Supplementary Material

Selective and sensitive detection of cysteine in water and live cells by a coumarin-Cu^{2+} fluorescence ensemble

Yue Wang,[a] Qingtao Meng,*[a,b] Qian Han,[a] Guangjie He,*[c] Yaoyun Hu,[a] Huan Feng,[a] Hongmin Jia [a] Run Zhang,[d] and Zhiqiang Zhang*[b]

[a] School of Chemical Engineering, University of Science and Technology Liaoning, Anshan, Liaoning, 114051, P. R. China. E-mail: qtmeng@ustl.edu.cn, Tel: +86-412-5929627

[b] Key Laboratory for Functional Material, Educational Department of Liaoning Province, University of Science and Technology Liaoning, Anshan 114051, P. R. China. E-mail: zhangzhiqiang@ustl.edu.cn, Tel: +86-421-5928002.

[c] Department of Forensic Medicine, Xinxiang Medical University, XinXiang, Henan, 453003, P. R. China. E-mail: guangjiehe@163.com.

[d] Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane, 4072, Australia.

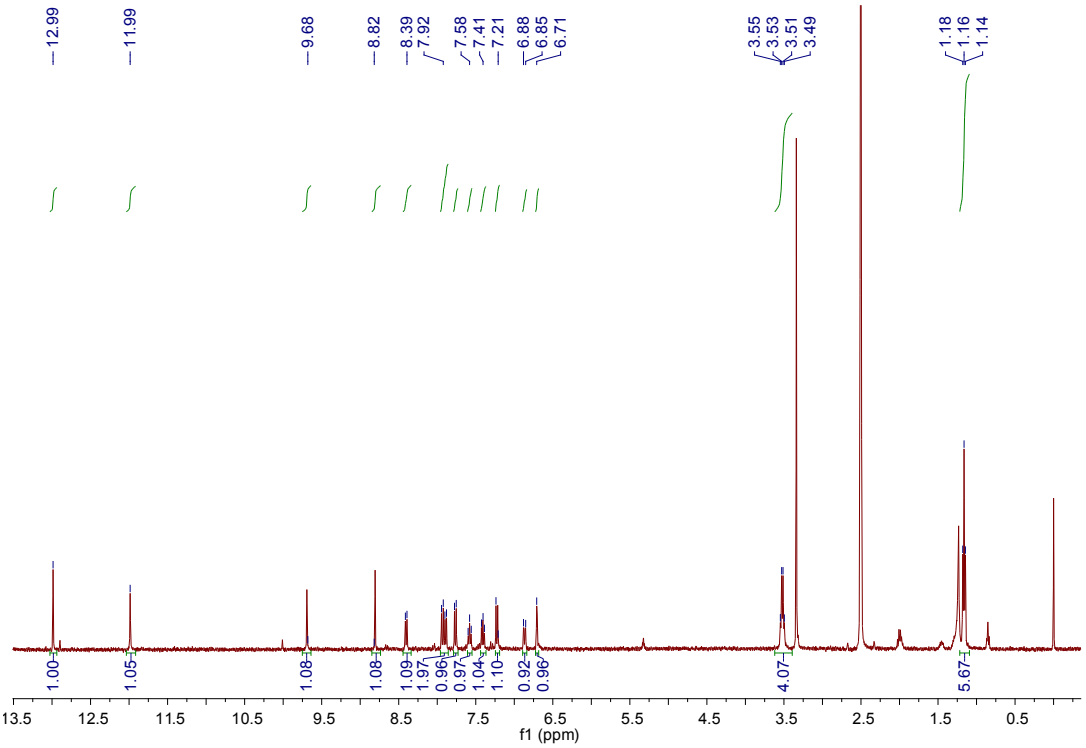

Fig. S1 ^{1}H NMR of **L** (DMSO-d_6)

