Electronic Supplementary Information (ESI)

A luminescent cerium metal-organic framework for the turn-on sensing of ascorbic acid

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Experimental Procedures

Materials and methods

All chemicals were analytical grade reagents and used directly without further purification, the organic linker H_4TPTC was obtained from Jinan Henghua Company and used as received. ZJU-136-Tb was prepared by a hydrothermal technique. Typically, a mixture of $Tb(NO_3)_3 \cdot 6H_2O$ (0.046 mmol, 20 mg), H_4TPTC (0.049 mmol, 20 mg), DMF (2 ml), H_2O (9 ml) and HNO_3 (0.05 ml) were sealed in a 25 ml Teflon-lined stainless-steel bomb at 160 ^oC for 48 h, which was then cooled to room temperature. After decanting the mother liquor, the white rhombus crystalline product was washed two times with DMF and dried at 60 ^oC for 20 min to obtain the sample. Yield: 52.9%. Elemental analysis calcd (%) for ZJU-136-Tb $(Me_2NH_2)[Tb(TPTC)] \cdot (H_2O)_2$: C, 44.79; H, 3.4; N, 2.3; Found: C, 44.68; H, 3.5; N, 2.27. Additionally, ZJU-136-Ce and ZJU-136-Gd was synthesized similarly to ZJU-136-Tb except for using a mixture containing the desired lanthanide nitrate. Elemental analysis calcd (%) for ZJU-136-Ce $(Me_2NH_2)_{0.6}\{[Ce^{IV}(TPTC)]_{0.4}[Ce^{III}(TPTC)]_{0.6}\}(H_2O)_2$: C, 45.97; H, 3.1; N, 1.38; Found: C, 45.48; H, 3.3; N, 1.56.

Characterization

All solvents and reagents were obtained from commercial sources and used without further purification. PXRD data were taken on a Shimadzu XRD7000 powder X-ray diffractometer with the recording rate 5^o/min in the 2θ=5-40 degree at room temperature. Thermogravimetric analyses (TGA) were carried out on a Netzsch TG209F3 with a heating rate of 10 K min^{-1} under N_2 atmosphere. Before the TGA measurement, the fresh samples were guest-exchanged with dry acetone at least 10 times, then filtered and degassed at 373 K for 2 h under high vacuum to obtain the activated samples. Elemental analyses for C, H, and N were performed on an EA1112 microelemental analyser. The emission and excitation spectra for the samples were recorded by a Hitachi F4600 fluorescence spectrometer. The decay lifetime test was carried out using an FLS920P Edinburgh Analytical Instrument apparatus equipped 295 nm and 360 nm laser as the excitation sources. Surface compositions were studied by X-ray photoelectron spectroscopy (XPS; Axis Supra, Kratos

Analytical Ltd). The binding energy data were calibrated with reference to the C 1s signal at 285 eV. UV-vis spectra were collected on a Shimadzu UV-2600 spectrophotometer.

Single-crystal data of ZJU-136-Tb was recorded on a Bruker APEX-II diffractometer with an CCD detector using graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å) at 293 K. The determination of the unit cells and data collections of ZJU-136-Tb were performed using CrysAlisPro. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. The structure was determined by direct methods, and refined by the full-matrix least-square method with the SHELX-2014 program package. All non-hydrogen atoms were refined with anisotropic thermal parameters, and all H atoms on C atoms were generated geometrically and refined with isotropic thermal parameters. The scattering from the highly disordered lattice guest molecules were removed using the SQUEEZE procedure implemented in the PLATON package.[1, 2] About one dimethylamine cations and two free water molecules were removed from the Formula unit by the SQUEEZE process. Selected crystal parameters, data collection, and refinement are summarized in Table S1. CCDC 1533082 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

Detection of AA

The dried powder of ZJU-136-Ce (1.00 mg) in 1 mL deionized water was ultrasonicated for 30 min, For the detection of AA, different concentrations of AA solutions prepared in deionized water were added into the ZJU-136-Ce suspension, For the selectivity of AA detection, 100 μM for Phe, Glu, Thr, Glc, Cys, Met, Ile, Leu, urea acid, urea, Gly, Ca^{2+}, I^{-}, HSO^{3-}, Na^{+}, K^{+}, Mg^{2+} and Zn^{2+} were added to each of the above ZJU-136-Ce suspension, respectively. All the fluorescence spectra were measured at an excitation of 316 nm light.

