Supporting Information

Ultra-Selective Recognition of UO_2^{2+} via Arousing its Intrinsic Luminescence by a Precisely Designed Europium Metal-Organic Framework

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1.1 EXPERIMENTAL SECTION

Materials and Reagents.

Eu(NO$_3$)$_3$•6H$_2$O, Gd(NO$_3$)$_3$•6H$_2$O and Tb(NO$_3$)$_3$•6H$_2$O was purchased from Aladdin Reagent (Shanghai, China). 2,5-pyridinedicarboxylic acid N-oxide (PDA) was obtained from Zhengzhou Alpha Chemical Co. UO$_2$(NO$_3$)$_2$ was purchased from Beijing HWRK Chem Co., Ltd (Beijing, China). All the other interfering compounds for UO$_2$$^{2+}$ detection experiments and Triethylamine (TEA) were purchased from Chengdu Kelong Chemical Reagent Factory. All suspensions were prepared using ultrapure water (resistivity > 18.2 MΩ cm^{-1})

Apparatus.

Fluorescence spectra were performed on an FLS1000 time-resolved fluorescence spectrometer. Quanta 200 scanning electron microscopy (SEM, U.S.A.) and JEOL2010 transmission electron microscope (TEM, Japan) were used to characterize the sizes and morphology. Fourier transform infrared (FTIR) spectra were performed over a Specturm 2 spectrometer (PerkinElmer, USA) using KBr as reference. The X-ray diffraction (XRD) patterns were recorded on a MiniFlex 600 (Rigaku, Japan). X-ray photoelectron spectra (XPS) was performed on a Thermo Scientific K-Alpha X-ray photoelectron spectrometer. The UV-vis spectra were collected on an UH4150 spectrophotometer (Hitachi, Japan).

Preparation of Eu-PDA.

Eu-PDA was synthesized by solvothermal method according to the previous method but with some modifications.[1] The specific synthesis procedure was as follows: an aqueous mixture (9 mL) containing 2,5-pyridinedicarboxylic acid (27.5 mg, 0.15 mM) and $Eu(NO_3)_3 \cdot 6H_2O$ (66.9 mg, 0.15 mM) was placed in a 25 mL Teflon-lined stainless steel autoclave. TEA (0.30 mL, 2.1 mM) was added to this mixture, the vessel was sealed and heated to 140 °C for 12 h and cooled to room temperature. The colorless powder of the product was collected and washed with 3×10 mL of ultrapure water and dried at 80°C for 12 h.

Fluorescent Analysis of UO_2^{2+}.

A stock suspension of 500 mg/L Eu-PDA probe was prepared by adding the prepared Eu-PDA into ultrapure water and continuously sonicated for 3 min. Then, the obtained stock suspension of Eu-PDA (60 μL) was mixed with different volumes of sample solution. The mixture was controlled to a final volume of 600 μL by adding ultrapure water. The mother solution of UO_2^{2+} (10 mM, 10 mL) was prepared with ultrapure water. Finally, the obtained mixtures were reacted for 20 min and photoluminescence spectra were collected under excitation at a wavelength of 330 nm. The fluorescence peak of UO_2^{2+} was at 517 nm. All experiments were performed in triplicate and the error in the graphs is the standard deviation of three parallel experiments.

Selectivity of the assay to UO_2^{2+}.

In order to evaluate the sensing selectivity of Eu-PDA for UO_2^{2+}, we chose potential interfering ions in the actual environment to study the anti-interference ability of Eu-PDA, such as metal ions Ca^{2+}, Al^{3+}, Pb^{2+}, Mg^{2+}, Ba^{2+}, and so on. The concentration of 60 μL Eu-PDA suspension (500 mg/L) was mixed with different volumes of interfering ions solution, and the mixture was controlled to a final volume of 600 μL by adding ultrapure water. The concentration of UO_2^{2+} was set to 20 μM, and the concentration of metal ions was 10 times that of UO_2^{2+}. Finally, the resulting mixture was reacted for 20 min and then fluorescence measurements were performed under the same conditions. All experiments were performed in triplicate and the error in the graphs is the standard deviation of three parallel experiments.

Analysis of UO_2^{2+} in real water samples.