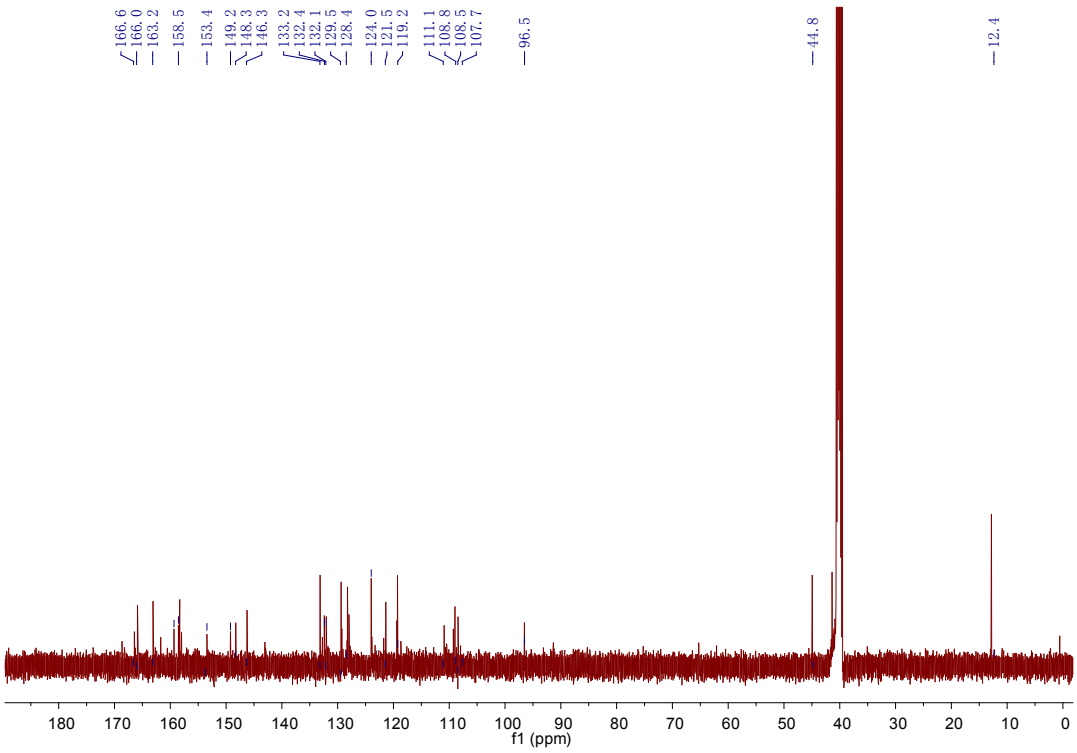

Fig. S2 ^{13}H NMR of **L** (DMSO-d_6).

