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Supporting Information for

A smart luminescent metal-organic framework-based logic system for simultaneous analysis of copper ions and hydrogen sulfide

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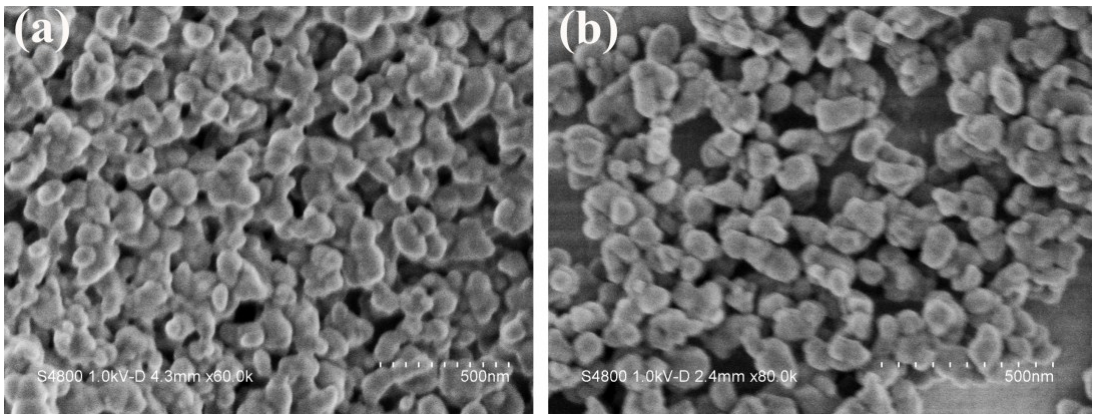


Fig. S1 SEM images of Zr-pydc (a) and Zr-pydc-Eu (b).

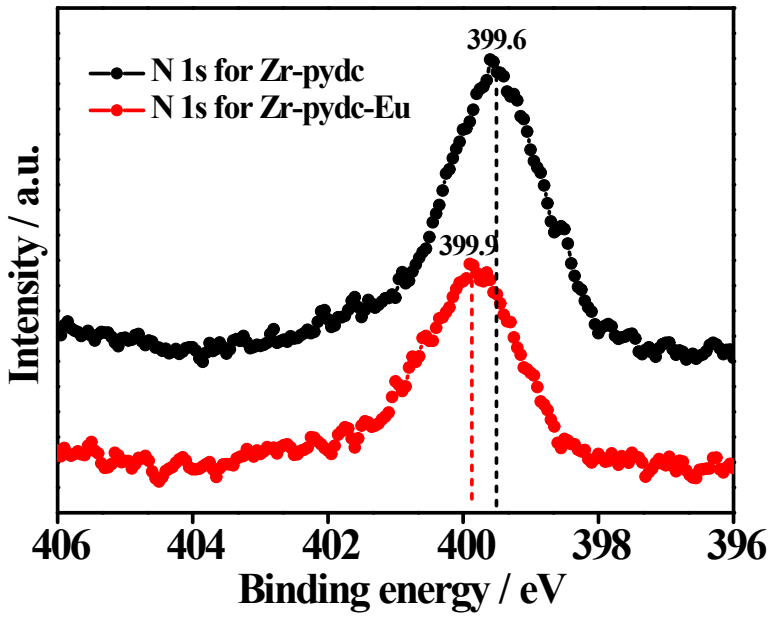


Fig. S2 N 1s XPS spectra for Zr-pydc (black line) and Zr-pydc-Eu (red line).