The feasibility of the proposed method was tested using real water samples. The water samples were taken from tap water and drinking water without any pretreatment before analysis. To assess the accuracy of the quantitative recovery results, the standard addition method was used. Different concentrations of UO_2^{2+} standard solutions were added to the water samples and measurements were made in triplicate for each concentration. The results reported are the average of three parallel samples at each concentration.
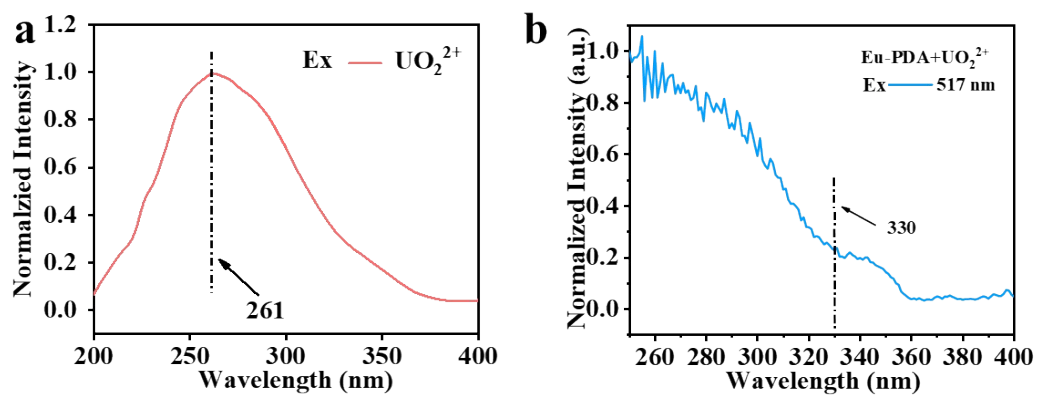
Figure S1. Excitation spectra of (a) free UO_2^{2+} and (b) Eu-PDA trapped UO_2^{2+} at 517 nm.
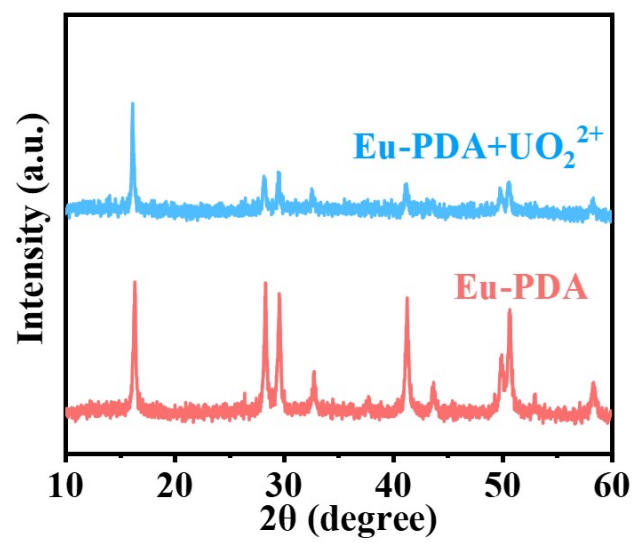
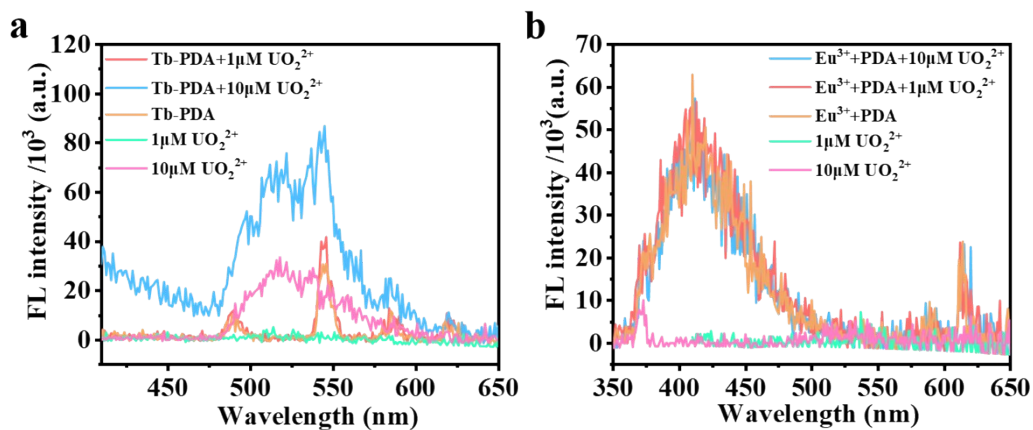**Figure S2**. PXRD pattern of Eu-PDA before and after addition of UO_2^{2+}.

