

Supporting Information

Structural Diversity of Bipyridinium-based Uranyl Coordination Polymers: Synthesis, Characterization and Ion-exchange Application

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S1 General Methods

Caution! While uranyl nitrate $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is a radioactive reactant containing chemical toxicity, strict care and suitable protection for handling such substances must be taken.

1, 1'-bis(4-carboxyphenyl)-4, 4'-bipyridinium bis(chloride) ($[\text{H}_2\text{bcbp}]\text{Cl}_2$) was synthesized using a multi-step reaction from N, N'-bis(2,4-dinitrophenyl)-4, 4'-bipyridinium dichloride and ethyl 4-aminobenzoate. The 0.5 M uranyl stock solution was made from dissolving the commercially purchased uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) into deionized water. All the other chemicals were commercially supplied and used without any further purification.

$[(\text{UO}_2)_2(\text{bcbp})(\text{TP})_2] \cdot 3\text{H}_2\text{O}$ (**1**). 0.5 M aqueous solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (100 μL , 0.05 mmol), H_2bcbp (11.7 mg, 0.025 mmol), H_2TP (8.31 mg, 0.05 mmol), ultrapure water (2.0 ml) was loaded into a 12 mL autoclave. The autoclave was sealed and heated to 150 °C in an oven for 2 days, then cooled to ambient temperature. Light yellow block crystals of compound **1** were produced in the autoclave. These crystals were filtered off, rinsed with ultrapure water, and subjected to air drying at room temperature. Yield: 11.5 mg, 35.1% based on uranium.

$[(\text{UO}_2)_2(\text{bcbp})(\text{PA})_2] \cdot 4\text{H}_2\text{O}$ (**2**). 0.5 M aqueous solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (100 μL , 0.05 mmol), H_2bcbp (23.4 mg, 0.05 mmol), and H_2PA (49.84 mg, 0.3 mmol) were added to a solution of 2 mL of water in a 12 mL autoclave. The pH of the solution was tested as 2.57. The autoclave was then placed in a stainless-steel Parr bomb, heated statically at 150 °C for 2 days, and slowly cooled to ambient temperature. Yellow block crystals were collected and filtered off, rinsed with ultrapure water, and air dried at room temperature. Yield: 18 mg, 54.2% based on uranium.

$[(\text{UO}_2)_2(\text{bcbp})(\text{bpdc})_2] \cdot 5\text{H}_2\text{O}$ (**3**). 0.5 M aqueous solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (100 μL , 0.05 mmol), H_2bcbp (23.4 mg, 0.05 mmol), biphenyl-4, 4'-dicarboxylic acid (24.22

mg, 0.1 mmol), ultrapure water (2.0 mL) was put in a 12 mL autoclave. The autoclave was sealed and heated to 150 °C in an oven. Two days later, the autoclave was cooled to ambient temperature. Lamellar crystals of compound **3** were got and filtered off, rinsed with ultrapure water, and subjected to air drying naturally. Yield: 8.46 mg, 45.2% based on uranium.

$[(\text{UO}_2)(\text{bcbp})(\text{OH})(\text{H}_2\text{O})]\cdot\text{Cl}$ (**4**). 0.5 M aqueous solution of $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (120 μL , 0.06 mmol), H_2bcbp (23.4 mg, 0.05 mmol), NH_4Cl (6.419 mg, 0.12 mmol), ultrapure water (2.0 ml) was put into a 12 ml autoclave. The autoclave was sealed and heated to 110 °C in an oven for 2 days, then cooled to ambient temperature. Brown block crystals of compound **4** were filtered off. These crystals were rinsed with ultrapure water, and subjected to air drying at room temperature. Yield: 11.4 mg, 54.4% based on uranium.

$[(\text{UO}_2)(\text{bcbp})\text{Cl}]\cdot\text{Cl}$ (**5**). 0.5 M aqueous solution of $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (80 μL , 0.04 mmol), H_2bcbp (19.0 mg, 0.04 mmol), CB7 (46.0 mg, 0.04 mmol), ultrapure water (2.0 mL) was put into a 12 mL autoclave. The autoclave was sealed and heated to 150 °C in an oven for 2 days, then cooled to ambient temperature. Brown prism-like crystals of compound **5** accompanied by small amount of yellow plate crystals of unreacted H_2bcbp as well as considerable amount of unidentified powders were produced.

Physical Properties

Powder X-ray diffraction (PXRD) spectra were carried out using a Bruker D8 Advance diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Thermogravimetric analyses (TGA) of all uranyl compounds were measured on a TA Q500 analyzer. Bruker Tensor 27 spectrometer with a xenon lamp and solid sample holder is the measuring instrument for the Fourier transform infrared (FTIR) spectra. Hitachi F-4600 fluorescence spectrophotometer is the measuring instrument for the solid-state fluorescence spectra.

Single crystal X-ray diffraction data were all collected carried on a Bruker D8 VENTURE X-ray CMOS diffractometer with a $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) or a $\text{Cu K}\alpha$ ($\lambda =$

1.54184 Å) X-ray source at 273 K or room temperature (297 K). All data were integrated by the software package of SAINT, and the absorption correction was made using SADABS. The crystallographic data of the five newly reported structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as CCDC 1922758 (1), 1922759 (2), 1922760 (3), 1922761 (4), 1922762 (5).

