

Supporting information for

A unique uranyl framework containing uranyl pentamers as secondary building units: synthesis, structure, and spectroscopic properties

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S1 Experimental section

Caution ! While all uranium compounds used in these studies contained depleted uranium, standard precautions were performed for handling radioactive material, and all studies were conducted in a laboratory dedicated to studies on actinide elements.

Materials: $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1,2,4-Benzenetricarboxylic acid (98%, TCI), Tetrahydrofuran (AR, Adamasbeta), N,N-Dimethylformamide (AR, Adamasbeta), Tetraethylammonium (TEA) hydroxide (35 wt% solution in water, TCI), Formic acid (AR, Adamasbeta). All chemical reagents and solvents purchased from commercial suppliers and directly used as received.

*Synthesis of **compound 1**:* the mixture of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (100.4 mg, 0.2 mmol), 1,2,4-Benzenetricarboxylic acid (63 mg, 0.3 mmol), H_2O (2 mL), THF (2 mL), and DMF (2 mL) was added into a 20 mL stainless steel PTFE vial. The vial was heated to 130 °C, maintained for 3 days, and then cooled to room temperature at a rate of 5 °C/h. Dark yellow crystals were finally obtained as a pure phase. The yield of **compound 1** is about 15% based on uranium.

*Synthesis of **compound 2**:* the mixture of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (50.2 mg, 0.1 mmol), 1,2,4-Benzenetricarboxylic acid (42 mg, 0.2 mmol), Tetraethylammonium hydroxide (100 μL), formic acid (50 μL), and H_2O (2 mL) was added into a 20 mL stainless steel PTFE vial. The vial was

heated to 160 °C, maintained for 4 days, and then cooled to room temperature at a rate of 5 °C/h. Yellow crystals were finally obtained as a pure phase. The yield of **compound 2** is about 52% based on uranium.

S2 X-ray Crystallography Studies:

Single crystal X-ray diffraction data collections of **compound 1** and **compound 2** were performed on a Bruker D8-Venture diffractometer with a Turbo X-ray Source (Mo–K α radiation, $\lambda = 0.71073 \text{ \AA}$) adopting the direct-drive rotating anode technique and a CMOS detector under 298 K. The data of **compound 1** and **compound 2** were collected using the program APEX3 and then processed using SAINT routine in APEX3. The structure of **compound 1** and **compound 2** were solved by direct methods and refined by the full-matrix least squares on F^2 using the SHELXTL.^[1]

S3 Characterizations

Instrumentations: Powder X-ray diffraction (PXRD) patterns were collected from 5° to 50° with a step of 0.02° on a Bruker D8 Advance diffractometer with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) and a Lynxeye one-dimensional detector. Elemental analysis (C, N, and H) were performed using a Vario EL CHNOS elemental analyzer. The FT-IR spectrum of **compound 1** without KBr were recorded in the range of 4000-400 cm^{-1}

on a Thermo Nicolet iS50 spectrometer. Thermogravimetric analyses were carried out on a NETZSCH STA449F3 instrument in the range of 30-900 °C under a nitrogen flow at a heating rate of 10 K/min for the dried samples of **compound 1** and **compound 2**. Luminescence spectra were collected on a Craic Technologies microspectrophotometer and accessory instrument. Second Harmonic Generation (SHG) signals were recorded on a Kurtz-Perry powder SHG test with an Nd:YAG laser (1064 nm). KH_2PO_4 was chosen as a reference substance to the signal of **compound 1**.

Hydrolytic Stability Measurements: Hydrolytic stability measurements for **compound 1** and **compound 2** were carried out by stirring the samples in aqueous solutions at various pH range from 5 to 12 for 1 day. The solid samples were then collected and dried for PXRD patterns analysis.

Table S1 The crystallographic data of compound 1Table S1. Crystallographic data of **compound 1**.

