A Dual-Emissive Europium-Based Metal Organic Framework for Selective and Sensitive Detection of Fe^{3+} and Fe^{2+}

Yuming Zhao,[a] Jinhui Liu,[b] Sha Wang,[a] Xu Zhai,[a] Lei Shao,[a] Yunling Liu,[c] Xuemin Zhang,[a] Junyi Chen,*[d], Fanbao Meng,*[a] and Yu Fu,*[a]

[a]Department of Chemistry, College of Sciences, Northeastern University, Shenyang 110819, P. R. China.

[b]Henan Province Industrial Technology Research Institute of Resources and Materials, Zhengzhou University, Zhengzhou 450001, P. R. China.

[c]State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R.China.

[d]College of Life Science, Tarim University, Xinjiang Uygur Autonomous Region, Alaer 843300, P. R. China.

Materials. Terbium(III) acetate hexahydrate [$Eu(OAc)_3·6H_2O$], 2-hydroxyterephthalic acid (H_2BDC-OH) were purchased from Energy Chemical (Shanghai, China). N,N-dimethylformamide (DMF), ethanol, methanol, acetonitrile (CH_3CN), N, N-dimethylacetamide (DMAC) were purchased from Sinopharm Chemical Reagent Co., Ltd. Zinc acetate [$Zn(OAc)_2$], potassium chloride (KCl), sodium chloride (NaCl), Nickel chloride hexahydrate ($NiCl_2·6H_2O$), Manganese chloride tetrahydrate ($MnCl_2·4H_2O$), Cobalt chloride hexahydrate ($CoCl_2·6H_2O$), Magnesium acetate tetrahydrate [$Mg(OAc)_2·4H_2O$], Chromium chloride hexahydrate ($CrCl_3·6H_2O$), Ferrous chloride tetrahydrate ($FeCl_2·4H_2O$), Ferric chloride hexahydrate ($FeCl_3·6H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Pure water was purchased from Shenyang Wahaha Group Co., Ltd. All chemicals used in this study are of analytical grade and have not been further purified before use.

Characterization. The crystalline structures were characterized by X-ray diffraction (Shimadzu XRD-6000) equipped with Cu Kα radiation (λ = 1.5406 Å) in the 2θ range of 5°-50°. A thermostability test was performed by thermal gravimetric analyzer (TGA-2050 TA Instruments) under N_2 from room temperature to 1000 ^{o}C with a heating rate of 10 ^{o}C min^{-1}. The morphology images were obtained by field-emission scanning electron microscopy (Hitachi SU8010). The optical photographs were taken by a positive fluorescence microscope (Olympus BX53M). The organic groups of MOF were determined by Fourier transform infrared spectroscopy (Bruker VERTEX 70) with KBr pellets. The compositions of the materials were analyzed through quantitative X-ray photoelectron spectroscopy (Thermo Scientific Escalab

250Xi). The absorption spectra at 200-800 nm were measured with an optical spectrometer (Ocean Optics, Maya 2000Pro). The fluorescence spectra were obtained through fluorescence spectrophotometer (FluoroMax-4 HORIBA) equipped with a 150 W xenon lamp as the excitation source. Single-crystal X-ray diffraction data of Eu-BDC-OH were collected on diffractometer (Bruker D8 Venture).

Preparation of text paper. The filter paper (0.7 cm×2 cm) was immersed in DMF solution of Eu-BDC-OH sample (1 mg mL^{-1}) and dispersed by ultrasound, then taken out and dried naturally at room temperature to prepare the test paper. 30 μL of 10 mM different metal ions were dropped on the test paper and the color change of the test paper was immediately observed with naked eye under the irradiation of UV light (365 nm).

Table S1 Crystal data and structure refinement for Eu-BDC-OH

Empirical formula	$C_{36}H_{40}N_4O_{19}Eu_2$
Formula weight	1136.64
Temperature	296.15 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 10.5002 (16) Å
	b = 11.1380(16) Å
	c = 12.5451(18) Å
	α= 103.803(4)°
	β= 109.918(4)°
	γ= 96.736(5)°
Volume	1307.5(3) Å^3
Z	1
Density (calculated)	1.444 g/m^3
Absorption coefficient	14.322 mm^{-1}
F(000)	562.0
Crystal size	0.12 x 0.1 x 0.1 mm^3
Theta range for data collection	3.417 to 63.380°
Index ranges	-15<=h<=16
	-17<=k<=17
	-18<=l<=20
Reflections collected	19673
Independent reflections	11211 [R(int) = 0.0641]
Completeness to theta=63.412°	95.4 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11211 / 66 / 344
Goodness-of-fit on F2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0548, wR2 = 0.1509
R indices (all data)	R1 = 0.0604, wR2 = 0.1565
Extinction coefficient	n/a
Largest diff. peak and hole	0.425 and -0.512 $e.\text{Å}^{-3}$

