Supporting Information for

Atypical Temperature-Dependence of Symmetry Transformation Observed in a Uranyl Phosphonate

Tao Zheng,[a, b] Yang Gao,[a, b] Daxiang Gui,[a, b] Lanhua Chen,[a, b] Daopeng Sheng,[a, b] Juan Diwu,* [a, b] Zhifang Chai,[a, b] Thomas E. Albrecht-Schmitt,[c] and Shuao Wang*[a,b]

[a]School for Radiological and Interdisciplinary Sciences (RAD-X), Soochow University, Jiangsu 215123, China

[b]Collaborative Innovation Center of Radiation Medicine of Jiangsu Higher Education Institutions, Jiangsu 215123, China

[c]Department of Chemistry and Biochemistry, Florida State University, 95 Chieftain Way, Tallahassee, Florida 32306, United States).

Caution! *As uranium compounds used in these experiments contains depleted uranium, handling radioactive materials should be performed carefully, and all experiments must be conducted in a laboratory authorized to study chemistry of actinide elements.*

Materials: All chemicals used in this work were obtained from commercial sources (J&K Chemical, Sinopharm Chemical Reagent and Alfa Aesar) and used without further purification. The ligand of 1,3-pbpH_4 was synthesized following the literature.[1]

Crystallographic Studies. Single Crystals of compound **1** was mounted on Cryoloops with paratone oil and optically aligned on a D8-Venture (Bruker) single crystal X-ray diffractometer equipped with a high-resolution digital camera. The diffraction data were collected using a CMOS area detector at variable temperature with a Turbo X-ray Source (Mo–Kα radiation, $\lambda = 0.71073$ Å, 50kV/50mA power). The data was reduced by SAINT package (Bruker) and the structures of all temperature were solved by the direct method and refined on F^2 by full–matrix least–squares methods using SHELXTL[2] (2014 version) and all the non–hydrogen atoms were refined anisotropically, and hydrogen atoms were put in the positon by calculation.

Absorption, Fluorescence, and Infrared Spectroscopy. UV-vis absorption and fluorescence spectroscopy were measured on single crystals of compound **1** from 200 to 800 nm at variable temperature, using the Craic Technologies microspectrophotometer. The room temperature infrared spectra were measured (4000-400 cm^{-1}) on a Nicolet spectrophotometer in ATR mode.

Thermal Stability. Thermogravimetric analysis was performed on a NETZSCH STA 449F3 instrument in the range of 30–900 °C under a nitrogen flow with a heating rate of 10 °C/ min for compound 1. The result shows that compound 1 began to collapse at 400 ^{o}C.