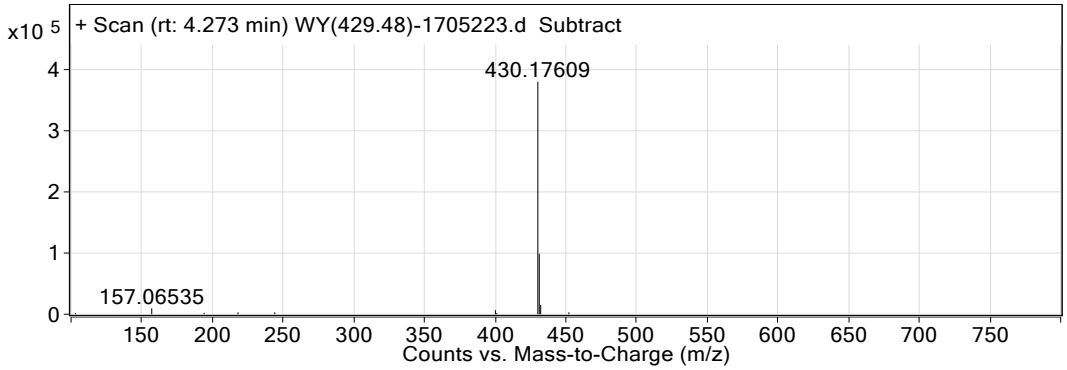

Fig. S3 HR MS of **L**

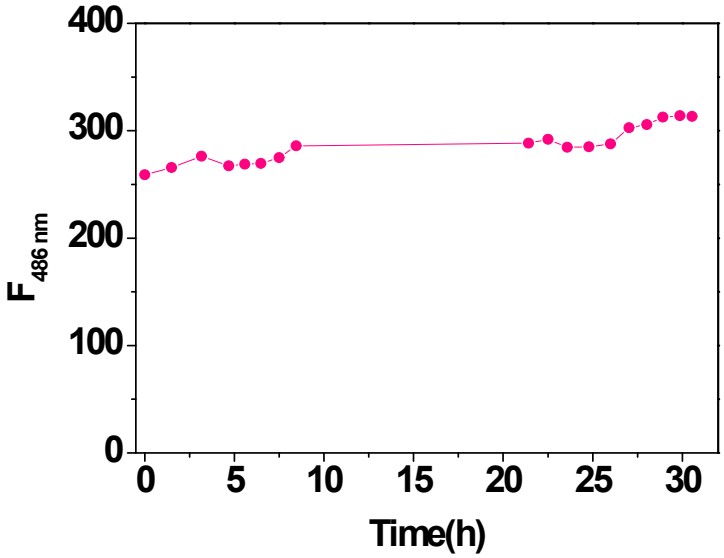

Fig. S4 Fluorescence responses of **L** (10 μM) at different time in HEPES aqueous buffer (CH_3CN: HEPES = 7:3, 20 mM, pH = 7.4). Excitation at 420 nm.

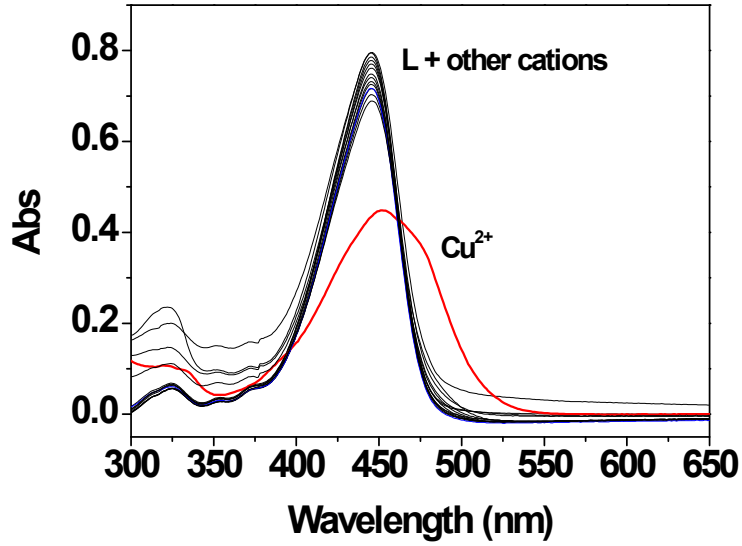

Fig. S5 Absorption spectra of **L** (10 μM) in HEPES aqueous buffer (CH_3CN: HEPES = 7:3, 20 mM, pH = 7.4) upon addition of various metal ions (10 μM).

