Electronic Supplementary Information

Manipulating surface structure of quantum dots based on dual response modes triggered by iron ions for visualization of hydrogen sulfide with a wide detection range

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Experimental section

Materials

Copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$, 99%), indium(III) chloride tetrahydrate ($InCl_3 \cdot 4H_2O$, 99.9%), zinc acetate ($Zn(Ac)_2$, 99.98%), sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$, 96+%), glutathione (GSH, 97%), iron(III) chloride ($FeCl_3$, 98%), 1,10-phenanthroline (Phen, 99%), ferrous sulfate ($FeSO_4$, 99%), L-cysteine (Cys, 99%), dithiothreitol (DTT, 99%), 3-mercaptopropionic acid (3-MPA, 98%), and sodium nitroprusside (SNP, 98%) were purchased from Energy Chemical. Sodium chloride (NaCl, 99.5+%), sodium fluoride (NaF, 99%), potassium bromide (KBr, 99+%), potassium iodide (KI, 99.5%), sodium acetate (NaAc, 99.5%), sodium carbonate (Na_2CO_3, 99.8+%), sodium bicarbonate ($NaHCO_3$, 99.5%), monopotassium phosphate (KH_2PO_4, 99.5%), disodium phosphate (Na_2HPO_4, 99+%), potassium nitrate (KNO_3, 99%), sodium sulfite (Na_2SO_3, 98+%), sodium sulfate (Na_2SO_4, 99+%), potassium thiocyanate (KSCN, 98.5+%), sodium thiosulfate ($Na_2S_2O_3$, 98%), and sodium hydroxide (NaOH, 98%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Trypsin (TRY, EC 3.4.4.4, 250 U mg^{-1}), Dulbecco`s modified Eagle`s medium (DMEM), fetal calf serum (FBS) and cell counting Kit-8/CCK8 were purchased from Dalian Chenyu Biotechnology. All chemical were used as received without further treatment.

Synthesis of $CuInS_2$/ZnS quantum dots

The synthesis of $CuInS_2$/ZnS quantum dots (CIS/ZnS QDs) refers to An` developed method with slight modification, which can been viewed in our previous research report.[1-2]

Cell viability assay

MCF-7 cells were provided by the Biological Laboratory of Dalian Medical University. We carried out CCK-8 assay to evaluate the cytotoxicity of the CIS/ZnS QDs against Hela cells. Briefly, cells were seeded at 2.5×10^4 cells/well in 96-well plates and incubated at 37 ºC for 24 h. Then, a fresh cultured DMEM medium (100 μL) containing CIS/ZnS QDs samples with concentrations of 0.07, 0.14, 0.28, 0.35, 0.42 μg/mL was added to plate and co-incubated with the cells for 12, 24 and 48 h, respectively. After incubation, 100 μL fresh DMEM solutions containing 10 μL reagents was added to each well and incubated at 37 ºC for 1h. Finally, a microplate reader (Bio-Rad, Model, 550, USA) was used to measure the absorbance at 450 nm. The free-QDs groups and culture medium (without cells and CIS/ZnS QDs) was marked as control and blank respectively, and incubated at the same conditions. The relative cell viability can be calculated with the following equation:

$$\text{cell viability (\%)} = \frac{A_s - A_b}{A_c - A_b} \times 100\%$$

where A_s, A_c and A_b are the absorbance of the test, control and blank sample.

Characterization

UV-vis absorption spectra were measured with a sp-2500 spectrophotometer (Shanghai Spectrum Instruments Co. ltd., China). Photoluminescence (PL) emission spectra were recorded on Hitachi F-4700 Fluorescence Spectrophotometer under the excitation wavelength of 410 nm. Fluorescence images were taken with an Olympus TH4-200 fluorescent inverted microscope at an excitation wavelength of 530-550 nm and imaged with the emission wavelength from 575 nm to near infrared region.