Formula	[DMPD][H ₃ O] [(CH ₃) ₂ NH ₂] ₂ [(UO ₂) ₅ O ₃ (OH)(HCOO) (C ₉ H ₃ O ₆) ₂]·(DMF) (H ₂ O)
<i>Mr</i> [g mol ⁻¹]	2174.00
Crystal system	Monoclinic
Space group	<i>Cc</i>
<i>a</i> (Å)	25.3322(19)
<i>b</i> (Å)	8.8310(7)
<i>c</i> (Å)	25.293(3)
α (°)	90
β (°)	118.825(2)
γ (°)	90
<i>V</i> (Å ³)	4957.2(8)
<i>Z</i>	4
ρ_{calcd} (g cm ⁻³)	2.791
<i>M</i> (mm ⁻¹)	16.371
<i>F</i> (000)	3668
<i>T</i> (K)	298
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (<i>I</i> >2 σ (<i>I</i>))	0.0305, 0.0706
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data)	0.0343, 0.0729

$$^aR_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

Table S2 Element analysis result of compound 1

Table S2. The element analysis result of **compound 1**

Name	Weight (mg)	Content (%)	Peak Area	Daily Factor	The theoretical content based on formula (%)
Compound 1	2.7710	N:2.546	2678	0.9915	2.569
		C:17.13	12918	0.9918	17.62
		H:2.526	4908	1.0587	2.478

Table S3 The crystallographic data of compound 2

Table S3. The crystallographic data of **compound 2**

Formula	(TEA) ₂ [(UO ₂) ₂ (H ₂ O)(C ₉ H ₃ O ₆) ₂]·5(H ₂ O)
<i>Mr</i> [g mol ⁻¹]	1322
Crystal system	monoclinic
Space group	<i>P2₁/n</i>
<i>a</i> (Å)	9.8823(13)
<i>b</i> (Å)	15.971(2)
<i>c</i> (Å)	27.569(3)
α (°)	90
β (°)	91.413(4)
γ (°)	90
<i>V</i> (Å ³)	4349.9(9)
<i>Z</i>	4
ρ_{calcd} (g cm ⁻³)	1.878
<i>M</i> (mm ⁻¹)	7.505
F(000)	2332
T(K)	298
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (<i>I</i> >2σ(<i>I</i>))	0.0371, 0.1434
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data)	0.0424, 0.1473

$$^aR_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

Table S4 Element analysis result of compound 2

Table S4. The element analysis result of **compound 1**

Name	Weight (mg)	Content (%)	Peak Area	Daily Factor	The theoretical content based on formula (%)
Compound 2	2.5730	N:2.513	1570	0.9915	2.121
		C:32.35	13124	0.9918	30.91
		H:4.670	7450	1.0587	4.546