Table S2 Selected bond lengths (Å) for Eu-BDC-OH

Eu(1-)O(1)	2.317(4)
Eu(1)-O(7)	2.415(4)
Eu(1)-O(9)	2.505(3)
Eu(1)-O(4)	2.354(2)
Eu(1)-O(10)	2.429(3)
Eu(1)-O(8)	2.424(6)
Eu(1)-O(1)	2.829(3)
Eu(1)-O(2)	2.383(3)
Eu(1)-O(5)	2.373(3)

Table S3 Selected bond angles (°) for Eu-BDC-OH

O(1)-Eu(1)-O(7)	144.8(1)
O(1)-Eu(1)-O(9)	131.7(1)
O(1)-Eu(1)-O(4)	77.5(1)
O(1)-Eu(1)-O(10)	84.5(1)
O(1)-Eu(1)-O(8)	80.5(2)
O(1)-Eu(1)-O(1)	75.0(1)
O(1)-Eu(1)-O(2)	123.9(1)
O(1)-Eu(1)-O(5)	76.8(1)
O(7)-Eu(1)-O(9)	75.7(1)
O(7)-Eu(1)-O(4)	75.1(1)
O(7)-Eu(1)-O(10)	104.9(1)
O(7)-Eu(1)-O(8)	71.8(2)
O(7)-Eu(1)-O(1)	112.5(1)
O(7)-Eu(1)-O(2)	73.5(1)
O(7)-Eu(1)-O(5)	138.4(1)
O(9)-Eu(1)-O(4)	150.2(1)
O(9)-Eu(1)-O(10)	52.6(1)
O(9)-Eu(1)-O(8)	100.3(2)
O(9)-Eu(1)-O(1)	121.0(1)
O(9)-Eu(1)-O(2)	83.9(1)
O(9)-Eu(1)-O(5)	71.7(1)
O(4)-Eu(1)-O(10)	143.3(1)
O(4)-Eu(1)-O(8)	76.3(2)
O(4)-Eu(1)-O(1)	66.1(1)
O(4)-Eu(1)-O(2)	82.1(1)
O(4)-Eu(1)-O(5)	129.9(1)
O(10)-Eu(1)-O(8)	69.3(2)
O(10)-Eu(1)-O(1)	138.8(1)
O(10)-Eu(1)-O(2)	133.9(1)
O(10)-Eu(1)-O(5)	74.7(1)
O(8)-Eu(1)-O(1)	138.5(2)
O(8)-Eu(1)-O(2)	142.7(2)
O(8)-Eu(1)-O(5)	138.9(2)
O(1)-Eu(1)-O(2)	49.0(1)
O(1)-Eu(1)-O(5)	66.0(1)
O(2)-Eu(1)-O(5)	77.8(1)

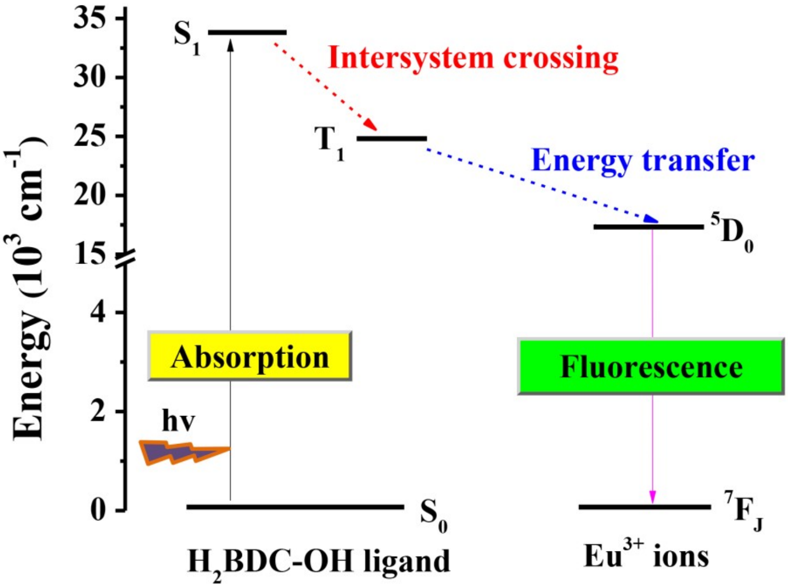

Figure S1 Schematic diagram of energy absorption, transfer and emission process of Eu-BDC-OH (S_0=ground state, S_1= the first excited singlet state, T_1=the first excited triplet state).