S2 Typical Figures

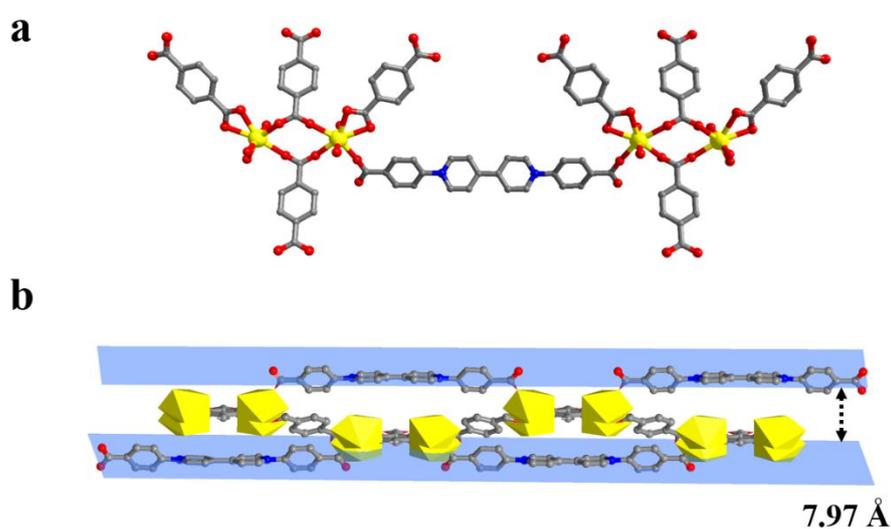


Figure S1. (a) Each dinuclear unit connects with four H₂TP and the interphase dinuclear units connect each other by a bcbp²⁻ ligand. (b) The double-layered 2D structure of compound 1. All solvent molecules are omitted for clarity.

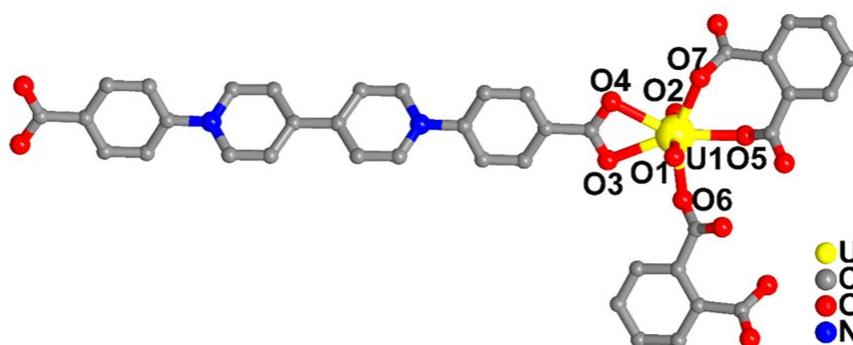


Figure S2. Coordination environment of the uranyl cation in compound 2. All hydrogen atoms are omitted for clarity.

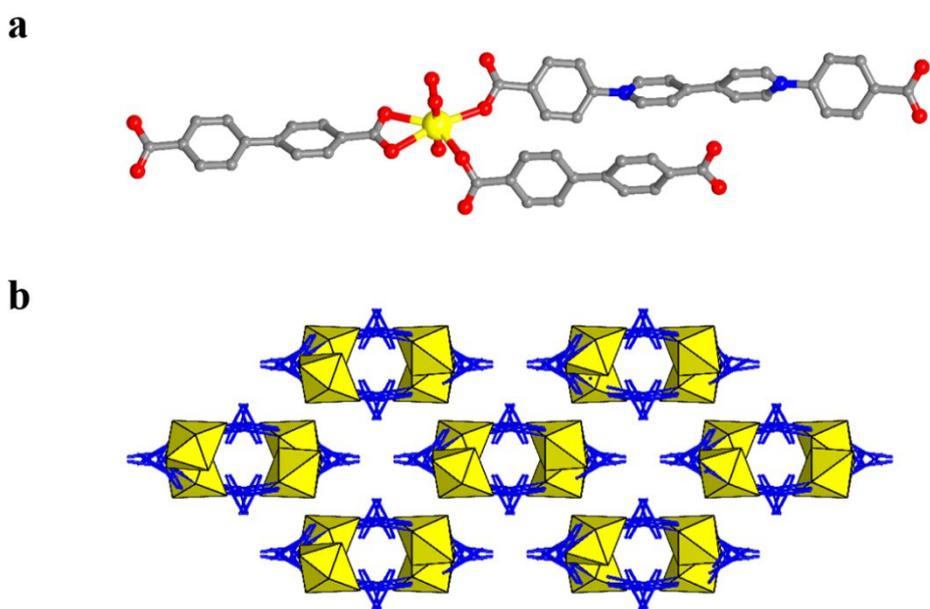


Figure S3. (a) Coordination environment of the uranyl cation of compound **3**. (b) Details of the extended 1D ribbon.

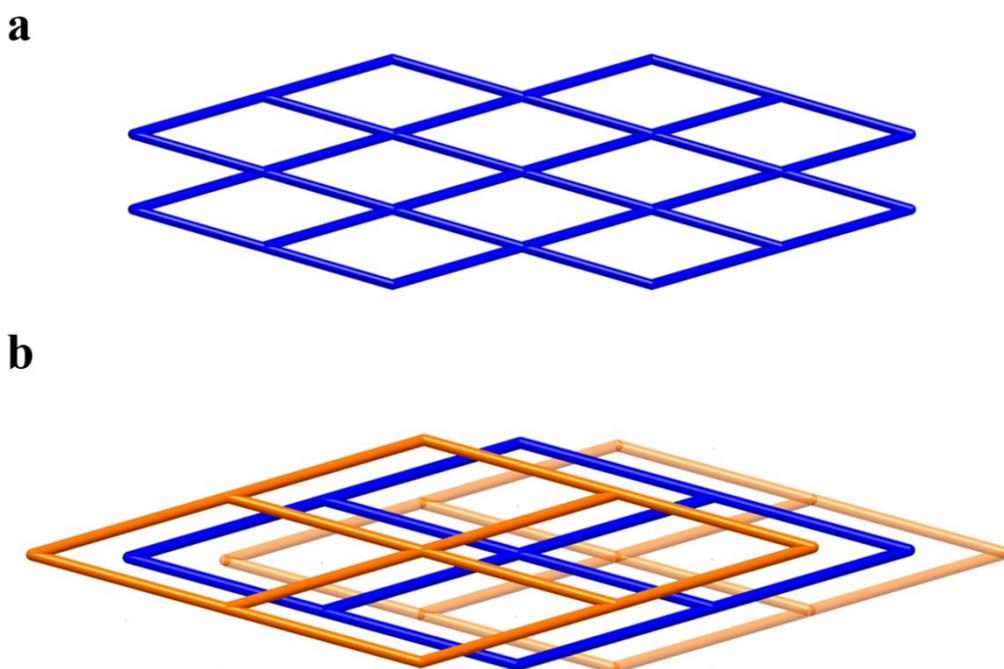


Figure S4. (a) The simplified 1D structure of compound **4**. (b) The layers of compound **4** along the *c* axis.

