

Surprising Coordination for Low-Valent Actinides Resembling Uranyl(VI) in Thorium(IV) Organic Hybrid Layered and Framework Structures Based on a Graphene-Like (6,3) Sheet Topology

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S1. Materials and instrumentations. All reagents and solvents were used from commercial suppliers without further purification. Powder X-ray diffraction (PXRD) data were collected from 5 to 50° with a step of 0.02° on a Bruker D8 Advance diffractometer with Cu K α radiation ($\lambda=1.54056$ Å) and a Lynxeye one-Dimensional detector. Thermalgravimetric analysis(TGA) was accomplished on a NETZSCH STA 449F3 instrument from 30 °C to 900 °C under a nitrogen flow at a heating rate of 10 °C/ min. The luminescence and UV-Vis absorption data was obtained using a Craic Technologies UV-vis-NIR microspectrophotometer, crystals were placed on quartz slides and data were collected after optimization of microspectro-photometer. An optical filter masking signal below 420 nm was applied in order to mask the broad feature of excitation light of 365 nm in the emission spectra. The quantum yield of compound **3** and H₃L2 were collected by Fluorolog-3 spectrofluorometers. Scanning electron microscopy/energy-dispersive spectroscopy (SEM/EDS) images and data were collected using FEI Quanta 200FEG. Elemental analyses was accomplished on a Vario EL CHNOS elemental analyzer.

S2. Synthetic methods.

Synthesis of [C₇H₁₁N₂]₅[Th₂(L1)₂Cl₆]·Cl (1**) and [C₇H₁₁N₂]₂[Th(L1)Cl₃] (**2**).** Th(NO₃)₄·6H₂O (58.8 mg, 0.1 mmol), H₃L1 (43.8 mg, 0.1 mmol), ionic liquid of 1-Allyl-3-methylimidazolium chloride (1 mL), and 1 drops of concentrated nitric acid were placed in a 20 mL closed glass vial and allowed to heated at 140 °C for 2 days. Colorless block crystals appeared and collected before washed with ethanol for both compound **1** and **2**. The PXRD pattern confirms the presence of the mixture as illustrated in **Figure S2**.

Synthesis of [(CH₃)₂NH₂][Th₂(L2)₃(H₂O)₂]·8H₂O·6DMF (3**).** A mixture of Th(NO₃)₄·6H₂O (39.2 mg, 0.067 mmol), and H₃L (43.9 mg, 0.1 mmol) was placed in scintillation vials before 5 mL of DMF and 3 drops of concentrated nitric acid were added. The mixture was then placed in oven and heated at 100 °C for 72 hours before it was cooled to room temperature at 5 °C·h⁻¹. Light brown block crystals were collected in ca. 92 % yield based on thorium and the phase purity was confirmed by the experimental PXRD (**Figure S3**).

S3. X-ray crystallography. Data collection was accomplished on a Bruker D8-Venture diffractometer with a Turbo X-ray Source (Mo–K α radiation, $\lambda = 0.71073$ Å) adopting the direct-

drive rotating anode technique and a CMOS detector at 123 K. The data collection, data integration, and absorption correction were accomplished using APEXII, SAINT, and SADABS software, respectively. 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 compounds **1**, **2**, and **3** are summarized in **Table S1**. Selected bond lengths for compounds **1**, **2**, and **3** are listed in **Tables S2**. Since not all the solvent molecules can be properly refined in the structure, the final formula of compound **3** was determined by a combination of CHN elemental analysis and TGA.

Table S1. Crystallographic data for all of the compounds

Sample	1	2	3
Formula	$[\text{C}_7\text{H}_{11}\text{N}_2]_5[\text{Th}_2(\text{L1})_2\text{Cl}_6]\cdot\text{Cl}$	$[\text{C}_7\text{H}_{11}\text{N}_2]_2[\text{Th}(\text{L1})\text{Cl}_3]$	$[(\text{CH}_3)_2\text{NH}_2][\text{Th}_2(\text{L2})_3(\text{H}_2\text{O})_2]\cdot 8\text{H}_2\text{O}\cdot 6\text{DMF}$
M_r [g mol ⁻¹]	2198.96	1020.16	2251.88
Crystal system	Monoclinic	Monoclinic	Trigonal
Space group	$C2/c$	$P2_1/c$	$R-3c$
a (Å)	17.427(3)	17.273(2)	24.8612(19)
b (Å)	30.021(5)	15.263(2)	24.8612(19)
c (Å)	18.374(4)	17.298(2)	28.260(4)
α	90.00	90.00	90.00
β	114.813(4)	118.669(3)	90.00
γ	90.00	90.00	120.00
V (Å ³)	8725(3)	4001.3(9)	15127(3)
Z	4	4	6
D_c (g cm ⁻³)	1.674	1.693	1.066
μ (mm ⁻¹)	3.686	3.979	2.993
$F(000)$	4336	2000	4650
T(K)	123(2)	123(2)	123(2)
GOF on F^2	1.039	1.035	0.957