Figure S3. (a) Emission spectra of UO_2^{2+} before and after trapped with Tb-PDA, and the emission spectra of Tb-PDA, respectively. (b) Emission spectra of UO_2^{2+} before and after comixed with uncoordinated PDA and Eu^{3+}, and the emission spectra of uncoordinated PDA and Eu^{3+}, respectively.
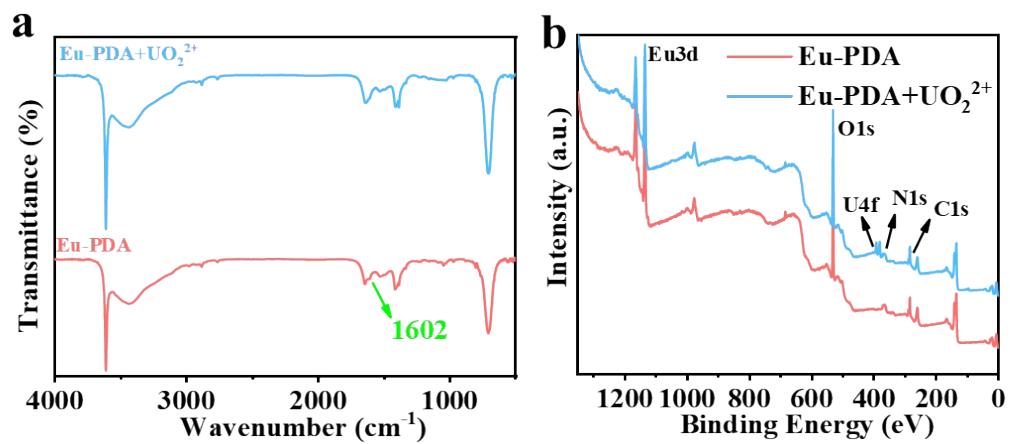
Figure S4. (a) FTIR spectra of Eu-PDA before and after incubated with UO_2^{2+}. (b) XPS spectra of Eu-PDA before and after incubated with UO_2^{2+}.
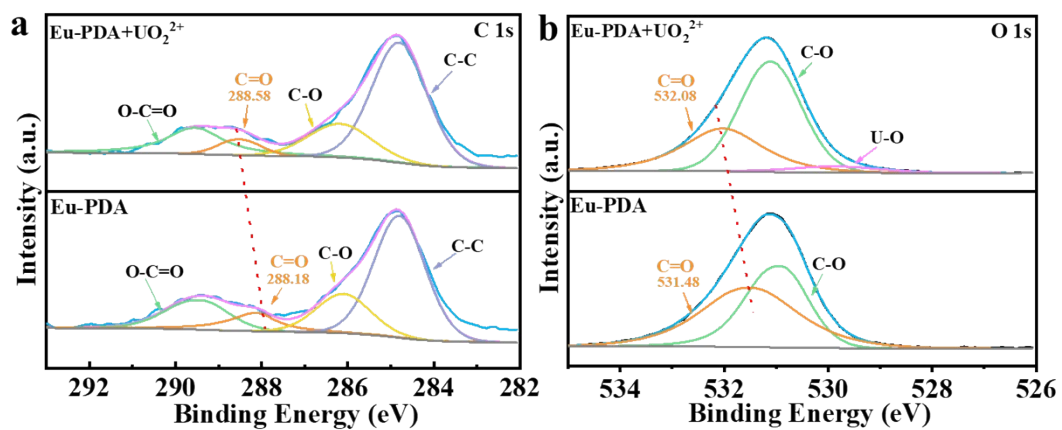
Figure S5. (a) C1s spectra of Eu-PDA before and after addition of UO_2^{2+};(b) O1s spectra of Eu-PDA before and after addition of UO_2^{2+}.
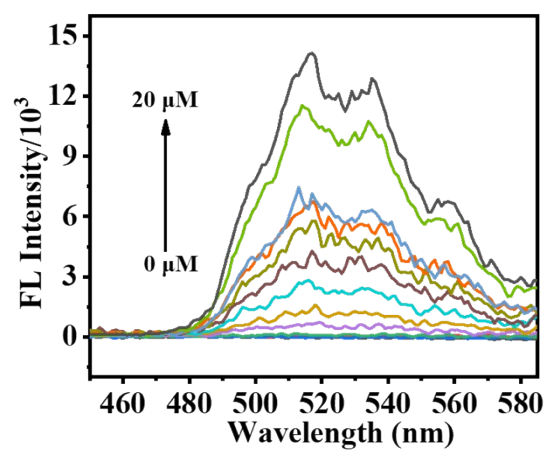
Figure S6. Fluorescent spectra of Eu-PDA after incubated with various UO_2^{2+} in the range from 0 to 20 μM.

Table S1. Various fluorescent sensing strategies for detection of UO_2^{2+}.

Method	Materials	Response time (min)	Linear range (μM)	LOD (nM)	Refs.
Fluorescence	ZIF-90	3	1.08-13.00	3.9	2
Fluorescence	DNAzyme	85	0.87-4333.33	0.43	3
Fluorescence	Eu-MOF	0	12.5-87.5	900	4
Fluorescence	Tb-MOF	40	0-700	296.3	5
Fluorescence	B-CDs@SiO$_2$@GSH-AuNCs/Ag$^+$	0.5	0.2-1	37	6
Fluorescence	TFPPy-BDOH	60	0-25	8.8	7
Fluorescence	Eu-PDA	20	0.5-20	83	This work

Table S2. Actual sample analysis by Eu-PDA.

Samples	Spiked (μM)	Measured (μM)	Recovery (%)	RSD (%, n=3)	ICP-MS (Consistency, %)
	0	N.D.	/	/	/
Sample 1	5	5.03	100.59	6.39	0.74
	10	10.91	109.10	3.30	0.79
	0	N.D.	/	/	/
Sample 2	5	5.24	104.80	3.13	0.80
	10	11.11	111.12	3.28	0.84

References

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