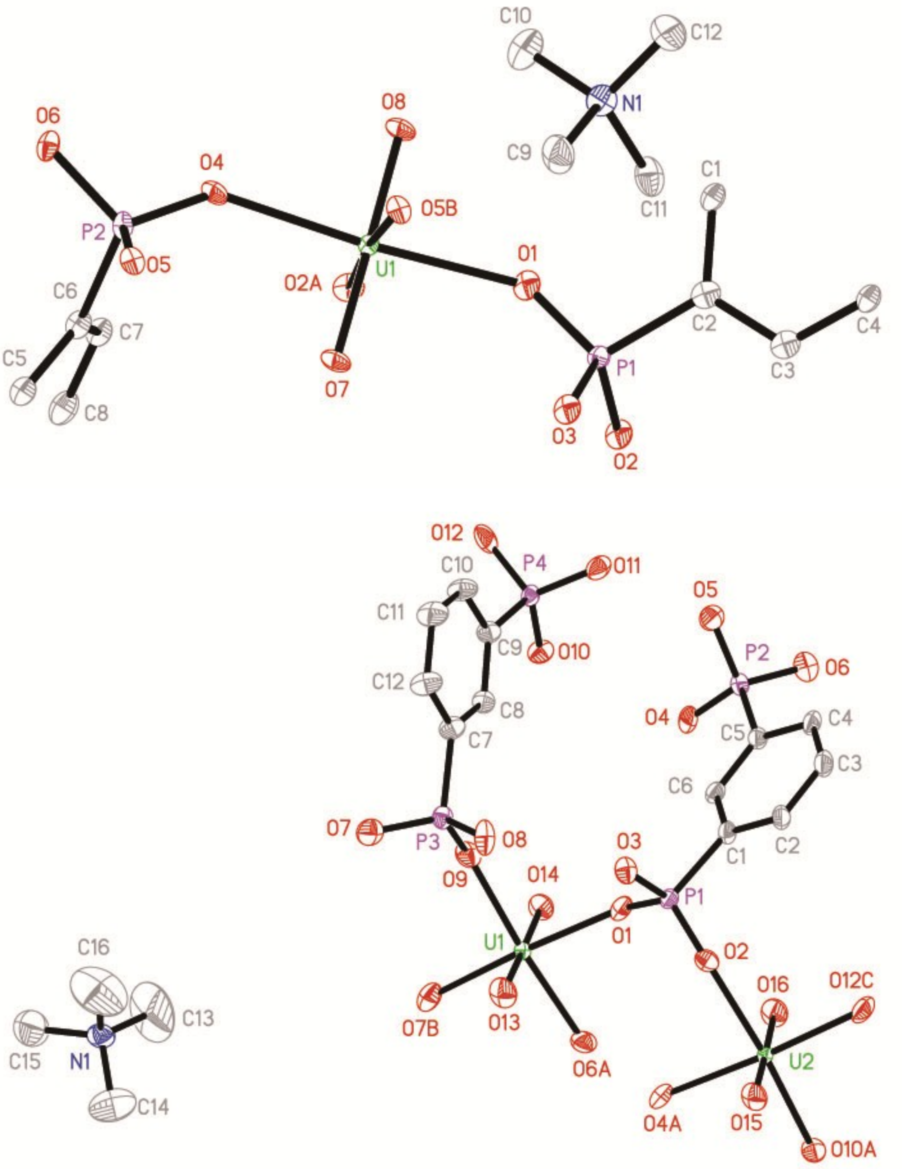


Fig. S1. Building unit of compound **1-98K** and **1-298K** with atomic labelling scheme at 50% probability, with all hydrogen atoms omitted for clarity.

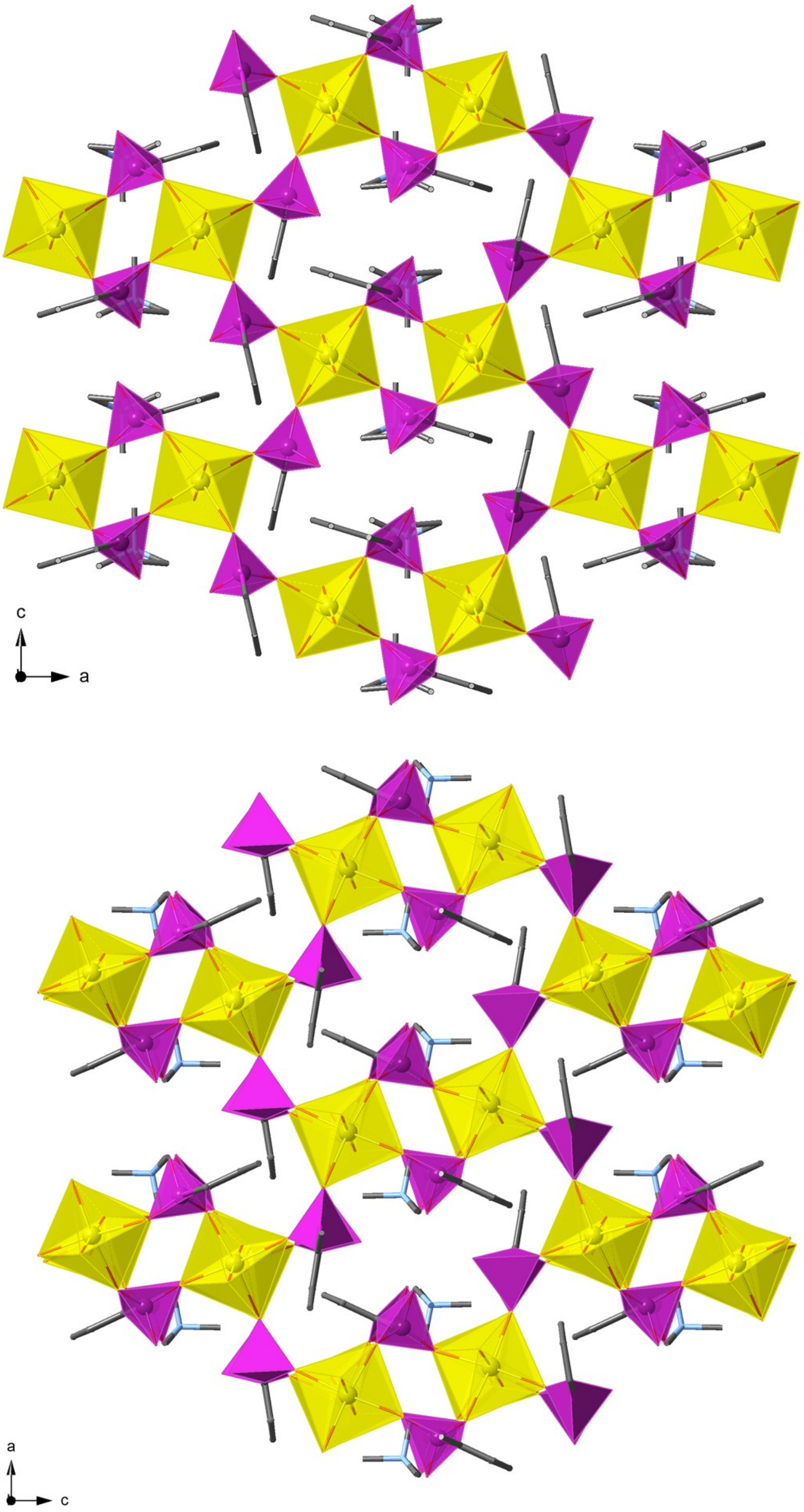


Fig. S2. Layered structure of **1-98K** (up) and **1-298K** (bottom).