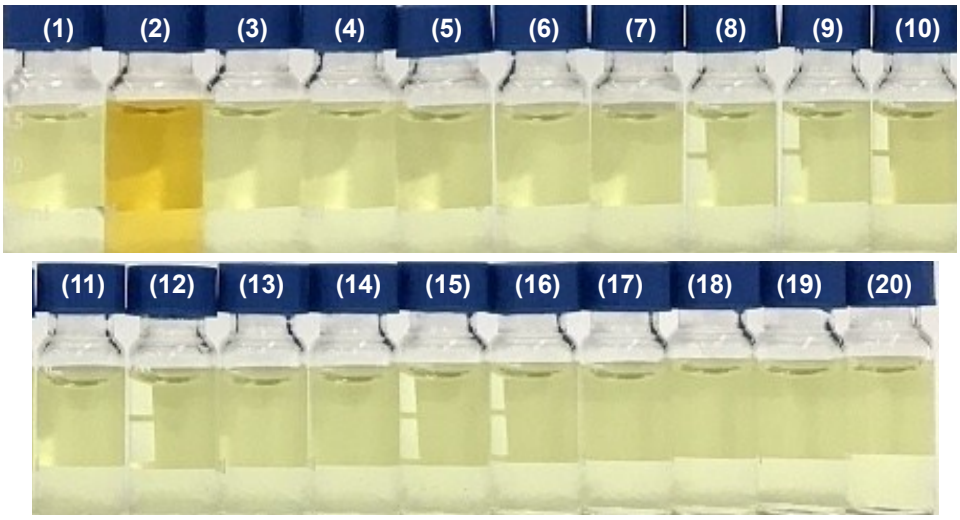

Fig. S6 Color responses of **L** (10 μM) in HEPES aqueous buffer (CH_3CN: HEPES = 7:3, 20 mM, pH = 7.4) upon addition of various metal ions (10 μM). From left to right: (1) free **L**, (2) Cu^{2+}, (3) Fe^{3+}, (4) Hg^{2+}, (5) Cd^{2+}, (6) Pb^{2+}, (7) Zn^{2+}, (8) Ni^{2+}, (9) Mn^{2+}, (10) Cr^{3+}, (11) Ag^{+}, (12) Ca^{2+}, (13) Mg^{2+}, (14) Ba^{2+}, (15) Li^{+}, (16) K^{+}, (17) Na^{+}, (18) All cations mixed.

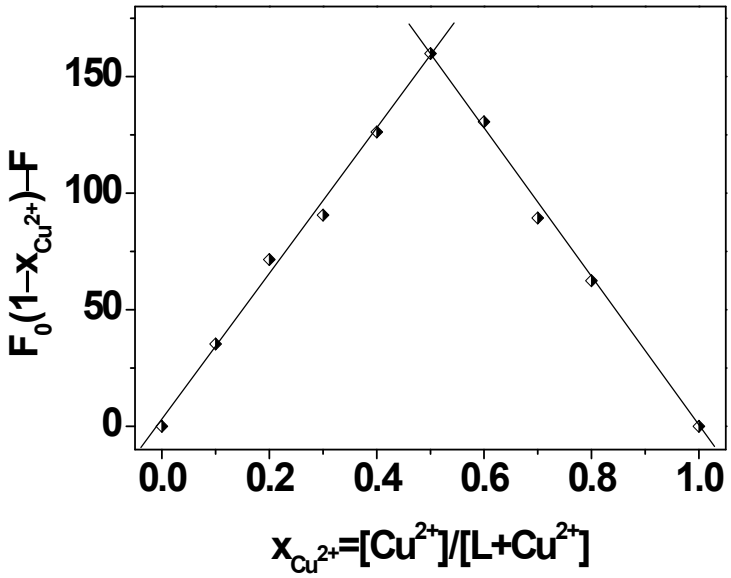

Fig. S7 Job's plots according to the method for continuous variations. The total concentration of **L** (10 μM) and Cu^{2+} is 10 μM. Excitation at 420 nm.