Table S1 ICP-OES analysis for the Zr and Eu elements in the Zr-pydc-Eu

Elements	Zr	Eu
Mass ratio / mg·L^{-1}	330	180
Molar ratio	3.62	1.18

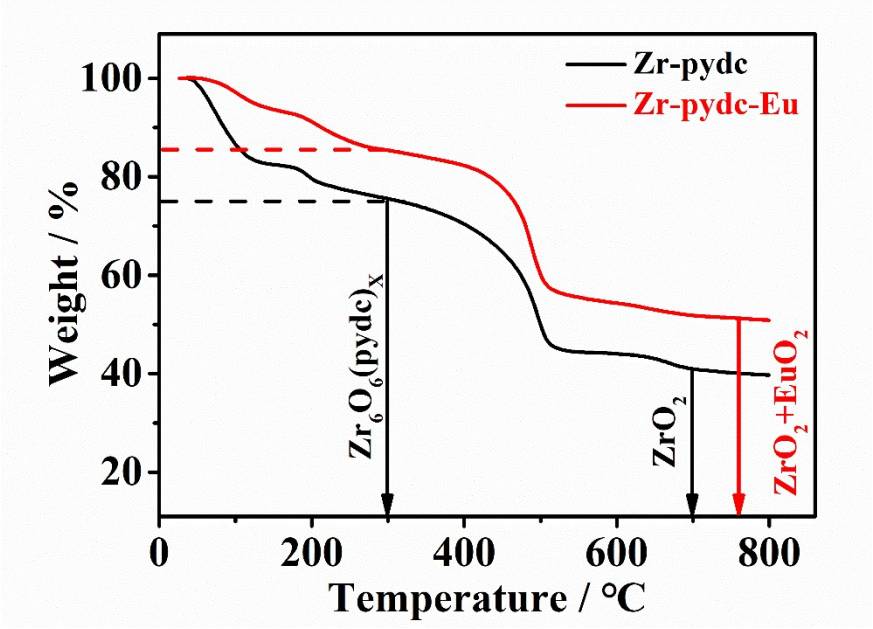


Fig. S3 Thermogravimetric analysis of Zr-pydc and Zr-pydc-Eu. The gradual weight loss from 100 to 300 °C can be ascribed to the dehydration of the $Zr_6O_4(OH)_4$ species and the units of MOFs turned into $Zr_6O_6(pydc)_6$ in this phase. The structure of both the Zr-pydc and Zr-pydc-Eu in air is thermally stable up to 400 °C, above which a further weight loss is attributed to decomposition of the framework. The residues are their corresponding metallic oxideand when the temperature rises to 700 °C.

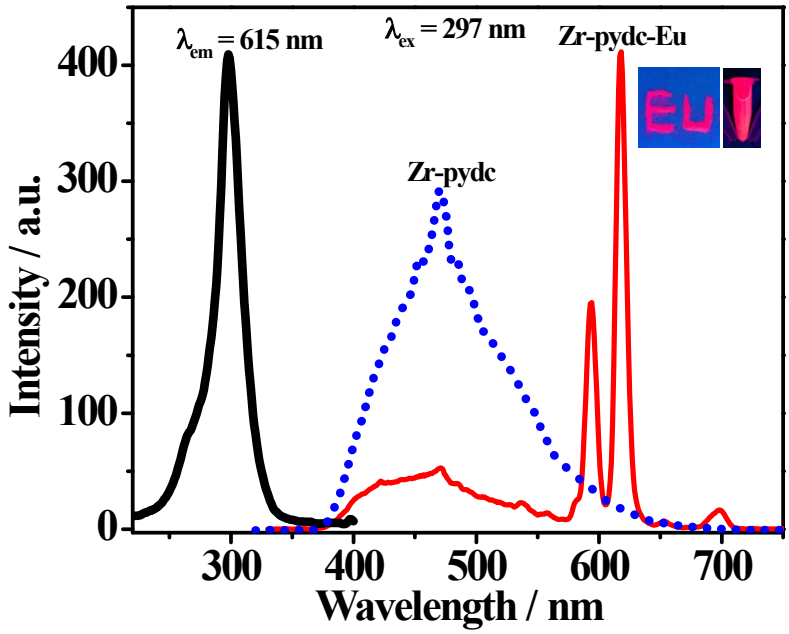


Fig. S4 Excitation (λ_{em} = 615 nm, black line) spectrum of Zr-pydc-Eu and emission spectra of Zr-pydc-Eu (red line) and Zr-pydc (blue dot line) under the excitation of 297 nm.

