Supporting Information

for

A Red-emitting Fluorescent Probe Based on Flavone for Hydrazine and Its Application in Aqueous Solution

Xueqiong Zhang,[a] Chunlong Shi,[a] Pengwei Ji,[a] Xiaodong Jin,[a] Jingning Liu[b] and Hongjun Zhu[a,*]

[a] *Department of Applied Chemistry, College of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing, 211816, P. R. China*

[b] *Department of Criminal Science and Technology, Jiangsu Police Institute, Nanjing, Jiangsu, 210031, P. R. China.*

Fax: +86-25-83172358. Phone: +86-25-58139480. E-mail: zhuhj@njtech.edu.cn

Content:

Determination of detection limit:

The detection limit was calculated based on the fluorescence titration. To determine the S/N ratio, the emission intensity of probe **1** without hydrazine was measured by 20 times and the standard deviation of blank measurements was determined.

The detection limit (CDL) of probe **1** for hydrazine was determined from the following equation: CDL = K × Sb1/S Where K = 2 or 3 (we take 3 in this case); Sb1 is the standard deviation of the blank solution; S is the slope of the calibration curve.

The detection limit (CDL) of probe **1** for hydrazine was determined from the following equation:

CDL = K × Sb1/S

$$Sb_1=\sqrt{\frac{\sum(\bar{x}-x_i)^2}{n-1}}$$

Where K = 2 or 3 (we take 3 in this case); Sb1 is the standard deviation of the blank solution; S is the slope of the calibration curve; Sb1 is the standard deviation of the blank solution; S is the slope of the calibration curve.

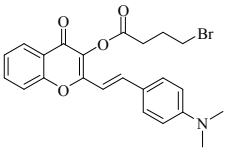
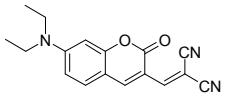
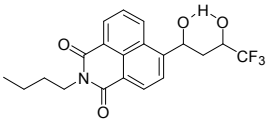
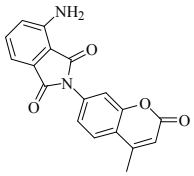
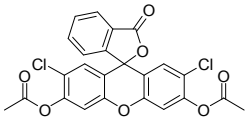
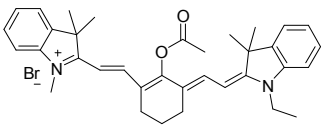
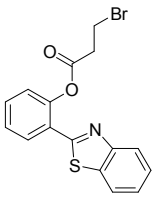
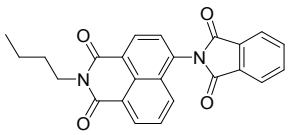
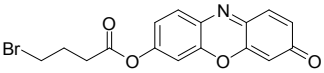
In aqueous solution: K=3, Sb_1= 0.7850 (n=20), S=6.5367

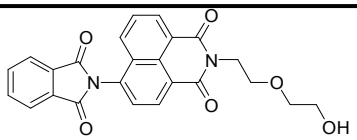
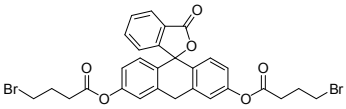
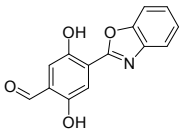
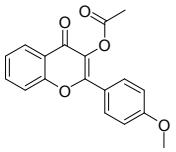
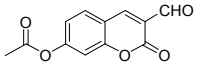
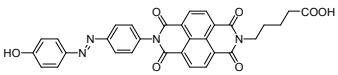
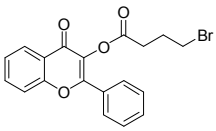
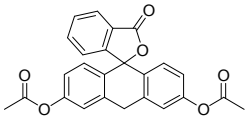
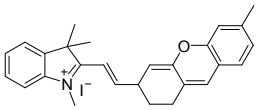
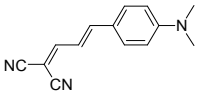
CDL= K × Sb_1/S