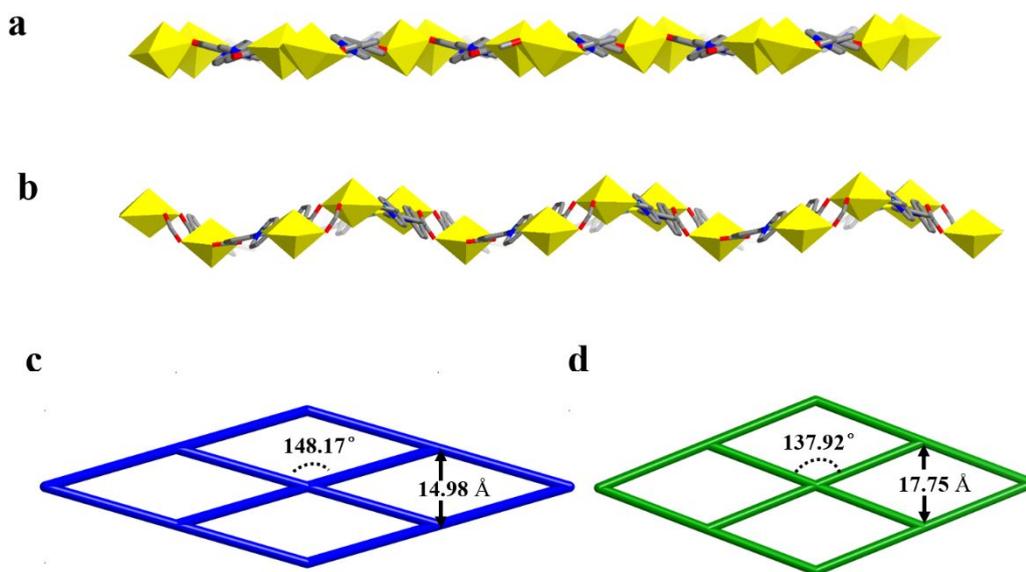


Figure S5. (a) A straight 2D plane of compound **4**. (b) A wave-shaped 2D plane of compound **5**. (c) The simplified rhombus shaped structure of compound **4**. (d) The simplified rhombus shaped structure of compound **5**.

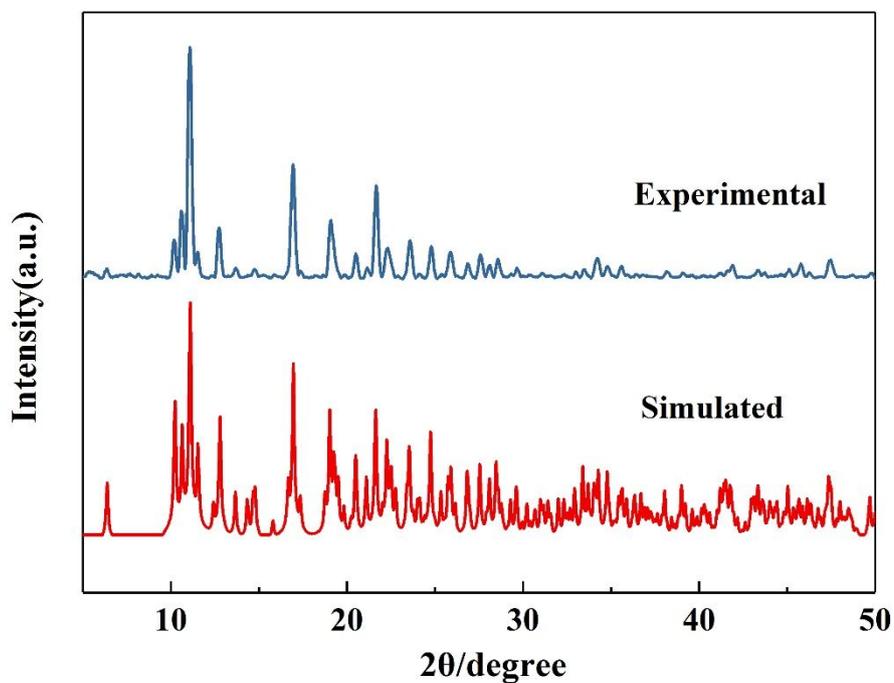


Figure S6. PXRD of compound **1**.