In order to mechanism of detecting AA, the different concentrations of $KMnO_4$ solutions prepared in deionized water were added into the ZJU-136-Ce with addition of 100 μM AA. Recyclability is an important parameter to assess the sensor's practicability. After the 20 μM $KMnO_4$ was added into the ZJU-136-Ce with addition of 100 μM AA, suspensions of ZJU-136-Ce / AA / $KMnO_4$ were centrifuged and washed several times with deionized water under ultrasonic. Three repeated cycles of adding VC and $KMnO_4$ and washing process was performed.

The sorption test: ZJU-136-Ce was immersed in 100 μM AA solution at room temperature for 1 hours to get ZJU-136-Ce⊃AA. After that, the ZJU-136-Ce⊃AA were collected by filtration, washed with ethanol and water several times to remove residual AA on the surface of ZJU-136-Ce, and dried at 60 ^{o}C for 1 hour. The UV–vis spectra of samples were measured.

Cell Culture, and Cytotoxicity of ZJU-136-Ce

PC12 cells were grown in Dulbecco's Modified Eagle's Medium (DMEM, Neuronbc) with 10% fetal bovine serum (FBS) and 1% penicillin/streptomycin (P/S, Boster) for 3 days in a cell incubator (37 ^{o}C, 5% CO_2). The cytotoxicity of ZJU-136-Ce was evaluated through employing a MTT assay in a 96-well plate. PC12 cells were incubated in the humidified incubator with ZJU-136-Ce at different concentrations (5, 20, 50, and 100 μg/mL). After that, 50 μL of 1 × MTT solutions were added to each well and incubated for 4 h with the tin foil covered. Then, 200 μL of the media were removed and 150 μL of dimethyl sulfoxide was added to each well. Thirty minutes later, the absorbance of each sample at 490 nm was measured using the microplate reader. The cell viability was calculated by the ratio of absorbance of the sample well to that of the control cell. The same concentration of the samples was sextuplicated, then the average calculated.

Table S1. Crystallographic data collection and refinement result for ZJU-136-Tb.

ZJU-136-Tb	$(Me_2NH_2)[Tb(TPTC)]\cdot(H_2O)_2$[a]
Empirical formula	$C_{22}H_{10}O_8Tb$
Formula weight	561.22
Temperature/K	293(2)
Wavelength/Å	0.71073
Crystal system	Triclinic
Space group	P-1
a/Å	9.933(2)
b/Å	11.292(3)
c/Å	13.383(3)
α/°	98.740(6)
β/°	99.894(7)
γ/°	106.303(4)
Z	2
Density (calculated g cm^{-3})	1.344
Absorption coefficient/ mm^{-1}	2.584
Reflections collected	10407
Independent reflections	4498 [Rint = 0.0458]
F(000)	542
Goodness of fit on F^2	1.080
R1,wR2(I>2σ(I))[b]	0.0393, 0.1143
R1,wR2(all date)[b]	0.0479, 0.1229

[a] the empirical formula is calculated after SQUEEZE process during refinement.

[b] $R1=\Sigma(|Fo|-|Fc|)/\Sigma|Fo|$; $wR2=[\Sigma w(|Fo|-|Fc|^2)/\Sigma wFo^2]^{1/2}$.

