## Temperature-induced Reversible Single-Crystal-to-Single-Crystal Isomerisation of Uranyl Polyrotaxane: An Exquisite Case of Coordination Variability of Uranyl Center

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## **Supporting Information**

Table of contents

### S1. Synthesis, Characterization and Theoretical Computation

**General Methods** 

Synthesis

X-ray Single Crystal Structure Determination.

**Computational methods** 

## **S2.** Typical figures

**Fig. S1** The indistinguishable  $\eta^2$ -coordination and  $\eta^1$ -coordination at two equivalent sites around the seven-fold coordinated uranium center of  $\alpha$ -**UP** gives three possible coordinated patterns including six-fold (a), seven-fold (b), and eight-fold (c) coordination. Due to the  $\eta^2$ -coordinated and  $\eta^1$ -coordinated carboxyl group taking fifty percent occupancy for two sites, respectively, the seven-fold coordinated pattern is the most probable in statistics (b in yellow block).

**Fig. S2** The corresponding snapshots of single-crystal samples in different phases during SCSC transformation, including α-UP(296K), α-UP(170K), α'-UP(170K), β-UP(320K) and β-UP(296K). **Fig. S3** Crystal structure of β-UP: a) the asymmetric unit with a monomeric uranyl center; b) six-fold coordination of uranyl coordination sphere with tetragonal-pyramid geometry; c) the 2D uranyl-organic rotaxane network with a minimum CB6-threaded square loop like a five-membered molecular necklace ([5]MN) with a minor variation in size compared to α-UP: two internal side lengths of 22.5106(22) and 20.1808(21) Å and an apical angle of 64.559(1)° for β-UP, and two internal side lengths of 22.628(1) Å and 20.958(1) Å and apical angle: 63.869(0)° for α-UP.

**Fig. S4** Close packing of 2D uranyl polyrotaxane sheets in  $\beta$ -**UP** (right) through widely distributed C-H•••O hydrogen bonding between cucurbituril macrocycles and uranyl motifs (left). Both the

cucurbituril macrocycles and uranyl motifs contribute to the hydrogen bonding network by interaction with functional groups of adjacent sheets from two different directions.

Fig. S5 IR spectra of  $\alpha$ -UP and  $\beta$ -UP in the range of 400-4000 cm<sup>-1</sup> revealing the difference in carboxylate coordination between them.

**Fig. S6** Crystal structure of  $\alpha$ '-**UP**: a) the asymmetric unit with a monomeric uranyl center; b) seven-fold coordination of uranyl coordination sphere with pentagonal-pyramid geometry; c) the 2D uranyl-organic rotaxane network with a minimum CB6-threaded square loop like a five-membered molecular necklace ([5]MN).

Fig. S7 PXRD patterns for  $\alpha$ -UP and  $\beta$ -UP. (SIM: simulated pattern based on crystal structure; EXP: experimental data)

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Fig. S9 Thermogravimetric results for  $\alpha$ -UP and  $\beta$ -UP.

Fig. S10 DSC curves of the  $\alpha$ -UP phase showing no change of thermal enthalpy throughout all the thermal circles.

Fig. S11 Decomposition process of  $\alpha$ -UP and analysis of decomposition product after being immersed in the water for 24 h: (a) dissolution kinetic curves at 55 °C (blue) and 25 °C (red) determined by the analysis of concentration of uranyl cation; (b) PXRD of decomposition product revealing it to be the C6BPCA@CB6 ligand;(c) Schematic diagram for the decomposition process. Fig. S12 The geometrical structures of two types of simplified fragments optimized using the hybrid exchange-correlation functional B3LYP method: (a) UO<sub>2</sub>(η<sup>1</sup>-L)<sub>3</sub>(η<sup>2</sup>-L) and UO<sub>2</sub>(η<sup>1</sup>-L)<sub>4</sub> (L: 1-methylpyridin-1-ium-4-carboxylate). The carbon atoms connected with carboxyl group of pyridine were fixed in the optimization to simulate the actual state in the crystal. It was found that the six-coordinated structure is higher 7.38 kcal/mol in energy compared to the seven-coordinated one, suggesting that the seven coordinated structure is more stable, which is in agreement with the experimental observation. (b) UO<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>(η<sup>2</sup>-L) and UO<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>(η<sup>1</sup>-L) (L: 1-methylpyridin-1-ium-4-carboxylate). The relative energy of the former structure is higher 6.25 kcal/mol than that of latter structures, which also indicate that the bi-dentate carboxyl group is favor with coordinated mode.