R1, ^a ($I > 2\sigma(I)$)	0.0844	0.0610	0.0242
R1, ^a (all data)	0.1163	0.1005	0.0430

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

Table S2. Selected bond lengths (Å) for compound **1**, **2**, and **3**

Bond	Distance (Å)	Bond	Distance (Å)
Compound 1			
Th1-O1	2.505(9)	Th1-O2	2.530(10)
Th1-O3A	2.566(9)	Th1-O4A	2.435(11)
Th1-O5B	2.450(10)	Th1-O6B	2.506(10)
Th1-Cl1	2.856(4)	Th1-Cl2	2.787(4)
Th1-Cl3	2.775(5)		
Compound 2			
Th1-O1	2.462(5)	Th1-O2	2.554(6)
Th1-O3D	2.490(5)	Th1-O4D	2.539(7)
Th1-O5E	2.527(6)	Th1-O6E	2.499(6)
Th1-Cl1	2.730(5)	Th1-Cl2	2.835(3)
Th1-Cl3	2.794(4)		
Compound 3			
Th1-O1	2.660(2)	Th1-O2	2.501(2)
Th1-O3C	2.408(2)	Th1-O5	2.569(5)
Symmetry codes: A = $1/2+x, 1/2+y, z$; B = $-1/2+x, 1/2+y, z$; C = $y, -x+y, -z$;			
D = $1+x, y, 1+z$; E = $1+x, y, z$;			

S4. Elemental analysis. Elemental analyses (C, N, and H) were performed with a Vario EL CHNOS elemental analyzer. Elemental analysis results: C calculated, 44.22%; found, 44.50%; N calculated, 6.217%; found, 6.032%; H calculated, 4.70%; found, 4.425%.

Table S2. The elemental analysis for compound **3**

Name	Wight. [mg]	Date Time	C/N Ratio	Content [%]	Peak Area	Daily Factor
Compound 3	2.8420	15.04.15	15.77	N: 6.032	6547	0.9811
				C: 44.50	35455	0.9875
				H: 4.425	11414	0.9983

S5. Additional crystal structure depiction.

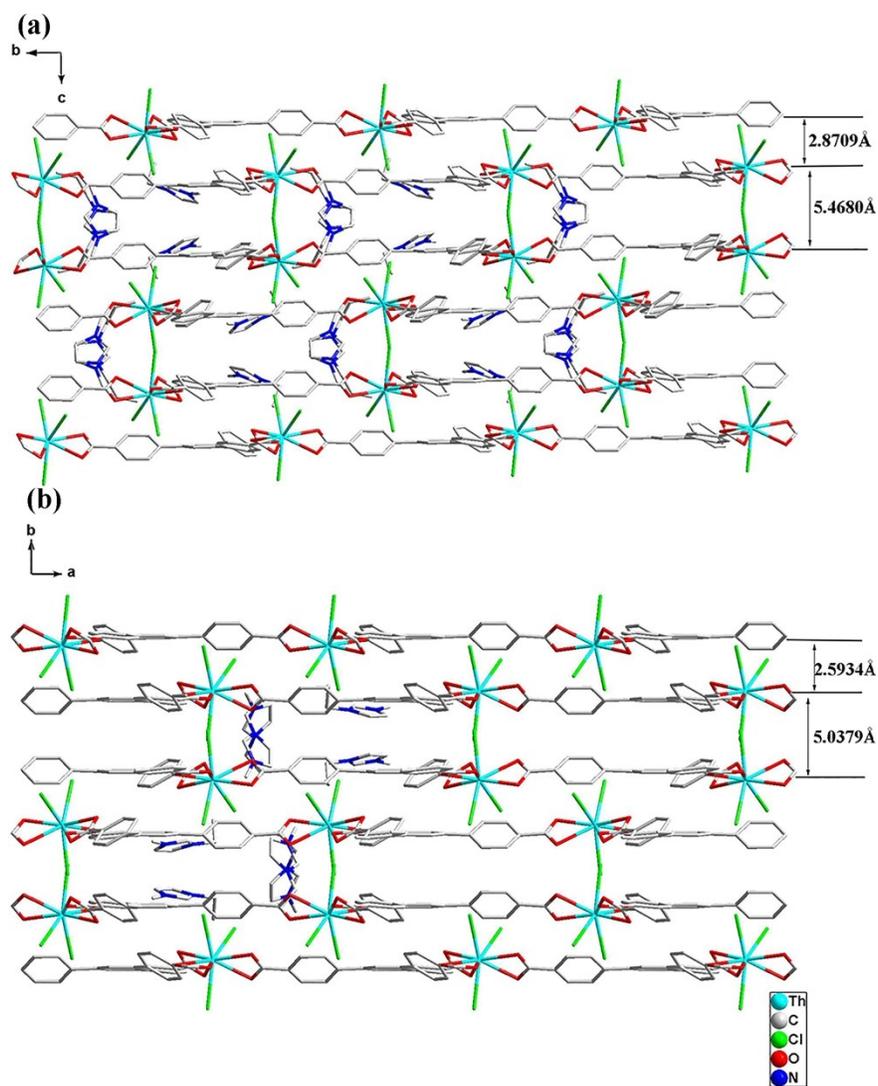


Figure S1. a) A view of 1-allyl-3-methylimidazolium cations piercing two layers of six-membered rings vertically in compound **1**; b) Crystal structure of compound **2** with an identical layered structure but a slightly different layer spacing from compound **1**.

