Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary information

An europium(III) metal–organic framework as a multi-responsive luminescent sensor for highly sensitive and selective detection of 4-nitrophenol, I^- and Fe^{3+} in water

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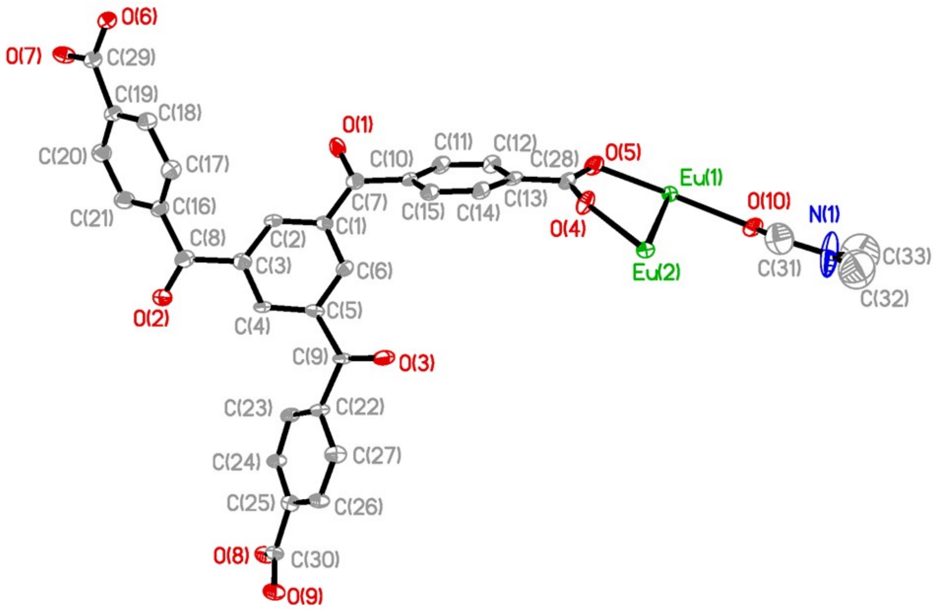

Fig. S1. ORTEP structure of compound **1** with hydrogen atoms omitted for clarity.

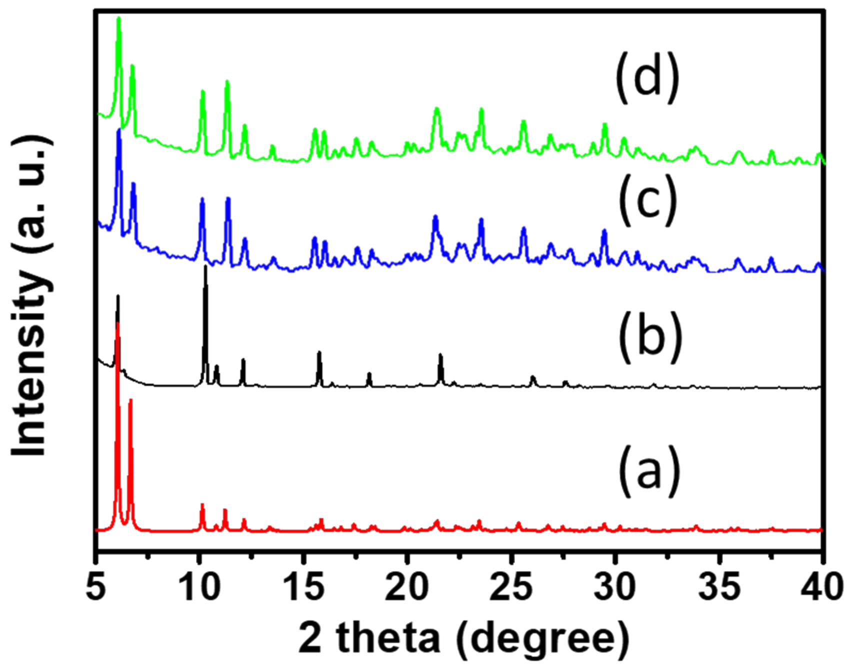

Fig. S2 Powder XRD patterns of **1** (a) simulated, (b) as-synthesized, (c) recycled from 4-NP, (d) recycled from I^-.