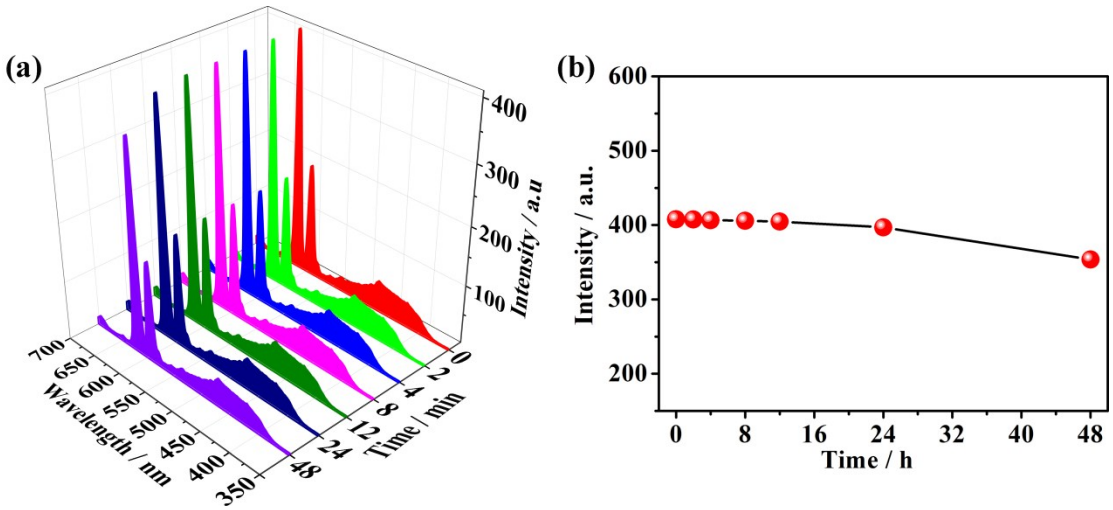


Fig. S5 Emission spectra (a) and the correspongding intensities at 615 nm (b) of Zr-pydc-Eu after immersing in Hepes solutions (pH = 7.4) with different time (0 - 48h).

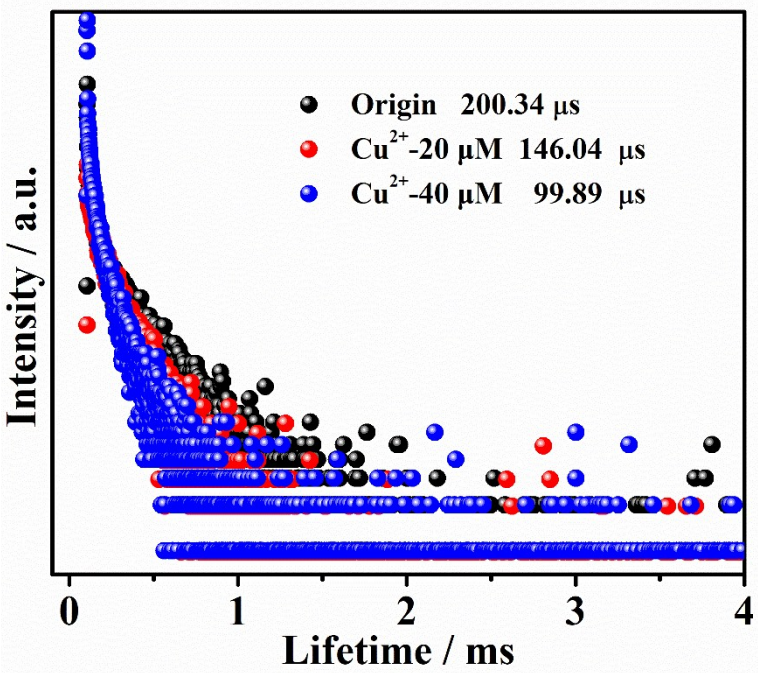


Fig. S6 Luminescence lifetimes of Zr-pydc-Eu at 615 nm in the absence and presence of different concentrations (20 and 40 μM) of Cu^{2+} under the excitation of 297 nm.

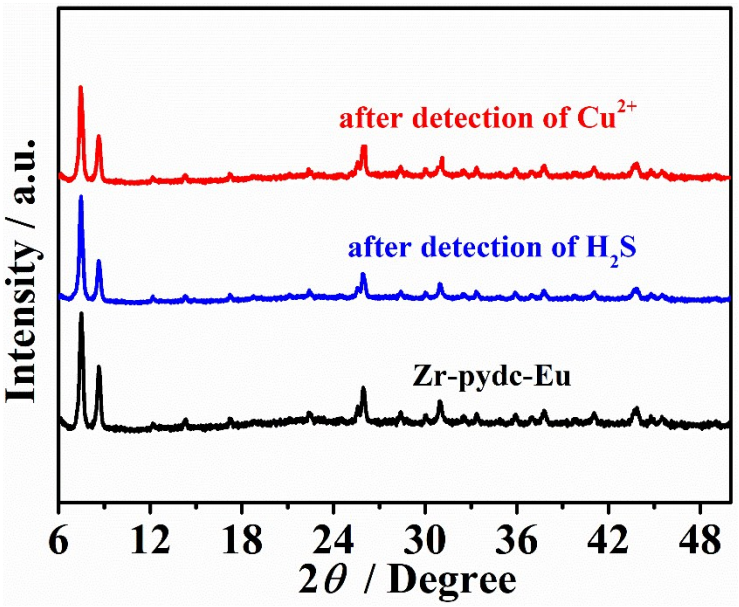


Fig. S7 PXRD patterns of Zr-pydc-Eu before and after detection of Cu^{2+} and H_2S.

