Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

A Hydrolytically Stable Uranyl-Organic Framework for Highly Sensitive and Selective Detection of Fe^{3+} in Aqueous Media

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KEYWORDS: Uranium; Luminescence; Metal organic framework; Detection

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S1. Experimental section

Materials and Instrumentations: All reagents and solvents were purchased from commercial suppliers and used as received without further purification. The elemental analyses (C, H, and N) were carried with a Vario EL CHNOS elemental analyzer. Powder X-ray diffraction (PXRD) data were collected from 5° to 50° with a step of 0.02° and data collection time of 0.2 s on a Bruker D8 Advance diffractometer with Cu Kα radiation (λ=1.54056 Å) and a Lynxeye one-Dimensional detector. The ATR-FTIR spectra of the samples without KBr were recorded in the range of 3000-400 cm^{-1} by a Thermo Nicolet iS 50 spectrometer. Scanning electron microscopy images and energy-dispersive spectroscopy data (SEM/EDS) were recorded on a FEI Quanta 200FEG Scanning Electron Microscope with the energy of the electron beam being 30 keV. Samples were mounted directly on the carbon conductive tape with Au coating. The photoluminescence spectra bulk samples were collected on FLS 980 Spectrometer. Thermalgravimetric (TG - DSC) analysis was carried out on a NETZSCH STA 449 F3 Jupiter instrument in the range of 30 - 900 °C under a nitrogen flow at a heating rate of 10 °C/ min.

Synthesis: A 0.0502 g of $UO_2(NO_3)_2{\cdot}6H_2O$, 0.0211 g H_2L, 0.0120 g H_3BO_3 and 5 ml mixed solvent (V_{H2O} : V_{DMF} (ml) = 2 : 3) were added into a 10 ml vials. The vials were then sealed and heated to 100 ^oC for 12 h and cooled to room temperature under ambient condition. Yellowish strip crystals were isolated as a pure product (**Figure X**).

Elemental analysis results: compound **1**, calculated C, 24.05 %; N, 5.34 %; H, 2.08 %; found C 24.03%; N, 5.27%; H, 1.92%. compound **1**', C, 19.00 %; N, 3.05 %; H, 1.69 %

X-ray Crystallography Studies: Single crystal X-ray diffraction data collection was accomplished on a Bruker D8-Venture diffractometer with a Turbo X-ray Source (Mo–Kα radiation, λ = 0.71073 Å) adopting the direct-drive rotating anode technique and a CMOS detector at 273 K. The data collection was carried out using the program APEX3 and processed using SAINT routine in APEX3. The structure of **1** was solved by direct methods and refined by the full-matrix least squares on F^2 using the SHELXTL-2014 program. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were placed in geometrically idealized positions. Crystallographic data of **1** are summarized in **Table S1** and **S2**.

Hydrolytic Stability Measurements: The hydrolytic stability of compound **1** was checked by PXRD pattern ahead of investigations of iron detection in different aqueous media. 30 mg of **1** was dispersed into aqueous solutions with various pH values (2-12), 200 ppm of multiple types of metal salt solutions, before PXRD analysis.

Fe^{3+} Concentration Dependent Luminescence Spectra: 3 mg of compound **1** was dispersed into 2 mL of $FeCl_3$ aqueous solution with the concentration varying from 0 to 60 ppm. The mixture was then treated with ultrasonic to form a homogeneous suspension, then aged for 1 hour. The Luminescence spectra of suspensions were collected after another 1.5 min ultrasonic treatment. All spectra were collected for three times and the data used for plotting is average value.

Influence of Competing Cations: 3 mg of compound **1** was dispersed into 2 mL of 200 ppm $M(Cl)_x \cdot n(H_2O)$ (M= Na^+, Mg^{2+}, Co^{2+}, Cu^{2+}, Cr^{3+}, Mn^{2+}, Ni^{2+}, Sr^{2+}, Fe^{3+}). The mixture was treated by ultrasonic for 1 min to form a homogeneous suspension. After aging for an hour, luminescence spectra for all samples were collected. 3 mg of

1 was dispersed into 2 mL deionized water and used as a blank sample following the same procedure. All the spectra were collected for three times to minimize instrumental fluctuation and the data used for plotting is average value.