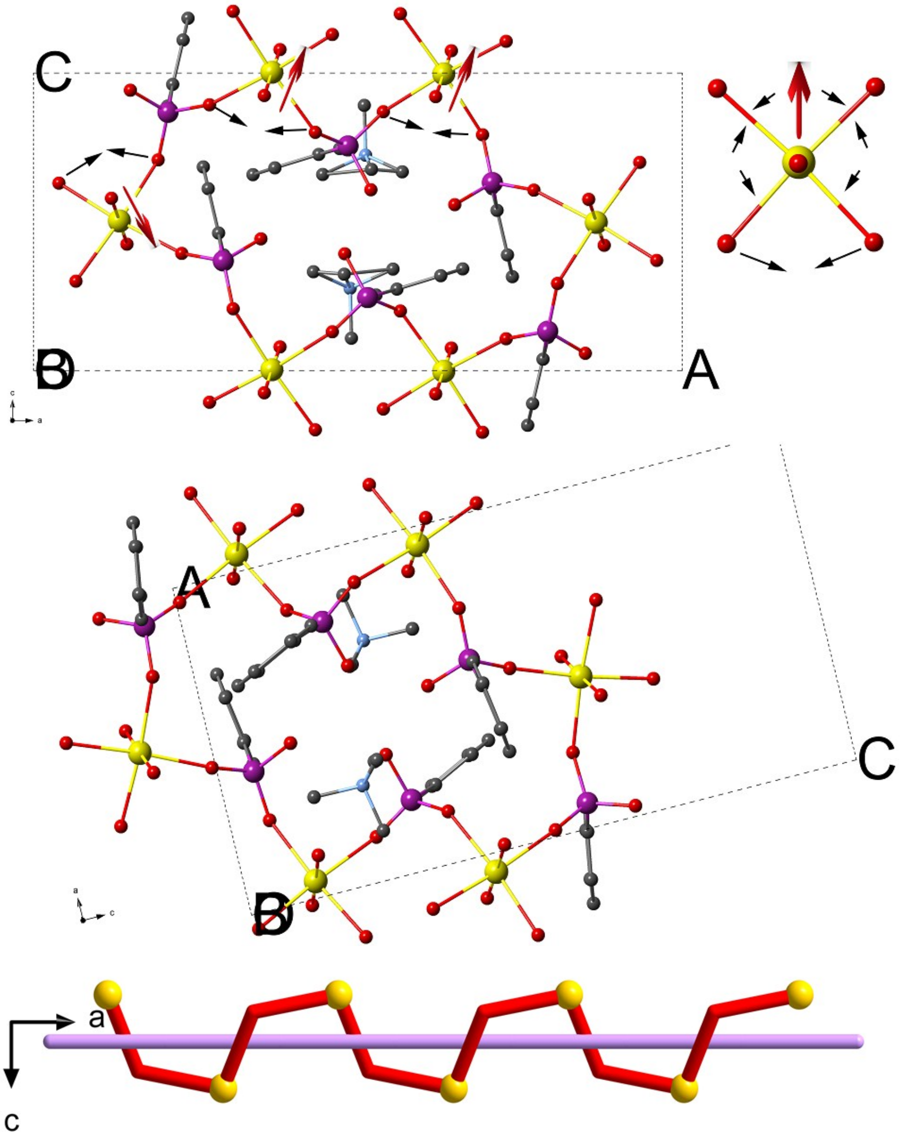


Fig. S3. Comparison of structures of **1-98K** and **1-298K** in *ac* plane and a chiral 2_1 screw axis along *a* direction in the structure of **1-298K**. The upper right figure shows the changes of O-U-O angles.

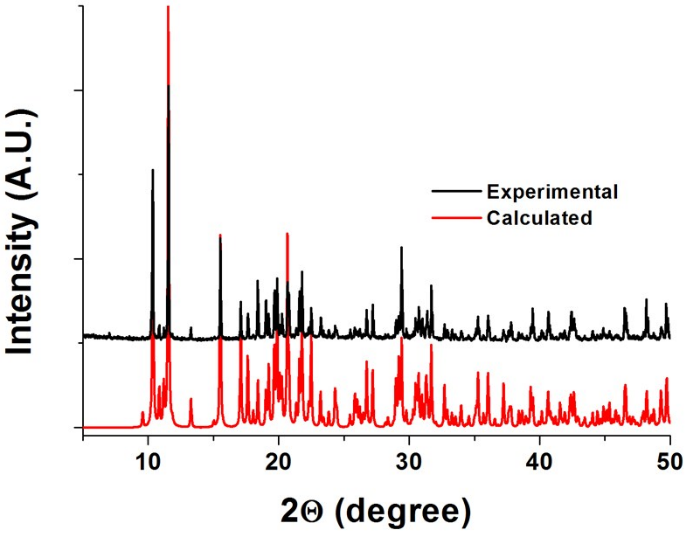


Fig. S4 PXRD pattern of compound **1-298K** at room temperature.