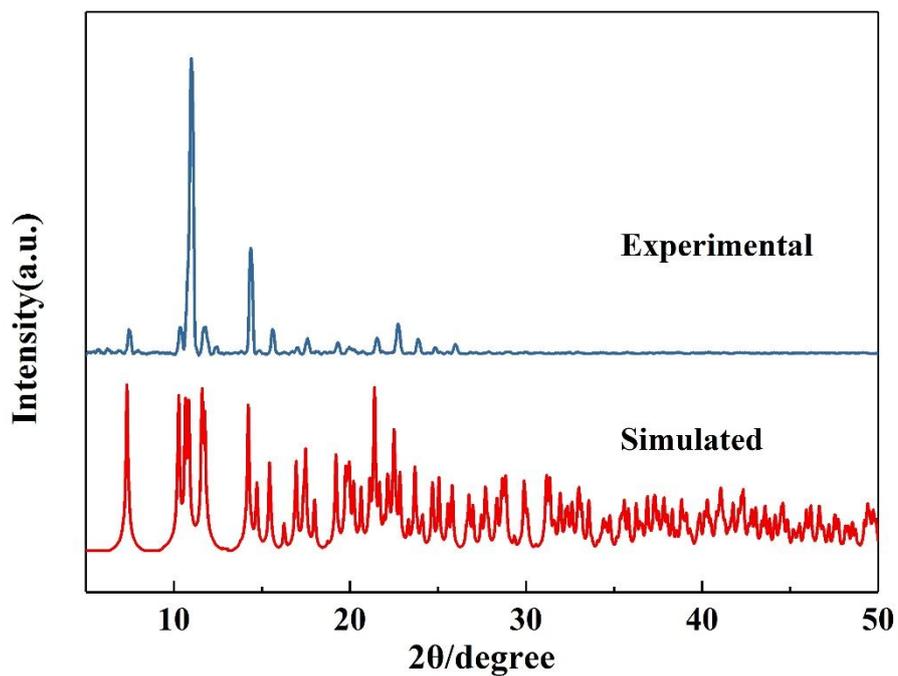


Figure S7. PXRD of compound 2.

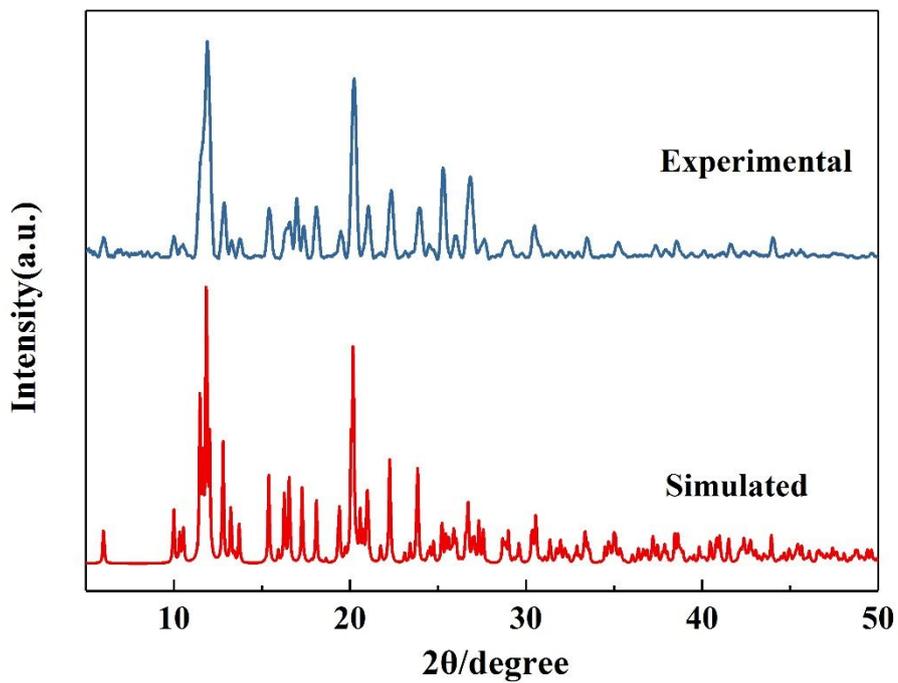


Figure S8. PXRD of compound 3.

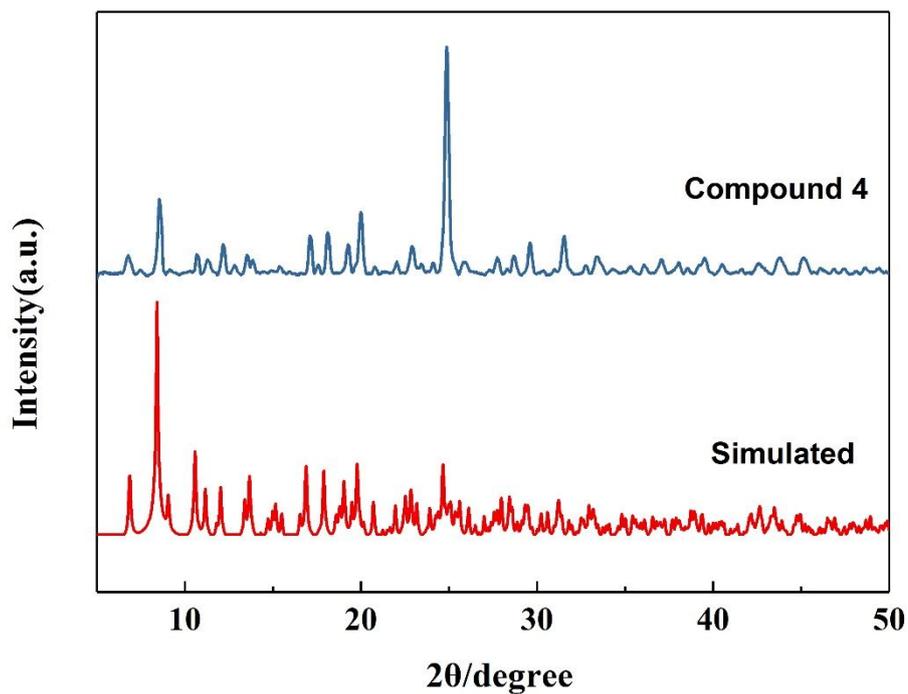


Figure S9. PXRD of compound 4.