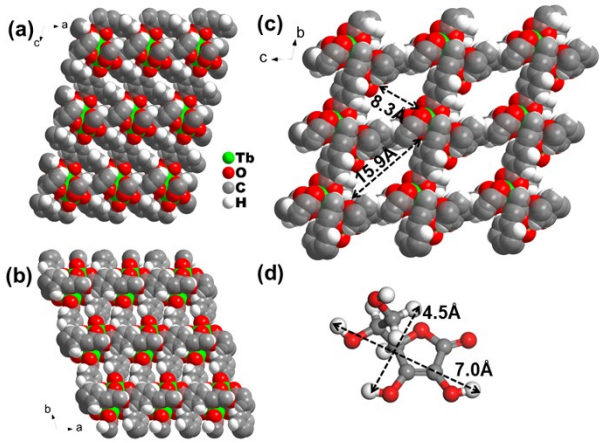


Fig. S1 The space filling model structure of ZJU-136-Tb viewed along (a) b-axis; (b) c-axis; (c) a-axis; (d) Ascorbic Acid.

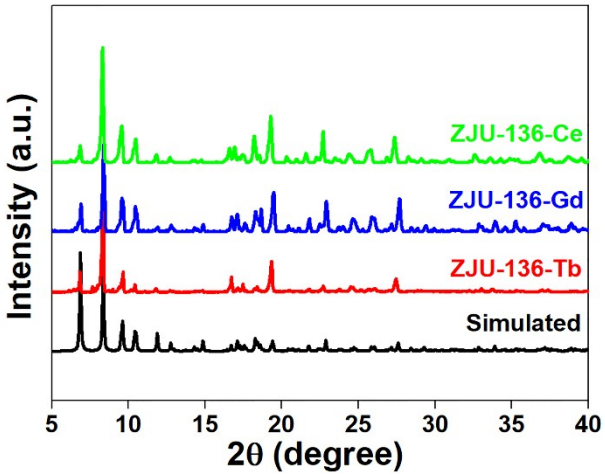


Fig. S2 PXRD patterns of ZJU-136-Ce, ZJU-136-Gd and ZJU-136-Tb.

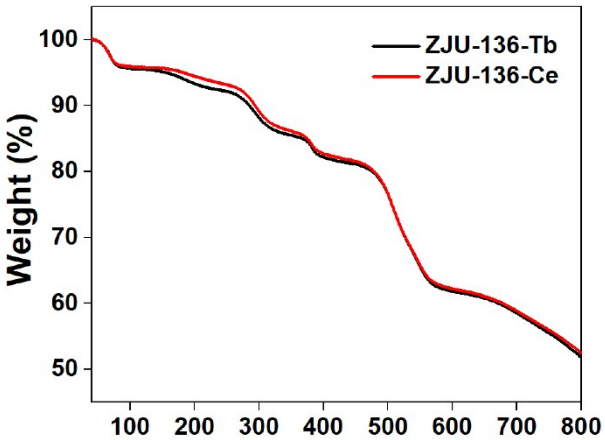


Fig. S3 TGA curve of activated ZJU-136-Tb and ZJU-136-Ce.

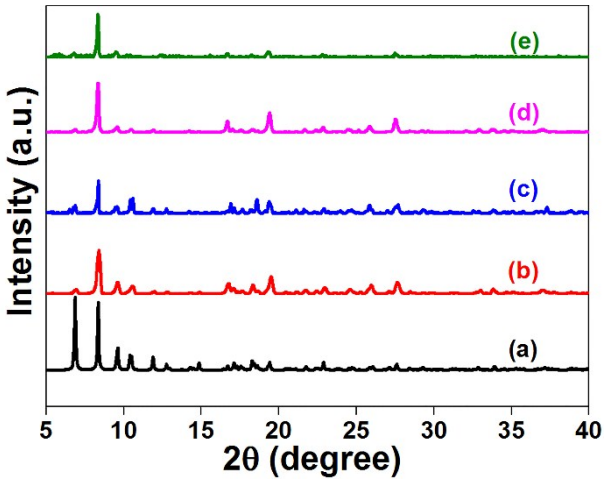


Fig. S4 XRD patterns of (a) simulated; (b) the original ZJU-136-Ce; (c) ZJU-136-Ce immersed in aqueous solution with pH=6.8 for 7 days; (d) ZJU-136-Ce in 100 μM AA for 1 hour; (e) ZJU-136-Ce with addition of 100 μM $KMnO_4$ to (d) for 1 hour.