Fig. S13 Twisted conformation of  $\eta^2$ -carboxyl group in  $\alpha\text{-}UP$  or  $\alpha^2\text{-}UP$ 

**Fig. S14** The large deflection angles of carboxyl against the uranyl axial direction  $(\Phi_1, \Phi_1, \Phi_2)$  or the pyridium ring  $(\Theta_1, \Theta_1, \Theta_2)$  for  $\alpha$ -UP,  $\alpha$ '-UP and  $\beta$ -UP.

**Fig. S15** A comparison between cell parameters of  $\alpha$ -UP,  $\alpha$ '-UP and  $\beta$ -UP: left shadow,  $\alpha$ -UP (296 K) and  $\beta$ -UP (320K); right shadow,  $\beta$ -UP (296 K),  $\alpha$ '-UP (170 K) and  $\alpha$ -UP (170 K).

**Fig. S16** Highly correlated isomeric structures between different isomers of uranyl polyrotaxanes ( $\alpha$ -UP and  $\beta$ -UP) ensured by the particular pseudorotaxane linker through multiple intermolecular weak interactions (hydrogen bond, ion-dipole and hydrophobic interactions).

#### S3. Tables

Table S1. Crystal data and refine details for the single crystal of  $\alpha$ -UP(296K),  $\alpha$ -UP(170K),  $\alpha'$ -UP(170K),  $\beta$ -UP(320K) and  $\beta$ -UP(296K).

**Table S2.** Selected bond distances (Å) related to uranyl centers and distances (Å) for hydrogen bonds observed in uranyl compounds  $\alpha$ -UP(296K),  $\alpha$ -UP(170K),  $\alpha$ '-UP(170K),  $\beta$ -UP(320K) and  $\beta$ -UP(296K).

Table S3. Bond lengths and angles of the optimized structures of  $UO_2(\eta^1-L)_3(\eta^2-L)$  and  $UO_2(\eta^1-L)_3(\eta^2-L)$ 

L)<sub>4</sub> (L: 1-methylpyridin-1-ium-4-carboxylate) from quantum chemical computation compared with the corresponding experimental data of  $\alpha$ -UP and  $\beta$ -UP.

#### S1. Synthesis, Characterization and Theoretical Computation

#### **General Methods**

Caution! Precautions with suitable care and protection for handling uranyl nitrate  $UO_2(NO_3)_2 \cdot 6H_2O$  should be followed, while natural uranium is a radioactive and chemically toxic reactant. 1,1'-(hexane-1,6-diyl)bis(4-(ethoxycarbonyl)pyridin-1-ium) bromide (**[C6BPCEt]Br**<sub>2</sub>) as well as cucurbit[6]uril (CB[6]) was synthesized according to refs.<sup>1</sup> The corresponding pseudorotaxane precursors **[C6BPCEt@CB6]Br**<sub>2</sub>, was synthesized according to the reported procedure previously.<sup>2</sup> Commercially purchased uranyl nitrate  $UO_2(NO_3)_2 \cdot 6H_2O$  (12.55g, 0.025mol) was dissolved in deionized water (50mL) to give 0.5 M uranyl nitrate solution. Other chemicals were commercially purchased and used without further purification.

Powder X-ray diffraction measurements (PXRD) were obtained with a Bruker D8 Advance diffractometer with Cu K $\alpha$  radiation ( $\lambda$ =1.5406 Å) in the range 5-70° (step size: 0.02°). Thermogravimetric analysis (TGA) was recorded from a TA Q500 analyzer over the temperature range of 25-800 °C in air atmosphere with a heating rate of 5 °C /min. The differential scanning calorimetry (DSC) measurement was performed on a TA Q2000 DSC analyzer at the rate of 5 °C min<sup>-1</sup> in N<sub>2</sub> flow and cycled as followed procedures (R.T. to -80 °C; -80 to 50 °C; 50 °C to -80 °C; -80 °C to 50 °C; 50 °C to R.T.). The Fourier transform infrared (IR) spectra were performed on KBr pellets in the range of 4000-400 cm<sup>-1</sup> on at Bruker Tensor 27 spectrometer. Solid-state fluorescence spectra were measured on a Hitachi F-4600 fluorescence spectrophotometer.