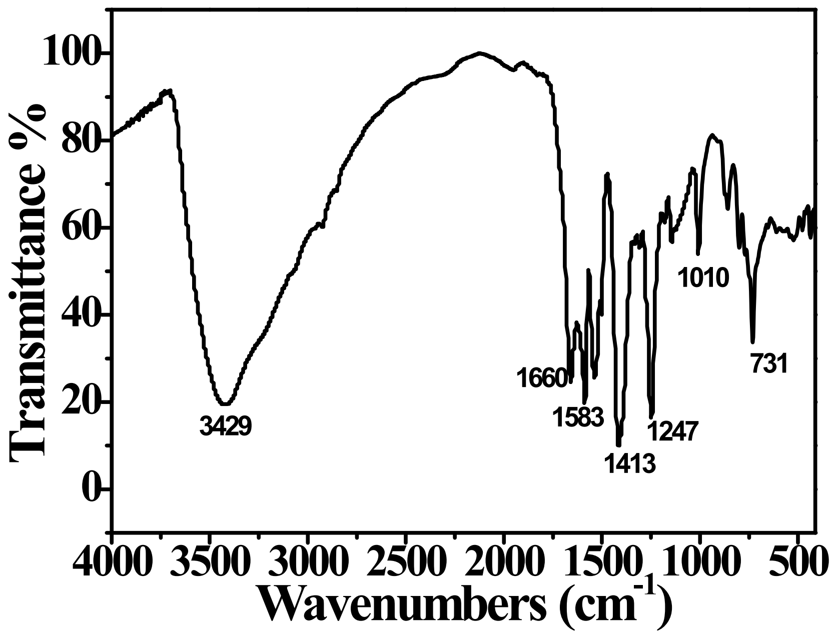

Fig. S3 IR spectrum of compound **1**.

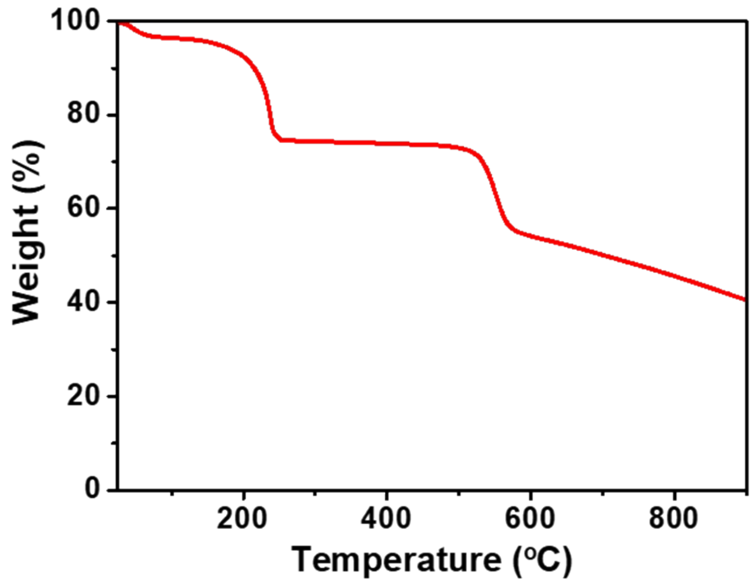

Fig. S4 The TGA curve of compound **1** under N_2 atmosphere at the heating rate of 5 °C·min^{-1}**.**

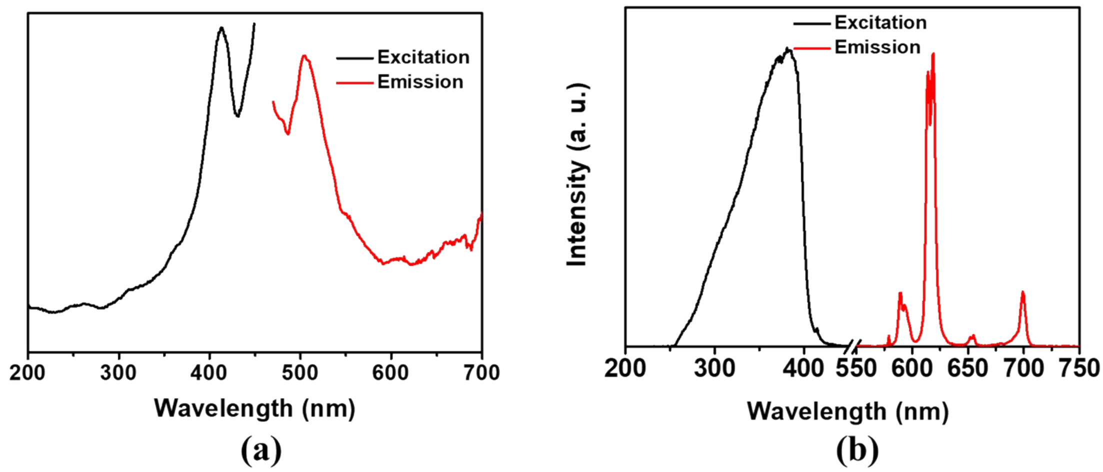

Fig. S5 Excitation and emission spectra of (a) free ligand H_3BCB and (b) compound **1**.