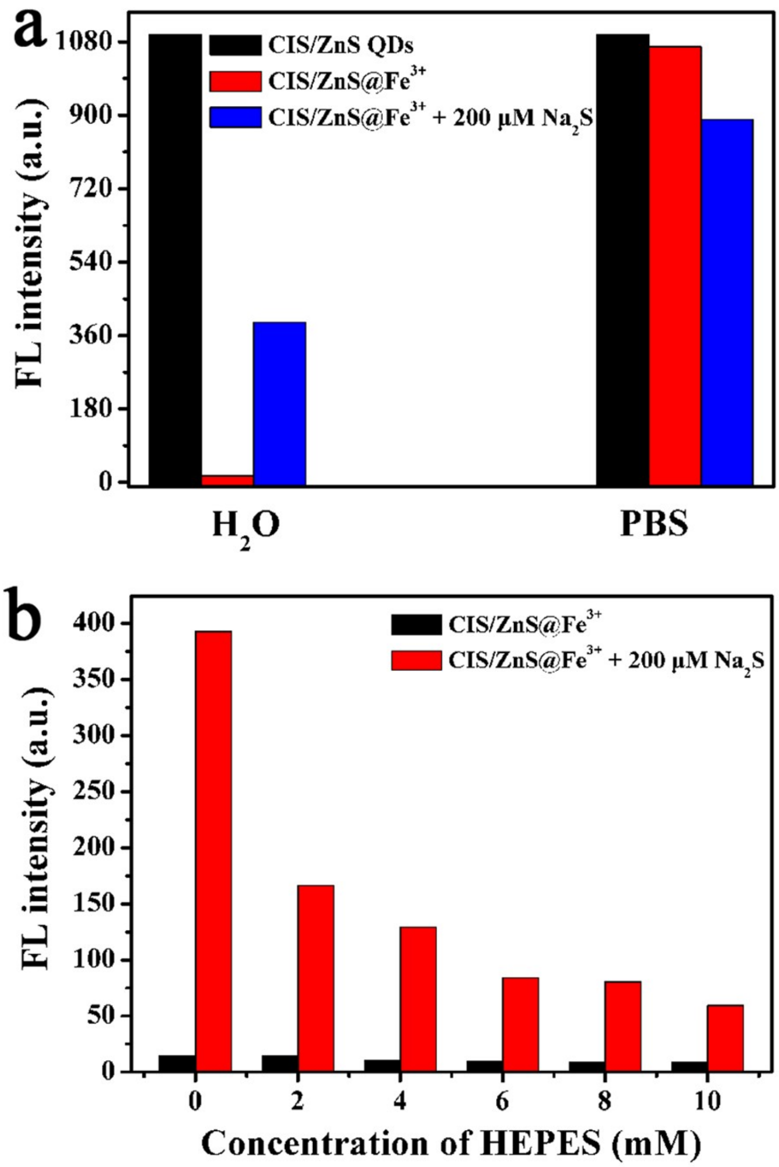

Fig. S1 (a) The emission peak intensity of CIS/ZnS QDs (black column), CIS/ZnS@Fe-200 nanoprobe (red column), and CIS/ZnS@Fe-200 nanoprobe upon the addition of 200 μM Na_2S (blue column) in the case of aqueous and PBS buffer (pH = 7.4, 10 mM) medium, respectively; (b) The emission peak intensity of CIS/ZnS@Fe-200 nanoprobe before (black column) and after (red column) adding 200 μM Na_2S in different concentration of HEPES buffers (pH = 7.4).

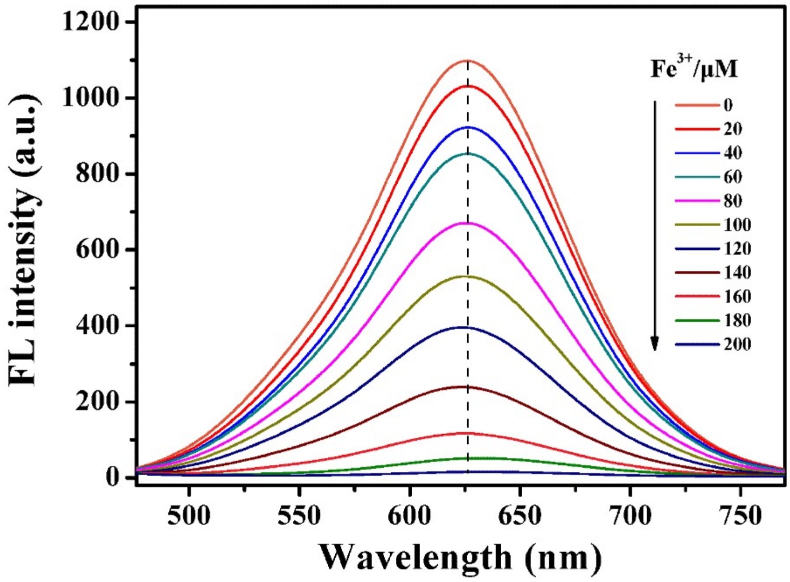

Fig. S2 Fluorescent titration spectra of CIS/ZnS QDs upon gradual addition of Fe^{3+} (0-200 μM) in the aqueous medium.