S2. Crystallographic Data of compound 1

Table S1. Crystallographic Data and structural refinement for **compound 1**

Sample	**compound 1**
Formula	$C_{11}H_{10}N_2O_9U$
*M*r [g·mol^{-1}]	552.24
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	6.5282(6)
b (Å)	10.9208(11)
c (Å)	10.9233(11)
α	93.983(4)
β	106.175(4)
γ	103.677(4)
V (Å^3)	719.04(12)
Z	2
D_c (g cm^{-3})	2.551
μ (mm^{-1})	11.339
F (000)	508
T(K)	296(2)
GOF on F^2	1.088
R1,[a] wR2[b] ($I>2\sigma(I)$)	0.0232, 0.0507
R1,[a] wR2[b] (all data)	0.0266, 0.0517

[a] $R_1 = \sum(F_o - F_c)/\sum F_o$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Table S2. Selected bond lengths (Å)

Selected Bond Lengths (Å)	
U1-O1	1.768(4)
U1-O2	1.746(4)
U1-O3	2.378(3)
U1-O4	2.287(3)
U1-O5	2.367(3)
U1-O6	2.470(3)
U1-O7	2.421(3)

S3. The TGA curve for compound 1

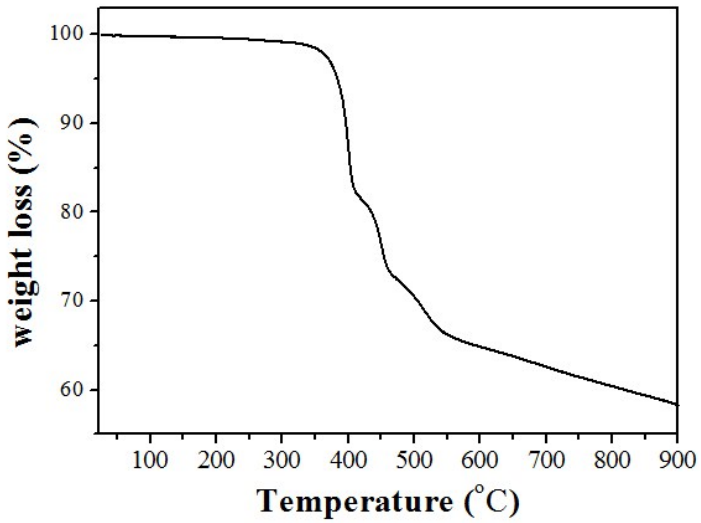

Figure S1. The TGA curve for compound 1