S6. Powder X-ray diffraction analysis. The experimental PXRD patterns of compound **3** match well with the simulated ones, revealing that it is a single phase without any impurity. The experimental PXRD patterns of mixtures (compounds **1** and **2**) is shown in **Figure S2**.

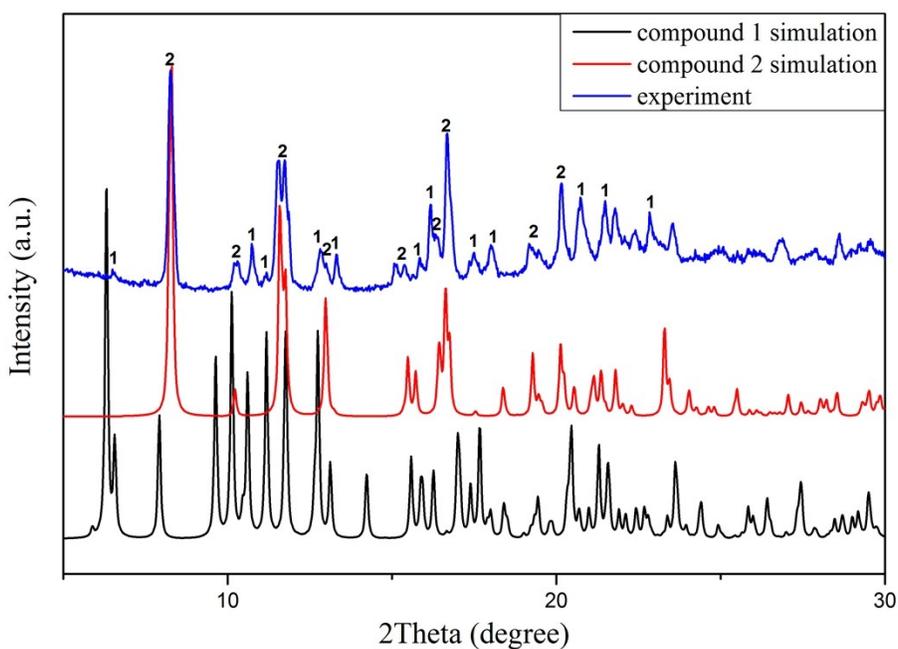


Figure S2. The powder X-ray diffraction (PXRD) for mixtures (compounds **1** and **2**).

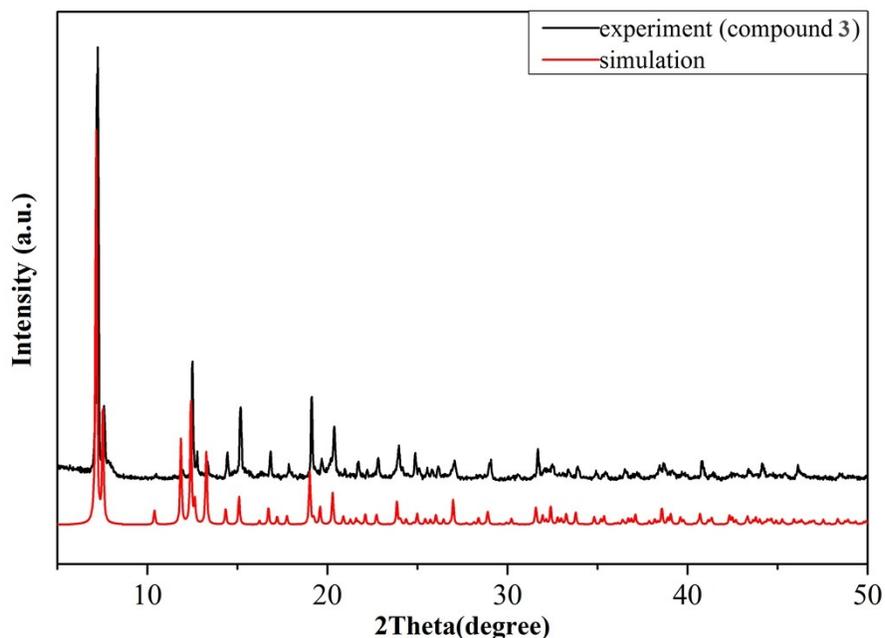


Figure S3. The powder X-ray diffraction (PXRD) for compound **3**.