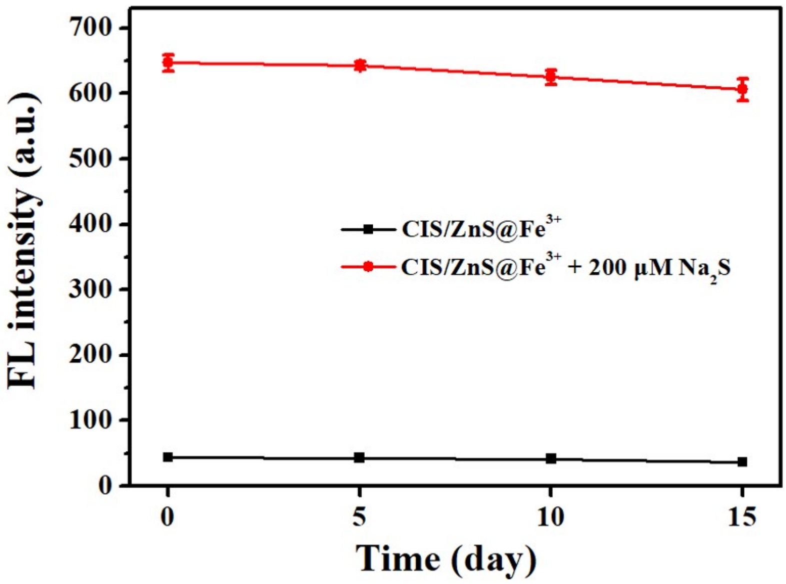

Fig. S3 The fluorescent intensity before (black line) and after (red line) adding 200 μM Na_2S for the CIS/ZnS@Fe-180 nanoprobe, which were prepared by the CIS/ZnS QDs that storing in a refrigerator at 4 ℃ for 0, 5, 10 and 15-day respectively.

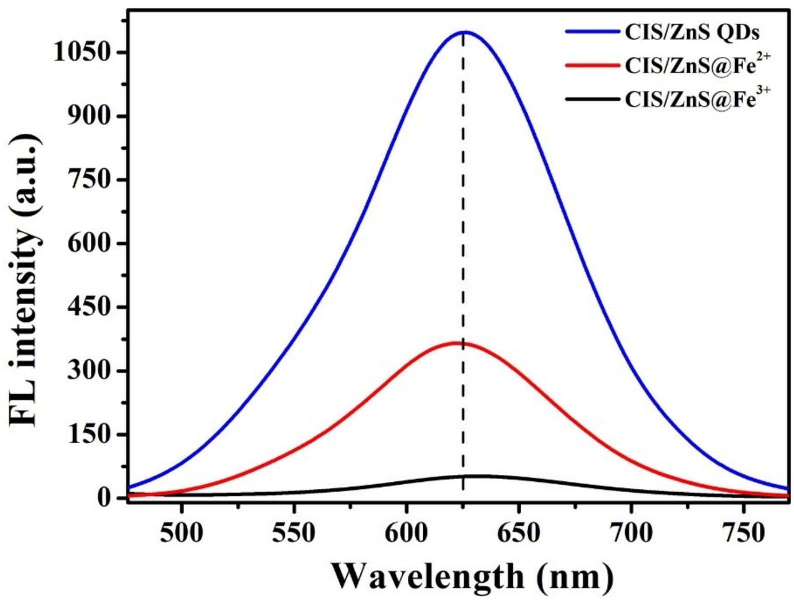

Fig. S4 The fluorescent spectra of CIS/ZnS QDs (blue line), CIS/ZnS QDs treated by 180 μM Fe^{3+} (CIS/ZnS@Fe^{3+}, black line) and 180 μM Fe^{2+} (CIS/ZnS@Fe^{2+}, red line)

