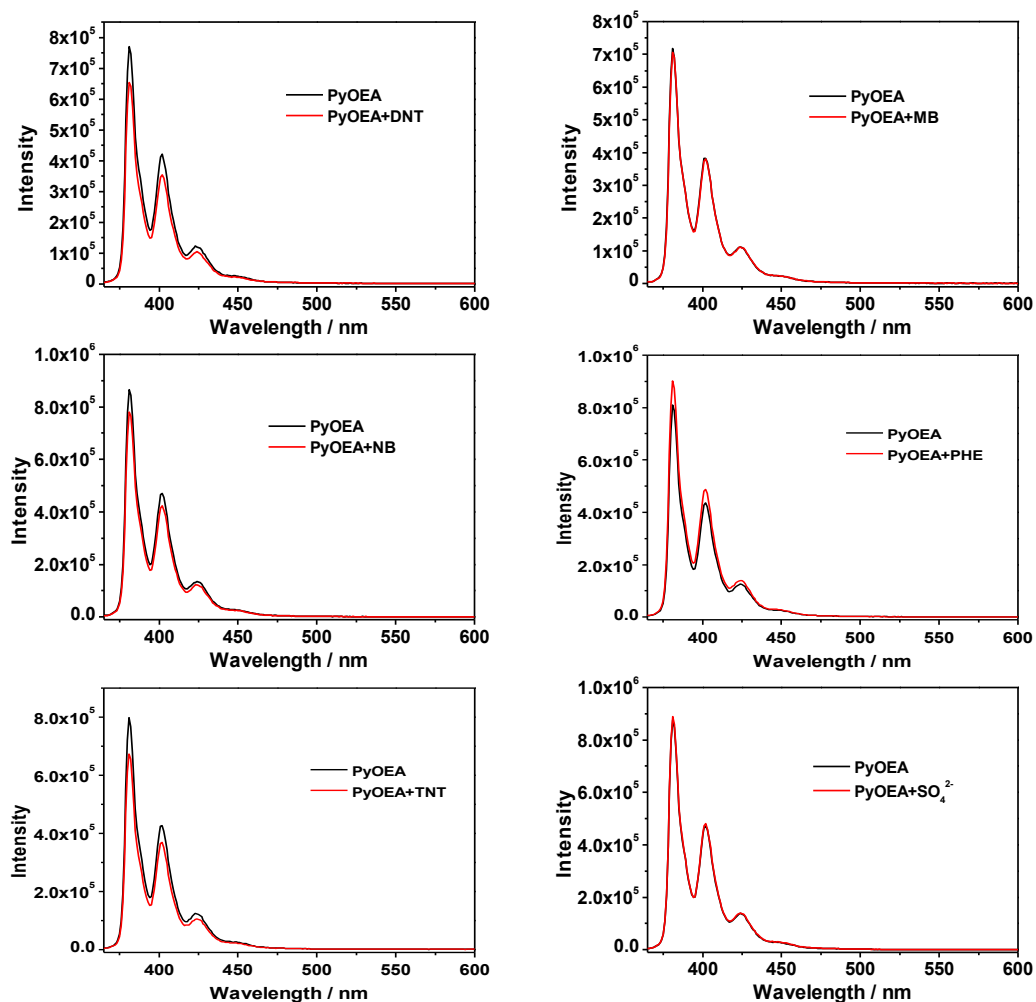

Fig. S7 Plots of I / I_0 vs. [PA] in HEPES buffer (pH 7.4) with different concentrations as indicated.

Fig. S8 Plots of I / I_0 vs [PA] in different buffer (10 mM, pH 7.4) as indicated.