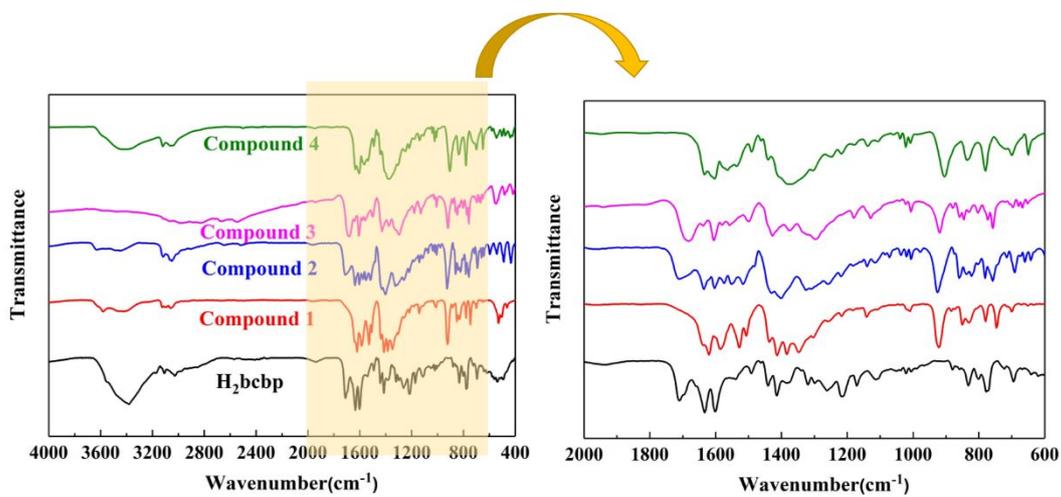


Figure S10. FTIR spectra of compounds 1-4. The left one is the wide spectra and the right one is the region-enlarged spectra for 2000-600 cm⁻¹.

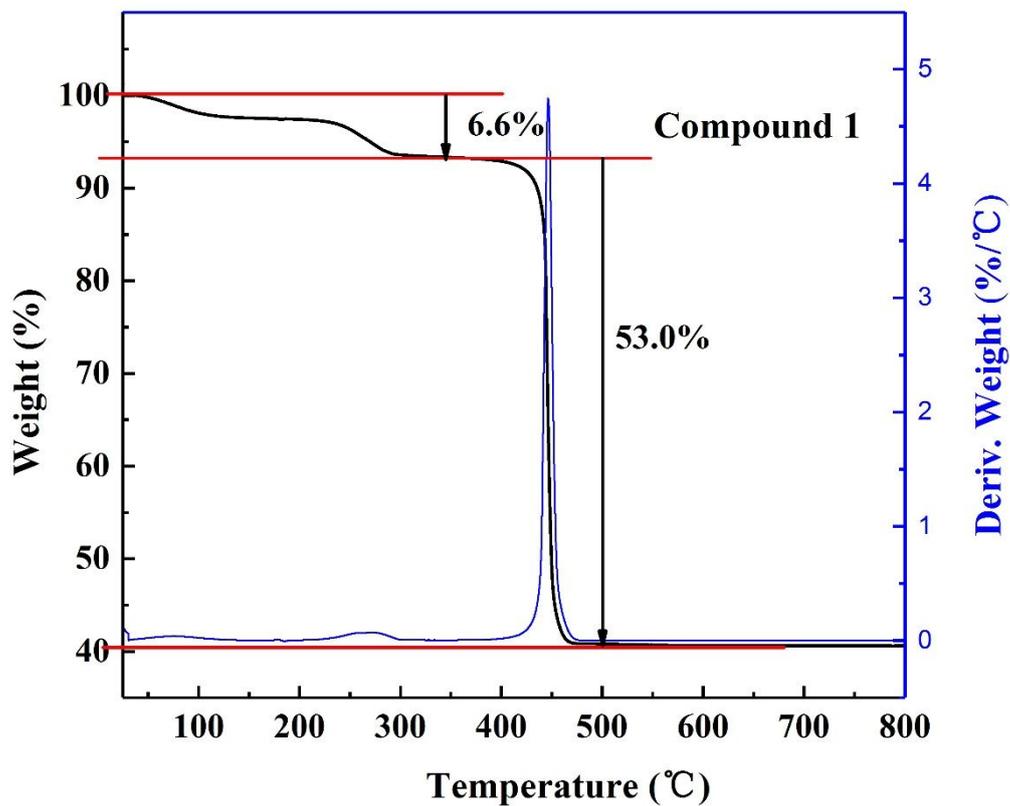


Figure S11. The TGA diagram of compound 1.

