A Turn-on Luminescent Probe for Fe^{3+} and Ascorbic Acid with Logic Gate Operation Based on a Zinc(II)-Based Metal-Organic Framework

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1. The process of fluorescence sensing experiment.

Firstly, 0.01M ascorbic acid (AA), amino acid (including Proline (Pro), Glycine (Gly) Glutamine (Glu), Leucine (Leu), Methionine (Met), Phenylalanine (Phe), Histidine (His), Threonine (Thr), Cysteine (Cys), Asparagine (Asn), Valine (Val), L-isoleucine (Lie)) and various cations (including Ag^{+}, Na^{+}, Co^{2+}, Cd^{2+}, Ba^{2+}, Fe^{2+}, Ca^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Hg^{2+} and Fe^{3+}) aqueous solutions were prepared at room temperature. Secondly, 2.0 mg of a powder sample of complex **1** was dispersed in different analytes (2 mL) and the fluorescence intensities of complex **1** in these analytes were collected. For Fe^{3+}@**1** sensing AA, firstly, 480 μL of Fe^{3+} ions at a concentration of 0.01M were added to the suspension of complex **1** (2 mL), the fluorescence intensity of complex **1** was collected, based on the first step, 102 μL of AA at a concentration of 0.01 M were added, the fluorescence intensity of Fe^{3+}@**1**-AA was collected.

2. The process of fluorescence titration for various analytes.

The process of fluorescence titration experiments were conducted by gradually adding various analytes of 0.01 M Fe^{3+} ions and AA aqueous solution to the suspensions of complex **1**.

3. The process of time-dependent fluorescence sensing.

For Fe^{3+} and AA, 480 μL and 220 μL of Fe^{3+} and AA at a concentration of 0.01 M were added to the suspension of complex **1** (2 mL), the fluorescence intensity of complex **1** was collected at 30 s, 1 min, 2 min, 3 min, 4 min, 6 min, 8 min and 10 min. For Fe^{3+}@**1** sensing AA, firstly, 480 μL of Fe^{3+} ions at a concentration of 0.01 M were added to the suspension of complex **1** (2 mL), secondly, based on the first step, 102 μL of AA at a concentration of 0.01 M were added, the fluorescence intensity of complex **1** was collected at next 30 s, 1 min, 2 min, 3 min, 4 min, 6 min, 8 min and 10 min.

4. The process of recyclable fluorescence experiments.

After the first fluorescence detection of various analytes, the powder sample of complex **1** was recovered by centrifugation and washed by water and EtOH. After drying, the samples collected were used again for the detection of various analytes.

Table S1 Selected bond lengths (Å) and angles (°) of complex **1**.

Zn1—O3	1.942 (4)	Zn1—N5^{i}	2.014 (4)
Zn1—N1	2.007 (4)	Zn1—O1^{ii}	2.021 (5)
Zn1—C1^{ii}	2.517 (8)	Zn1—O2^{ii}	2.340 (6)
O3—Zn1—N1	99.25 (2)	O3—Zn1—N5^{i}	99.79 (2)
O3—Zn1—O1^{ii}	103.6 (2)	O3—Zn1—C1^{ii}	126.8 (2)
O3—Zn1—O2^{ii}	147.0 (2)	N1—Zn1—N5^{i}	106.69 (2)
N1—Zn1—O1^{ii}	101.2 (2)	N1—Zn1—C1^{ii}	106.2 (2)
N1—Zn1—O2^{ii}	108.4 (3)	N5^{i}—Zn1—O1^{ii}	139.8 (2)
N5^{i}—Zn1—C1^{ii}	115.7 (2)	N5^{i}—Zn1—O2^{ii}	89.4 (2)
O1^{ii}—Zn1—C1^{ii}	26.5 (2)	O1^{ii}—Zn1—O2ii	54.1 (2)
O2^{ii}—Zn1—C1^{ii}	27.61 (2)	C12—O3—Zn1	129.4 (4)
C13—N1—Zn1	129.2 (4)	C23—N5—Zn1^{i}	129.7 (4)
C1—O1—Zn1^{iii}	101.7 (6)	C2—C1—Zn1^{iii}	172.9 (6)
O1—C1—Zn1^{iii}	51.8 (5)	O2—C1—Zn1^{iii}	67.7 (5)

Symmetry codes: (i) 1-x,1-y,1-z; (ii) 1/2-x,-1/2+y,3/2-z; (iii) 1/2-x,1/2+y,3/2-z.