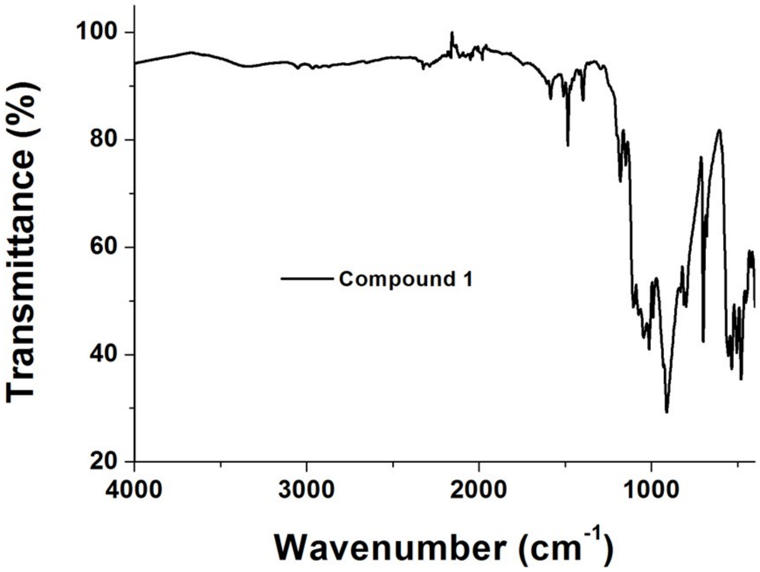


Fig. S5 IR spectrum of compound **1** at room temperature.

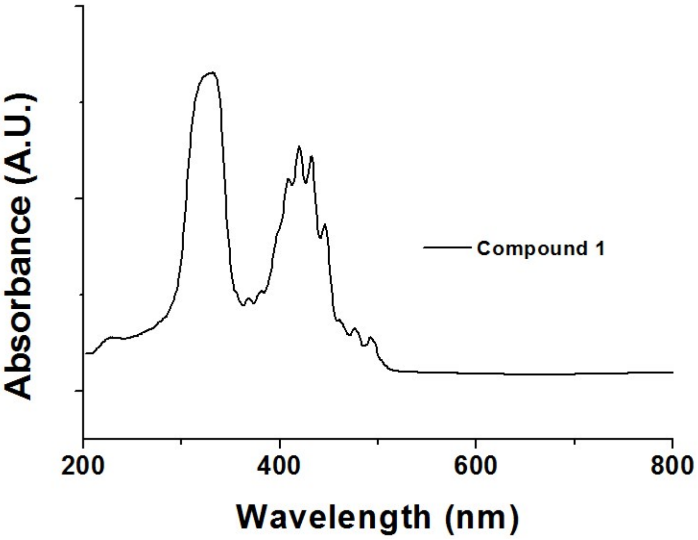
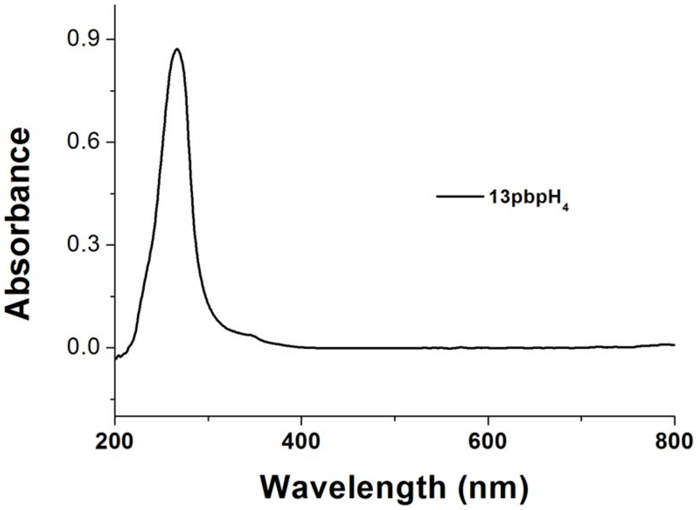


Fig. S6 Uv-vis spectrum of compound **1** at room temperature.