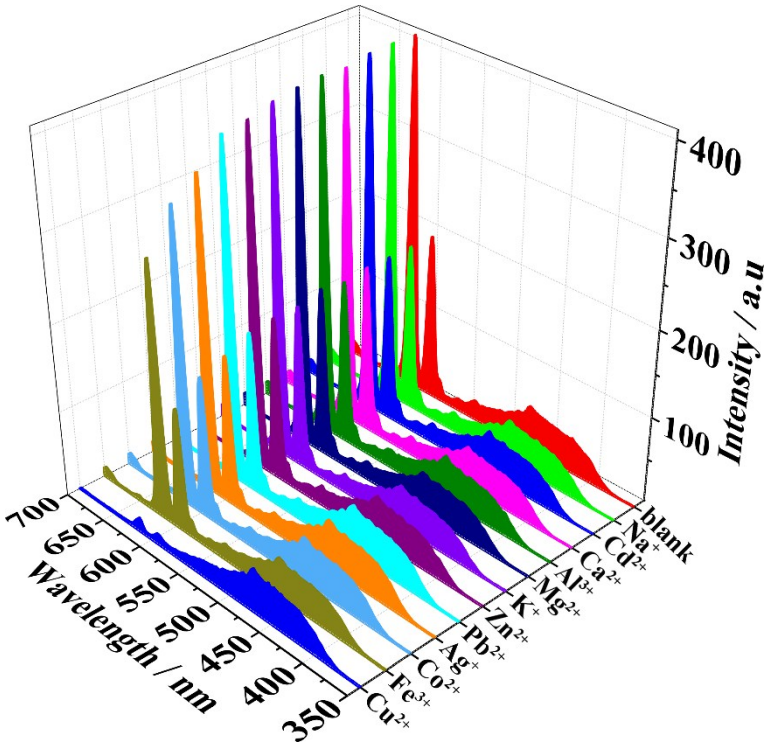


Fig. S8 Emission spectra of Zr-pydc-Eu upon the addition of different cations (100 μM, λ_{ex} = 297 nm).