#### Synthesis.

 $\alpha$ -UP: 0.5 M uranyl nitrate solution (70 µL, 0.035 mmol) were added to a suspension of the pseudorotaxane ligand of **[C6BPCEt@CB6]Br<sub>2</sub>** (0.052 g, 0.035 mmol) in water (2 mL) in a stainless-steel bomb. After treating with HNO<sub>3</sub> (40 µL, 0.16 mmol) to adjust the initial pH to about 1.30, the bomb was sealed, kept at 150 °C for 48 h and gradually cooled to room temperature. The resulting product showing a pale yellow prismatic crystallites, namely as  $\alpha$ -UP, was then filtered off, washed with water, and dried at room temperature. The final pH of the reaction mixture was 2.7.

 $\beta$ -UP: The new  $\beta$ -UP phase was found after raising the initial temperature (296 K) of  $\alpha$ -UP up

to above 320K at the ramp rate of 360 K/h, while a considerable amount of solid sample of  $\beta$ -UP was prepared by incubating crystals of  $\alpha$ -UP at 120 °C in an oven for 90 min, followed by fast cooling to ~30 °C (303 K).

Phase transition between  $\alpha$ -UP and  $\beta$ -UP: The initial single crystal of  $\alpha$ -UP was mounted on the loop at 296 K, then a set of variable-temperature conducted by raising or lowering the temperature at the ramp rate of 360 K/h by a cryogenic system: route A,  $\alpha$ -UP (296K)  $\Rightarrow \beta$ -UP (320K); route B1,  $\beta$ -UP (320K)  $\Rightarrow \beta$ -UP (296K); route B2,  $\beta$ -UP (296K)  $\Rightarrow \beta$ -UP (300K); route C,  $\beta$ -UP (296K)  $\Rightarrow \alpha$ -UP (296K); route D1,  $\beta$ -UP (296K)  $\Rightarrow \alpha$ '-UP (170K); route D2,  $\alpha$ '-UP (170K) $\Box \beta$ -UP (296K); route E,  $\alpha$ '-UP (170K)  $\Rightarrow \alpha$ -UP (170K); route F,  $\alpha$ -UP (296K)  $\Rightarrow \alpha$ -UP (170K); route G,  $\alpha$ -UP (170K)  $\Rightarrow \beta$ -UP (296K). In order to complete all the transition processes, many repeating experiments are needed and the identical procedure was applied.

Additionally, when being placed in air atmosphere at room temperature for 2 days, the crystal of  $\beta$ -UP at 296K transformed into  $\alpha$ -UP (route C,  $\beta$ -UP (296K)  $\rightarrow \alpha$ -UP (296K)).

#### X-ray Single Crystal Structure Determination.

Single crystals suitable for X-ray single crystal structure determination isolated from each bulk sample were mounted on micromounts. For all the compounds here, X-ray diffraction data of each compound was performed on Bruker D8 VENTURE X-ray diffractometer equipped with a Photon CMOS detector using a Mo K $\alpha$  X-ray source ( $\lambda = 0.71073$  Å) in different temperature. All data was integrated using the SAINT software package, and an absorption correction was applied using SADABS. All the crystal structures were solved by means of direct methods (SHELXS-97) and refined with full-matrix least squares on SHELXL-2014 within APEX III software package.<sup>3-4</sup> The aromatic and hydroxyl hydrogen atoms were placed in calculated, ideal positions and refined as riding on their respective carbon or oxygen atoms. For  $\alpha$ -UP(296K),  $\alpha$ -UP(170K) and  $\alpha$ '-UP(170K), PLATON/SQUEEZE<sup>5-6</sup> was employed to calculate the diffraction contribution of the solvent water molecules and, thereby, to afford a new set of solvent-free diffraction intensities because the unit cell for each compound includes a large region of disordered solvent water molecules, which could not be modeled as discrete atomic sites. The crystal data of all these four compounds are given in Table S1. Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos.