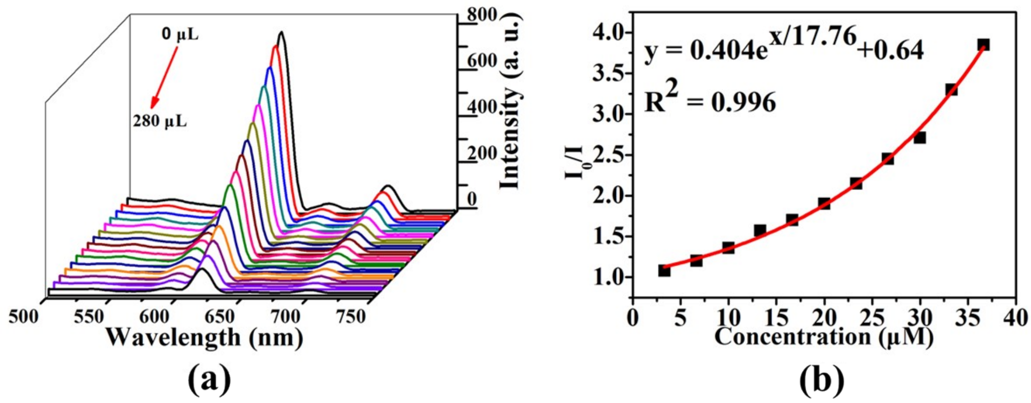

Fig. S6 (a) Photoluminescence spectra of **1** upon progressive addition of 4-NP aqueous solution (0.33 mM, 20 μL each time); (b) Stern-Volmer plot of I_0/I versus 4-NP concentration in water.

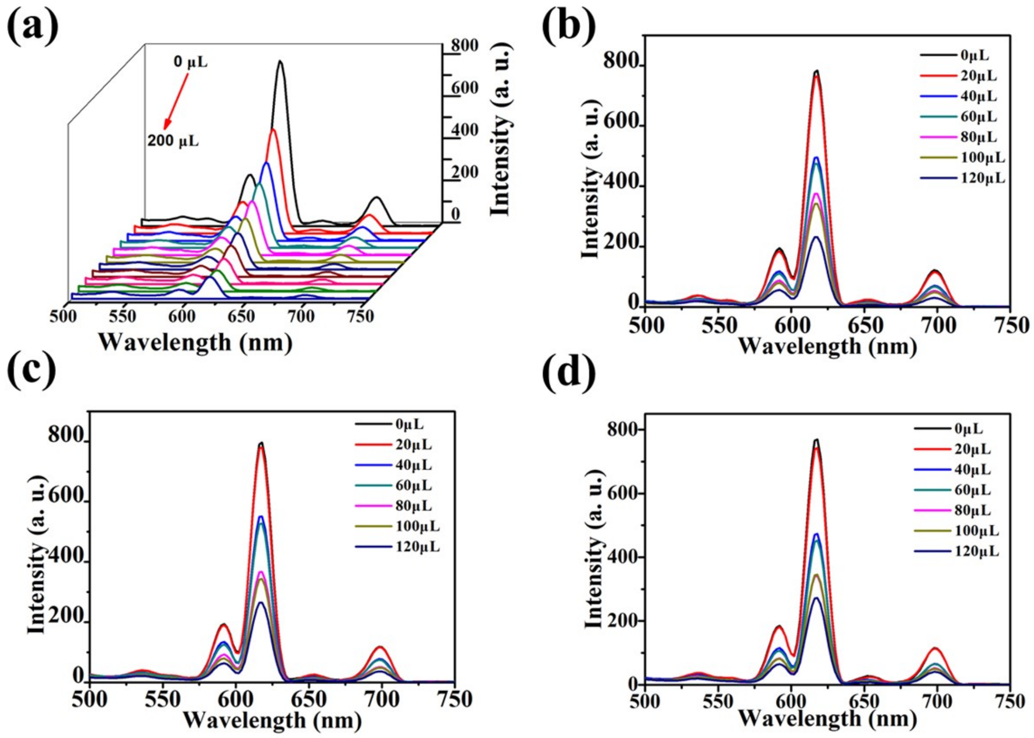

Fig. S7 Photoluminescence spectra of compound **1** upon progressive addition of the 4-NP aqueous solution (1.25 mM, 20 μL addition each time) (a); Tracked emission spectra of compound **1** upon the addition of 4-NP in the presence and absence of toluene (b); m-NT (c); 2,4-DNT(d).