Fig. S1 Thermal-gravimetric analysis (TGA) data of compound 1

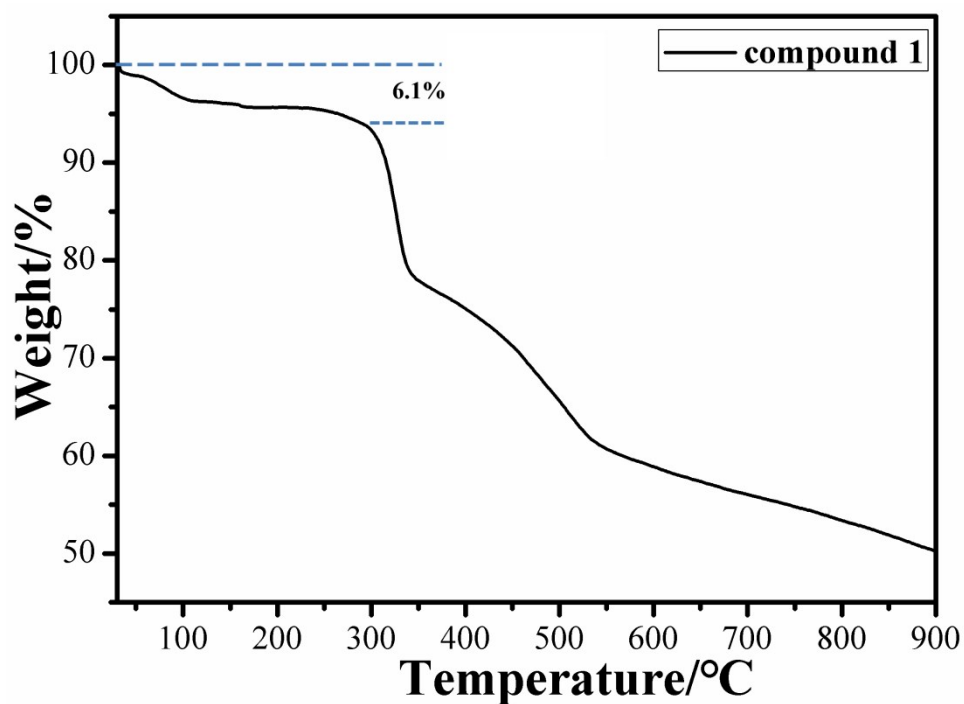


Fig. S1. The Thermal-gravimetric analysis curve of **compound 1**

Fig. S2 FT-IR spectrum

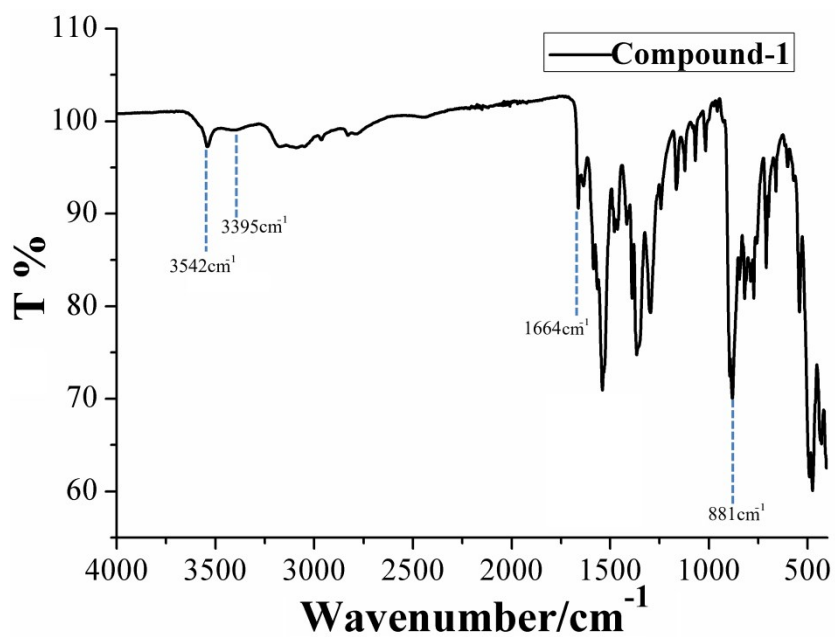


Fig. S2. FT-IR spectrum of **compound 1**

Fig. S3 Thermal-gravimetric analysis (TGA) data of compound 2

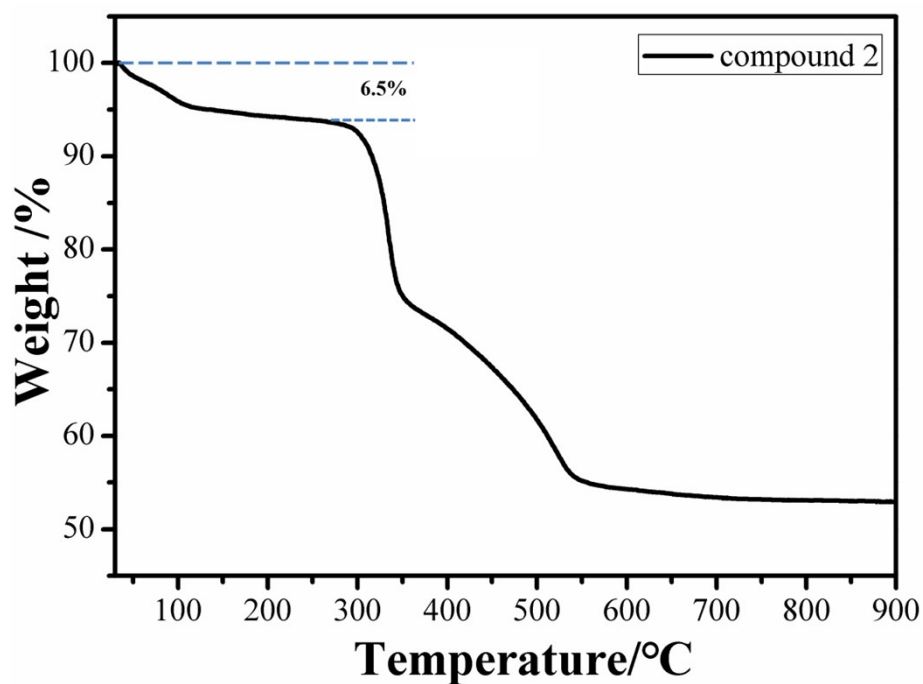


Fig. S3. The Thermal-gravimetric analysis curve of **compound 2**

Fig. S4 pH stability measurement results of compound 1