S4. Influence of competing metal ions

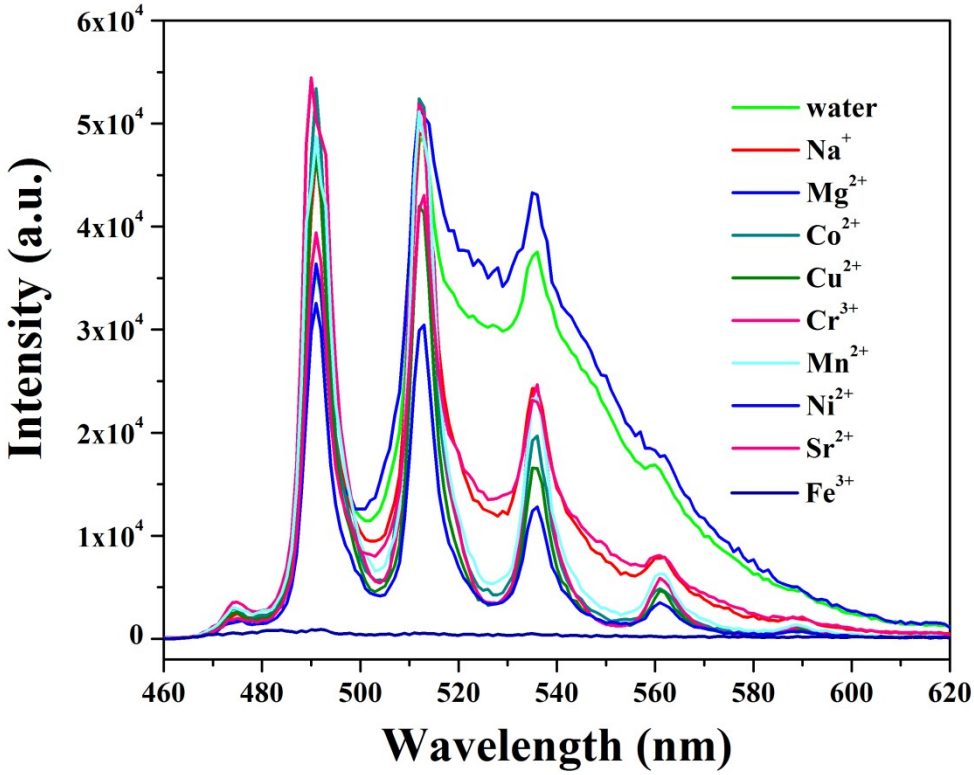

Figure S2. Emission spectra of **compound 1** immersed in different cation solution.

Table S3. Quenching constants (K_{SV}) of various 200 ppm $M(Cl)_x \cdot n(H_2O)$ (M = Na^+, Mg^{2+}, Co^{2+}, Cu^{2+}, Cr^{3+}, Mn^{2+}, Ni^{2+}, Sr^{2+}, Fe^{3+},) solution and 100 ppm $K_2Cr_2O_7$ solution.

Sample	Blank	Na^+	Mg^{2+}	Co^{2+}	Cu^{2+}	Cr^{3+}	Mn^{2+}	Ni^{2+}	Sr^{2+}
K_{SV}	0	0.06	-4.48	7.63	58.4	-10.47	-13.63	150.01	59.33
Sample	Fe^{3+}								
K_{SV}	25526.34								

S4. EDS analysis

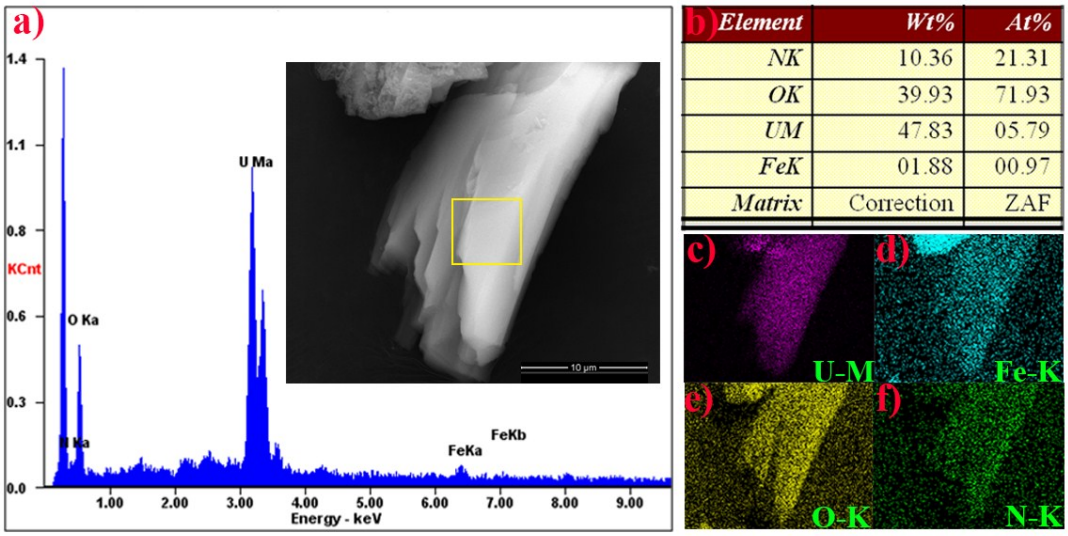

Figure S3. a), b) EDS analysis of the Fe loaded simple of **1**, inset is the SEM photograph of a single crystal of **1**. c), d), e),f) U, Fe, O and N elements EDS mapping of a single crystal of **1** showing the elemental distribution on the surface of a crystal of **1**.