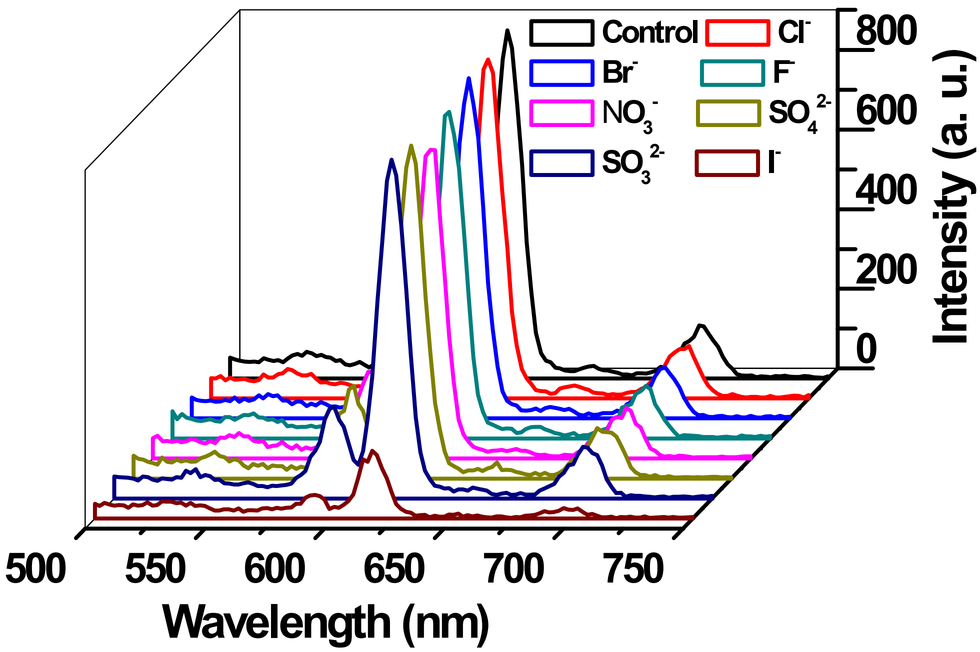

Fig. S8 Emission spectra (λ_{ex} = 230 nm) of **1** dispersed in water after the addition of different anion aqueous solutions (0.10 M, 20 μL).

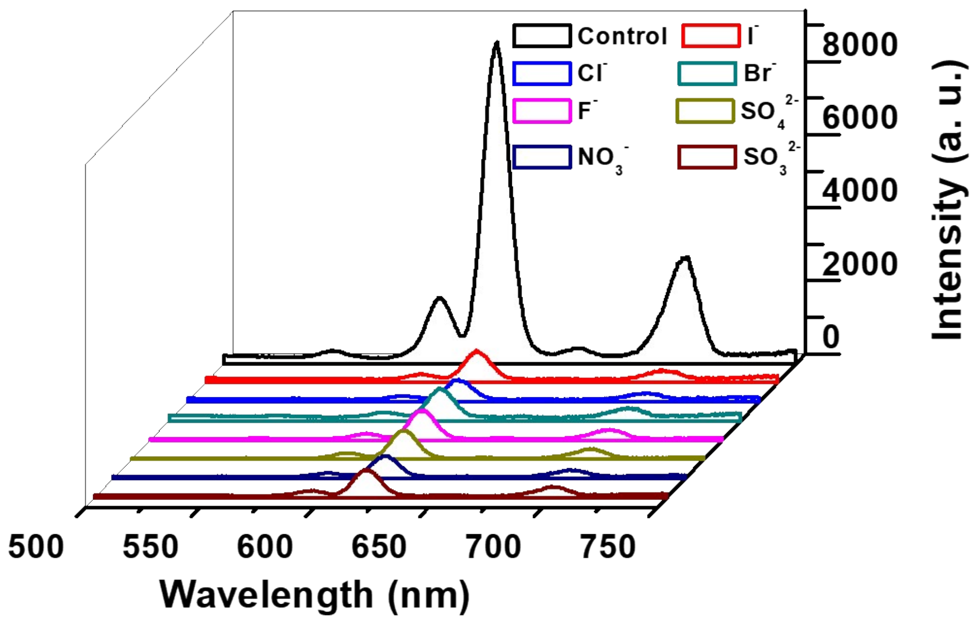

Fig. S9 Luminescence intensity of **1** in water in the presence of I⁻ and other different anions excited at 230 nm.

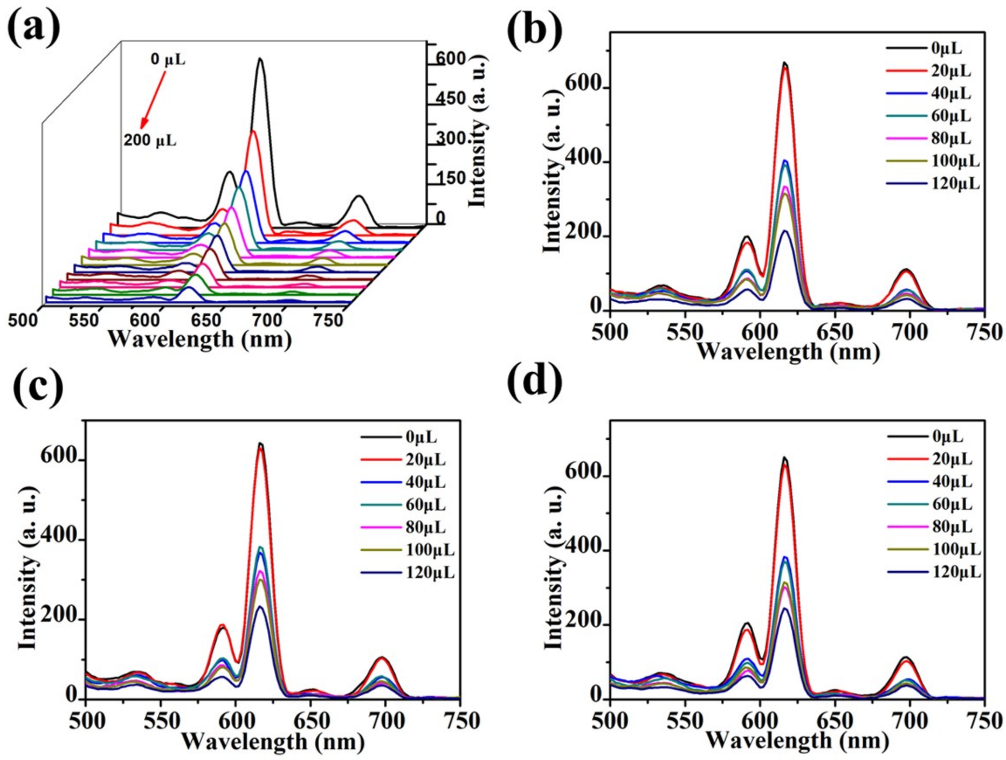

Fig. S10 Photoluminescence spectra of compound **1** upon progressive addition of the Fe^{3+} ion aqueous solution (5 mM, 20 μL addition each time) (a); Tracked emission spectra of compound **1** upon the addition of Fe^{3+} in the presence and absence of Na^{+} (b); Ca^{2+} (c); Ni^{2+} (d).