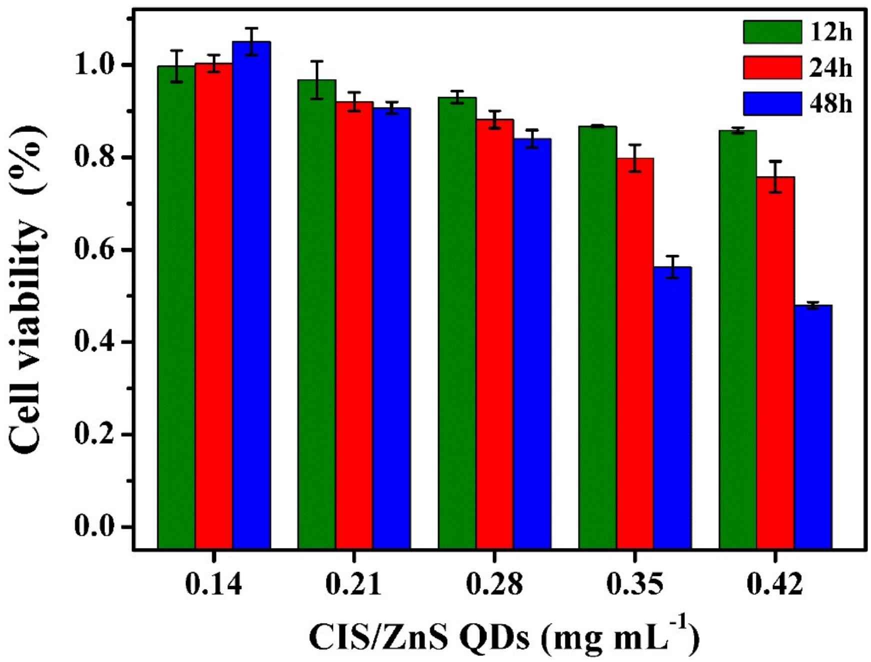

Fig. S5 The cell viability of CIS/ZnS QDs with concentration of 0.14, 0.21, 0.28, 0.35 and 0.42 mg mL^{-1} at different incubation time.

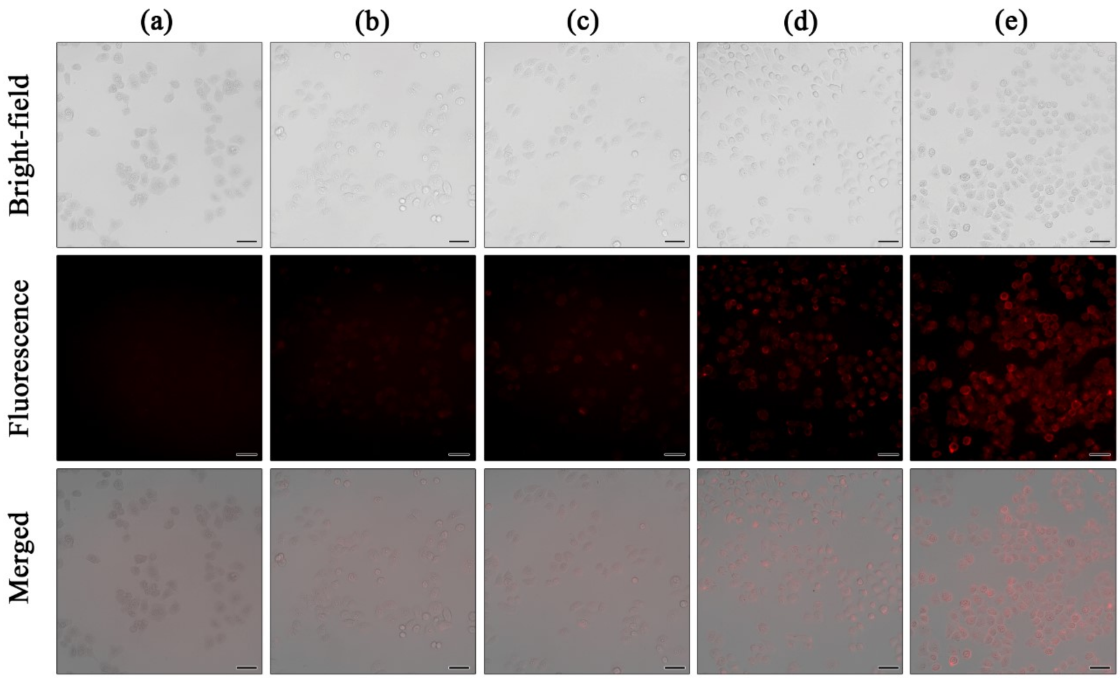

Fig. S6 Fluorescence images of MCF-7 cells. From left to right: CIS/ZnS@Fe-200 labeled cells incubated with exogenous 200 μM Na_2S for (a) 0 min, (b) 5 min, (c) 10min, (d) 20 min and (e) 50 min. All scale bars = 100 μm.