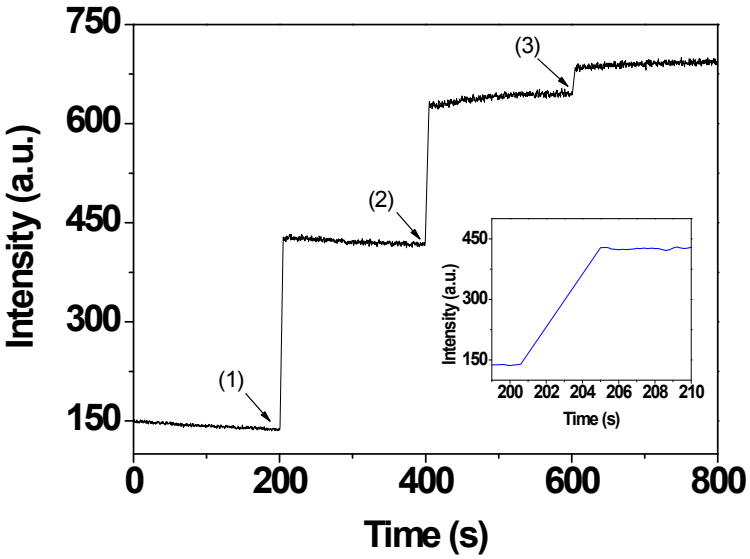

Fig. S8 Time course of fluorescence intensity of **L**-Cu^{2+} (10 μM) at 486 nm upon addition of Cys. Arrows represent sequentially addition of (1) 5 μM, (2) 15 μM and (3) 20 μM Cys. Excitation was performed at 420 nm.

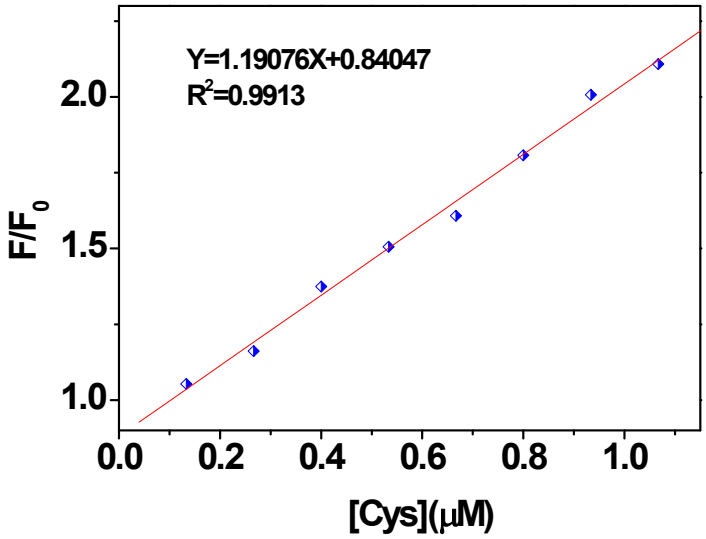

Fig. S9 Linear relationship between fluorescence intensity of **L**-Cu^{2+} (2 μM) at 486 nm versus the concentration of Cys (0–1.0 μM) in HEPES aqueous buffer (CH_3CN: HEPES = 7:3, 20 mM, pH = 7.4). Excitation was performed at 420 nm.

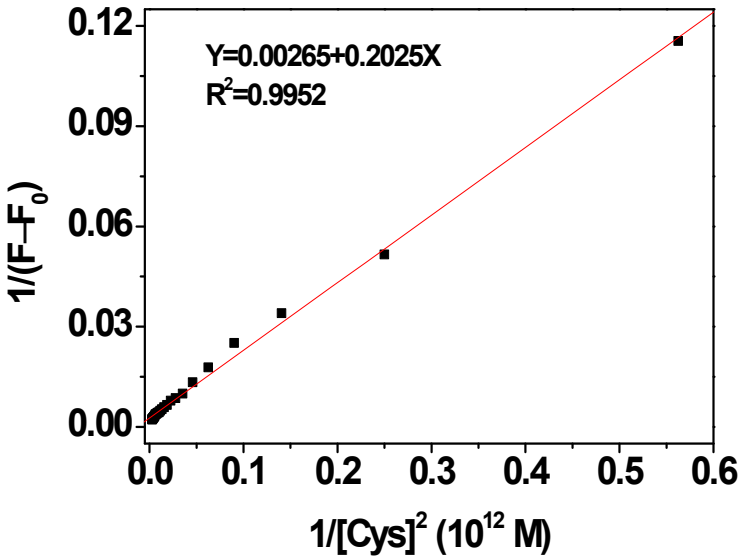

Fig. S10 Benesi-Hildebrand plot (emission at 486 nm) of **L**-Cu^{2+} based on 1:2 binding stoichiometry with Cys. Excitation was performed at 420 nm.