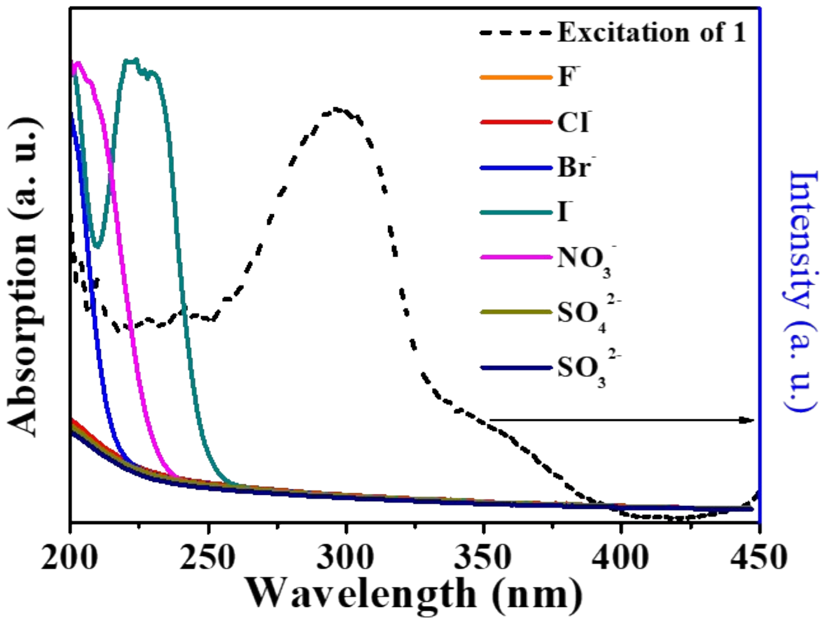

Fig. S11 The excitation spectra of the suspension of **1** and the absorption spectra of anions in water.

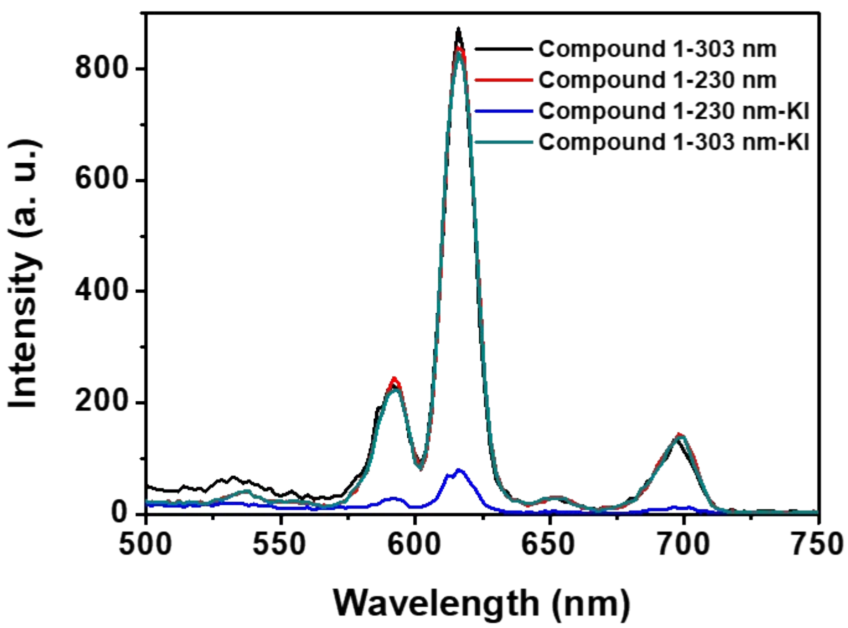

Fig. S12 Photoluminescence spectra of compound **1** in the presence or absence of I^- (Conc. =1 mM) in water excited upon 230 or 303 nm.