=3×0.7850/6.5367

=0.36 μM= 3.6×10^{-7} M

Table. S1 Summary of representative fluorescent probes for hydrazine

No	Solvent	Chemical structure	pH	E_x/E_m(nm)	CDL
This Work	DMSO:H_2O = 9:1		7.3	445/590	0.36 μM
1	DMSO:H_2O = 9:1		3.7	510/639	0.70 nM
2	CH_3CN:H_2O = 9:1		No mentioned	445/501	0.1 μM
3	DMSO:H_2O = 3:7		6.0	410/480	0.1 μM
4	DMSO:H_2O = 1:1		8.0	480/534	2.9 ppb
5	DMSO:H_2O = 9:1		4.5	740/820	0.81 ppb
6	DMSO:H_2O = 3:2		7.4	300/368	2.2 ppb
7	DMSO:H_2O = 3:2		7.0	420/540	0.3 ppb
8	CH_3CN:H_2O = 9:1		7.4	560/584	2 μM

9	EtOH:H_2O = 9:1		7.2	405/528	4.2 nM
10	MeOH:H_2O = 1:1		7.1	460/516	38.8 nM
11	CH_3CN:H_2O = 1:2		7.4	390/560	2.7 ppb
12	DMSO:H_2O = 9:1		7.4	370/540	320 ppb
13	DMSO:H_2O = 7:3		6.0	410/480	20 μM
14	DMSO		-	320/500	-
15	DMSO:H_2O = 9:1		7.0	350/536	0.15 μM
16	H_2O		7.5	480/515	31 nM
17	DMSO:H_2O = 4:1		7.4	585/706	0.17 μM
18	DMSO:H_2O = 9:1		7.2	400/582	8.87 nM

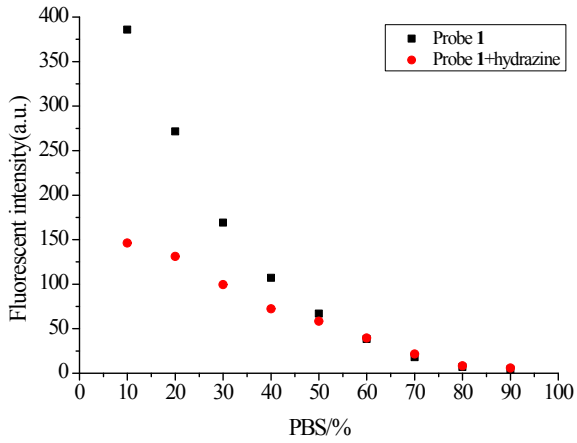


Fig. S1 *The fluorescence spectra of probe* ***1*** *(10 μM) incubated with hydrazine (10 equiv) in DMSO-H_2O (v/v, 9:1, 8:2, 7:3, 6;4, 5:5, 4:6, 3:7, 2:8,1:9) at room temperature.*