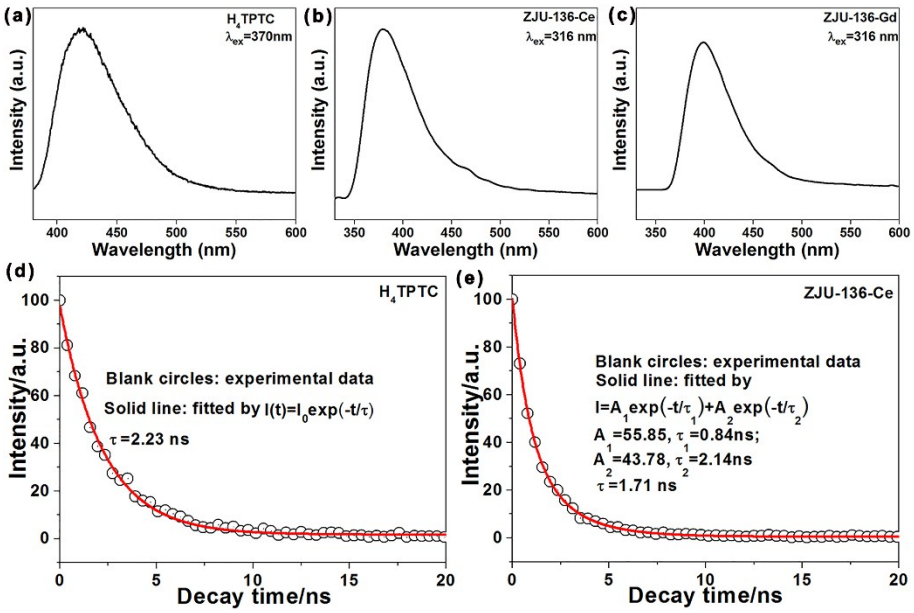


Fig. S5 The emission spectrum of (a) H_4TPTC; (b) ZJU-136-Ce; (c) ZJU-136-Gd, the decay time of (d) H_4TPTC; (e) ZJU-136-Ce.

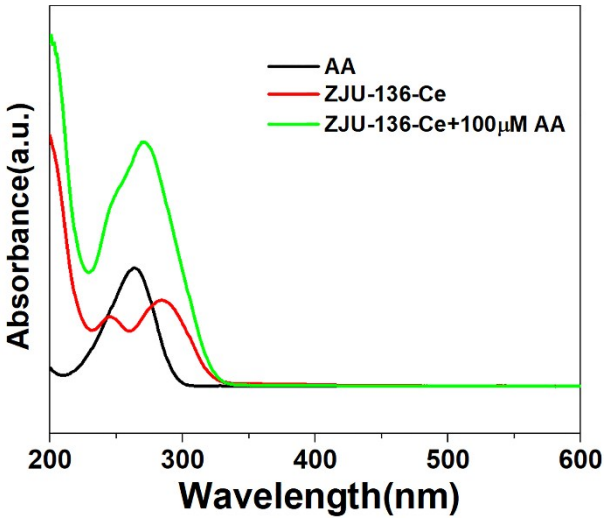


Fig. S6 UV-vis absorption spectra of AA, ZJU-136-Ce and ZJU-136-Ce was immersed in 100 μM AA solution.