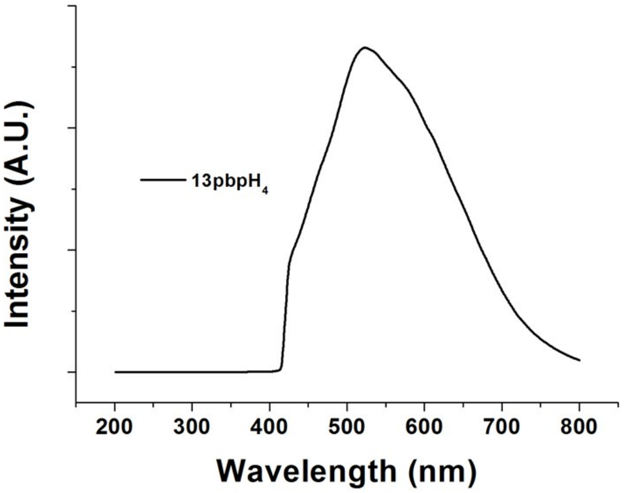


Fig. S7 UV-vis (top) absorption and fluorescence (bottom) spectra of 1,3-pbpH_4.

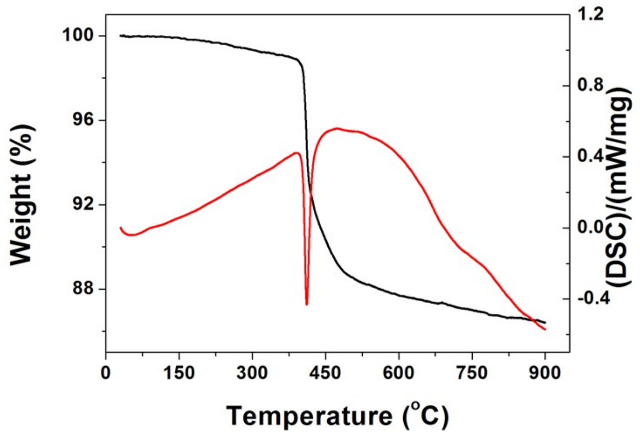


Fig. S8 TG (black) and DSC (red) curves of compound **1**.

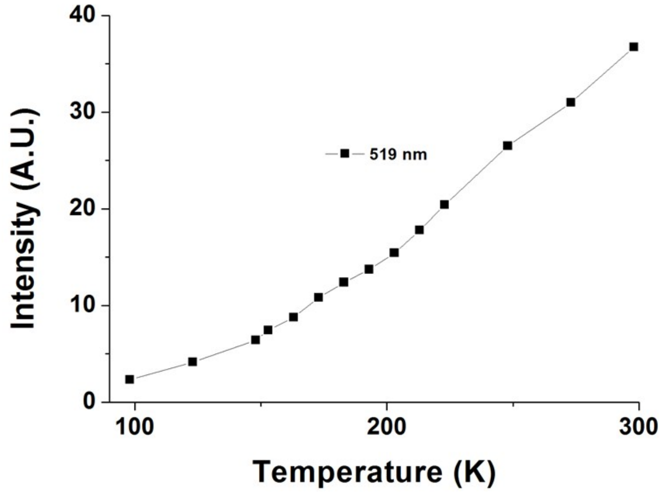


Fig. S9 The curve of intensity vs. temperature at 519 nm that can be assigned to ligand based emission in the temperature dependent photoluminescence spectra of Compound **1**.

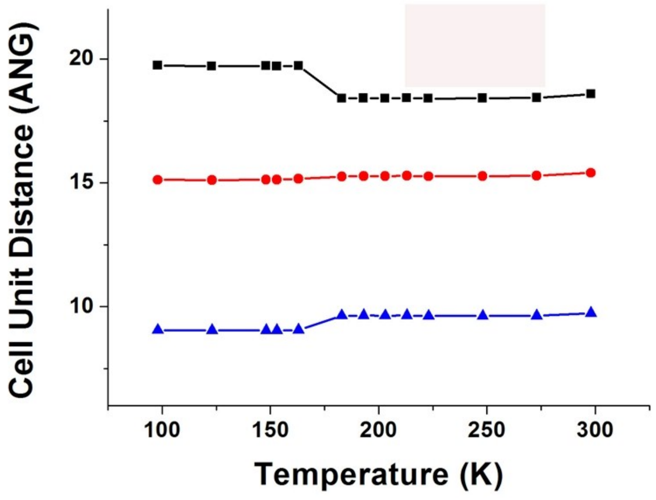


Fig. S10 Cell parameters of compound **1** at different temperature.