S7. Thermogravimetric analysis. The samples were heated at a rate 10 K/min in nitrogen from 30 °C to 900 °C. In compound **3**, three weight loss steps were observed. A first loss of 6.13 % occurs before 135 °C, which corresponds to the loss of eight water molecules (cal. 6.39 %). The DMF molecular (cal. 19.48 %) further departs between 135 and 170 °C (observed 18.87 %). In 270-500 °C interval, the dimethylamine cation and coordinated water are slowly removed. The benzene fragments starts losing around 500 °C with collapse of the structure.

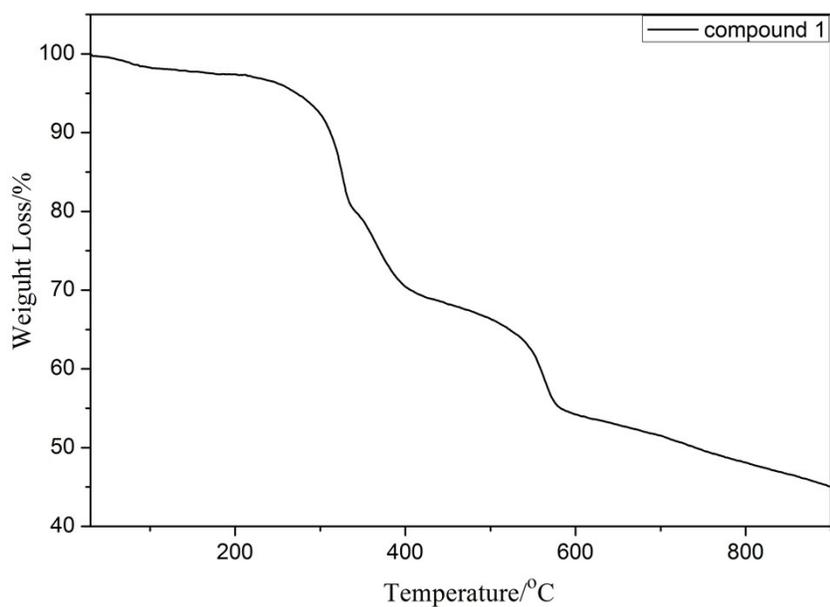


Figure S4. The TGA curve for mixtures (compounds **1** and **2**).

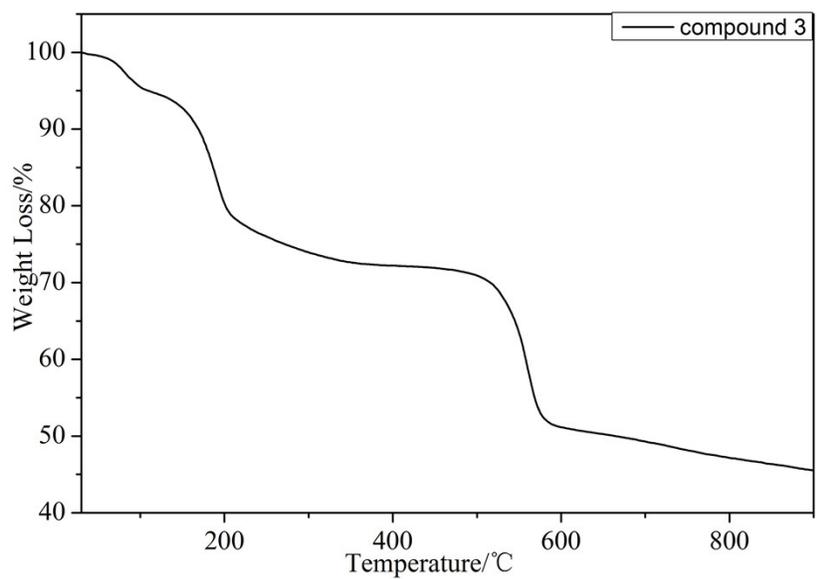


Figure S5. The TG curve for compound **3**.

S8. Thermostability Measurements. Thermostability measurements for compound **3** was studied by variable-temperature PXRD from 25 °C to 600 °C under the nitrogen flow.