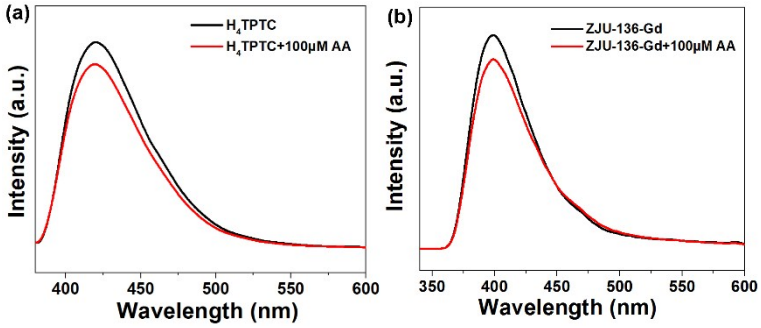


Fig. S7 Fluorescence response of (a) H_4TPTC and (b) ZJU-136-Gd in the absence and presence of 100 μM AA, respectively.

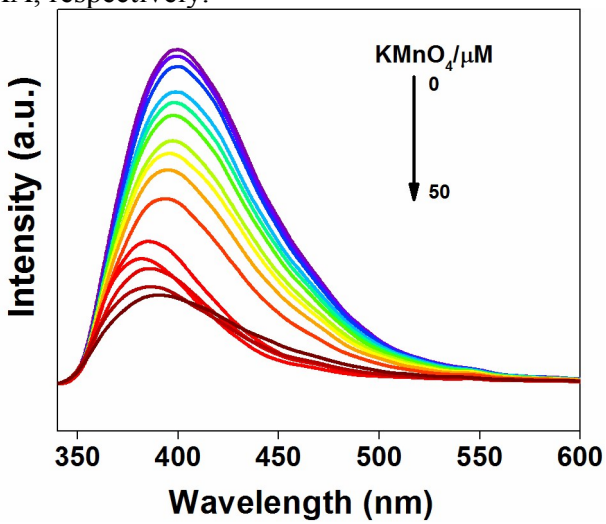


Fig. S8 Fluorescence response of the samples with the addition of various concentrations of $KMnO_4$ to ZJU-136-Ce enhanced by 100 μM AA.

Table S2 Corresponding binding energy and integrated peak areas of ZJU-136-Ce with addition 100 μM AA and 50 μM $KMnO_4$.

Ce 3d region	Peak assignment	Ce species	ZJU-136-Ce		ZJU-136-Ce+ 100 μM AA		ZJU-136-Ce+100μM AA+50μM $KMnO_4$	
			Peak (eV)	Area (%)	Peak (eV)	Area (%)	Peak (eV)	Area (%)
$3d_{5/2}$	v_0	Ce^{3+}	881.41	6.39	881.70	8.50	881.40	4.84
	v	Ce^{4+}	882.81	10.34	883.63	15.10	883.09	15.54
	v'	Ce^{3+}	885.56	31.03	885.97	26.52	886.01	29.05
	v''	Ce^{4+}	887.72	7.21	888.07	5.36	888.29	5.04
	v'''	Ce^{4+}	898.47	3.06	—	—	897.93	2.54
$3d_{3/2}$	u_0	Ce^{3+}	899.96	5.31	899.58	4.48	899.53	6.57
	u	Ce^{4+}	901.33	9.38	901.22	10.92	901.35	8.66
	u'	Ce^{3+}	904.02	18.10	904.31	23.00	904.24	20.52
	u''	Ce^{4+}	907.05	6.46	907.17	6.12	907.27	5.22
	u'''	Ce^{4+}	917.55	2.73	—	—	917.55	2.02