Fig. S9 Relative intensity of I / I_0 vs incubation time for the detection of PA in 10 mM HEPES buffer (pH 7.4). [PyOEA] $= 2.0 \times 10^{-7}$ M; [PA] $= 9.0 \times 10^{-5}$ M.
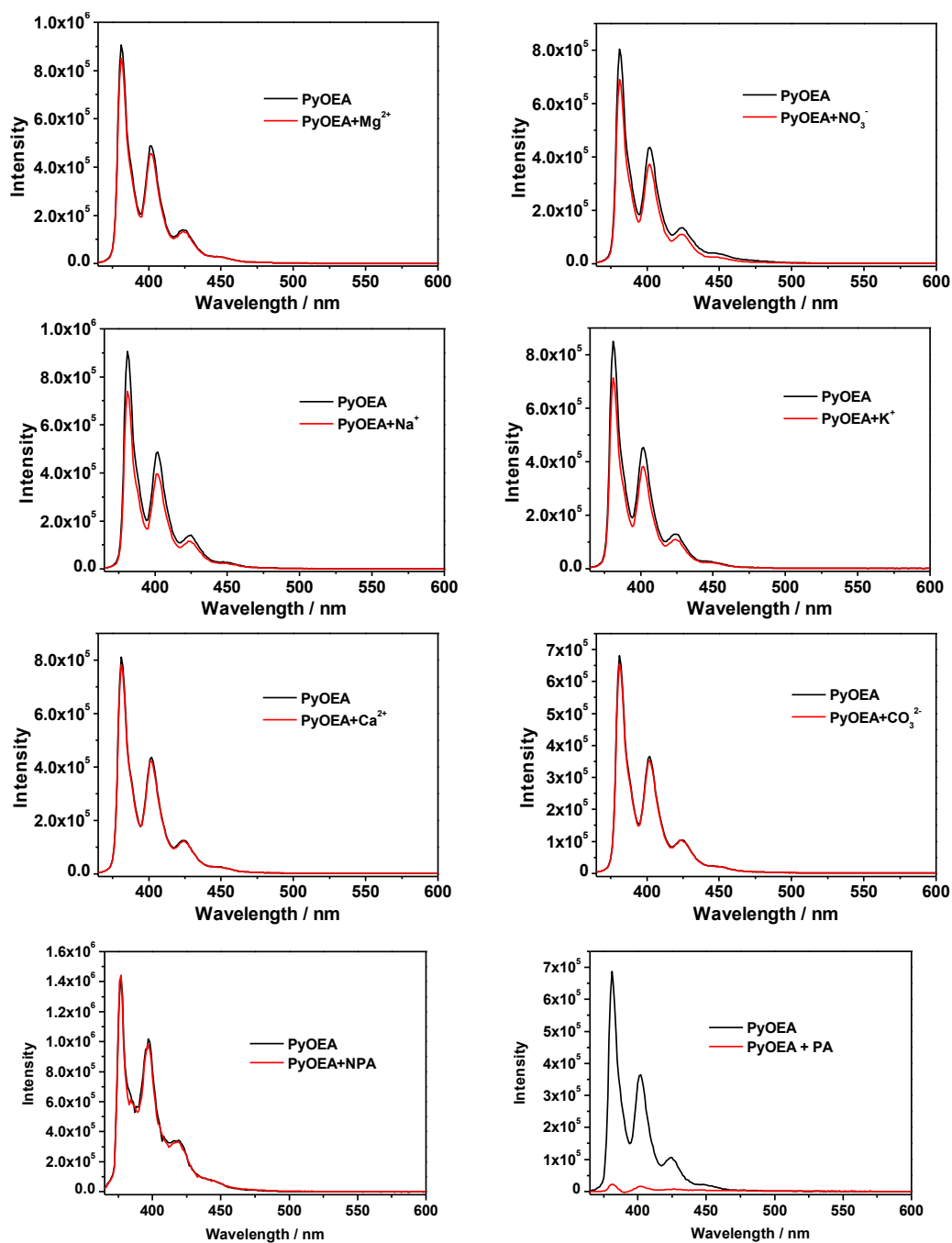
Fig.S10 Emission spectra of PyOEA (2.0×10^{-7} M) in the absence and presence of various analytes (9.0×10^{-5} M) as indicated in 10 mM HEPES buffer (pH 7.4). λ_{ex} = 345 nm.

Fig.S11 Time-resolved decay of PyOEA (2.0×10^{-7} M) with different concentrations of PA (μM) as indicated in 10 mM HEPES buffer (pH 7.4).
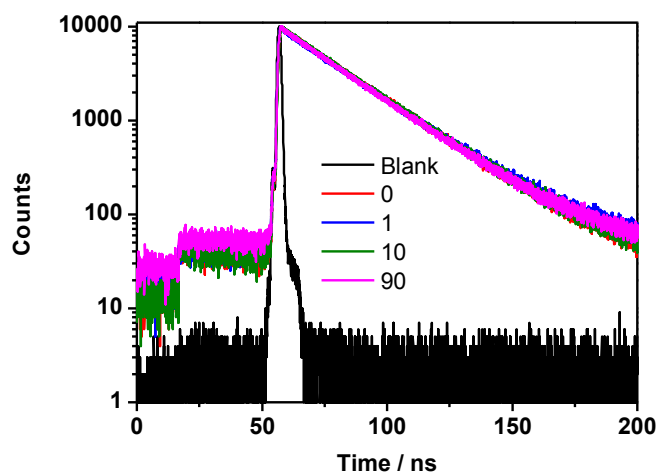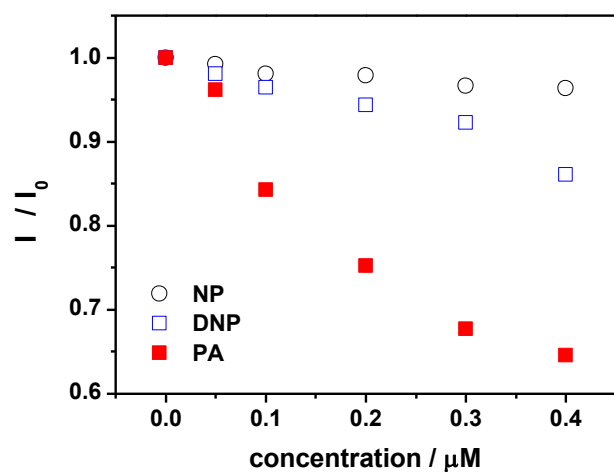