S5. Determination of the detection limit

Based on the fluorescence measurement shown in Figure 5, the linear domain in low dose range can be fitted as

$y = 5.22\ x + 6.23$

where y is the relative decrease of luminescence intensity ($100 \times (I_0\text{-}I)/I_0$) monitored at 512 nm, and x is the Fe^{3+} concentration.

The standard deviation (σ) is defined as $100 \times (I_{SE}/I_0)$, where I_{SE} is the standard error of the emission measurement, as determined by the baseline measurement of blank samples (monitored at 512 nm), I_0 is the luminescence intensity of compound 1 in

deionized water (also monitored at 512 nm). If defining three times of the standard deviation as the detectable signal, the detection limit can be projected as 3σ/slope = 6.3×10^{-3} ppm

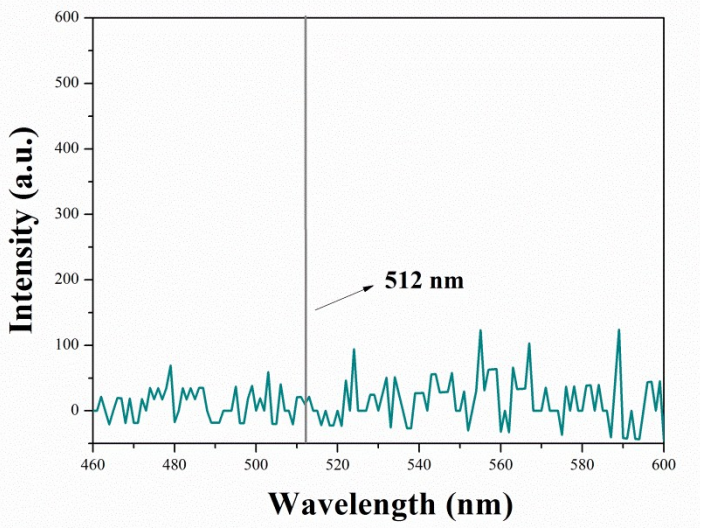

Figure S4. Emission spectra of deionized water, (excited at 365 nm, I_{SE}: deionized water 10.12).

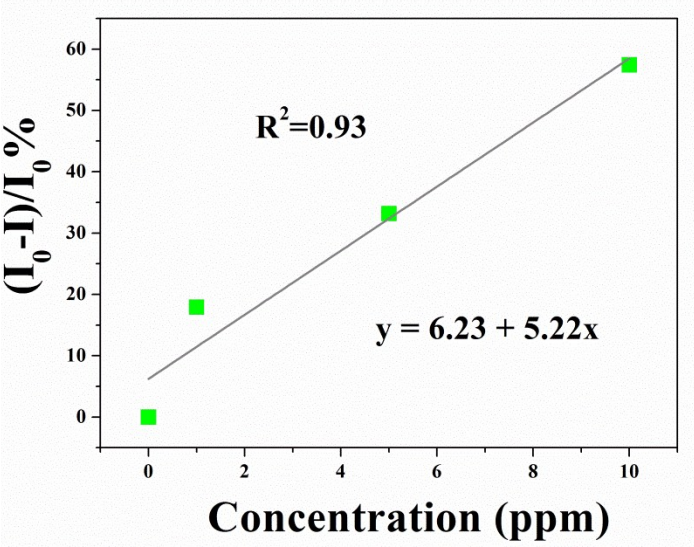

Figure S5. The plot showing the quenching ratio of PL intensity (measured at 512 nm) of **compound 1** as a function of the Fe^{3+} concentration, the data points in low concentration range from 0 to 10 ppm are fitted in linear relationship to obtain the slop.