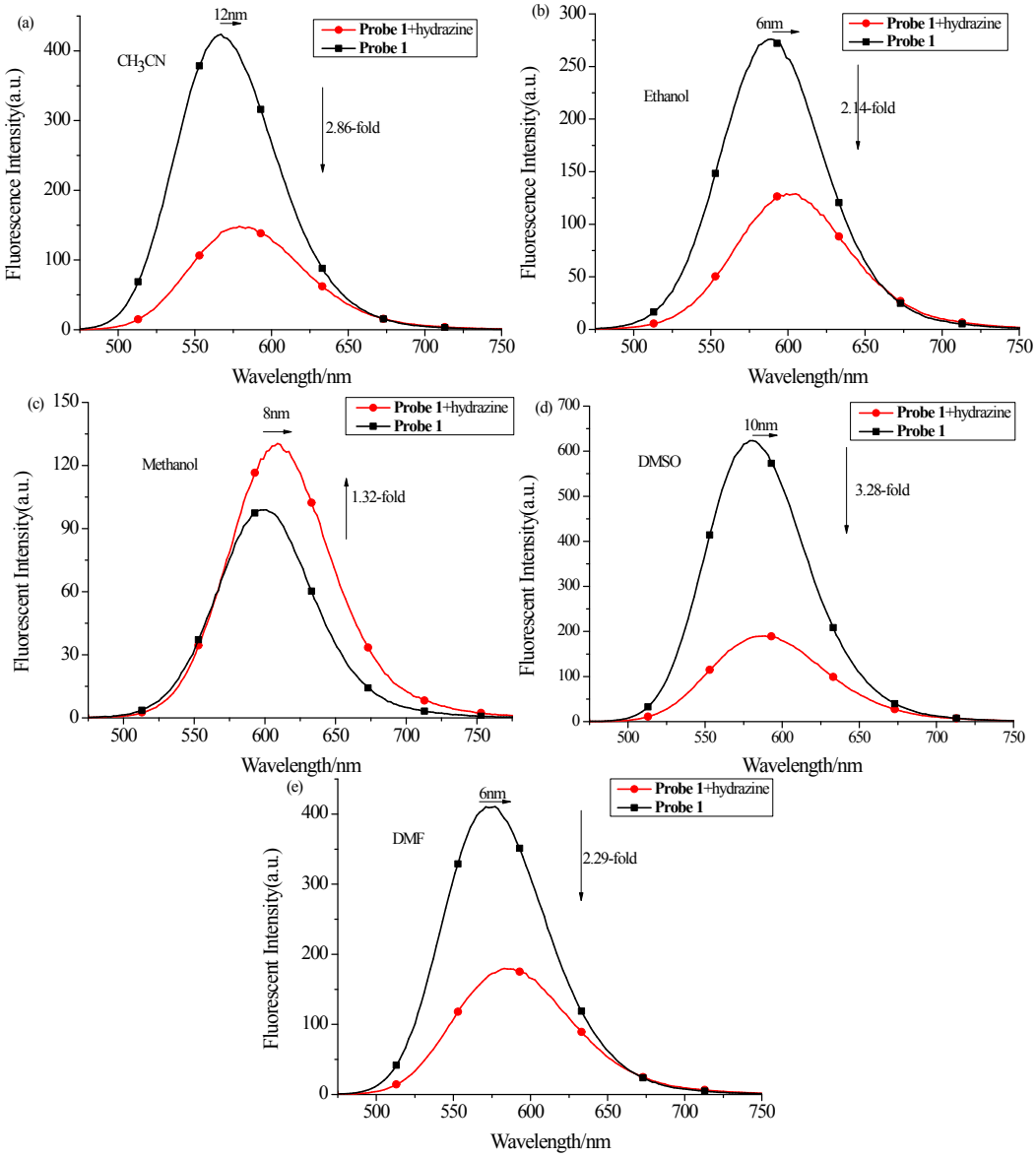


Fig. S2 *Emission spectra of probe* ***1*** *(10 μM) with the absence and presence of hydrazine (100 μM) in different solvents at room temperature.*