Fig.S12 Relative fluorescence intensity of PyOEA (2.0×10^{-7} M) in the presence of various amounts of PA, DNP, and NP as indicated in HEPES buffer (10 mM, pH 7.4).
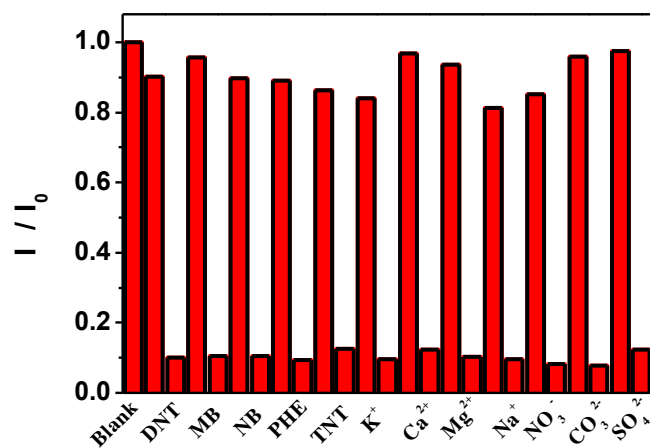
Fig.S13 Relative fluorescence intensity of PyOEA/PA in the absence and presence of interferents in HEPES buffer (10 mM, pH 7.4). [PyOEA] = 2.0×10^{-7} M, [PA] = [interferents] = 9.0×10^{-5} M.

Table S1. Comparison of advantages and disadvantages of present work and previous methods

	LOD	Advantages	Disadvantages
This work	23.2 nM	Visual and rapid detection, simple synthesis, high selectivity and water solubility, easy to fabricate into test papers	Visual detection with UV lamp
Zwitterionic squaraine dye[1]	70 nM	Colorimatric detection	Complicated synthesis and poor water solubility
BODIPY derivative[2]	0.65 ppb (2.84 nM)	Turn on response	Complicated synthesis and poor water solubility
Triphenylene derivatives[3]	35 nM	Rapid response, easy to fabricate into test papers	Poor selectivity, complicated synthesis and poor water solubility
1,8-Naphthyridine[4]	4.16 μM	Ease of preparation	Poor sensitivity
Anthracene-functionalized fluorescent tris-imidazolium salts[5]	354 ppb (1.54 μM)	Good selectivity in both organic and aqueous media	Complicated synthesis
Amine-functionalized α-cyanostilbene derivatives[6]	1.96 μM	Good sensitivity and selectivity	Complicated synthesis and the use of organic solvent
Anthracene Derivatives[7]	500 ppb (2.13 μM)	Visual detection, good selectivity	Complicated synthesis and the use of organic solvent
Bispyrene fluorophore[8]	1 μM	Good water solubility	Poor selectivity
Pyrene based copper complex array[9]	0.14 μM	Rapid response	Poor water

			solublility and selectivity
Cationic iridium(III) complex[10]	0.5 ppm (2.13 μM)	Good water solublility	Poor sensitivity
Cationic conjugated Polymer Nanoparticles[11]	30.9 pM	High sensitivity	Complicated preparation

References:

1. Y. Xu, B. Li, W. Li, J. Zhao, S. Sun and Y. Pang, *Chem. Commun.*, 2013, **49**, 4764.

2. Y. Erande, S. Chemate, A. More and N. Sekar, *RSC Adv.*, 2015, **5**, 89482.

3. H. Arora, V. Bhalla and M. Kumar, *RSC Adv.*, 2015, **5**, 32637.

4. M. K. Chahal and M. Sankar, *Anal. Methods*, 2015, **7**, 10272.

5. B. Roy, A. K. Bar, B. Gole and P. S. Mukherjee, *J. Org. Chem.*, 2013, **78**, 1306.

6. A. Ding, L. Yang, Y. Zhang, G. Zhang, L. Kong, X. Zhang, Y. Tian, X. Tao and J. Yang, *Chem. – Eur. J.*, 2014, **20**, 12215.

7. D. C. Santra, M. K. Bera, P. K. Sukul and S. Malik, *Chem. – Eur. J.*, 2016, **22**, 2012.

8. L. Ding, Y. Bai, Y. Cao, G. Ren, G. J. Blanchard and Y. Fang, *Langmuir*, 2014, **30**, 7645.

9. R. Pandey, L. Reddy, S. Ishihara, A. Dhir and V. Krishnan, *RSC Adv.*, 2013, **3**, 21365.

10. X. G. Hou, Y. Wu, H. T. Cao, H. Z. Sun, H. B. Li, G. G. Shan and Z. M. Su, *Chem. Commun.*, 2014, **50**, 6031.

11. A. H. Malik, S. Hussain, A. Kalita and P. K. Iyer, *ACS Appl. Mater. Interfaces*, 2015, **7**, 26968.