## **Supporting Information**

# A dual-ligand lanthanide-based metal-organic framework for highly selective and sensitive colorimetric detection of Fe<sup>2+</sup>

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#### 1. Absorption curve

Under optimized conditions, in general, 940  $\mu$ L of 0.1 mM PBS (pH =5.0), 50  $\mu$ l Eu-BDC/TPY solution (1.0 × 10<sup>-6</sup> g/L) and 10  $\mu$ L Fe<sup>2+</sup> (1.0 × 10<sup>-2</sup> M) standard solution were added to

1 mL centrifugal tubes, incubated for 5 min. Subsequently, the absorption spectra were collected on an ultraviolet-visible spectrophotometer.



## 2. SEM images of Eu-BDC/TPY at different temperatures

Fig. S1. SEM images of Eu-BDC/TPY with different temperatures (a-d: 25, 40, 80, 120 °C, 200°C).

#### 3. Absorption spectra of Eu-BDC/TPY with different temperatures reaction mixture with Fe<sup>2+</sup>



Fig. S2. Absorption spectra of Eu-BDC/TPY with different temperatures reaction mixture with  $Fe^{2+}$  in PBS buffer (0.1 M, pH = 5.0) at 25 °C.

#### 4. Absorption spectra including Eu-BDC/TPY, TPY, Eu-DBC reaction mixture with Fe<sup>2+</sup>



Fig. S3. Absorption spectra including Eu-BDC/TPY, TPY, Eu-DBC (50  $\mu$ g/mL) reaction mixture with Fe<sup>2+</sup> (100  $\mu$ M) in PBS buffer (0.1 M, pH = 5.0) at 25 °C.

#### 5. Selectivity of Eu-BDC/TPY in Tris-HCl and HEPES buffer

Under the same conditions, dissolve Eu-BDC/TPY in solution Tris-HCl<sub>\</sub> HEPES, and then add equal amounts of Fe<sup>2+</sup> and other metal ions(K<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Ba<sup>2+</sup>, Cu<sup>2+</sup>, Cr<sup>3+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Mn<sup>2+</sup>, Pb<sup>2+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup>, Ca<sup>2+</sup>, Hg<sup>2+</sup>), and observe the ultraviolet absorption peaks and changes in the color of the solution.



Fig. S4. (a) UV-vis and (b) color changes of Eu-BDC/TPY  $(1.0 \times 10^{-5} \text{ M})$ , to varied metal ions (K<sup>+</sup>; Na<sup>+</sup>; Mg<sup>2+</sup>; Ba<sup>2+</sup>; Cu<sup>2+</sup>; Cr<sup>3+</sup>; Fe<sup>2+</sup>; Ni<sup>2+</sup>; Zn<sup>2+</sup>; Cd<sup>2+</sup>; Mn<sup>2+</sup>; Pd<sup>2+</sup>; Fe<sup>3+</sup>; Al<sup>3+</sup>; Ca<sup>2+</sup>; Hg<sup>2+</sup>, 1.0 × 10<sup>5</sup> µM) in Tris-HCl buffe (0.1 M, pH = 5.0). (c) UV-vis and (d) color changes of Eu-BDC/TPY  $(1.0 \times 10^{-5} \text{ M})$ , to varied metal ions (K<sup>+</sup>; Na<sup>+</sup>; Mg<sup>2+</sup>; Ba<sup>2+</sup>; Cu<sup>2+</sup>; Cr<sup>3+</sup>; Fe<sup>2+</sup>; Ni<sup>2+</sup>; Zn<sup>2+</sup>; Cd<sup>2+</sup>; Mn<sup>2+</sup>; Pd<sup>2+</sup>; Fe<sup>3+</sup>; Al<sup>3+</sup>; Ca<sup>2+</sup>; Hg<sup>2+</sup>, 1.0 × 10<sup>5</sup> µM) in HEPES buffer (0.1 M, pH = 5.0) at 25 °C. Absorbance at 552 nm before (A<sub>0</sub>) and after (A<sub>1</sub>) the addition of Fe<sup>2+</sup> to the sample.

#### 6. Anti-interference test of TPY



**Fig. S5.** UV-vis spectra change of TPY (50  $\mu$ g/mL) in the presence of Fe<sup>2+</sup> (100  $\mu$ M), other metal ions are added. (1000  $\mu$ M). The metal ions are (K+; Na<sup>+</sup>; Mg<sup>2+</sup>; Ba<sup>2+</sup>; Cu<sup>2+</sup>; Cr<sup>3+</sup>; Ni<sup>2+</sup>; Zn<sup>2+</sup>; Cd<sup>2+</sup>; Mn<sup>2+</sup>; Pd<sup>2+</sup>; Fe<sup>3+</sup>; Al<sup>3+</sup>; Ca<sup>2+</sup>; Hg<sup>2+</sup>); in PBS buffer (0.1 M, pH = 5.0) at 25 °C. Absorbance at 552 nm before (A<sub>0</sub>) and after (A<sub>1</sub>) the addition of Fe<sup>2+</sup> to the sample.