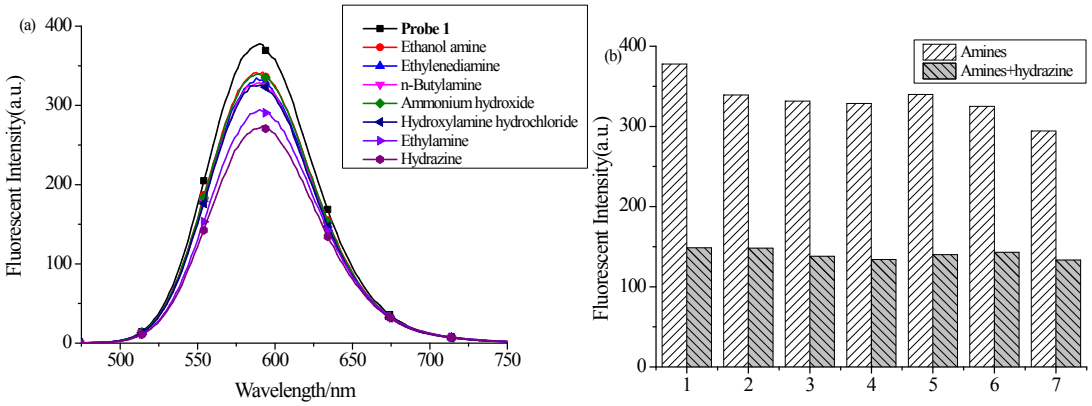


Fig. S3 *Fluorescence emission of probe* ***1*** *(10 μM) upon the addition of different hydrazine-structure related potentials (100 μM) and 100 μM N_2H_4 in DMSO-H_2O (9:1, v/v) solution (PBS, pH = 7.3, 15 mM). (a) Represents the addition of hydrazine or other amines to a solution of probe 1. (b) Represents the addition of hydrazine to the above solutions. (1. Blank, 2. Ethanolamine 3. Ethylenediamine, 4. n-Butylamine, 5.Ammonium hydroxide, 6. Hydroxylamine Hydrochlorid, 7. Ethylamine)*