	MOF	Methods	Detection Limit	Medium Used	Ref.
1	[Zn(bimpy)(1,4-ndc)]•H_2O	FL (turn-on)	6.12×10^{-7} M	H_2O	This work
2	ZJU-136-Ce	FL (turn-on)	7 nM	H_2O	42
3	$[\{(H_3O)[Eu(SBDB)H_2O)_2]\}_n]$	FL (turn-off)	5×10^{-6} M	H_2O	24
4	MOF-Cd-abtz	FL (turn-off)	75 μM	H_2O	8
5	ZJU-137	FL (turn-off)	34 nM	H_2O	43
6	Eu HDSs	FL (turn-off)	0.0015 μM	H_2O	44
7	Cu-MOFs-MPC/GCE	ESC	3.5 μM		72
8	ZIF-8	ESC	740 μM		73
9	PCN-333 (Al) MOFs	ESC	4.6 μM		74
10	GOD/AuNPs/Cu-BTC	ESC	14.77 μM		75
11	MIL-68/MIL-100	ESC	6 μM		76
12	Cu-MOF	ESC	0.24 μM		77
13	$\{[Tb(Cmdcp)(H_2O)_3]_2(NO_3)_25H_2O\}_n$	FL (off-on)	5.9 μM	PBS buffer	56
14	RhB@DiCH$_3$MOF-5	FL (on-off on)	0.31 μM	NaAc−HAc buffer	57
15	$Hf_6O_4(OH)_4(Cl_5H_8O_4S_2)_6$	FL (on-off on)	2.9 μM	H_2O	58
16	ZJU-136-$Ce_{0.76}Eu_{0.24}$	ratiometric	12.6 μM	H_2O	78
17	5-5-Eu/BPyDC@MOF-253-NH_2	ratiometric	0.73 μM	Tris-HCl	79

Table S2. Comparison of reported MOF-based sensors for AA detection.

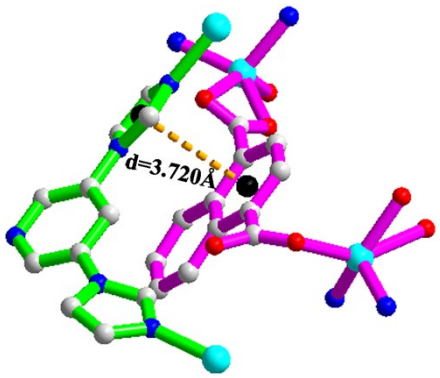

Fig. S1 The π-stacking interaction between the pyridine ring of bimpy and the naphthalene ring of 1,4-ndc ligand.

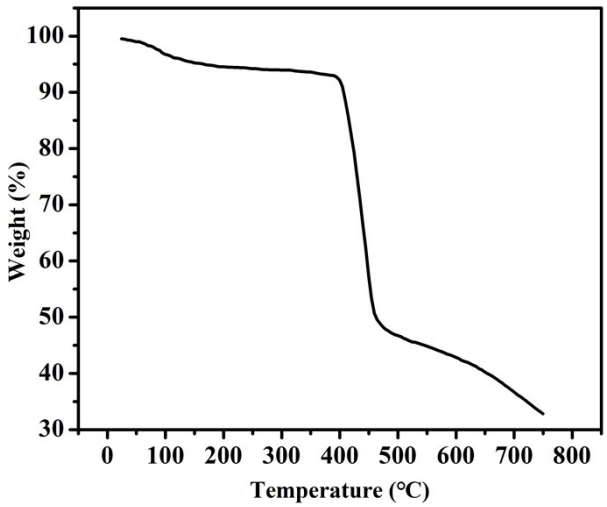

Fig. S2 TGA pattern of complex **1**.

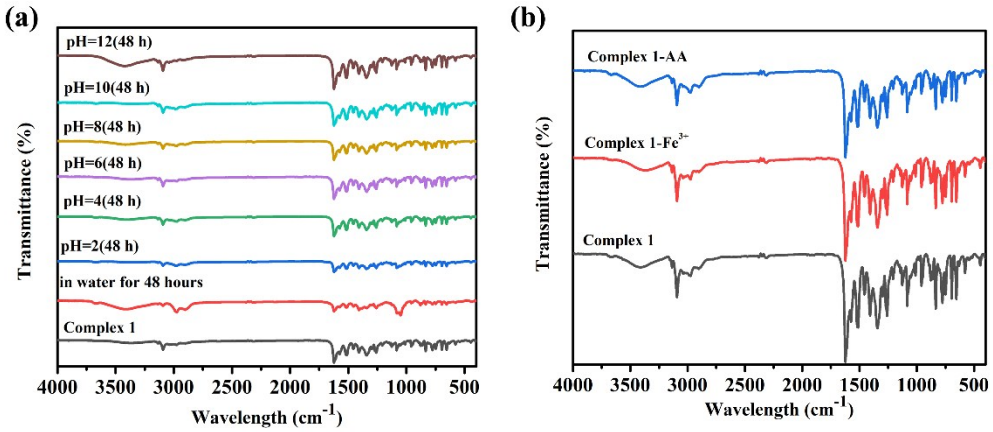

Fig. S3 FTIR spectra of complex **1** recorded in aqueous solution and different pH ranges for 48 h (a); and after immersing various analytes for 48 h (b).