Table S4 The singlet and triplet energy levels of H_2BDC-OH ligand.

Multiplicity	Excited state	Excitation energy
T	1	3.0733 eV (24786 cm^{-1})
S	1	4.2095 eV (33949 cm^{-1})

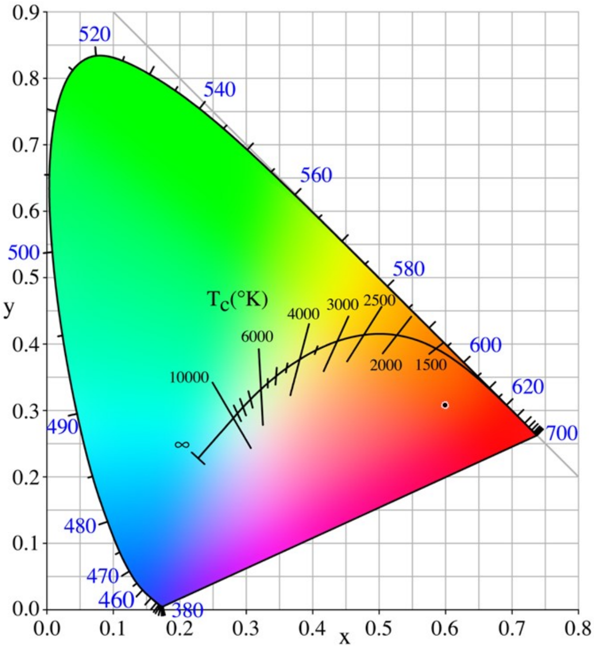

Figure S2 The CIE chromaticity diagram of Eu-BDC-OH.

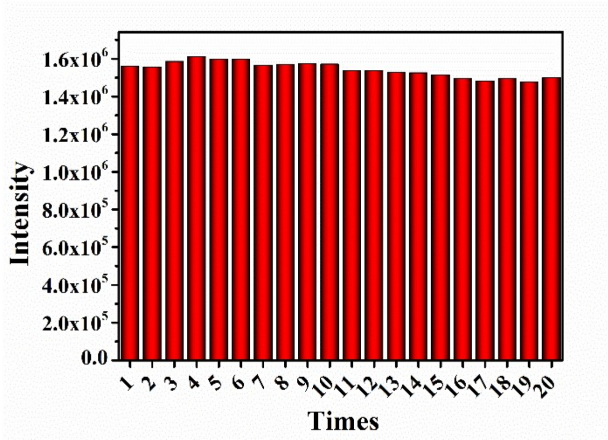

Figure S3 The fluorescence performance of Eu-BDC-OH in DMF for 20 times.

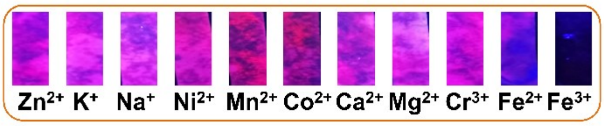

Figure S4 The corresponding text paper photographs under UV light irradiation.

Table S5 *K*sv comparison between various MOF materials for Fe^{3+}.

	*K*sv	Ref
Eu@MIL-124	3.874×10^4	[1]
$[Tb(Cmdcp)(H_2O)_3]_2(NO_3)_2\cdot5H_2O$	5.532×10^3	[2]
EuL_3	4.1×10^3	[3]
$[(CH_3)_2NH_2][Ca(Me_2tcpbH)(H_2O)$	1.18×10^5	[4]
$(Me_2NH_2)[Tb(OBA)_2]\cdot(Hatz)\cdot(H_2O)_{1.5}$	3.4×10^4	[5]
Eu-BDC-OH	1.303×10^5	This work

$H_3CmdcpBr$ = N-carboxymethyl-(3,5-dicarboxyl)pyridinium bromide
L = 4’-(4carboxyphenyl)-2,2’:6’,2”-terpyridine
Me_2tcpbH_4 = 1,2,4,5-tetrakis(4-carboxyphenyl)-3,6-dimethylbenzene).
H_2oba = 4,4’-oxybis(benzoic acid); Hatz = 3-amino-1,2,4-triazole.