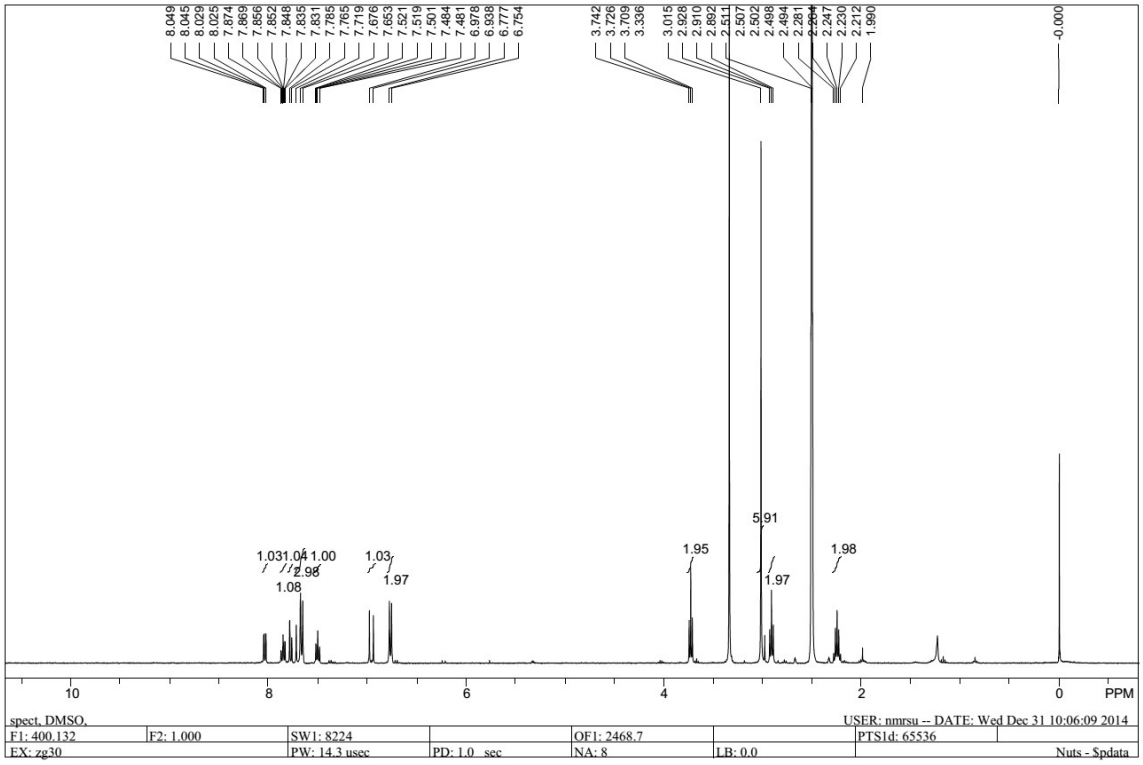


Fig. S4 *^{1}H NMR of probe* ***1***

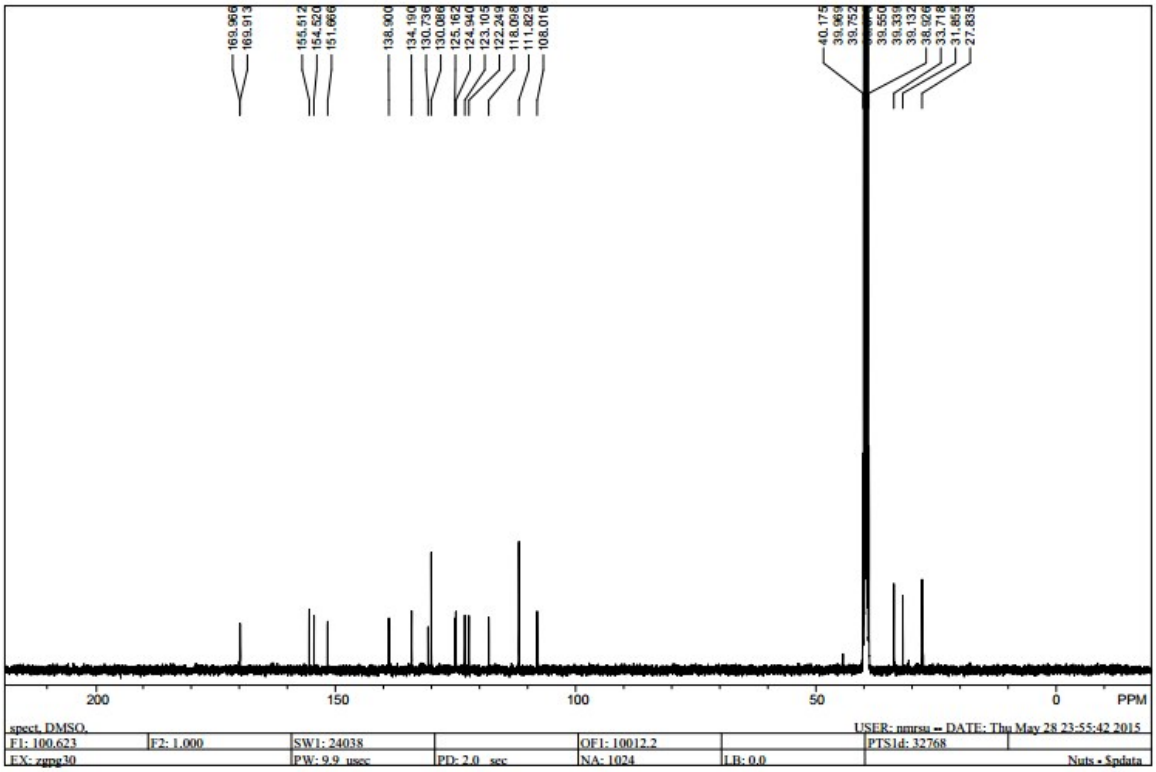


Fig. S5 *^{13}C NMR of probe **1***

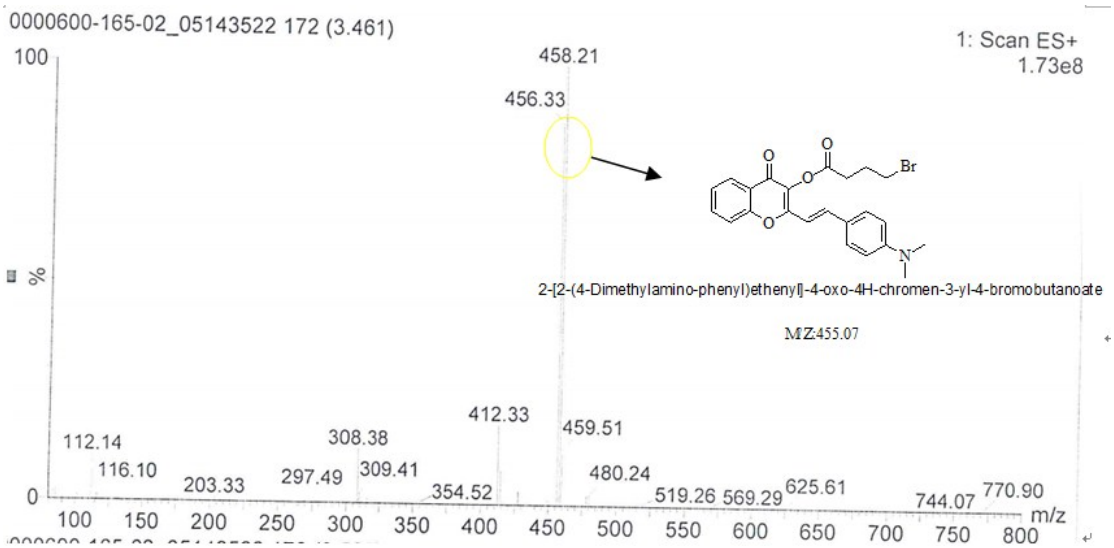