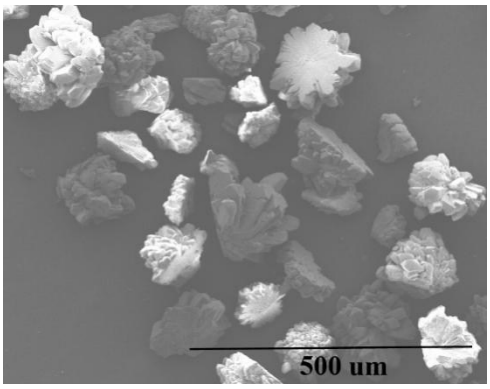

Fig. S4 Overall SEM image of complex **1**.

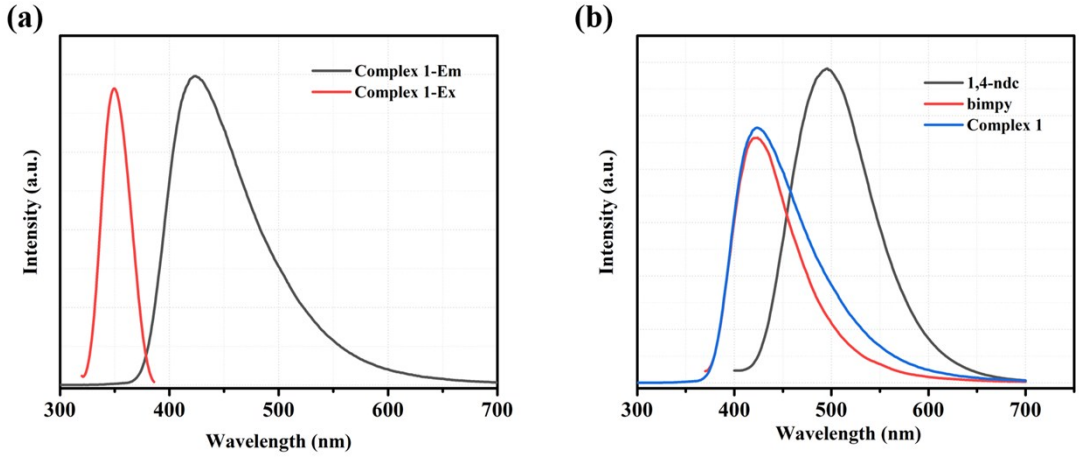

Fig. S5 (a) Fluorescence excitation and emission spectra of complex **1**. (b) Fluorescence emission spectrum of free ligands and complex **1**.

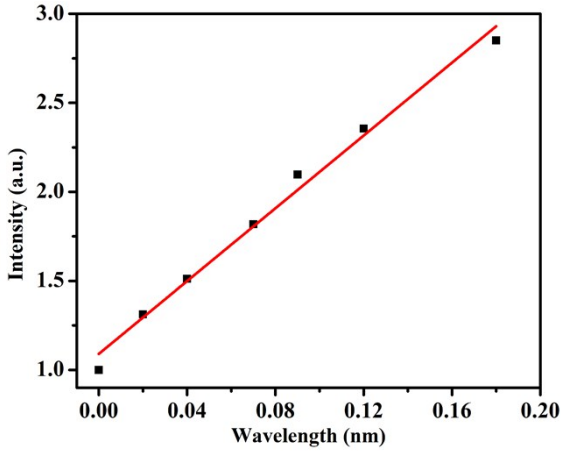

Fig. S6 The *SV* plot for the fluorescence titration experiments of Fe^{3+}.