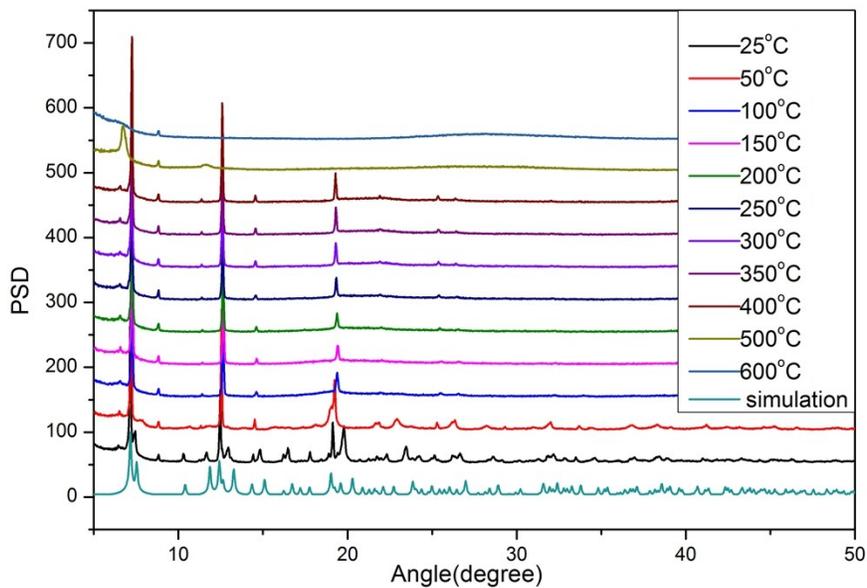


Figure S6. The variable-temperature PXRD for compound **3**.

S9. Spectroscopic characterizations.

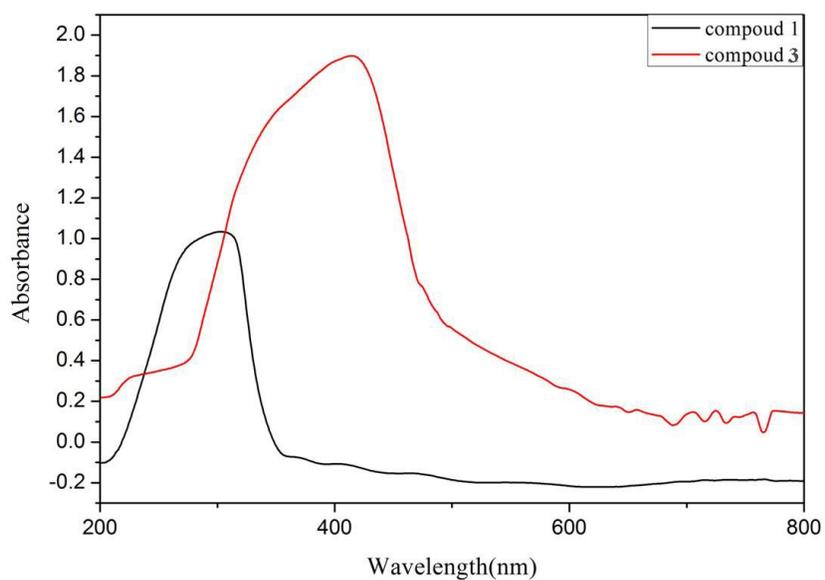


Figure S7. The UV-vis absorption spectra for compounds **1** and compound **3** measured at 298 K.

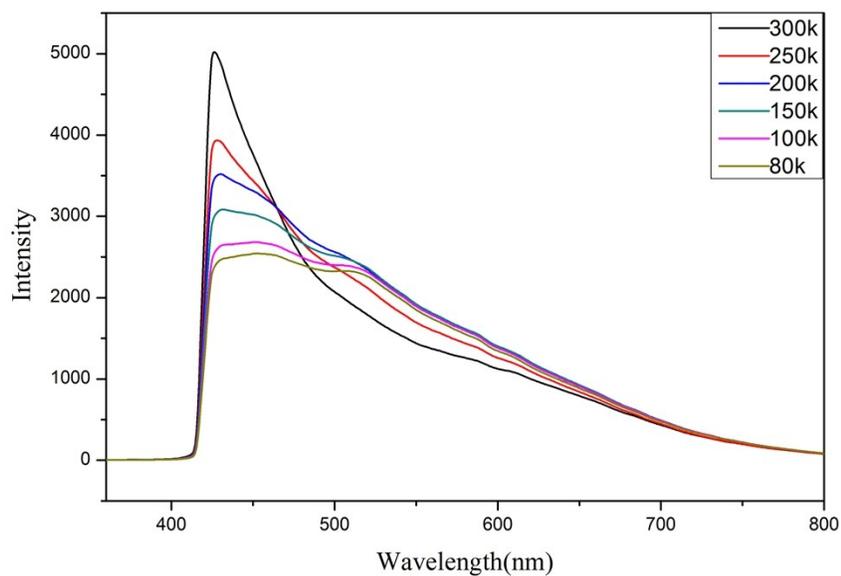


Figure S8. Temperature-dependent photoluminescence spectra of compound **1** with the excitation at 365 nm.