# CCDC-1534039 (α-UP(296K)), CCDC-1534040 (α-UP(170K)), CCDC-1534042 (α'-UP(170K)), CCDC-1534043 (β-UP(320K)), and CCDC-1534046 (β-UP (296K)).

#### **Computational methods**

To insight into the nature of the different coordination of uranyl ions with ligands, the two types of simplified coordinated structures cut from the crystal, six and seven coordination, were considered using the quasi-relativistic density functional theory. The geometrical structures of the complexes were optimized using the hybrid exchange-correlation functional B3LYP method<sup>7-8</sup> with the Gaussian 09 program.<sup>9</sup> The relativistic effects were taken into account by using the quasi-relativistic effective core potentials (RECPs), which substitute 60 core electrons for U atom<sup>10-11</sup> without considering spin-orbit coupling effects. The corresponding ECP60MWB-SEG valence basis sets were used to describe U atom<sup>11-12</sup>, respectively. As for other light atoms including O, N, C and H, the 6-31G\* basis set was applied. The structural optimizations were carried out in the gas phase at the B3LYP/6-31G\*/RECP level of theory.

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## S2. Typical figures



Fig. S1 The indistinguishable  $\eta^2$ -coordination and  $\eta^1$ -coordination at two equivalent sites around the seven-fold coordinated uranium center of  $\alpha$ -UP gives three possible coordinated patterns including six-fold (a), seven-fold (b), and eight-fold (c) coordination. Due to the  $\eta^2$ -coordinated and  $\eta^1$ -coordinated carboxyl group taking fifty percent occupancy for two sites, respectively, the seven-fold coordinated pattern is the most probable in statistics (b in yellow block).



**Fig. S2** The corresponding snapshots of single-crystal samples in different phases during SCSC transformation, including  $\alpha$ -UP(296K),  $\alpha$ -UP(170K),  $\alpha$ '-UP(170K),  $\beta$ -UP(320K) and  $\beta$ -UP(296K).



**Fig. S3** Crystal structure of  $\beta$ -UP: a) the asymmetric unit with a monomeric uranyl center; b) six-fold coordination of uranyl coordination sphere with tetragonal-pyramid geometry; c) the 2D uranyl-organic rotaxane network with a minimum CB6-threaded square loop like a five-membered molecular necklace ([5]MN) with a minor variation in size compared to  $\alpha$ -UP: two internal side lengths of 22.5106(22) and 20.1808(21) Å and an apical angle of 64.559(1)° for  $\beta$ -UP, and two internal side lengths of 22.628(1) Å and 20.958(1) Å and apical angle: 63.869(0)° for  $\alpha$ -UP.



**Fig. S4** Close packing of 2D uranyl polyrotaxane sheets in  $\beta$ -**UP** (right) through widely distributed C-H•••O hydrogen bonding between cucurbituril macrocycles and uranyl motifs (left). Both the cucurbituril macrocycles and uranyl motifs contribute to the hydrogen bonding network by interaction with functional groups of adjacent sheets from two different directions.



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Fig. S7 PXRD patterns for  $\alpha$ -UP and  $\beta$ -UP. (SIM: simulated pattern based on crystal structure; EXP: experimental data)



Fig. S8 Fluorescence spectra for  $\alpha$ -UP and  $\beta$ -UP, displaying similar quenching of fluorescence.



Fig. S9 Thermogravimetric results for  $\alpha$ -UP (left) and  $\beta$ -UP (right).



Fig. S10 DSC curves of the  $\alpha$ -UP phase showing no change of thermal enthalpy throughout all the thermal circles.



Fig. S11 Decomposition process of  $\alpha$ -UP and analysis of decomposition product after being immersed in the water: (a) dissolution kinetic curves at 55 °C (blue) and 25 °C (red) determined by the analysis of concentration of uranyl cation (enlarged kinetic curve for the first 24 h); (b) PXRD of decomposition product revealing it to be the C6BPCA@CB6 ligand;(c) Schematic diagram for the decomposition process.