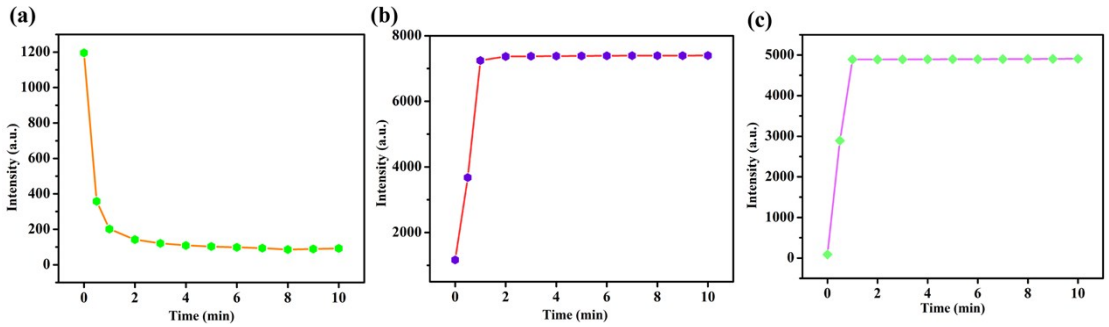

Fig. S7 Time-dependent fluorescence intensity of complex **1** with the addition of Fe^{3+} (a), AA (b), Fe^{3+}@**1**-AA (c).

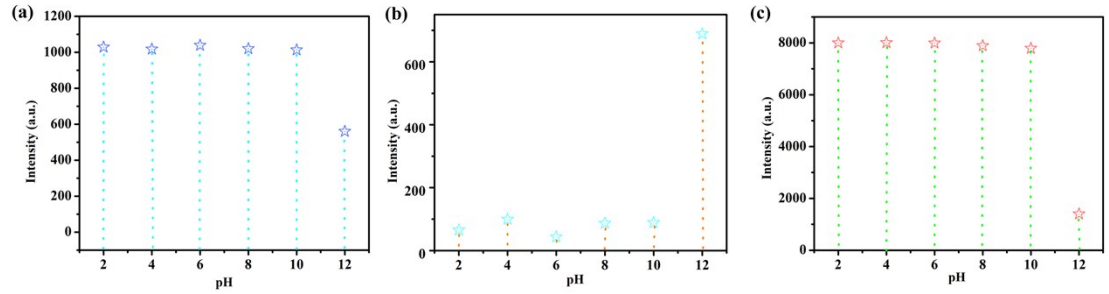

Fig. S8 Fluorescence intensity in different pH solutions of complex **1** (a), sensing Fe^{3+} (b), sensing AA (c).

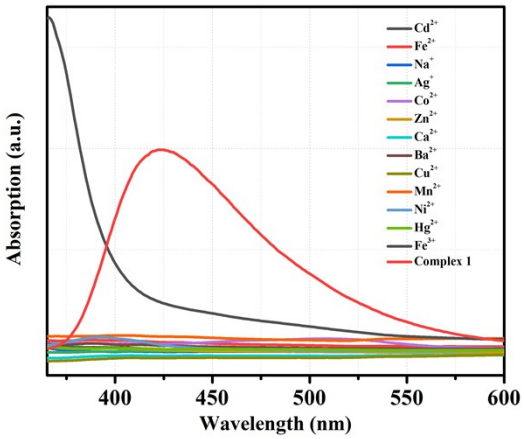

Fig. S9 The UV-vis absorption spectra of different cations and the emission spectrum of complex **1.**

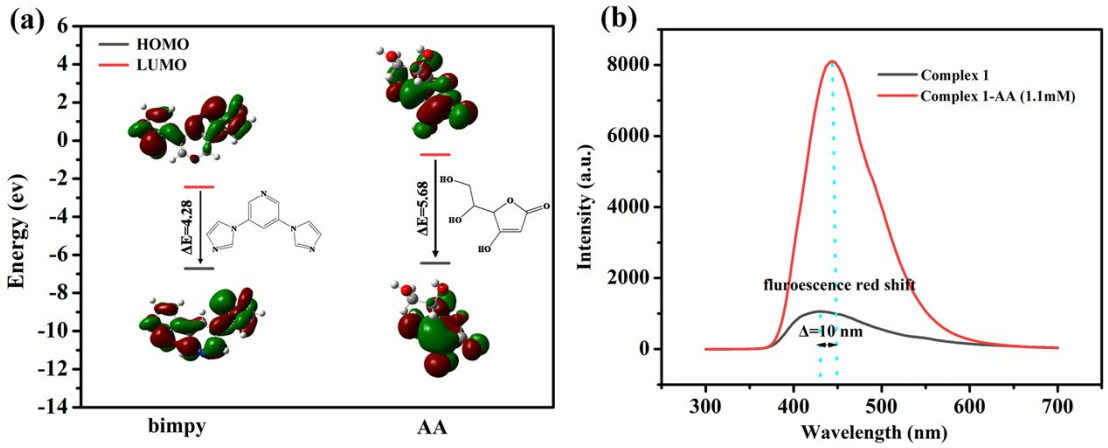

Fig. S10 (a) HOMO−LUMO energy levels of bimpy ligand and AA. (b) Fluorescence intensity of complex **1** before and after adding AA.