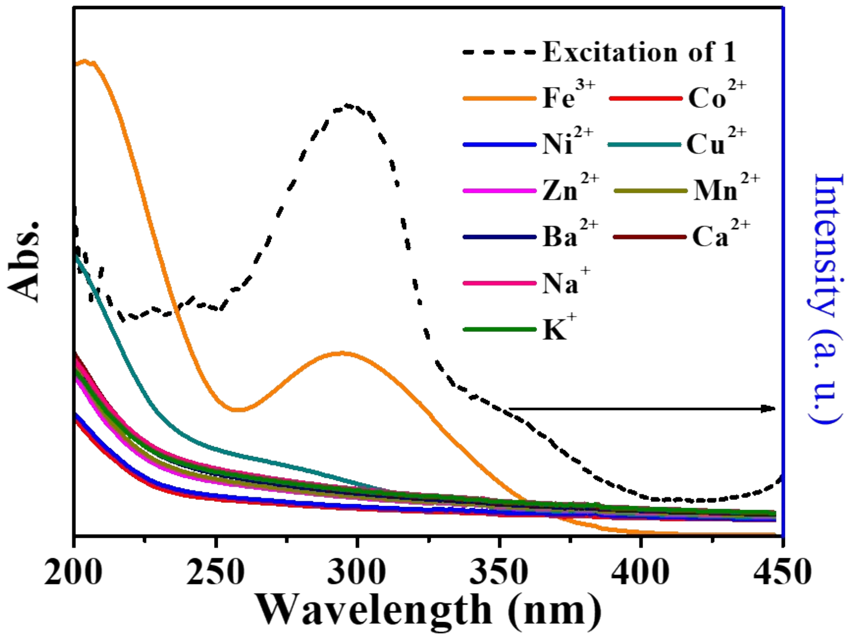

Fig. S13 The excitation spectra of the suspension of **1** and the absorption spectra of metal ions in water.

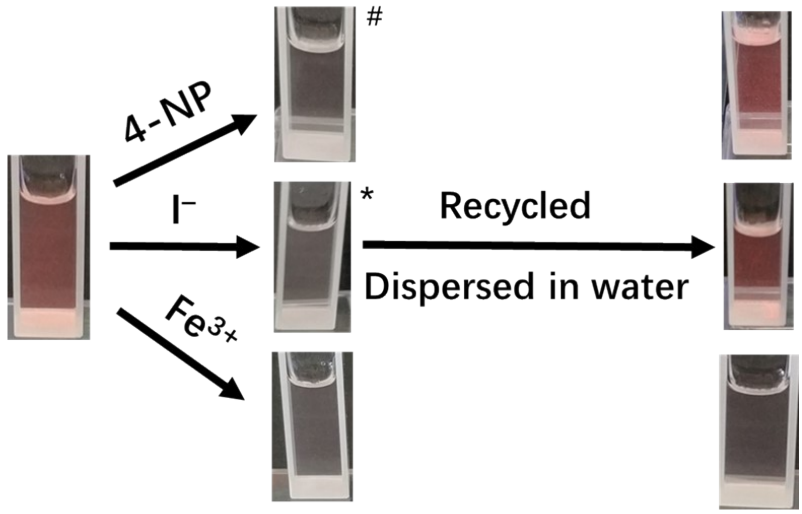

Fig. S14 The visual color change of aqueous suspension of **1** before and after adding 4-NP, I^- and Fe^{3+} and the recyclable samples dispersed in water under UV light (λ_{ex} = 365 nm; #: λ_{ex} = 303 nm; *: λ_{ex} = 230 nm).

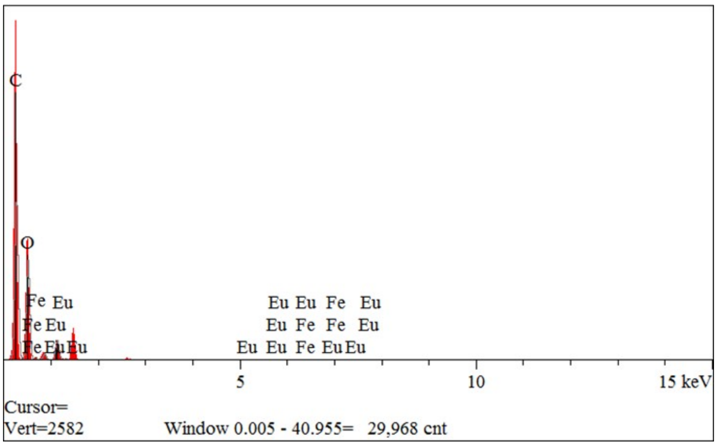

Fig. S15 Energy-dispersive X-ray spectroscopy (EDS) spectrum of **1** after treatment with the Fe^{3+} aqueous solution.

Table S1. Comparison of the 4-NP Detection Efficiency of **1** with Other Sensors