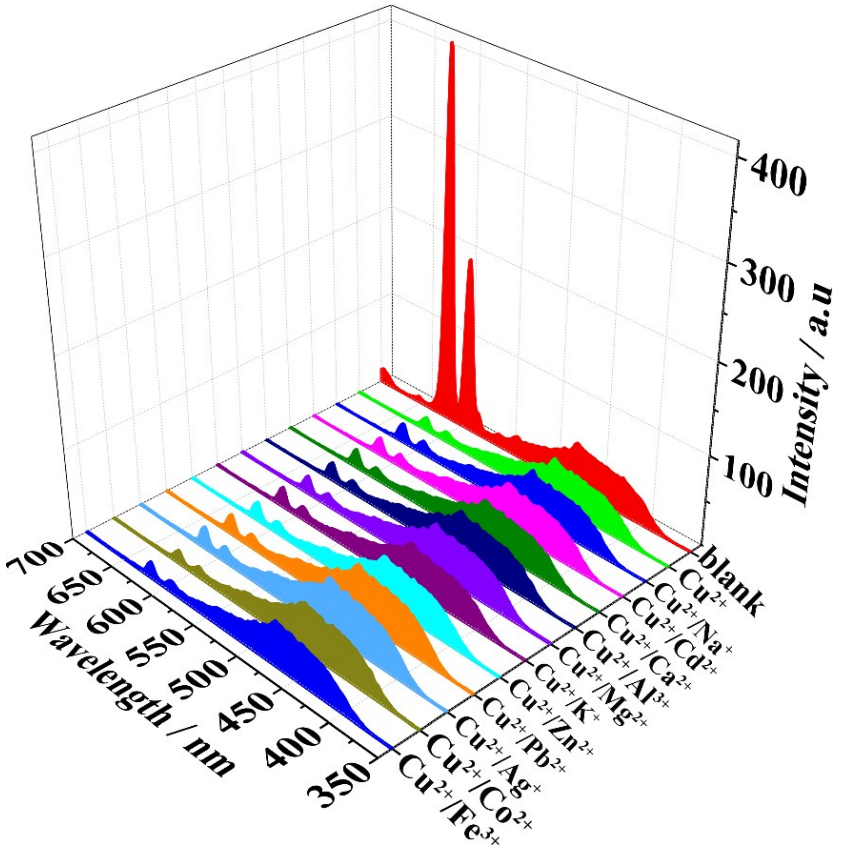
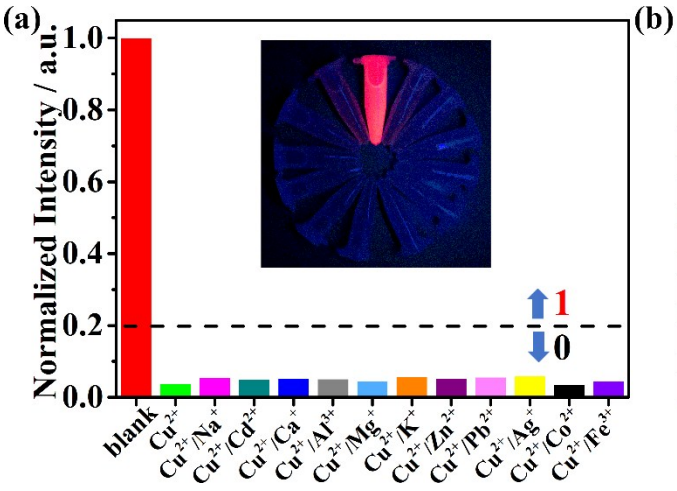


Fig. S9 Luminescence spectra of Zr-pydc-Eu towards Cu^{2+} (100 μM) in the presence of other various cations (100 μM, λ_{ex} = 297 nm).



(b)

Input												Output
Cu (II)	Na (I)	Cd (II)	Mg (II)	Al (III)	K (I)	Ca (II)	Zn (II)	Fe (III)	Pb (II)	Ag (I)	Co (II)	I_{615}
0	0	0	0	0	0	0	0	0	0	0	0	1
1	1	0	0	0	0	0	0	0	0	0	0	0
1	0	1	0	0	0	0	0	0	0	0	0	0
1	0	0	1	0	0	0	0	0	0	0	0	0
1	0	0	0	1	0	0	0	0	0	0	0	0
1	0	0	0	0	1	0	0	0	0	0	0	0
1	0	0	0	0	0	1	0	0	0	0	0	0
1	0	0	0	0	0	0	1	0	0	0	0	0
1	0	0	0	0	0	0	0	1	0	0	0	0
1	0	0	0	0	0	0	0	0	1	0	0	0
1	0	0	0	0	0	0	0	0	0	1	0	0
1	0	0	0	0	0	0	0	0	0	0	1	0
1	0	0	0	0	0	0	0	0	0	0	0	0

Fig. S10 Column diagram (a) of the normalized fluorescence intensity (threshold, 0.2) of the Zr-pydc-Eu^{3+} at 615 nm toward Cu^{2+} in the presence of other cations, and the corresponding truth table (b) of the logic operation with different cations inputs.