Fig. S6 *MS of probe **1** with the absence of hydrazine*

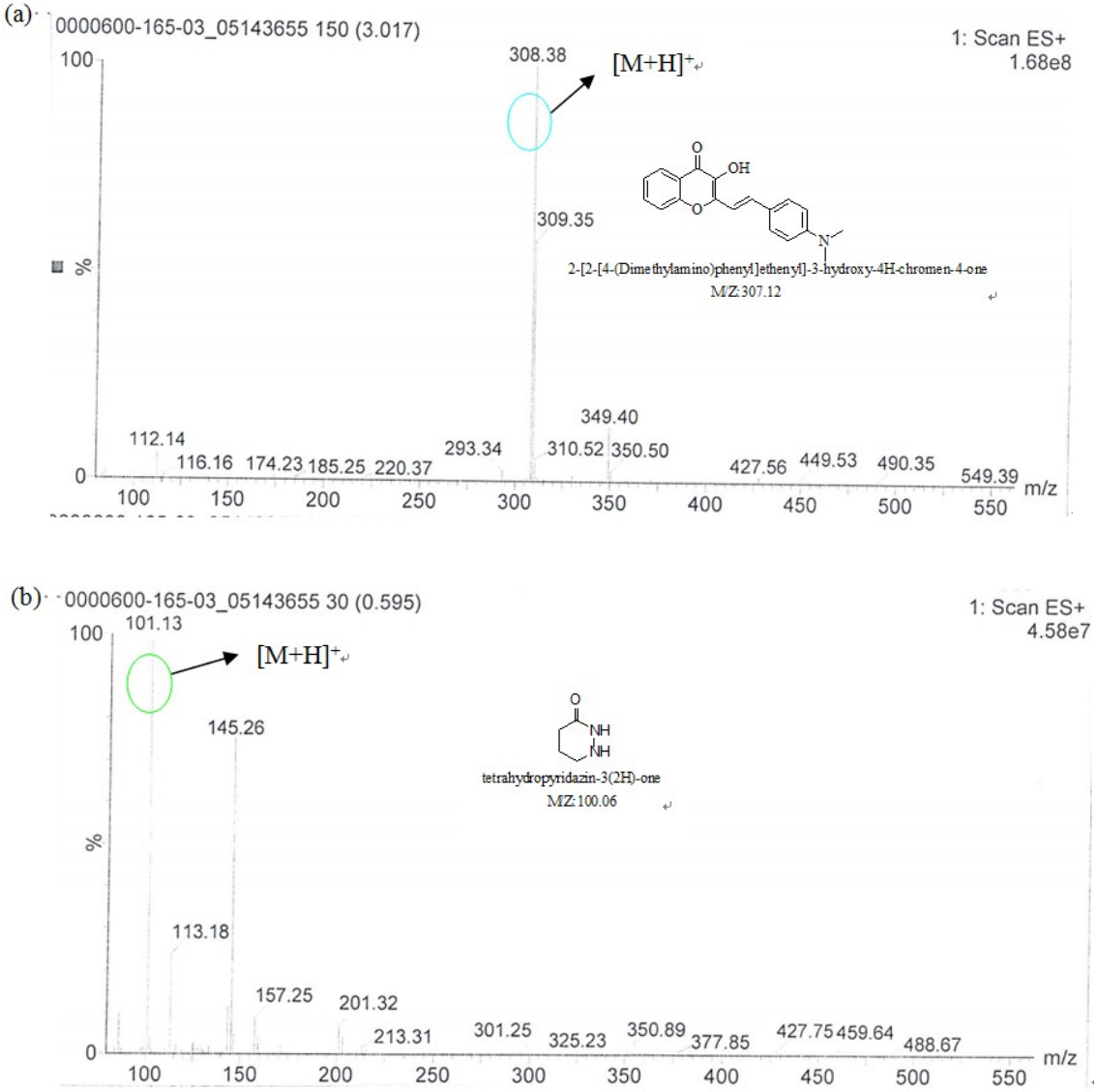


Fig. S7 (a) *MS of probe **1** with the presence of hydrazine in methanol;* ***(b)*** *MS of probe **1** with the presence of hydrazine in methanol.*