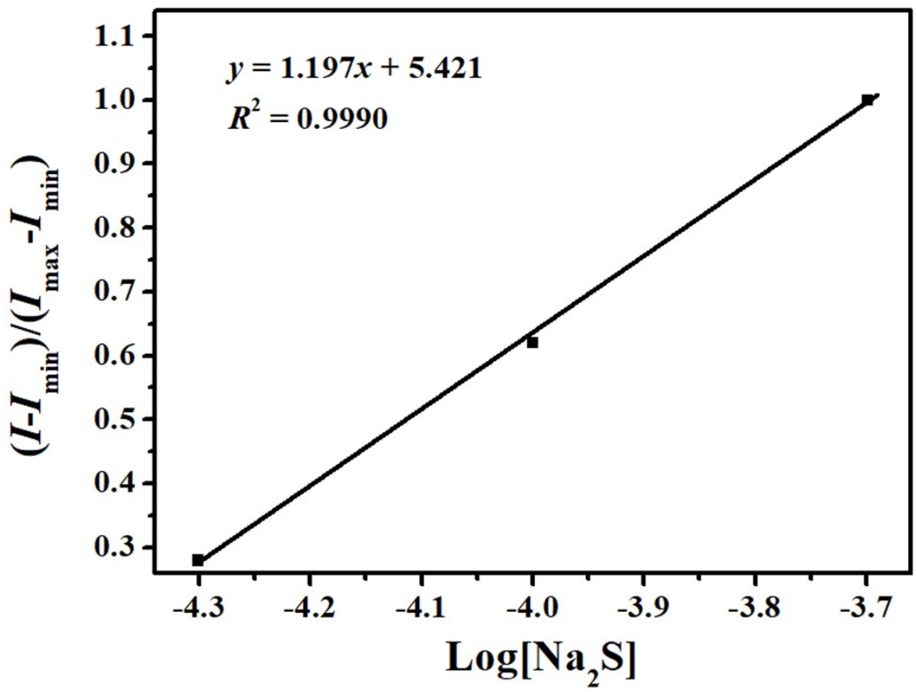

Fig. S7 The regression curve of normalized emission peak intensity obtained by using

Image J software versus the logarithm of exogenous Na_2S in MCF-7 cells.

Table S1 The detection performance of representatively reported fluorescent turn-on H_2S bio-probes

No.	Probe	LOD (μM)	Linear range (μM)	Ref.
1	CLSS-2	4.6 ± 2.0	0-250	[3]
2	Mn-doped ZnS QDs	0.2	2-100	[4]
3	TPP-H_2S	0.12	0.5-20	[5]
4	BH-HS	1.7	0-40	[6]
5	Ag-NPs@DNA-FAM	0.01	0.01-100	[7]
6	Flu-N_3	0.031	0-140	[8]
7	CdTe QDs/AgNP	0.015	0.0495-5.2	[9]
8	Mito-NIR-SH	0.0893	0-30	[10]
9	Lyso-HA-HS	0.34	0-40	[11]
10	SXR	0.70	0-80	[12]
11	QCy7-HS	1.0	0-14	[13]
12	SNARF-SeSPy	0.034	0-20	[14]
13	TPA-Pz-NBD	0.70	0-125	[15]
14	NT-SH	0.080	0-50	[16]
15	CMHS	0.23	0-260	[17]
16	CPs/MOFs	7.2	0-80	[18]
17	NTR-HS	0.104	3.33-20	[19]
18	SS-N_3	0.010	0-80	[20]
19	RDM-HS	0.31	0-80	[21]
20	ER-Nap-NBD	5.2	0-450	[22]
21	T-HS	3.6	0-100	[23]
22	WFP-PC	0.47	0-20	[24]
23	DCI-Br-NBD	0.40	0-50	[25]
24	CFB-H_2S	0.046	0-100	[26]
25	HN8DNP	0.31	0-50	[27]
26	DCM-H_2S	0.13	5-50	[28]
27	CIS/ZnS@Fe-160	0.68	0-300	**This work**
28	CIS/ZnS@Fe-180	0.68	0-300	**This work**
29	CIS/ZnS@Fe-200	0.70	0-300	**This work**

Additional References:

[1] X. An, Y. Zhang, J. Wang, D. M. Kong, X. W. He, L. Chen and Y. Zhang, *ACS Omega*, 2021, **6**, 17501-17509.

[2] R. Li, X. Qi, F. Wu, C. Liu, X. Huang, T. Bai and S. Xing, *Anal. Chim. Acta*, 2024,

1287, 342121.