	4-NP sensors	Ksv (M^{-1})	Detection Limit	Refs.
1	$[Zn_2(TCPE)(tta)_2]\cdot 2DMF\cdot 4H_2O\cdot 2Me_2NH_2$	0.16×10^4	94.59 ppb	1
2	$[Zn(L^4)(H_2O)]\cdot H_2O$	1.25×10^4	0.52 ppm	2
3	$[Zn_2(1,4\text{-bdc})(1,4\text{-Hbdc})_2(NI\text{-bpy-}34)_2]$	1000	13.25×10^{-6} mol/L	3
4	$\{[Eu(L)(HCOO)]\cdot H_2O\}n$	13784	3×10^{-9} mol/L	4
5	$[Eu(L)(H_2O)]\cdot 1.5H_2O$	75130	9.2×10^{-7} mol/L	5
6	$[In_3O(ADBA)_3(H_2O)_3](NO_3)\cdot(H_2O)_6$	5.1×10^4	Not given	6
7	$\{[Tb(TATAB)\ (H_2O)_2]\cdot NMP\cdot H_2O\}n$	3.7×10^5	140 ppm	7
8	$[Tb(TAIP)(DMF)_2]$	3.35×10^4	6×10^{-7} mol/L	8
9	$[Gd_6(L)_3(HL)_2(H_2O)_{10}]1_8\cdot H_2O\cdot x(solvent)$	8.4×10^3	1.7ppm	9
10	$[Pb(BPDP)]$	6.45×10^4	6×10^{-4} mol/L	10
11	$[Pb_3(BPDP)_{1.5}(OOCC_6H_4COOH)_3]$	4.2×10^4	7×10^{-4} mol/L	10
12	$[Zn(L)(H_2O)]\cdot H_2O$	1.25×10^4	3.74×10^{-6} mol/L	2
13	**1**	4.7×10^4	4.15×10^{-7} mol/L	This work

1. X. D. Zhang, G. J. Ren, M. L. Li, W. T. Yang, and Q. H. Pan, Cryst. Growth Des., 2019, 19,6308-6314.
2. X. Y. Guo, F. Zhao, J. J. Liu, Z. L. Liu, and Y. Q. Wang, J. Mater. Chem. A, 2017,5, 20035-20043.
3. M. J. Tsai, C. Y. Li and J. Y. Wu, CrystEngComm, 2018, 20, 6762-6774.
4. Y. Liu, J. Ma, C. Xu, Y. Yang, M. Xia, H. Jiang and W. Liu, Dalton Trans., 2018, 47, 13543-13549.
5. Y. Tao, P. Zhang, J. Liu, X. Chen, X. Guo, H. Jin, J. Chai, L. Wang and Y. Fan, New J. Chem., 2018, 42, 19485-19493.
6. X. Liu, B. Liu, G. Li and Y. Liu, J. Mater. Chem. A., 2018, 6, 17177-17185.
7. G. X. Wen, M. L. Han, X. Q. Wu, Y. P. Wu, W. W. Dong, J. Zhao, D. S. Li and L. F. Ma, Dalton Trans., 2016, 45, 15492-15499.
8. D. Wang, L. Sun, C. Hao, Y. Yan and Z. Liang, RSC Adv., 2016, 6, 57828-57834.
9. Q. H. Tan, Y. Q. Wang, X. Y. Guo, H. T. Liu and Z. L. Liu, RSC Adv., 2016, 6, 61725-61731.
10. B. Xing, H. Y. Li, Y. Y. Zhu, Z. Zhao, Z. G. Sun, D. Yang and J. Li, RSC Adv., 2016, 6, 110255- 110265.

Table S2. Comparison of the I^- Detection Efficiency of **1** with Other Sensors

	I^- sensors	Ksv (M^{-1})	LOD(μM)	Refs.
1	IPF	4310	0.80	1
2	Cz-TPM	2372	7.9	2
3	benzimidazole-based tripodalreceptor	$(1.5 \pm 0.2) \times 10^3$	7.45	3
4	imidazolium-based cyclophane	Not given	10	4
5	quinoxaline-based azine derivatives	Not given	4.77	5
6	D–A type Zn(II) complexes	Not given	0.58	6
7	NC-PNPs-Hg(II)nanocomplex	Not given	0.9	7
8	Cu(I)-MOF	Not given		8
9	Tb/Zn Hetero-MOF	1.8×10^5	0.01	9
10	Cd-MOF	1.8×10^4	0.63	10
11	$[Tb(cpia)(H_2O)_2]n\cdot nH_2O$	1.23×10^4	2.29	11
12	**1**	1.57×10^4	1.57	This work

1. Z. Chen, R. Sun, S. Feng, D. Wang and H. Liu, ACS Appl. Mater. Interfaces, 2020, 12, 11104−11114.
2. Q. Q. Dang, H. J Wan, and X. M. Zhang, ACS Appl. Mater. Interfaces, 2017, 9, 21438−21446.
3. D. Y. Lee, S. Narinder, J. K. Min and O. J. Doo, Org. Lett., 2011, 13, 3024−3027.
4. V. Suresh, N. Ahmed, I. S. Youn and K. S. Kim, Chem-Asian J., 2012, 7, 658−663.
5. B. Gopal and S. Velmathi, Sens. Actuators B, 2018, 256, 126−134.
6. H. Su, L. Hao, W. Hussain, Z. Li and H. Li, CrystEngComm, 2020, 22, 2103−2109.
7. Y. Fan, L. Han, S. Liu, Y. Zhang, H. Luo and N. Li, J. Mater. Chem. C, DOI: 10.1039/d0tc01983f.
8. Y. Q. Chen, G. R. Li, Z. Chang, Y. K. Qu, Y. H. Zhang and X. H. Bu, Chem. Sci., 2013, 4, 3678−3682.
9. P. F. Shi, H. C. Hu, Z. Y. Zhang, G. Xiong and B. Zhao, Chem. Commun., 2015, 51, 3985−3988.
10. D. K. Singha, P. Majee, S. K. Mondal and P. Mahata, J. Photochem. Photobiol. A: Chem., 2018, 356, 389−396.
11. L. J. Liu, M. Y. Zhang, Q. Z. Guo, Z. H. Zhang, and J. F. Guo, Dalton Trans., 2021, 50, 1697–1702.