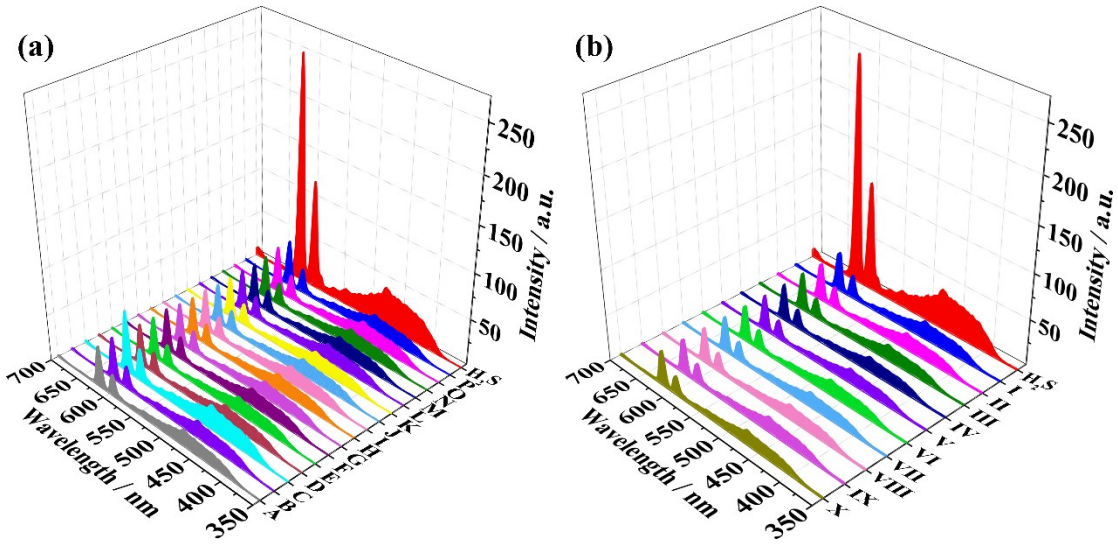
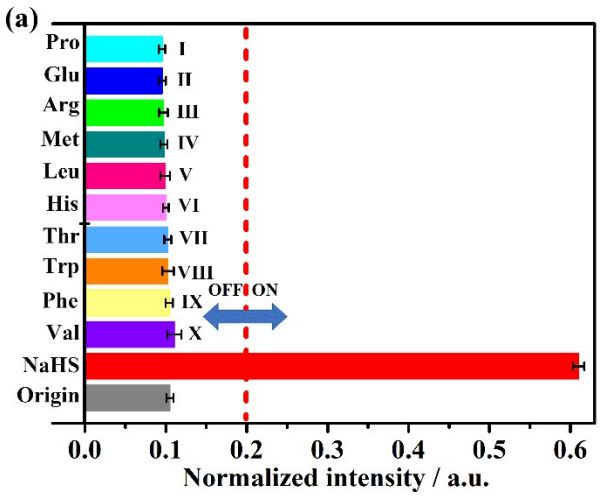


Fig. S11 The emission responses of Cu^{2+}(100 μM)-assisted Zr-pydc-Eu to H_2S and various biologically relevant interferents (A-P and I-X, 120 μM, λ_{ex} = 297 nm).



(b)

Input												Output
Cu^{2+}	NaHS	I	II	III	IV	V	VI	VII	VIII	IX	X	I_{615}
1	1	0	0	0	0	0	0	0	0	0	0	1
1	0	1	0	0	0	0	0	0	0	0	0	0
1	0	0	1	0	0	0	0	0	0	0	0	0
1	0	0	0	1	0	0	0	0	0	0	0	0
1	0	0	0	0	1	0	0	0	0	0	0	0
1	0	0	0	0	0	1	0	0	0	0	0	0
1	0	0	0	0	0	0	1	0	0	0	0	0
1	0	0	0	0	0	0	0	1	0	0	0	0
1	0	0	0	0	0	0	0	0	1	0	0	0
1	0	0	0	0	0	0	0	0	0	1	0	0
1	0	0	0	0	0	0	0	0	0	0	1	0

Fig. S12 (a) The emission intensities of Cu^{2+}-assisted Zr-pydc-Eu to NaHS and various biologically relevant interferents (I-X, 120 μM, λ_{ex} = 297 nm). (b) Truth table of the logic Zr-pydc-Eu with Cu^{2+} (100 μM) and different components (I-X, 120 μM) as inputs.