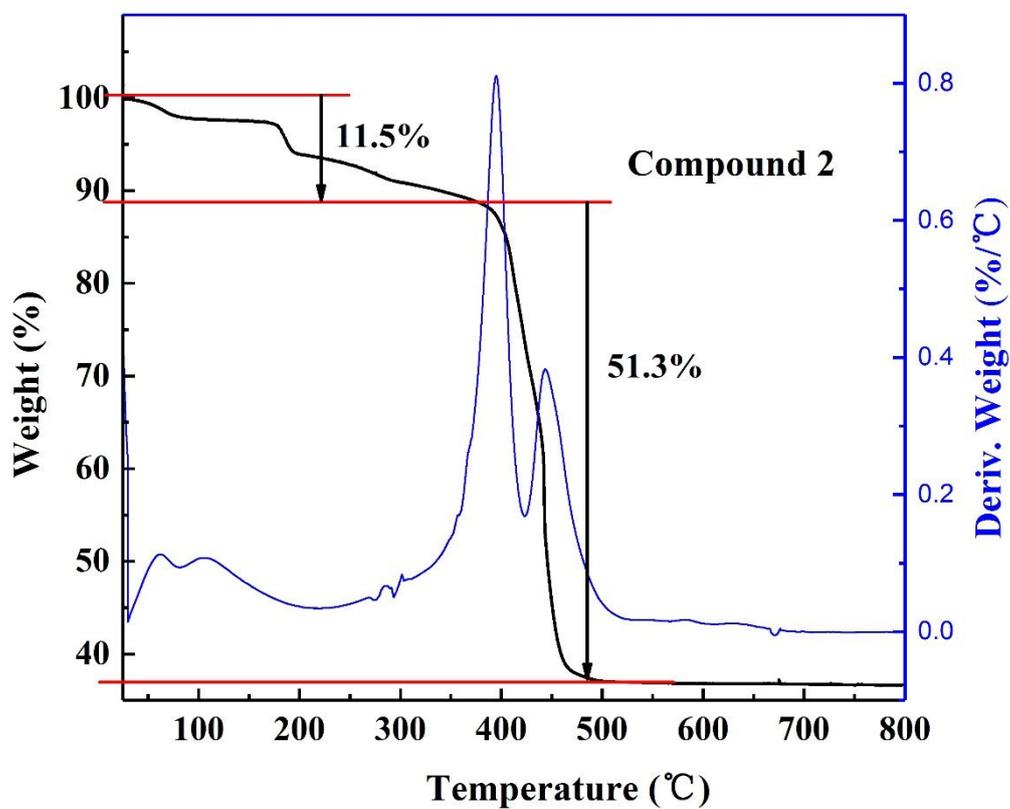


Figure S12. The TGA diagram of compound 2.

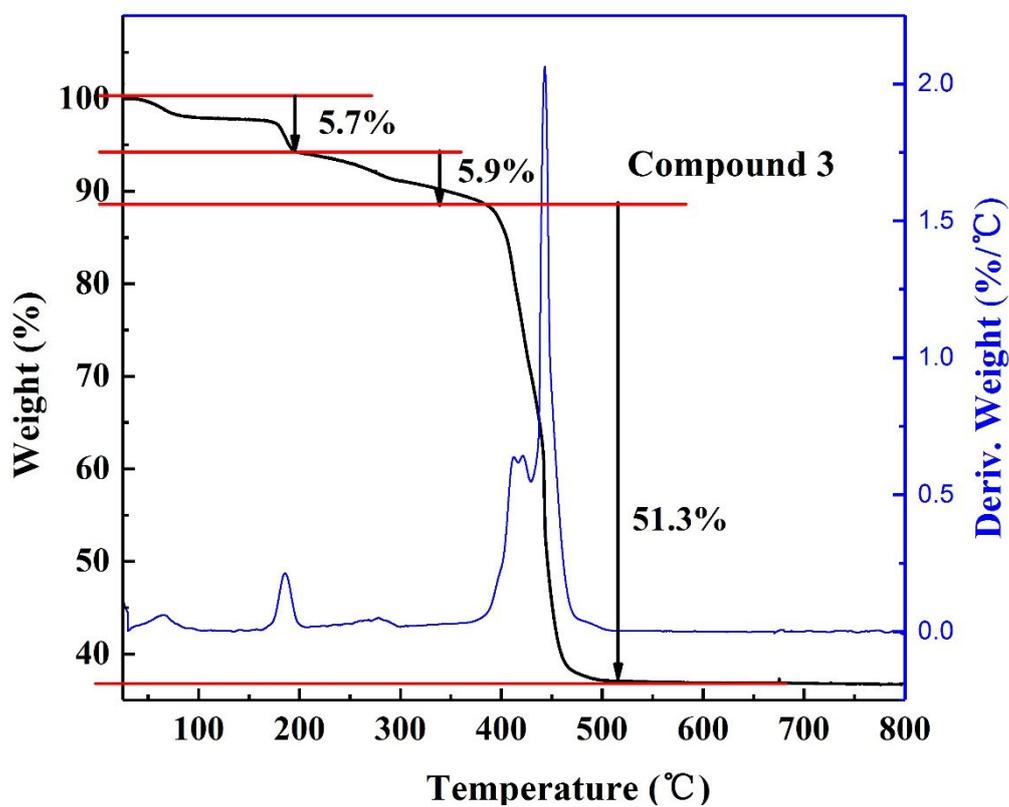


Figure S13. The TGA diagram of compound 3.

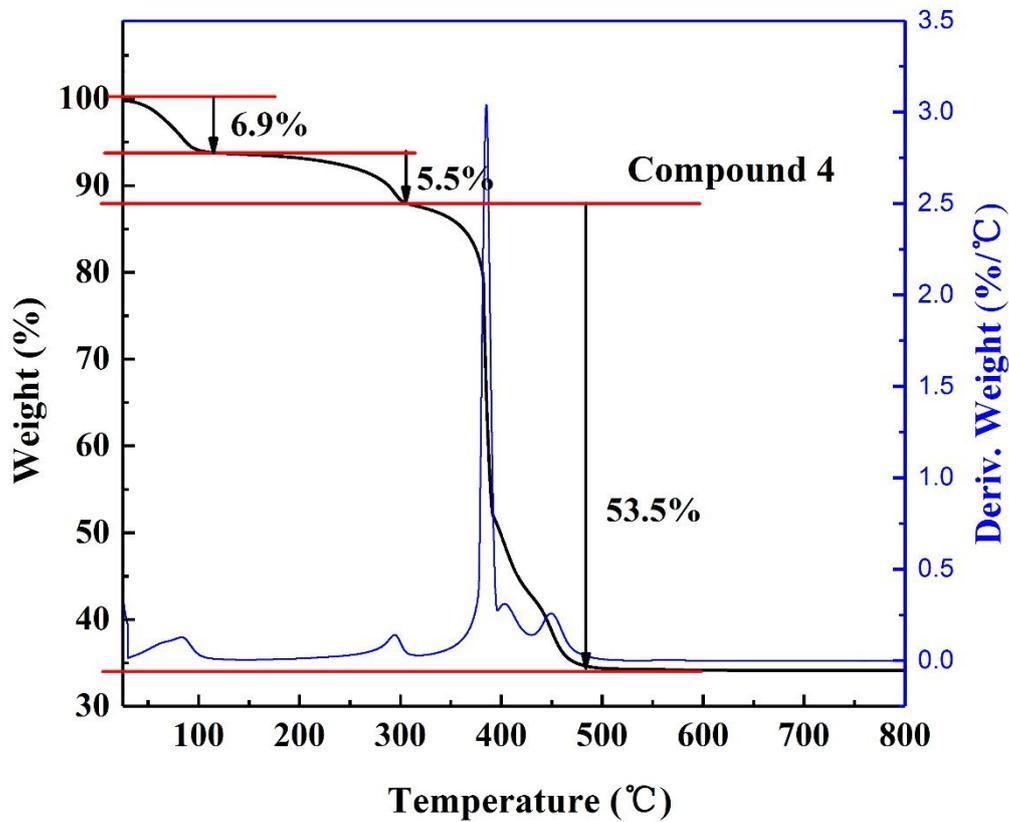


Figure S14. The TGA diagram of compound 4.