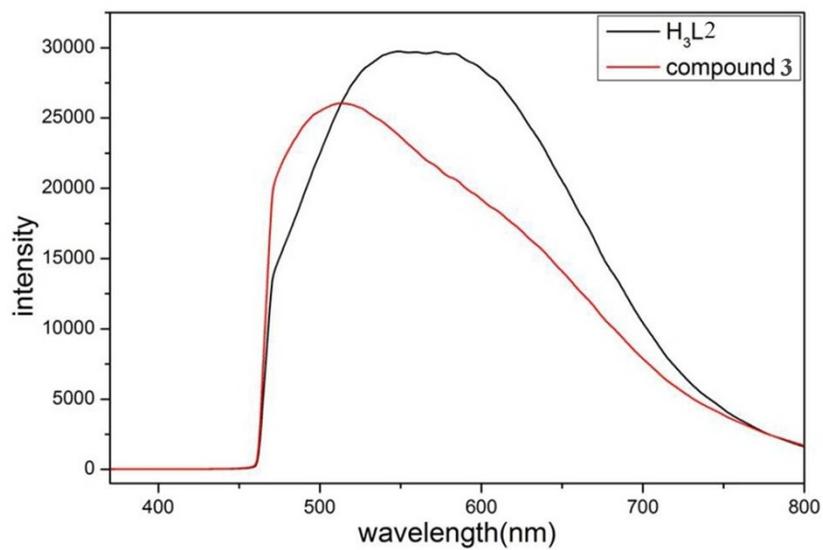


Figure S9. Photoluminescence spectra of compound **3** and H₃L₂ with the excitation at 420 nm.

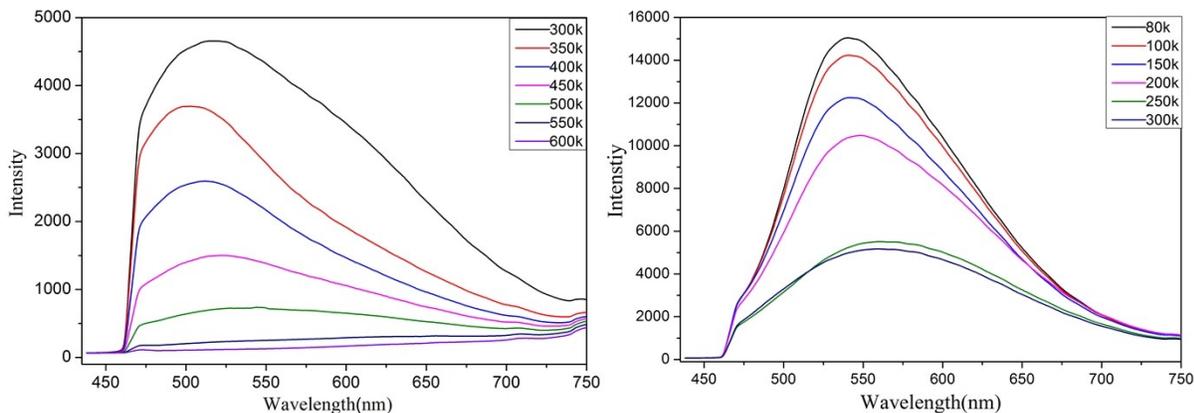


Figure S10. Temperature-dependent photoluminescence spectra of compound **3** with the excitation at 420 nm.

As shown in **Figure S8**, the abnormal monotonic decrease in intensity for compound **1** is observed with the decrease of temperature, which is likely attributed to special energy transfer mechanism involving the guests in the interlayer space. On the contrary, the intensity of luminescence for compound **3** is decreasing as the temperature rises (**Figure S10**), and this is owing to the fact that the non-radiative emission of phonon is promoted as elevated temperature. The observation of the emission at over 500 K also shows the potential application as high temperature luminescent material of compound **3**.

S10. Quantum yield.

The quantum yield of compound **3** and H₃L2 were collected by Fluorolog-3 spectrofluorometers showing similar values (H₃L2: $\Phi_{QY} = 4.4\%$ and Compound **3**: $\Phi_{QY} = 5.9\%$) for H₃L and compound **3**.

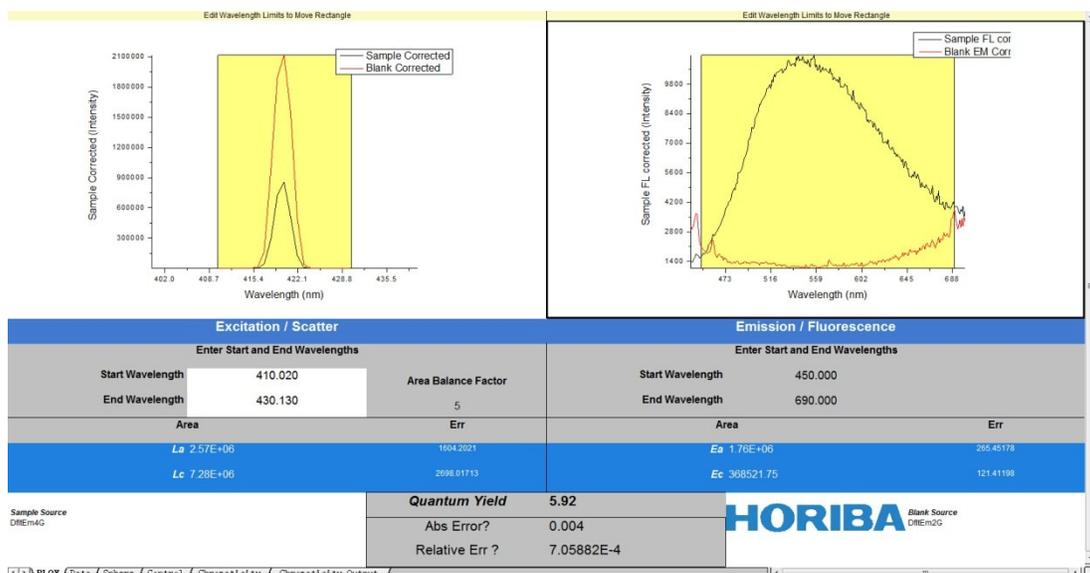


Figure S11. The analysis of quantum yield of compound **3**.