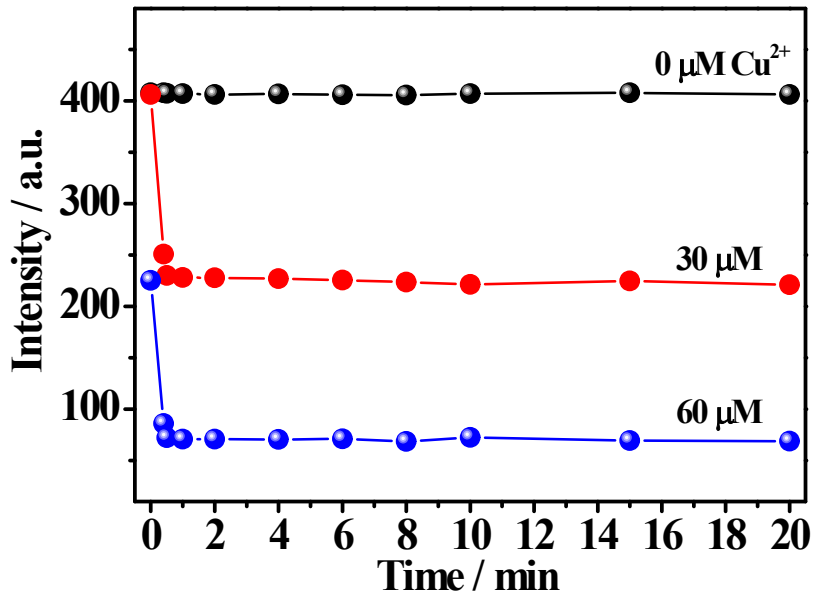


Fig. S13 Luminescence intensity changes of Zr-pydc-Eu at 615 nm as a function of time after successive addition of Cu^{2+} from 30 to 60 μM.

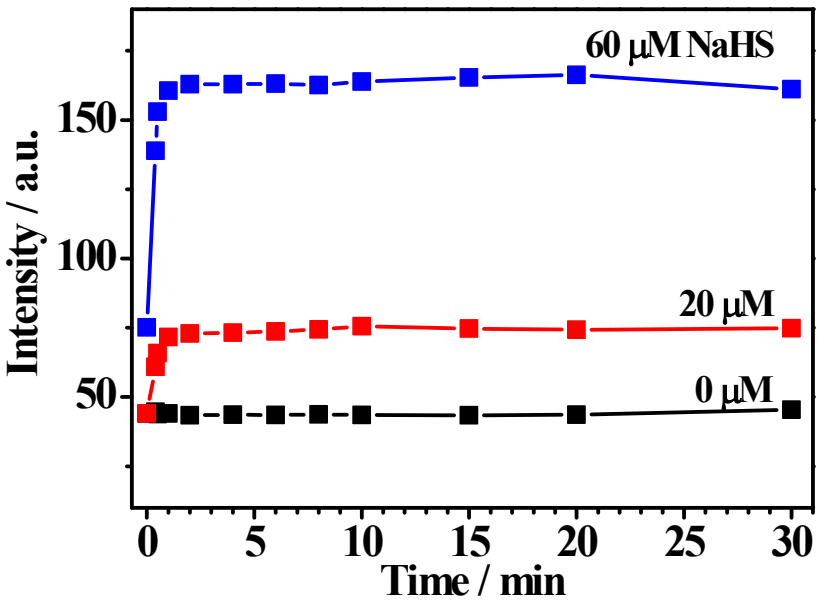


Fig. S14 Luminescence intensity changes of Cu^{2+}/Zr-pydc-Eu at 615 nm as a function of time after successive addition of NaHS from 20 to 60 μM.

Table S2. Comparison of analysis performances of various systems for determination of Cu^{2+} and H_2S.

No	Methods	Systems	Analyte	LOD/ μM	Response time/min	Assay media	Ref.
1	Luminescence	$[Cd(L)_2]\cdot(DMF)_{0.92}$	Single Cu^{2+}	16.9	-	DMF	18a
2	Luminescence	Cd-MOF-74	Single Cu^{2+}	78.7	-	Water	18b
3	Luminescence	$\{[Nd_2(NH_2\text{-}BDC)_3(DMF)_4]\}_n$	Single Cu^{2+}	24.95	-	DMF	18c
4	Luminescence	NH_2-MIL-101(Al)@ZIF-8	Single Cu^{2+}	0.17	-	Water	18d
5	Luminescence	$[Zn(OBA)_2(PTD)_2DMF_2H_2O]_n$	Single Cu^{2+}	4.43	-	DMF	18e
6	Luminescence	Eu^{3+}/Ag^{+}@UiO-66-$(COOH)_2$	Single H_2S	23.53	0.5	Serum	5a
7	Luminescence	$Zr_6O_4(OH)_4((NDC\text{-}(NO_2)_2)_6$	Single H_2S	20	55	Blood plasma, living cells	19a
8	Luminescence	UiO-66-$(NO_2)_2$	Single H_2S	14.14	40	Blood plasma, living cells	19b
9	Luminescence	Eu^{3+}/Cu^{2+}@UiO-66-$(COOH)_2$	Single H_2S	5.45	0.5	Water	19c
10	Luminescence	Tb^{3+}@Cu1	Single H_2S	1.2	2	Water	19d
11	Luminescence	Cy-N_3	Single H_2S	0.08	20	Living cells	19e
12	Luminescence	SF4	Single H_2S	0.125	60	Living cells	19f
13	Luminescence	PSS-PA-Cu NC aggregates	Single H_2S	0.65	30	Water	19g
14	UV-vis spectroscopy	Bare gold NPs	Single H_2S	0.08	1	Water	19h
15	Luminescence	Zr-pydc-Eu	Cu^{2+} H_2S	0.09 0.06	1 2	Water/ Serum Water/ Serum	This work