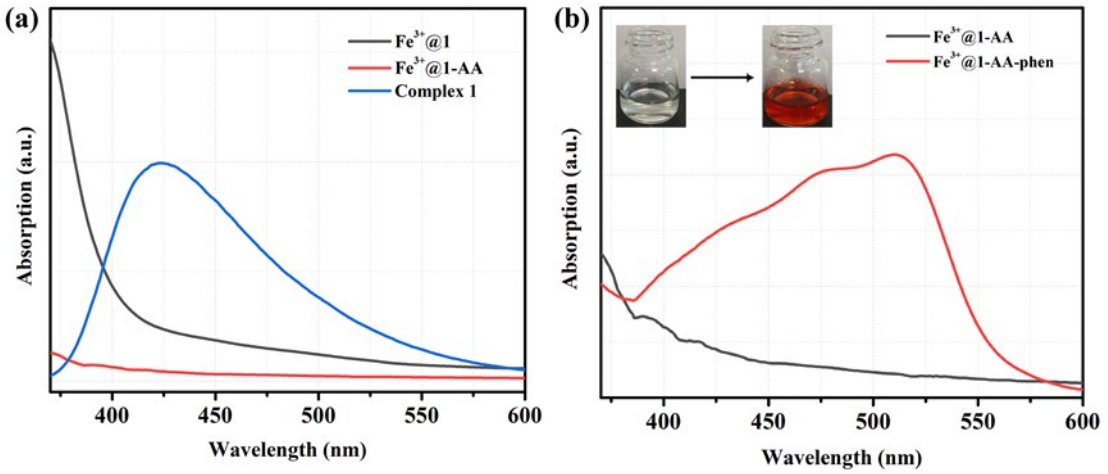

Fig. S11 (a) Fluorescence emission spectrum of **1** (blue)and the UV-vis absorption spectra of Fe^{3+}@**1** (black) and Fe^{3+}@**1**-AA (red). (b) UV-vis absorption spectrum of Fe^{3+}@**1**-AA system before (black) and after (red) addition of 1,10-phen. Inset: The photograph of the solutions of Fe^{3+}@**1**-AA before (left) and after (right) addition of 1,10-phen under visual light.

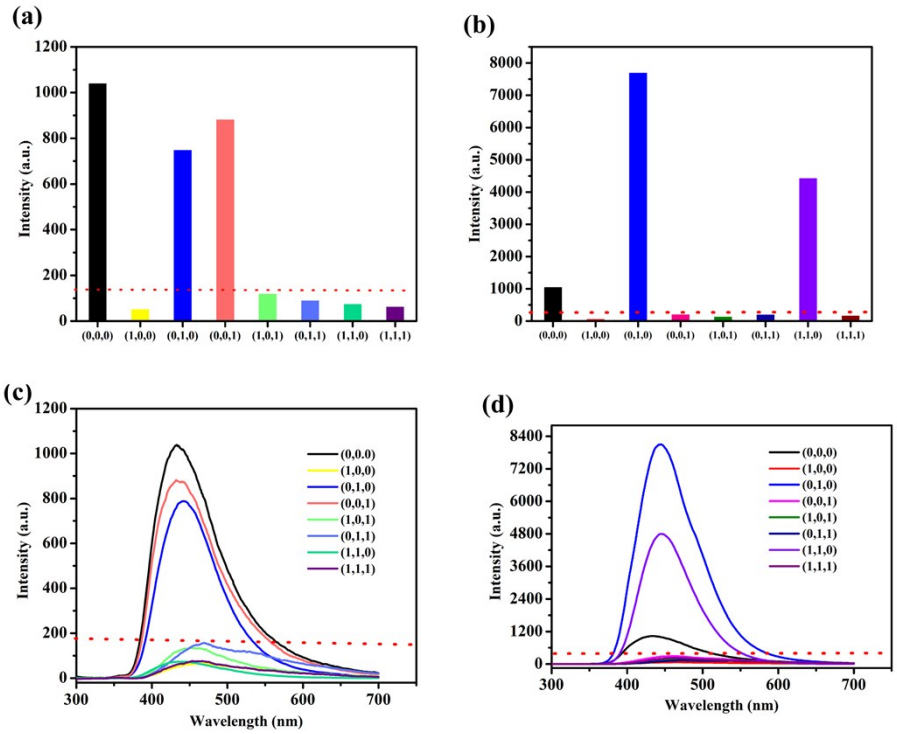

Fig. S12 Fluorescence intensity based on molecular logic gate (a,b). Fluorescence spectrum based on molecular logic gate (c,d).