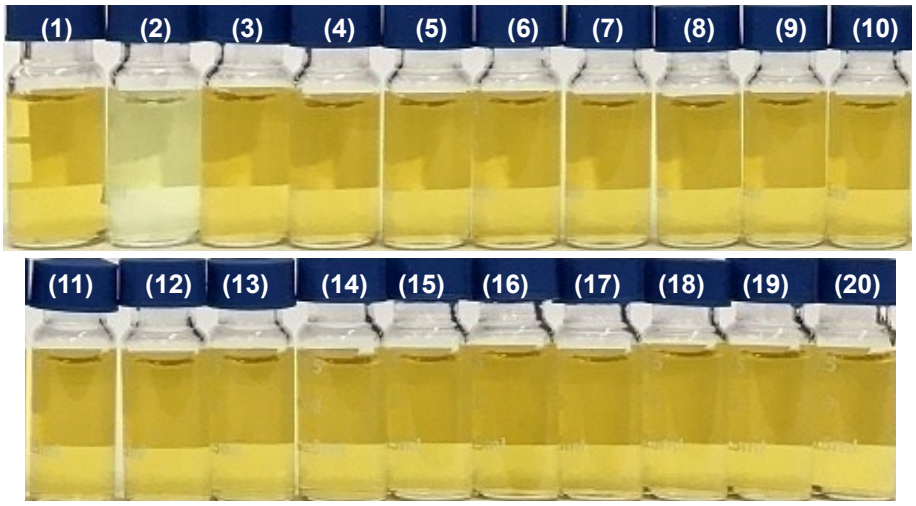

Fig. S11 Colour responses of **L**-Cu^{2+} (10 μM) in HEPES aqueous buffer (CH_3CN: HEPES = 7:3, 20 mM, pH = 7.4) upon addition of various biothiols and amino acids (30 μM): (1) free **L**-Cu^{2+}, (2) Cys, (3) Ala, (4) Asp, (5) Gln, (6) Gly, (7) Hcy, (8) Lys, (9) Phe, (10) Pro, (11) Ser, (12) Thr, (13) Try, (14) Val, (15) Leu, (16) His, (17) Arg, (18) Asn, (19) GSH, (20) Glu.

Table S1. Comparison of **L**-Cu^{2+} with recently reported fluorescent probes for biothiols detection.

Probes	Selectivity	Limit of detection (LOD)	Colour changes	Response time	Ref.
1	Cys, Hcy and GSH	Cys: 0.518 μM Hcy: 0.658 μM GSH: 0.246 μM	-	＞10 min	1