Table S3. Comparison of the Fe^{3+} Detection Efficiency of **1** with Other Sensors

	Fe^{3+} sensors		Ksv (M^{-1})	Detection Limit	Refs.
1	Bio-MOF-1@RhB	Fe^{3+}	Not given	1.1 ppm	1
2	UiO-66@N	Fe^{3+}	Not given	0.69 ppm	2
3	{[$Cd_2(L)_2(bpe)_2$]·3DMF·2.5H_2O}	Fe^{3+}	1.74×10^4	6.1×10^{-7} mol/L	3
4	{[Cd(L)(bibp)]·2DMF}n	Fe^{3+}	3.39×10^4	1.24×10^{-6} mol/L	3
5	{[Eu(L)(HCOO)]·H_2O}n	Fe^{3+}	7461	1×10^{-9} mol/L	4
6	{[Zn(nBuOip)(bpp)]·2H_2O}n	Fe^{3+}	1474	5.442×10^{-5} mol/L	5
7	[$Tb_4L4(NO_3)_2(Piv)_2$]·2CH_3OH	Fe^{3+}	1.86×10^4	1×10^{-5} mol/L	6
8	[$Eu(IMS1)_2$ Cl·4H_2O	Fe^{3+}	5873.4	2.3×10^{-5} mol/L	7
9	{[$Zn(L)_{0.5}$(btdpe)]·H_2O}n	Fe^{3+}	5.1×10^4	5.9×10^{-7} mol/L	8
10	{$Zn_2(NO_3)_2$(4,4'-bpy)$_2$(TBA)}	Fe^{3+}	7×10^4	7.18×10^{-6} mol/L	9
11	TMU-16	Fe^{3+}	2.8×10^4	2×10^{-7} mol/L	10
12	[$Zn_2(L)_2$(TPA)]·2H_2O	Fe^{3+}	6.4×10^3	3.84×10^{-6} mol/L	11
13	NKU-115	Fe^{3+}	3.092×10^3	1.61×10^{-6} mol/L	12
14	[$Zn_3(L)_2$(bipy)(μ_3-OH)$_2$]·3H_2O	Fe^{3+}	2.3×10^4	Not given	13
15	**1**	Fe^{3+}	2.35×10^4	1.78×10^{-6} mol/L	This work

1. S. Let, P. Samanta, S. Dutta and S. K. Ghosh, Inorg. Chim. Acta, 2020, 500, 119205.
2. S. Fajal, P. Samanta, S. Dutta and S. K. Ghosh, Inorg. Chim. Acta, 2020, 502, 119359.
3. Z. Chen, X. Mi, J. Lu, S. Wang, Y. Li, J. Dou and D. Li, Dalton Trans., 2018, 47, 6240-6249.
4. Y. Liu, J. Ma, C. Xu, Y. Yang, M. Xia, H. Jiang and W. Liu, Dalton Trans., 2018, 47, 13543-13549.
5. R. R. Zhu, T. Wang, D. W. Wang, T. Yan, Q. Wang, H. X. Li, Z. Xue, J. Zhou, L. Du and Q. H. Zhao, New J. Chem., 2019, 43, 1494-1504.

6. Y. Qin, Y. Ge, S. Zhang, H. Sun, Y. Jing, Y. Li and W. Liu, RSC Adv., 2018, 8, 12641-12652.
7. Y. Q. Huang, H. Y. Chen, Y. Wang, Y. H. Ren, Z. G. Li, L. C. Li and Y. Wang, RSC Adv., 2018, 8, 21444-21450.
8. C. Xu, C. Bi, Z. Zhu, R. Luo, X. Zhang, D. Zhang, C. Fan, L. Cui and Y. Fan, CrystEngComm, 2019, 21, 2333-2344.
9. X. Zhang, X. Zhuang, N. Zhang, C. Ge, X. Luo, J. Li, J. Wu, Q. Yang and R. Liu, CrystEngComm, 2019, 21, 1948-1955.
10. Y. D. Farahani, V. Safarifard, J. Solid State Chem., 2019, 275, 131-140.
11. X.Y. Guo, Z. P. Dong, F. Zhao, Z.L. Liu, Y.Q. Wang, New J. Chem., 2019, 43, 2353-2361.
12. W. H. Wang, Q. Gao, X. Y. Li, J. H. Wang, C. P. Wang, Y. H. Zhang, X. H. Bu, Chin. Chem. Lett., 2019, 30, 75-78.
13. J. L. Dua, X.Y. Zhang, C.P. Li, J.P. Gao, J.X. Hou, X. Jing, Y.J. Mu, L.J. Li, Sens. Actuators B., 2018, 257, 207-213.