[3] T. S. Bailey and M. D. Pluth, *J. Am. Chem. Soc.*, 2013, **135**, 16697-166704.

[4] P. Wu, J. Zhang, S. Wang, A. Zhu and X. Hou, *Chem. Eur. J.*, 2014, **20**, 952-956.

[5] Q. Chen, J. Yang, Y. Li, J. Zheng and R. Yang, *Anal. Chim. Acta*, 2015, **896**, 128-136.

[6] M. Ren, B. Deng, X. Kong, K. Zhou, K. Liu, G. Xu and W. Lin, *Chem. Commun.*, 2016, **52**, 6415-6418.

[7] Y. Dong, L. Wang, F. Wang, N. Li, Y. Jin, J. Zhang and X. Yang, *Analyst*, 2017, **142**, 4703-4707.

[8] Q. Zhao, F. Huo, J. Kang, Y. Zhang and C. Yin, *J. Mater. Chem. B*, 2018, **6**, 4903-4908.

[9] Y. Wu, Q. Wang, T. Wu, W. Liu, H. Nam, S. Xu and Y. Shen, *ACS Appl. Mater. Interfaces*, 2018, **10**, 43472-43481.

[10] X. Zhao, Y. Li, Y. Jiang, B. Yang, C. Liu and Z. Liu, *Talanta*, 2019, **197**, 326-333.

[11] M. Ren, Z. Li, B. Deng, L. Wang and W. Lin, *Anal. Chem.*, 2019, **91**, 2932-2938.

[12] X. Song, Y. Wang, J. Ru, Y. Yang, Y. Feng, C. Cao, K. Wang, G. Zhang and W. Liu, *Sens. Actuators B Chem.*, 2020, **312**, 127982.

[13] D. Su, D. Cheng, Y. Lv, X. Ren, Q. Wu and L. Yuan, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, 2020, **226**, 117635.

[14] X. Zhang, W. Qu, H. Liu, Y. Ma, L. Wang, Q. Sun and F. Yu, *Anal. Chim. Acta*, 2020, **1109**, 37-43.

[15] S. Pei, J. Li, C. Zhang, W. Liang, G. Zhang, L. Shi, W. Wang, S. Shuang and C.

Dong, *Analyst*, 2021, **146**, 2138-2143.

[16] Q. Sun, H. Liu, Y. Qiu, J. Chen, F. Wu, X. Luo and D. Wang, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, 2021, **254**, 119620.

[17] L. Ou, R. Guo and W. Lin, *Anal. Methods*, 2021, **13**, 1511-1516.

[18] S. Saha, P. K. Roy, K. Maity, M. Mandal and K. Biradha, *Chem. Eur. J.*, 2022, **28**, e202103830.

[19] B. Li, M. Wang, X. Gu, J. Chen, X. Yang, X. Liu and K. Xu, *Microchim. Acta*, 2022, **189**, 291.

[20] J. Peng, Q. Ju, B. An, Z. Yin, N. Wei and Y. Zhang, *Talanta*, 2022, **250**, 123741.

[21] K. Wang, X. Yang, M. Guo, X. Chen, T. Li, R. Yan, Y. Yang, H. Zhu and Z. Hu, *Sens. Actuators B Chem.*, 2022, **369**, 132285.

[22] Y. S. Kafuti, S. Zeng, X. Liu, J. Han, M. Qian, Q. Chen, J. Wang, X. Peng, J. Yoon, H. Li, *Chem. Commun.*, 2023, **59**, 2493-2496.

[23] C. Xu, Y. Zhang, H. Sun, J. Ai and M. Ren, *Anal. Methods*, 2023, **15**, 1948-1952.

[24] M. Wang, J. Chen, X. Gu, X. Yang, J. Fu and K. Xu, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, 2023, **295**, 122587.

[25] Y. Xiao, P. Wang, Q. Wang, N. Ma, S. Feng, G. Zhang and Y. Gong, *Sens. Actuators B Chem.*, 2023, **396**, 134515.

[26] F. Chu, B. Feng, M. Liu, M. Liu, F. Chen, J. Dong and W. Zeng, *Dyes Pigments*, 2024, **222**, 111894.

[27] Q. Wang, P. Wang, Y. Xiao, S. Feng, G. Zhang and Y. Gong, *Talanta*, 2024, **271**, 125734.

[28] Y. Wang, J. Wang, R. Liu, J. Chen, Y. Shu, J. Wang and H. Qiu, *Microchem. J.*, 2024, **199**, 109950.