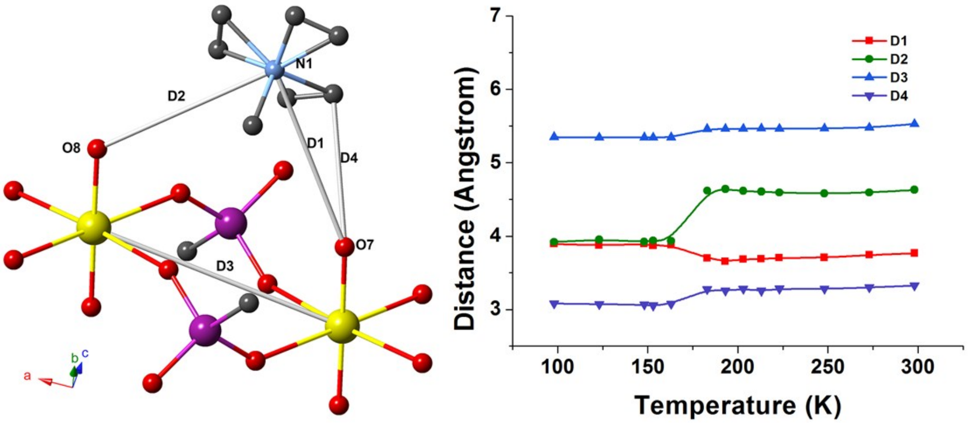


Fig. S11. The pattern of selected distances *v.s* temperature. (Inset: D1 is the distance between N1 and O7, D2 is the distance between N1 and O8, D3 is the distance of two uranium atoms bridging by two phosphonate groups, D4 is the nearest distance between O7 and the carbon atom from tetramethylammonium.)

Table S1. Crystal Data and Refinement Details for **1** at 98 and 298 K.

	1-98K	**1-298K**
Formula	$C_{16}H_{23}NO_{16}P_4U_2$	$C_{16}H_{23}NO_{16}P_4U_2$
M	1085.29	1085.29
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pnma*	$P2_12_12_1$
a / Å	19.7287(17)	9.6374(18)
b / Å	15.1632(14)	15.312(3)
c / Å	9.0568(8)	18.465(4)
α / °	90	90
β / °	90	90
γ / °	90	90
V /Å^3	2709.3(4)	2724.8(9)
Z	4	4
ρ_{calcd} / g cm^{-3}	2.661	2.646
F (000)	1992	1992
μ /mm^{-1}	12.251	12.181
GooF on F^2	1.079	1.093
R_1,wR_2 [I>2σ(I)]	0.0199, 0.0551	0.0242, 0.0613
R_1, wR_2 (all data)[a]	0.0254, 0.0573	0.0304, 0.0706
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / eÅ^{-3}	1.136, -1.149	1.071, -2.251

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

Table S2. Selected Bond Distances (Å) for **1-98K**.

U1=O8	1.769(3)	P1-O1	1.510(3)
U1=O7	1.774(3)	P1-O2	1.509(3)
U1-O2A	2.282(3)	P1-O3	1.560(3)
U1-O5B	2.297(3)	P2-O4	1.521(3)
U1-O1	2.309(3)	P2-O5	1.518(3)
U1-O4	2.310(3)	P2-O6	1.556(3)

Symmetry code of **1-98K**: A: -x+1/2, -y, z-1/2; B: -x, -y, -z+1.

Table S3. Selected Bond Distances (Å) for **1-298K**.

U1=O14	1.763(6)	P1-O2	1.493(6)
U1=O13	1.780(6)	P1-O1	1.514(6)
U1-O6A	2.265(6)	P1-O3	1.572(6)
U1-O7B	2.298(6)	P2-O6	1.515(6)
U1-O1	2.297(6)	P2-O4	1.511(6)
U1-O9	2.306(6)	P2-O5	1.538(6)
U2=O15	1.765(5)	P3-O9	1.506(6)
U2=O16	1.786(6)	P3-O7	1.495(6)
U2-O12C	2.262(6)	P3-O8	1.567(6)
U2-O10A	2.295(6)	P4-O12	1.516(6)
U2-O4A	2.316(6)	P4-O11	1.530(6)
U2-O2	2.341(7)	P4-O10	1.519(6)

Symmetry code of **1-298K**: A: -x+1, y-1/2, -z+3/2; B: x+1/2, -y+3/2, -z+1; C: -x+1/2, -y+2, z+1/2.

Table S4. Cell parameters of compound **1** at different temperature.

	a/ Å	*b*/ Å	*c* / Å	*V*/ Å^3	CCDC No.
98 K	19.7287(17)	15.1632(14)	9.0568(8)	2709.3(4)	1472437
123 K	19.7115(17)	15.1120(12)	9.0434(7)	2693.8(4)	1476554
148 K	19.7192(9)	15.1289(7)	9.0463(4)	2698.8(2)	1476637
153 K	19.7092(10)	15.1296(7)	9.0454(4)	2697.3(2)	1476638
163 K	19.7241(17)	15.1635(13)	9.0592(8)	2709.5(4)	1476639
183 K	9.6369(4)	15.2543(6)	18.4124(7)	2706.70(19)	1476640
193 K	9.6448(6)	15.2691(10)	18.4142(12)	2711.8(3)	1476641
203 K	9.6409(4)	15.2670(7)	18.4119(9)	2710.0(2)	1476642
213 K	9.6435(5)	15.2842(7)	18.4269(8)	2716.0(2)	1476643
223 K	9.6279(4)	15.2605(7)	18.4075(9)	2704.6(2)	1476644
248 K	9.6248(4)	15.2647(7)	18.4148(9)	2705.5(2)	1476645
273 K	9.6297(7)	15.2888(12)	18.4333(14)	2713.9(4)	1476646
298 K	9.6374(18)	15.312(3)	18.465(4)	2724.8(9)	1472440

Table S5. Selected Bond Distances (Å) for compound **1** at low temperature.