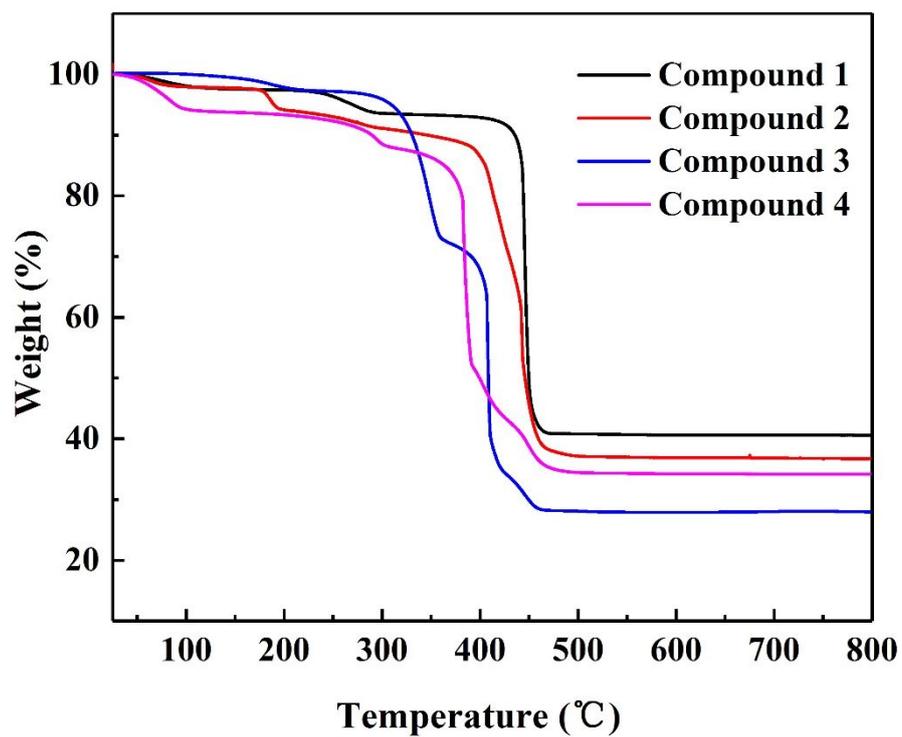


Figure S15. TGA results for compounds 1-4.

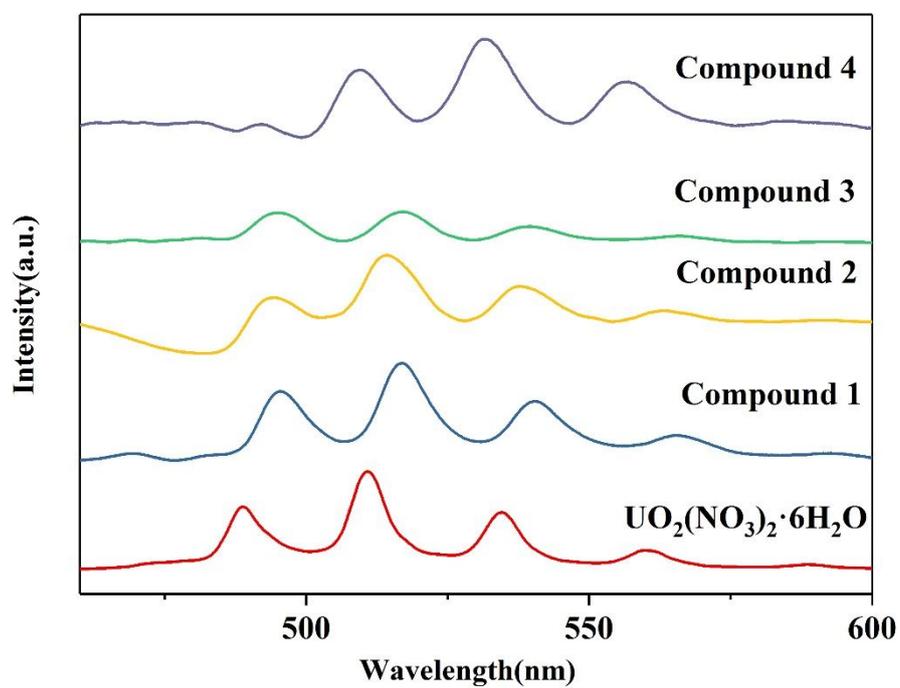


Figure S16. Fluorescence spectra of compounds 1-4 and uranyl nitrate.