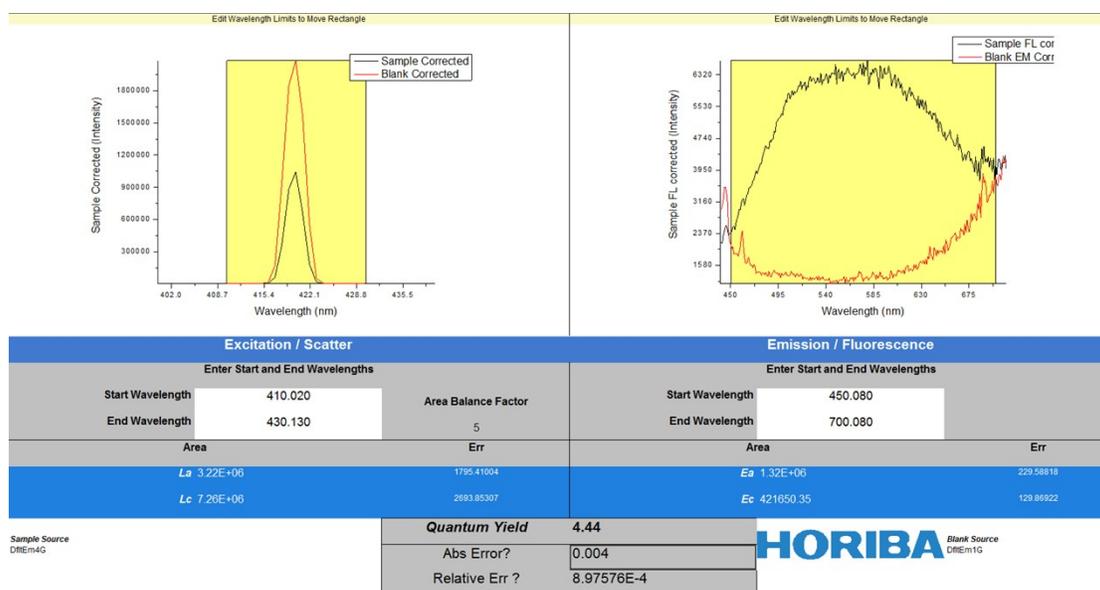


Figure S12. The analysis of quantum yield of **H₃L₂**.

S11. The doping experiment of uranium and thorium

The doping experiment of uranium and thorium was achieved by adding one equivalent of uranyl cation into the synthetic reaction of compound **1**: Th(NO₃)₄·6H₂O (58.8 mg, 0.1 mmol), UO₂(NO₃)₂·6H₂O (50.2 mg, 0.1 mmol), H₃L1 (43.8 mg, 0.1 mmol), ionic liquid of 1-Allyl-3-methylimidazolium chloride (1 mL) and one drop of concentrated nitric acid were placed in a 20

mL of closed glass vial and allowed to be heated at 140 °C for 2 days. The formation of structure same as undoped experiment (compounds **1** and **2**) is confirmed by PXRD data (**Figure S13**). The successful doping of uranium onto the thorium site is demonstrated by the EDX elemental analysis measurements. As shown in the **Figure S14**, the molar ratio of Th : U is 9.03 : 1 in the crystals, indicating 10% doping rate of uranium for thorium in the compound (see discussion in the main text).