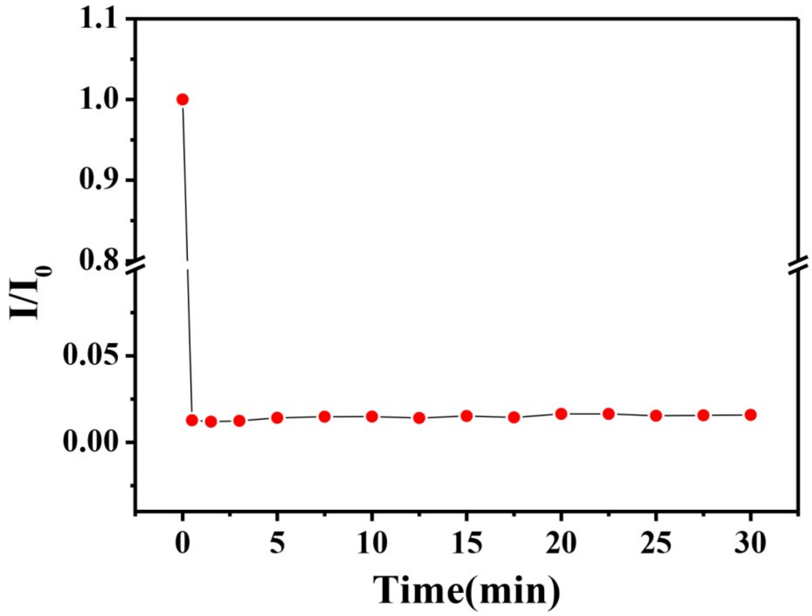

Figure S5 The quenching efficiency (I/I_0) of Eu-BDC-OH for Fe^{3+} (0.5 mM) with time.

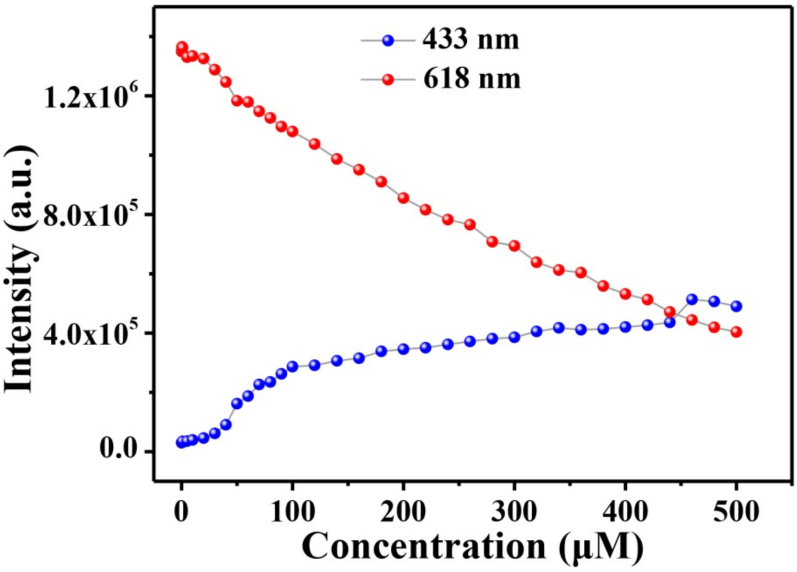

Figure S6 Relationship between fluorescence intensity (λ_{em}=618 nm and λ_{em}=433 nm) and concentration of Fe^{2+}.

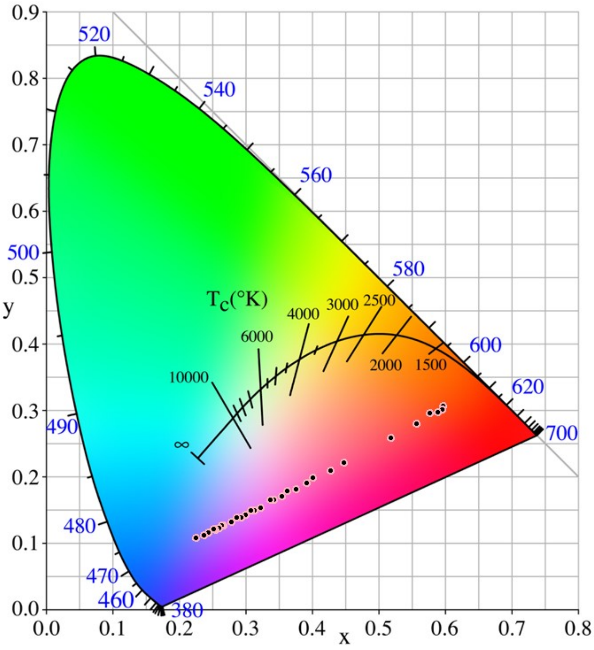

Figure S7 The CIE chromaticity diagram of Eu-BDC-OH.

Reference

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