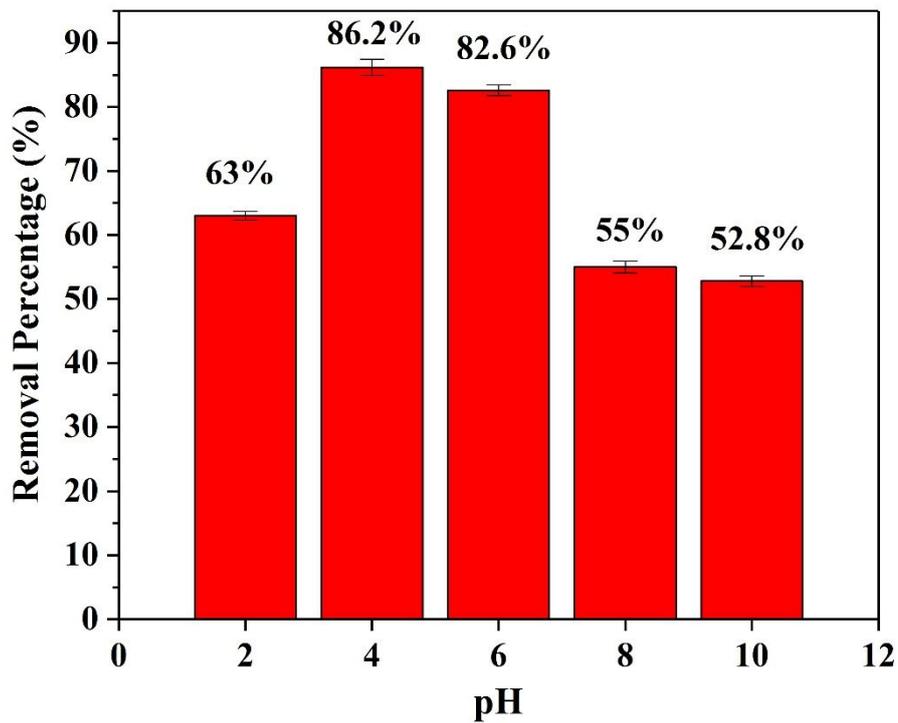


Figure S17. Effect of pH on the removal percentage of $10\text{mg L}^{-1} \text{ReO}_4^-$ ($T = 300\text{ K}$, $t = 12\text{ h}$, $m/V = 0.5\text{g L}^{-1}$).

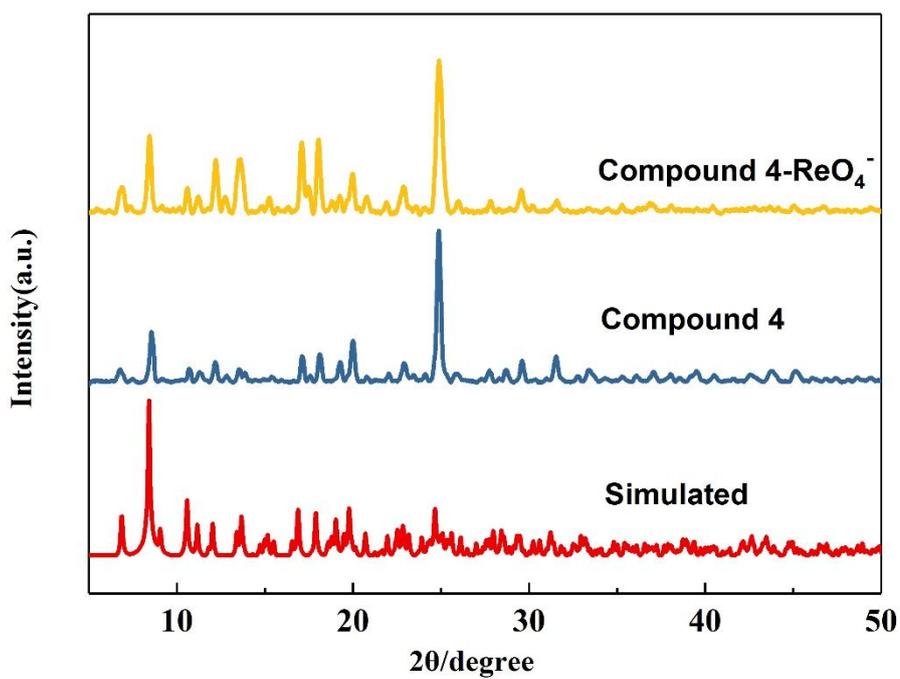


Figure S18. PXRD patterns before ReO_4^- sorption and after ReO_4^- sorption.

Table S1. Selected bond distances (Å) and bond angles (°) related to uranyl centers in Compound 1-5.

Compound 1			
U(1)-O(1)	1.7539(34)	U(1)-O(5)	2.2680(45)
U(1)-O(2)	1.7738(34)	U(1)-O(6)	2.3315(35)
U(1)-O(3)	2.4770(32)	U(1)-O(7)	2.3328(33)
U(1)-O(4)	2.4717(35)	U(1)-U(2)	5.8631(8)
O(1)-U(1)-O(2)	178.09(17)°		

Compound 2			
U(1)-O(1)	1.7630(22)	U(1)-O(5)	2.3333(19)
U(1)-O(2)	1.7622(23)	U(1)-O(6)	2.3798(20)
U(1)-O(3)	2.4469(21)	U(1)-O(7)	2.3240(17)
U(1)-O(4)	2.4607(23)	U(1)-U(2)	5.0252(7)
O(1)-U(1)-O(2)	178.804(97)		

Compound 3			
U(1)-O(1)	1.7600(24)	U(1)-O(5)	2.2685(23)
U(1)-O(2)	1.7627(24)	U(1)-O(6)	2.3293(25)
U(1)-O(3)	2.4402(25)	U(1)-O(7)	2.4578(30)
U(1)-O(4)	2.4820(25)		
O(1)-U(1)-O(2)	177.660(108)		

Compound 4			
U(1)-O(1)	1.8819(89)	U(1)-O(7)	2.4578(30)
U(1)-O(2)	1.8289(104)	U(1)-O(7A)	2.4402(25)
U(1)-O(3)	2.3311(99)	U(1)-O(8)	2.4820(25)
U(1)-O(5)	2.3292(25)	U(1)-U(2)	3.8995(6)
O(1)-U(1)-O(2)	177.660(108)		

Compound 5			
U(1)-O(1)	1.7605(94)	U(1)-O(5)	2.3501(107)
U(1)-O(2)	1.7723(96)	U(1)-O(6)	2.3564(109)
U(1)-O(3)	2.5225(127)	U(1)-Cl(1)	2.6903(57)
U(1)-O(4)	2.4067(132)	U(1)-U(2)	5.1184(10)
O(1)-U(1)-O(2)	177.566(481)		