**Fig. S12** The geometrical structures of two types of simplified fragments optimized using the hybrid exchange-correlation functional B3LYP method: (a)  $UO_2(\eta^1-L)_3(\eta^2-L)$  and  $UO_2(\eta^1-L)_4$  (L: 1-methylpyridin-1-ium-4-carboxylate). The carbon atoms connected with carboxyl group of pyridine were fixed in the optimization to simulate the actual state in the crystal. It was found that the six-coordinated structure is higher 7.38 kcal/mol in energy compared to the seven-coordinated one, suggesting that the seven coordinated structure is more stable, which is in agreement with the experimental observation. (b)  $UO_2(H_2O)_3(\eta^2-L)$  and  $UO_2(H_2O)_3(\eta^1-L)$  (L: 1-methylpyridin-1-ium-4-carboxylate). The relative energy of the former structure is higher 6.25 kcal/mol than that of latter structures, which also indicate that the bi-dentate carboxyl group is favor with coordinated mode.



Fig. S13 Twisted conformation of  $\eta^2$ -carboxyl group in  $\alpha$ -UP or  $\alpha'$ -UP



 $\Theta_1$ : angle between C1 and Ax;  $\Theta_1$ : angle between C1' and Ax;  $\Theta_2$ : angle between C2 and Ax.  $\Phi_1$ : dihedral angle between C1 and Py1;  $\Phi_1$ ': dihedral angle between C1' and Py1;  $\Phi_2$ : dihedral angle between C2 and Py2.

	e	)/°			Ф/°	
	b	$\Theta_1$	73.5(1)	2 0	Φ <sub>1</sub>	3.5(1)
α- <b>UP</b>	ortho	Θ <sub>1</sub> ,	4.8(8)	8	$\Phi_{1'}$	81.7(7)
		$\Theta_2$	25.3(2)	the	Φ <sub>2</sub>	9.6(3)
		$\Theta_1$	90.0(1)	e 1	Φ <sub>1</sub>	14.0(2)
α'- <b>UP</b>	000	$\Theta_{1}$	19.4(1)	8	Φ <sub>1</sub> ,	66.3(9)
		Θ <sub>2</sub>	24.1(8)		Φ <sub>2</sub>	28.4(5)
β- <b>UP</b>	Dr. A	Θ1	57.7(3)		Φ <sub>1</sub>	6.2(5)
		$\Theta_2$	37.5(3)	X	Φ <sub>2</sub>	8.7(4)

**Fig. S14** The large deflection angles of carboxyl against the uranyl axial direction  $(\Phi_1, \Phi_1, \Phi_2)$  or the pyridium ring  $(\Theta_1, \Theta_1, \Theta_2)$  for  $\alpha$ -UP,  $\alpha$ '-UP and  $\beta$ -UP.



Fig. S15 A comparison between cell parameters of  $\alpha$ -UP,  $\alpha$ '-UP and  $\beta$ -UP: left shadow area,  $\alpha$ -UP (296 K) and  $\beta$ -UP (320K); right shadow area,  $\beta$ -UP (296 K),  $\alpha$ '-UP (170 K) and  $\alpha$ -UP (170 K).



**Fig. S16** Highly correlated isomeric structures between different isomers of uranyl polyrotaxanes ( $\alpha$ -UP and  $\beta$ -UP) ensured by the particular pseudorotaxane linker through multiple intermolecular weak interactions (hydrogen bond, ion-dipole and hydrophobic interactions).

## S3. Tables

	α-UP	α-UP	α'-UP	β-UP	β-UP	
Т, К	296	170	170	320	296	
Formula	$C_{108}H_{112}Br_2N_{52}O_3$	$C_{108}H_{112}Br_2N_{52}O_3$	$C_{108}H_{112}Br_2N_{52}O_3$	$C_{108}H_{112}Br_2N_{52}O_3$	$C_{108}H_{112}Br_2N_{52}O_3$	
	<sub>4</sub> U					
Formula	2080.22	2080.22	2080.22	22 2000.22	2080 22	
weight	3080.33	3080.33	3080.33	3080.33	5080.55	
Crystal	trialinia	trialinia	trialinia	trialinia	trialinia	
system	unenine	utennic	utennie	unennine	ulennie	
Space	רמ	רמ	רמ	רמ	רמ	
group	<i>P</i> 1					
a, Å	12.7767(13)	12.6201(4)	12.6946(10)	12.8248(15)	12.7846(5)	
b, Å	15.3536(16)	15.5773(6)	14.7727(11)	14.8362(16)	14.7915(6)	
c, Å	17.0453(16)	17.0824(6)	17.0721(12)	17.044(2)	17.0792(7)	
α, deg	90.559(5)	89.556(2)	90.387(3)	91.439(5)	91.261(2)	
β, deg	97.590(5)	81.972(2)	98.122(4)	96.887(6)	97.291(2)	
γ, deg	94.644(5)	84.793(2)	94.716(4)	93.574(5)	93.699(2)	
V, Å <sup>3</sup>	3302.9(6)	3311.5(2)	3158.2(4)	3211.6(6)	3195.5(2)	
Z	1	1	1	1	1	
F(000)	1558.0	1558.0	1558.0	1558.0	1558.0	
Dx,	1.540	1 5 4 5	1.620	1 502	1 601	
g/cm <sup>3</sup>	1.349	1.343	1.020	1.393	1.001	
μ (mm <sup>-1</sup> )	1.930	1.925	2.018	1.985	1.995	
R <sub>int</sub>	0.0484	0.0466	0.0585	0.0437	0.0390	
R <sub>1</sub> , wR <sub>2</sub> (all data)	0.0507, 0.1438	0.0739, 0.2178	0.0973, 0.2472	0.0468, 0.1357	0.0573, 0.1683	