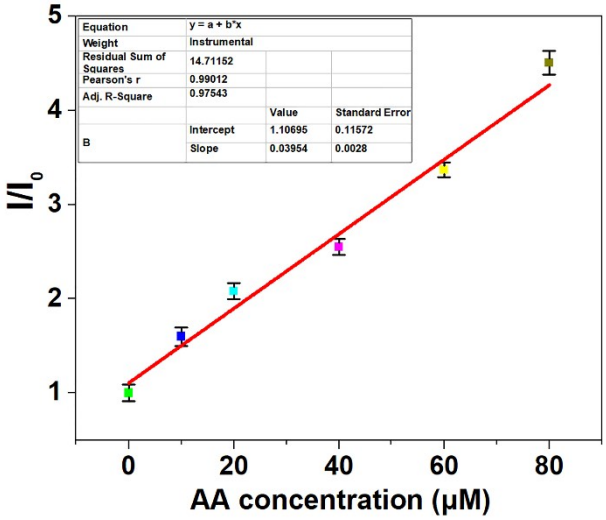


Fig.S9 The corresponding calibration curve of AA detection, the error bars represent standard deviations based on three independent measurements.

Linear Equation: $y = 1.10695+0.03954\times C_{AA}$ $R^2 = 0.9754$

$S = 2.4 \times 10^7 M^{-1}$

$\delta = \sqrt{\frac{\sum (F_0 - F_1)^2}{N-1}} = 0.056$ (N = 20)

$LOD = 3\delta/S = 7$ nM

Where S is the slope of the calibration curve, Standard deviation (δ) is calculated from twenty measurements of blank solutions. F_0 is the fluorescence intensity of ZJU-136-Ce in water, F_1 is the average of the F_0. [3, 4]

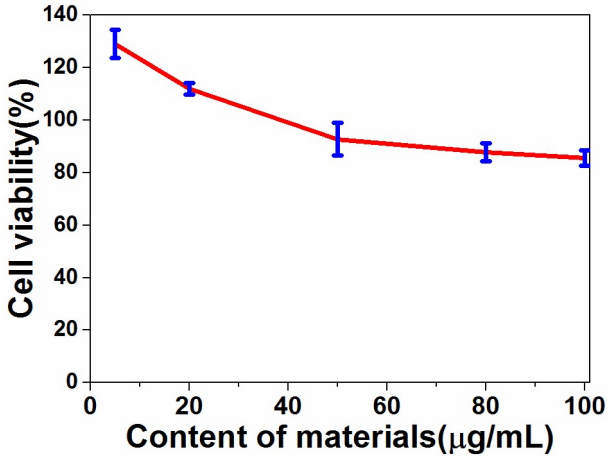
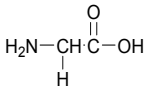
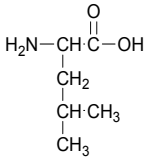
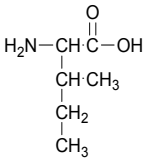
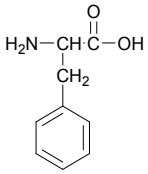
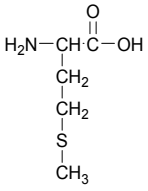
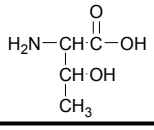
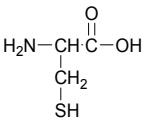
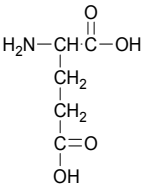
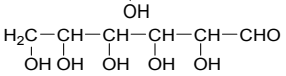
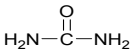
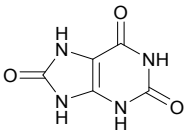


Fig. S10 Cell viability data of ZJU-136-Ce obtained from cultured PC12 cells with the untreated cell as a control. Error bars represent the standard deviation of uncertainty for each point.

Table S3 Structure and name of various small biomolecules.

Name	Abbreviation	Structure
Glycine	Gly	
Leucine	Leu	
Isoleucine	Ile	
Phenylalanine	Phe	
Methionine	Met	
Threonine	Thr	

Cysteine	Cys	
Glutamic acid	Glu	
Glucose	Glc	
Urea	Urea	
Uric acid	UA	

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