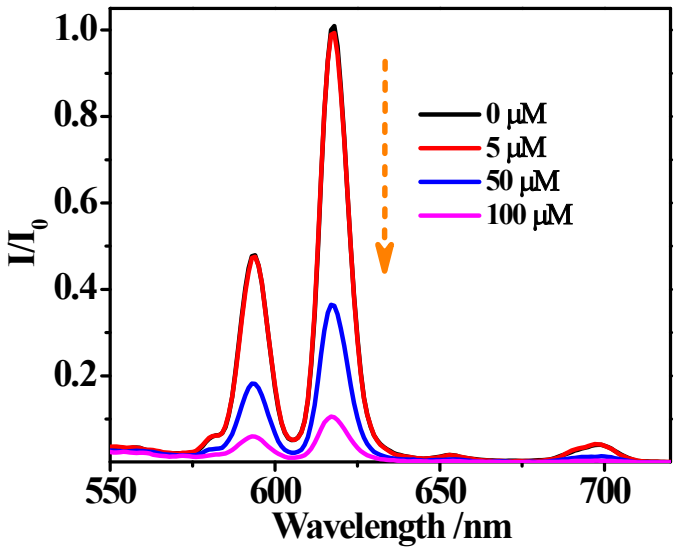


Fig. S15 Fluorescent responses of Zr-pydc-Eu to pretreated FBS spiked with different concentrations of Cu^{2+}.

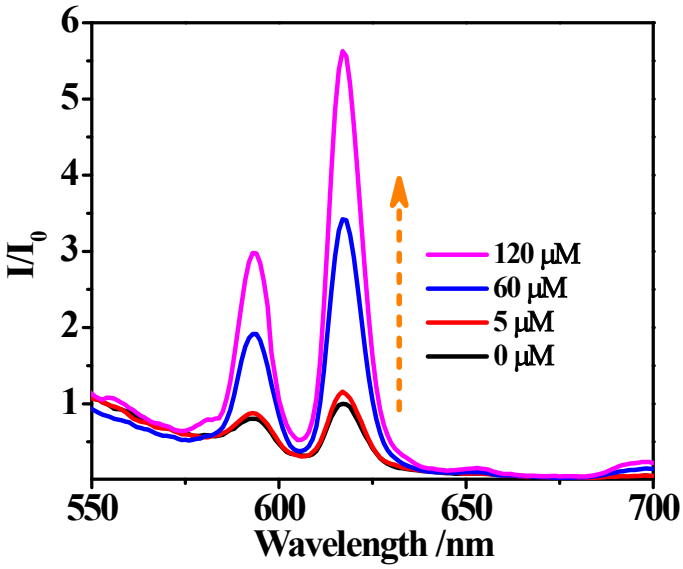


Fig. S16 Fluorescent responses of Cu^{2+}(100 μM)-assisted Zr-pydc-Eu to pretreated FBS spiked with different concentrations of NaHS.

Table S3. Determination of Cu^{2+} in the pretreated FBS samples by the Zr-pydc-Eu.

Serum Samples	Spiked (μM)	Measured (μM, *n* = 6)	Recovery (%)	RSD (%, *n* = 6)
1	5.0	5.21±0.10	104.20	1.92
2	50.0	46.37±1.22	92.74	2.63
3	100.0	103.0±1.42	103.00	1.38

Table S4. Determination of NaHS in the pretreated FBS samples by the Cu^{2+}-assisted Zr-pydc-Eu.

Serum Samples	Spiked (μM)	Measured (μM, *n* = 6)	Recovery (%)	RSD (%, *n* = 6)
1	5.0	4.78 ± 0.11	95.60	2.30
2	60.0	63.54 ± 1.10	105.90	1.73
3	120.0	120.8 ± 1.35	100.67	1.12