**Table S1.** Crystal data and refine details for the single crystal of  $\alpha$ -UP(296K),  $\alpha$ -UP(170K),  $\alpha'$ -UP(170K),  $\beta$ -UP(320K) and  $\beta$ -UP(296K).

Compound	bond type	bond length (Å)	bond type	bond length (Å)
α-UP (296K)	U1-01	1.727(4)	U1-O2	2.253(4)
	U1-O4	2.595(10)	U1-05	2.653(9)
	U1-O6	2.231(7)	С43-Н43…О3	2.663
	C42-H42A…O3	2.314	C44-H44…O1	2.314
α-UP(170K)	U1-O1	1.763(4)	U1-O2	2.268(5)
	U1-O4	2.658(9)	U1-O5	2.651(9)
	U1-O6	2.250(9)	С26-Н26…О1	2.362
	С25-Н25…ОЗ	2.639	С27-Н01Q…О3	2.263
α'-UP	U1-O1	1.739(10)	U1-O2	2.241(8)
(170K)	U1-O4	2.593(17)	U1-O5	2.681(15)
	U1-O6	2.289(14)	C54-H54…O1	2.428
	С55-Н55…О2	2.516	С3-Н3…О4	2.523
	С3-Н3…О4	2.946		
β-UP (320K)	U1-O1	1.756(3)	U1-O2	2.306(3)
	U1-O4	2.273(3)	C47-H47…O1	2.457
	С12-Н12…О3	2.836	С55-Н55…О1	2.511
	С50-Н50А…О5	2.313	С55-Н55…О5	2.911
β-UP (296K)	U1-O1	1.758(4)	U1-O2	2.269(4)
	U1-O4	2.301(3)	С32-Н32…О1	2.428
	С33-Н33…О3	2.877	С35-Н35В…О3	2.301
	С6-Н6…О5	2.840		

**Table S2.** Selected bond distances (Å) related to uranyl centers and distances (Å) for hydrogen bonds observed in uranyl compounds  $\alpha$ -UP(296K),  $\alpha$ -UP(170K),  $\alpha$ '-UP(170K),  $\beta$ -UP(320K) and  $\beta$ -UP(296K).

	$UO_2(\eta^1-L)_3(\eta^2-L)$ vs $\alpha$ -UP		$UO_2(\eta^1-L)_4 \text{ vs } \beta-UP$	
	Calculated	Experimental	Calculated	Experimental
U=O	1.770	1.780	1.772	1.758
	1.772	1.783	1.772	1.758
U-O	2.313	2.252	2.324	2.269
	2.343	2.252	2.324	2.269
	2.340	2.230	2.322	2.300
	2.473	2.623	2.322	2.300
	2.797	2.652		
O=U=O	180.0	177.5	180.0	180.0

**Table S3.** Bond lengths and angles of the optimized structures of  $UO_2(\eta^1-L)_3(\eta^2-L)$  and  $UO_2(\eta^1-L)_4$  (L: 1-methylpyridin-1-ium-4-carboxylate) from quantum chemical computation compared with the corresponding experimental data of  $\alpha$ -UP and  $\beta$ -UP.