	98 K	123 K	148 K	153 K	163 K
U1=O8	1.767(6)	1.776(8)	1.767(8)	1.769(8)	1.775(6)
U1=O7	1.775(6)	1.777(8)	1.771(8)	1.779(8)	1.774(6)
U1-O2A	2.266(6)	2.266(8)	2.257(8)	2.263(8)	2.281(6)
U1-O5B	2.293(6)	2.303(8)	2.299(8)	2.296(6)	2.300(6)
U1-O1	2.313(6)	2.288(8)	2.299(7)	2.291(7)	2.305(6)
U1-O4	2.319(6)	2.311(9)	2.305(8)	2.320(8)	2.327(6)
P1-O1	1.511(7)	1.524(9)	1.517(8)	1.517(8)	1.516(6)
P1-O2	1.521(7)	1.523(9)	1.531(8)	1.523(8)	1.507(6)
P1-O3	1.554(7)	1.547(9)	1.553(8)	1.550(9)	1.552(7)
P2-O4	1.516(7)	1.524(8)	1.537(8)	1.506(8)	1.510(6)
P2-O5	1.522(6)	1.506(8)	1.514(8)	1.519(7)	1.518(6)
P2-O6	1.551(7)	1.563(9)	1.552(8)	1.545(9)	1.553(7)

Symmetry code of **1-98K**: A: -x+1/2, -y, z-1/2; B: -x, -y, -z+1.

Table S6. Selected Bond Distances (Å) for compound **1** at high temperature.

	298 K	273 K	248 K	223 K	213 K	203 K	193 K	183 K
U1=O14	1.763(6)	1.755(8)	1.766(8)	1.760(8)	1.767(8)	1.764(8)	1.765(8)	1.761(7)
U1=O13	1.780(6)	1.782(8)	1.774(8)	1.786(8)	1.784(8)	1.782(8)	1.783(8)	1.781(8)
U1-O6A	2.265(6)	2.248(9)	2.260(8)	2.262(8)	2.271(9)	2.270(8)	2.262(8)	2.258(8)
U1-O7B	2.298(6)	2.279(9)	2.287(8)	2.293(8)	2.292(8)	2.289(8)	2.292(8)	2.285(8)
U1-O1	2.297(6)	2.305(9)	2.305(7)	2.309(8)	2.312(9)	2.303(7)	2.305(7)	2.288(7)
U1-O9	2.306(6)	2.296(8)	2.295(8)	2.295(8)	2.327(9)	2.297(8)	2.292(8)	2.294(8)
U2=O15	1.765(5)	1.774(8)	1.768(8)	1.766(8)	1.771(8)	1.769(8)	1.775(8)	1.777(7)
U2=O16	1.786(6)	1.759(8)	1.779(8)	1.768(8)	1.767(8)	1.772(8)	1.780(8)	1.775(8)
U2-O12C	2.263(6)	2.263(9)	2.261(7)	2.267(8)	2.267(9)	2.265(7)	2.271(8)	2.255(7)
U2-O10A	2.295(6)	2.286(8)	2.282(8)	2.293(8)	2.277(8)	2.296(7)	2.287(8)	2.290(7)
U2-O4A	2.316(6)	2.313(9)	2.312(7)	2.306(7)	2.296(8)	2.300(7)	2.314(8)	2.312(7)
U2-O2	2.341(7)	2.321(9)	2.322(8)	2.322(8)	2.318(9)	2.329(8)	2.326(8)	2.327(8)
P1-O2	1.493(6)	1.497(9)	1.502(8)	1.497(8)	1.502(8)	1.493(8)	1.505(8)	1.502(8)
P1-O1	1.514(6)	1.501(10)	1.498(8)	1.492(8)	1.495(9)	1.502(8)	1.500(8)	1.514(8)
P1-O3	1.572(6)	1.575(9)	1.579(8)	1.577(8)	1.569(9)	1.584(8)	1.570(8)	1.574(8)
P2-O6	1.515(6)	1.536(9)	1.520(8)	1.515(8)	1.520(9)	1.516(8)	1.527(8)	1.522(7)
P2-O4	1.511(6)	1.511(9)	1.508(8)	1.509(8)	1.522(9)	1.524(8)	1.507(8)	1.518(8)
P2-O5	1.538(6)	1.546(9)	1.539(8)	1.545(8)	1.547(8)	1.544(8)	1.543(8)	1.549(8)
P3-O9	1.506(6)	1.517(9)	1.512(8)	1.511(8)	1.487(9)	1.509(8)	1.523(8)	1.513(8)
P3-O7	1.495(6)	1.505(9)	1.496(8)	1.493(8)	1.493(8)	1.499(8)	1.493(8)	1.504(8)
P3-O8	1.567(6)	1.551(10)	1.557(8)	1.567(8)	1.556(10)	1.560(8)	1.560(8)	1.571(8)
P4-O12	1.516(6)	1.507(10)	1.512(8)	1.505(9)	1.513(10)	1.513(8)	1.509(8)	1.521(8)
P4-O11	1.530(6)	1.522(8)	1.522(8)	1.529(8)	1.528(8)	1.519(8)	1.518(8)	1.523(8)
P4-O10	1.519(6)	1.526(8)	1.524(8)	1.521(8)	1.533(8)	1.519(7)	1.526(8)	1.523(7)

Symmetry code of **1-298K**: A: -x+1, y-1/2, -z+3/2; B: x+1/2, -y+3/2, -z+1; C: -x+1/2, -y+2, z+1/2.