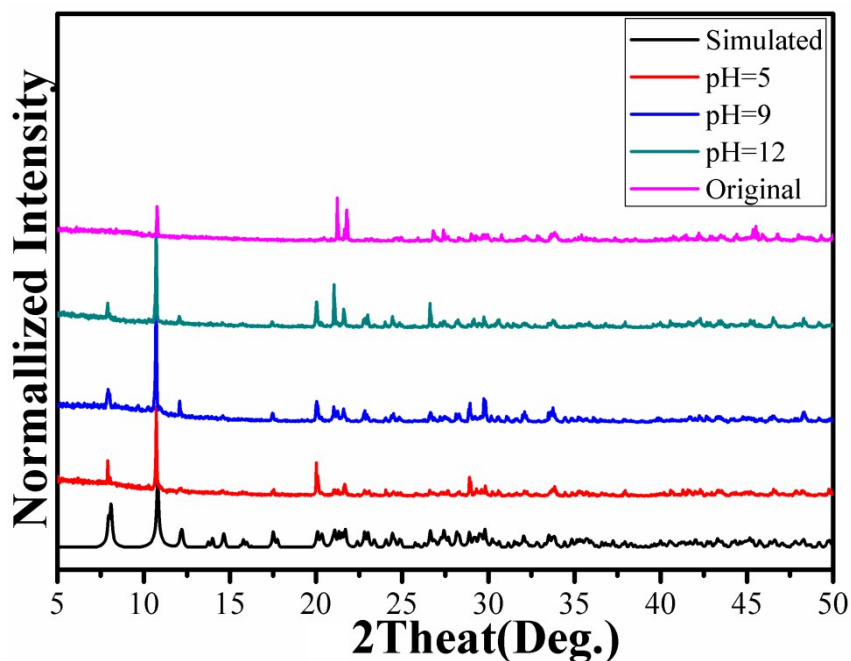


Fig. S4. The Powder X-ray diffraction (PXRD) patterns for solid samples of **compound 1** after soaking in solutions with pH ranging from 5 to 12

Fig. S5 pH stability measurement results of compound 2

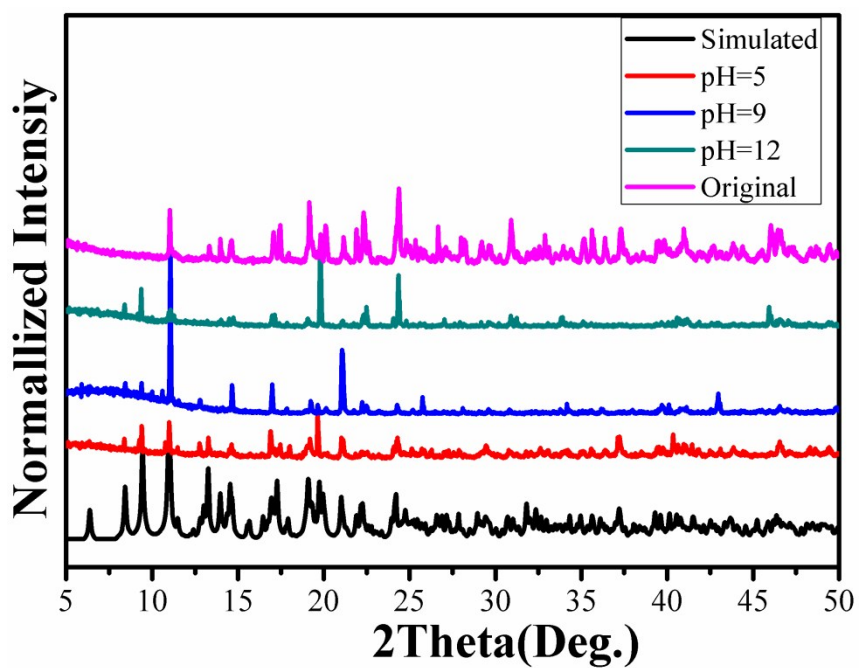


Fig. S5. The powder X-ray diffraction (PXRD) patterns for solid samples of **compound 2** after soaking in solutions with pH ranging from 5 to 12.

Reference:

- [1]. G. Sheldrick, P. SHELXTL, *Madison, WI* 1990.