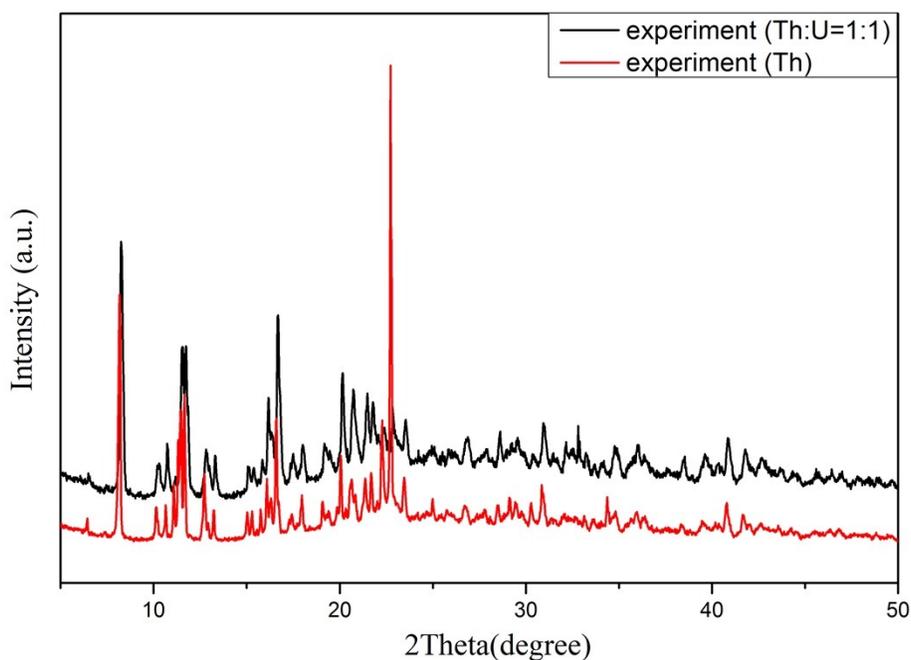


Figure S13. The PXRD pattern for products of doping experiments confirming the formation of same structure as before.

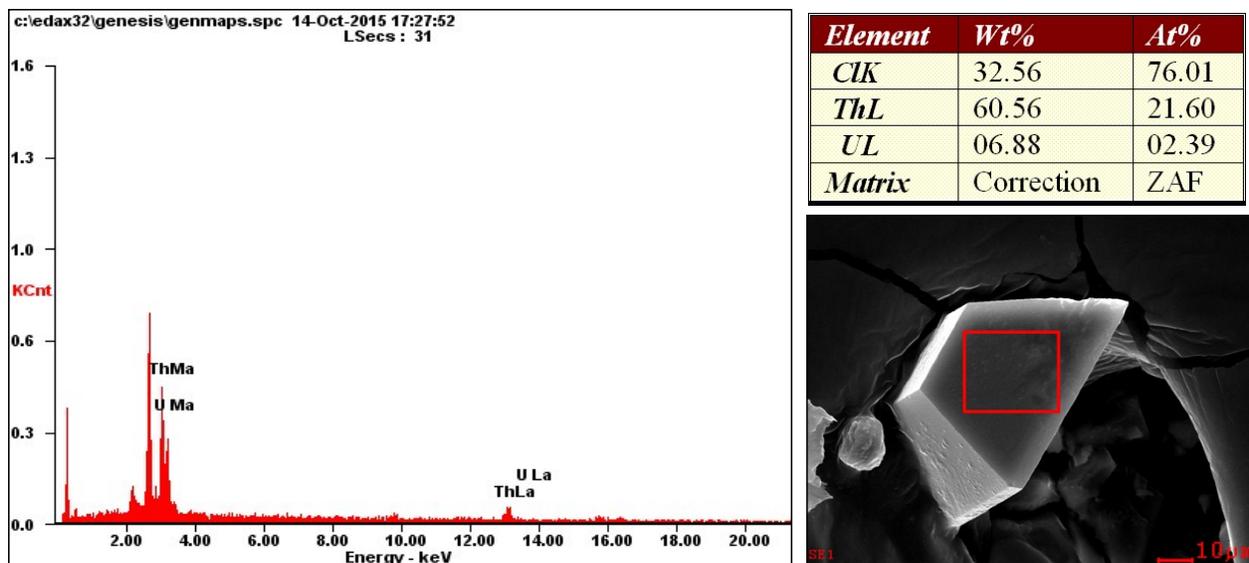


Figure S14. The EDX results for crystals of doping products.

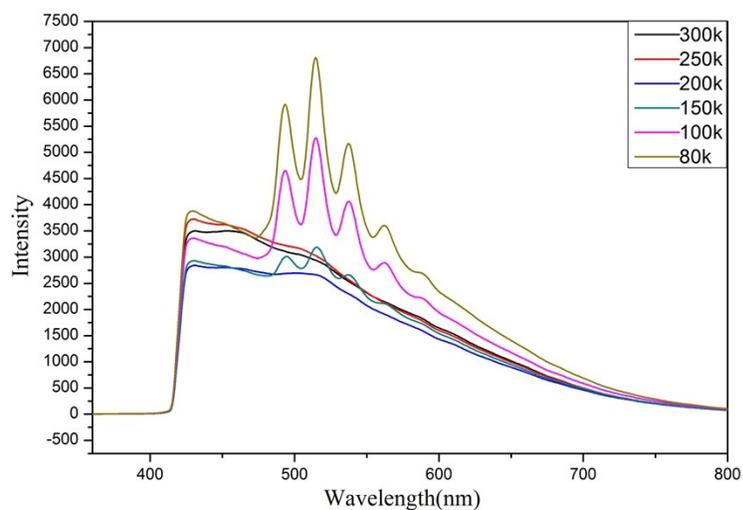


Figure S15. Temperature-dependent photoluminescence spectra on crystals of doping products under the excitation at 365nm.