DACP-1 and **DACP-2**	Cys, Hcy and GSH	For GSH: 10.1 nM (**DACP-1**) and 17.0 nM (**DACP-2**) For Cys: 0.31 μM (**DACP-1**) and 1.27 μM (**DACP-2**)	-	within ~5−10 min	2
CNF	Cys/Hcy, GSH and H_2S	0.59 μM (for Cys) 0.56 μM (for Hcy) 0.78 μM (for GSH) 0.52 μM (for H_2S)	-	Cys/Hcy: 30 min H_2S: 5 min	3
CS-thiols	Cys, Hcy and GSH	4.3×10^{-5} (for Cys)	-	within 10 min	4
1–Cu(II)	Cys, Hcy and GSH	10^{-8} M (GSH)	Pink to green	10 min	5
NP	Cys, Hcy and GSH	1.5 μM (for Cys) 1.8 μM (for Hcy) 2.2 μM (for GSH)	-	-	6
HNA	Cys, Hcy and GSH	1.5 μM (for Cys) 1.0 μM (for Hcy) 0.8 μM (for GSH)	Yellow to yellowish	-	7
Probe **2**	Cys (slight interference from Hcy and GSH)	0.084 μM	Colorless to yellow	5 min	8
probe 1	Cys and Hcy	1.6×10^{-7} M (Cys) 1.8×10^{-7} M (Hcy)	Dark blue to yellow-green	25 min	9
AQDA	Cys	1.58×10^{-7} M	Colorless to orange	90 min	10
R1	Cys	4.61×10^{-8} M	Pink to colorless	within 1.0 min	11
Cy-NB	Cys	0.2 μM	Blue to green	within 5 min	12
TP-NIR	Cys	0.2 μM	Yellowish to yellow	within 2 min	13
SBD-Cl	Cys	1.4×10^{-6} M	Yellowish to yellow	within about 1 h	14
BTAC	Cys	124 nM	Colorless to yellow	within 3 min	15
L-Cu^{2+}	Cys	15 nM	Yellow-yellowish	< 4 s	This work

References:

1. Q. Miao, Q. Li, Q. Yuan, L. Li, Z. Hai, S. Liu and G. Liang, *Anal. Chem*., 2015, **87**, 3460−3466.
2. S. V. Mulay, Y. Kim, M. Choi, D. Y. Lee, J. Choi, Y. Lee, S. Jon and D. G. Churchill, *Anal. Chem*., 2018, **90**, 2648−2654.
3. L. He, X. Yang, K. Xu, Y. Yang and W. Lin, *Chem. Commun*., 2017, **53**, 13168−13171.
4. K. Liu, H. Shang, X. Kong and W. Lin, *J. Mater. Chem. B*, 2017, **5**, 3836–3841.
5. H. S. Jung, J. H. Han, Y. Habata, C. Kang and J. S. Kim, *Chem. Commun*., 2011, **47**, 5142–5144.
6. Y. Wang, Z. Q. Zhang, Q. T. Meng, C. He, R. Zhang and C. Y. Duan, *J. Lumin*., 2016, **175**, 122–128.

7. H. M. Jia, M. Yang, Q. T. Meng, G. J. He, Y. Wang, Z. Z. Hu, R. Zhang and Z. Q. Zhang, *Sensors*, 2016, **16**, 79; doi:10.3390/s16010079.
8. J. Guo, Z. Kuai, Z. Zhang, Q. Yang, Y. Shan and Y. Lia, *RSC Adv*., 2017, **7**, 18867–18873.
9. Z.-H. Fu, X. Han, Y. Shao, J. Fang, Z.-H. Zhang, Y.-W. Wang and Y. Peng, *Anal. Chem*., 2017, **89**, 1937−1944.
10. H. Lv, X.-F. Yang, Y. Zhong, Y. Guo, Z. Li and H. Li, *Anal. Chem*., 2014, **86**, 1800−1807.
11. U. Diwan, V. Kumar, R. K. Mishra, N. K. Rana, B. Kochc and K. K. Upadhyay, *RSC Adv*., 2016, **6**, 95722–95728.
12. K. Yin, F. Yu, W. Zhang, L. Chen, *Biosens. Bioelectron*., 2015, **74**, 156−164.
13. J. Wang, B. Li, W. Zhao, X. Zhang, X. Luo, M. E. Corkins, S. L. Cole, C. Wang, Y. Xiao, X. Bi, Y. Pang, C. A. McElroy, A. J. Bird and Y. Dong, *ACS Sens*., 2016, **1**, 882−887.
14. L. He, X. Yang, K. Xu and W. Lin, *Anal. Chem*., 2017, **89**, 9567−9573.
15. S. Manna, P. Karmakar, S. S. Ali, U. N. Guria, R. Sarkar, P. Datta, D. Mandalc and A. K. Mahapatra, *New J. Chem*., 2018, **42**, 4951−4958.