Table S7. Distances (Å) of tetramethylammonium cation and surrounding oxygen atoms.*

	C10 - **O7** / **O7** / **O8** / **O8** / O5 / O5	C9 - **O7** / O3 / O6	C11 - **O8** / O4/ O6	C12 - O6 / O6 / O3
98 K	3.504/3.504/3.450/ 3.450/3.417 /3.417	3.094/3.576/3.663	3.158/3.415/3.580	3.147/3.244/3.805
	C15 - **O13** / **O16**	C16 - **O16** / **O13** / **O14** / O1 / O4	C14 - **O13** / O3 / O8 / O5 / O11	C13 - **O16** / O5 / O8 / O3 / O11
298 K	3.316/3.277	3.504/3.514/3.673/ 3.790/3.647	3.554/3.184/3.820/ 3.517/3.439	3.653/3.257/3.734/ 3.492/3.967

*: The oxygen atoms in bold are part of O=U=O.

Table S8. Cation-Cation Interaction induced elongation of O=U=O (Å).

		U=O		U=O
98 K	C9···O7 3.094	1.775(6)	C11···O8 3.158	1.767(6)
298 K	C15···O13 3.316	1.791(8)	C15···O16 3.277	1.785(8)
	C16···O14 3.673	1.773(7)		

Table S9. Crystal Data and Refinement Details for **1** at 298K.

	A	**B**	**C**
Formula	$C_{16}H_{23}NO_{16}P_4U_2$	$C_{16}H_{23}NO_{16}P_4U_2$	$C_{16}H_{23}NO_{16}P_4U_2$
M	1085.29	1085.29	1085.29
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a / Å	9.6504(19)	9.6434(12)	9.6329(18)
b / Å	15.330(3)	15.3254(18)	15.311(3)
c / Å	18.490(4)	18.473(2)	18.463(4)
α / °	90	90	90
β / °	90	90	90
γ / °	90	90	90
V /Å^3	2735.3(9)	2730.1(6)	2723.2(9)
Z	4	4	4
ρ_{calcd} / g cm^{-3}	2.635	2.640	2.647
F (000)	1992	1992	1992
μ /mm^{-1}	12.524	12.157	12.188
GooF on F^2	1.133	1.075	1.070
R_1,wR_2 [I>2σ(I)]	0.0163, 0.0385	0.0211, 0.0608	0.0253, 0.0668
R_1, wR_2 (all data)[a]	0.0187, 0.0453	0.0239, 0.0672	0.0301, 0.0785
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / eÅ^{-3}	0.644, -1.006	1.035, -2.505	1.057, -2.913

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

Table S10. Crystal Data and Refinement Details for **1** at 98K.

	A	**B**	**C**
Formula	$C_{16}H_{23}NO_{16}P_4U_2$	$C_{16}H_{23}NO_{16}P_4U_2$	$C_{16}H_{23}NO_{16}P_4U_2$
M	1085.29	1085.29	1085.29
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pnma*	*Pnma*	*Pnma*
a / Å	19.7277(15)	19.7304(16)	19.746(2)
b / Å	15.1536(11)	15.1555(13)	15.1635(16)
c / Å	9.0520(7)	9.0485(8)	9.0544(9)
α / °	90	90	90
β / °	90	90	90
γ / °	90	90	90
V /$Å^3$	2706.1(4)	2705.7(4)	2711.1(5)
Z	4	4	4
ρ_{calcd} / g cm^{-3}	2.634	2.635	2.629
F (000)	1944	1944	1944
μ /mm^{-1}	12.264	12.266	12.242
GooF on F^2	1.240	1.175	1.098
R_1,wR_2 [$I>2\sigma(I)$]	0.0261, 0.0805	0.0504, 0.1403	0.0261, 0.0638
R_1, wR_2 (all data)[a]	0.0371, 0.0972	0.0579, 0.1532	0.0327, 0.0670
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / e$Å^{-3}$	2.214, -2.604	4.787, -3.815	2.069, -1.409

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

1. T. Zheng, Y. Gao, L. Chen, Z. Liu, J. Diwu, Z. Chai, T. E. Albrecht-Schmitt and S. Wang, Dalton Transactions, 2015, **44**, 18158.
2. G. M. Sheldrick, SHELXTL, Siemens Analytical X-ray Instruments, Inc: Madison, WI, 2001.