## 7. Colorimetric testing of cellular phones

Fig. S6 Relationship with Fe2+ concentration in the results of different color data processing

#### 8. Effect of temperature on smart detection of cell phones.



Fig. S7. RGB values of samples spiked with different concentrations of  $Fe^{2+}$  were determined at (a) 20 °C;(b)30 °C;(c) 40 °C.

## 9. Detection Fe<sup>2+</sup> levels in serum



**Fig. S8.** UV-vis absorption spectra including Serum, Serum + Eu-BDC/TPY (50 μg/mL), Serum + EDTA (0.1mM) + Eu-BDC/TPY; Serum + phen (0.1mM) + Eu-BDC/TPY with PBS (0.1 M, pH = 5.0) at 25°C.

#### 10. Compare the proposed methods for the determination of Fe<sup>2+</sup>

S. No	Method	Solvent	LOD/µM	Ref
1	Fluorescence	DMF/H <sub>2</sub> O	0.10	[1]
2	Fluorescence	THF/H <sub>2</sub> O	7.78	[2]
3	Fluorescence	DMSO/PBS	4.50	[3]
4	Fluorescence	H <sub>2</sub> O	6.50	[4]
5	Fluorescence	ACN/H <sub>2</sub> O	15.70	[5]
6	Colorimetric	DMSO/H <sub>2</sub> O	0.43	[6]
7	Colorimetric	DMSO/H <sub>2</sub> O	11.0	[7]
8	Colorimetric	HAc-NaAc	0.59	[8]
9	Colorimetric	H <sub>2</sub> O	0.34	This work

Table S1. Compare the proposed methods for the determination of Fe<sup>2+</sup>

[1]. Y. Ding, C. Zhao, P. Zhang, Y. Chen, W. Song, G. Liu, Z. Liu, L. Yun and R. Han, J. Mol. Struct. 2021, 1231, 129965.

[2]. X. Gong, H. Zhang, N. Jiang, L. Wang and G. Wang, Microchem. J. 2019, 145, 435.

[3]. X. Yang, Y. Wang, R. Liu, Y. Zhang, J. Tang, E. Bing Yang, D. Zhang, Y. Zhao and Y. Ye, Sens. Actuators B., 2019, 288, 217.

[4]. P. Siahcheshm and P. Heiden, J.Photochem. Photobiol. A., 2023, 435, 114284.

[5]. S. S. Mati, D. Singharoy, B. Samai, S. Konar, N. Santra, S. Pal, P. Das, S. Murmu, J. Mol. Struct. 2019, 1184, 102.

[6]. J. M. Jungb, S. Y. Lee and C. Kim, Sensors Actuat. B-Chem., 2017, 251, 291-301.

[7]. X. Zhao, R. He, M. Li, N. Zhao, Y. Li and C. Huang, RSC Adv., 2013, 3, 111-116

[8]. X. Sun, J. Zhang, X. Wang, J. Zhao, W. Pan, G. Yu, Y. Qu and J. Wang, Arab. J. Chem., 2020, 13, 5075-5083.

#### 11. Digital image colorimetric card production using cell phone software

编	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
号															
R	181	181	173	165	156	148	148	140	140	140	136	132	132	132	123
G	178	162	138	117	105	89	60	56	48	40	64	44	48	44	65
В	181	173	156	156	148	140	132	115	115	115	112	115	107	107	107
I <sub>tota</sub>	540	516	467	438	409	377	340	311	303	295	312	287	287	283	295
Y	312	298	271	255	239	222	207	190	187	186	187	181	177	176	176
Gr	179	169	151	136	125	112	94.	87.	83.	78.	91.	78.	79.	77.	87.1
	175	107	1.51	150	125	112	5	8	1	4	0	4	8	5	07.1
Vr	1.0	1.0	1.1	1.2	1.2	1.3	1.5	1.5	1.6	1.7	1.5	1.6	1.6	1.7	1 /1
	1	7	5	2	5	2	7	9	8	8	0	8	5	0	1.41

Table S2. Cell phone photos and cell phone software colorimetric photos after color development of materials with different concentrations of Fe<sup>2+</sup>.

#### 12. Detection in real samples

Table S 3. Determination of Fe<sup>2+</sup> concentration in in real sample by cell phone colorimetry

Sample	Spiked/µM	Found/µM	Recovery/%	RSD/%
	5	5.08	101.6	1.04
Human blood	10	9.75	97.5	2.32
	20	20.42	102.1	1.12
	5	4.88	97.6	1.94
Tap water	10	10.32	103.2	1.02
	20	20.52	102.6	1.29
	5	5.10	102.0	3.20
Lake water	10	9.91	99.1	2.36
	20	20.26	101.3	1.23
	5	4.93	98.6	3.67
Industrial wastewater	10	10.18	101.8	2.29
	20	20.62	103.1	1.45

### TableS 4. Determination of Fe<sup>2+</sup> concentration in iron supplements by cell phone colorimetry

Sample	Theoretical /µM	Found/µM	Recovery/%	RSD/%	errors/%
	10	10.22	102.2	1.38	2.2
Iron supplement	20	20.36	101.8	2.32	1.8
	30	29.62	98.7	2.25	2.3