References

1. J.L. Fan, W. Sun, M.M. Hu, J.F. Cao, G.H. Cheng, H.J. Dong, K.D. Song, Y.C. Liu, S.G. Sun and X.J. Peng, *Chem. Comm.*, 2012, **48**, 8117-8119.
2. M.H. Lee, B. Yoon, J.S. Kim and J.L. Sessler, *Chem. Sci.*, 2013, **4**, 4121-4126.
3. L. Cui, C. Ji, Z. Peng, L. Zhong, C. Zhou, L. Yan, S. Qu, S. Zhang, C. Huang, X. Qian, and Y. Xu, *Anal. Chem*., 2014, **86**, 4611-4617.
4. M.G. Choi, J.O. Moon, J. Bae, J.W. Lee and S. Chang, *Org. Biomol. Chem.*, 2013, **11**, 2961-2965.
5. C. Hu, W. Sun, J.F. Cao, P. Gao, J.Y. Wang, J.L. Fan, F.L. Song, S.G. Sun and X.J. Peng, *Org Lett.*, 2013, **15**, 4022-4025.
6. S. Goswami, S. Das, K. Aich, B. Pakhira, S. Panja, S. K. Mukherjee and S. Sarkar, *Org Lett*, 2013, 15, 5412-5415.
7. L. Cui, Z.X. Peng, C.F. Ji, J.H. Huang, D.T. Huang, J. Ma, S.P. Zhang, X.H. Qian and Y.F. Xu, *Chem. Comm.*, 2014, **50**, 1485-1487.
8. Y. Qian, J. Lin, L. J. Han, L. Lin and H. L. Zhu, *Biosens. Bioelectron*., 2014, **58**, 282-286.
9. M. V. Ramakrishnam Raju, E. Chandra Prakash, H. Chang and H. Lin, *Dyes Pigments*, 2014, **103**,

9-20.
10. S. Goswami, K. Aich, S. Das, S.B Roy, B. Pakhira and S. Sarkar, *RSC Adv.*, 2014, **4**, 14210-14214.
11. L.L. Xiao, J. Tu, S.G. Sun, Z. Pei, Y.X. Pei, Y. Pang and Y.Q. Xu, *RSC Adv.*, 2014, **4**, 41807-41811.
12. B. Liu, Q. Liu, M. Shah, J.F. Wang, G. Zhang and Y. Pang, *Sens. Actuators B Chem.*, 2014, **202**, 194-200.
13. K. Li, H.R. Xu, K.K. Yu, J.T. Hou and X.Q. Yu, *Anal. Methods*, 2013, **5**, 2653-2656.
14. D.Y. Zhou, Y.Y. Wang, J. Jia, W.Z. Yu, B.F. Qu, X. Li and X. Sun, *Chem. Comm.*, 2015, **51**, 10656-10659.
15. X.D. Jin, C.Z. Liu, X.M. Wang, H. Huang, X.Q. Zhang and H.J. Zhu, *Sens. Actuators B Chem.*, 2015, **216**, 141-149.
16. D.Y. Qu, J.L. Chen and B. Di, *Anal. Methods*, 2014, **6**, 4705-4709.
17. J.J. Zhang, L.L. Ning, J.T. Liu, J.X. Wang, B.F. Yu, X.Y. Liu, X.J. Yao, Z.P. Zhang and H.X. Zhang, *Anal. Chem.*, 2015, **87**, 9101-9107.
18. S.I. Reja, N. Gupta, V. Bhalla, D. Kaur, S. Arora, M. Kumar, *Sens. Actuators B Chem.*, 2016, 222, 923-929.