

A Uranyl Phosphonate Framework with Temperature Induced Order-disorder Transition and Temperature Correlated Photoluminescence.

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***Caution!** As depleted uranium is involved in all uranium compounds employed in the experiments, standard precautions are performed for handling radioactive materials. Crystallographic study and UV, Fluorescence, Raman and Infrared studies are conducted in a laboratory dedicated to studies on actinide elements.*

Materials and methods. (1,3-phenylenebis(phosphonic acid) (1,3-pbpH₄) was synthesized by similar procedure reported in the literature and the characterization was provided in our previous work¹. UO₂(NO₃)₂·6H₂O, and HF (40 %) were used as received without further purification.

Crystallographic studies. Crystal of **UPF-1** is mounted on loop with paratone and optically aligned on a Bruker D8-Venture single crystal X-ray diffractometer equipped with a digital camera. The diffraction data is collected using 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 100 K. The structures were solved by the direct method and refined on F² by full-matrix least-squares methods using SHELXTL². All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms except those attached to water molecules were put in calculated positions, except disordered moieties.

Powder X-ray diffraction (PXRD). Powder X-ray diffraction (PXRD) pattern is collected from 5° to 50°, with a step of 0.02°, and the data collection time was 0.2 s, using a Bruker D8 advance X-ray diffractometer with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) equipped with a Lynxeye 1D detector. PXRD pattern of **UPF-1** reveals that they are all single phases without impurities.

Thermogravimetric analysis (TGA). Thermogravimetric analysis were performed on a NETZSCH STA 449F3 instrument in the range of 30–900 °C under a nitrogen flow at a heating rate of 10 °C/min for the samples of **UPF-1**.

UV, Fluorescence, Raman and Infrared spectroscopies. UV spectroscopy data were recorded from single crystals of three phases using a Craic Technologies microspectrophotometer. Fluorescence spectroscopy is collected with 365 nm wavelength as excitation light. Crystals were placed on quartz slides under Krytox oil, and the data was collected after optimization of microspectrophotometer.

Table S1. Crystal data and refinement details for **UPF-1** and **UPF-1(298K)**.

	UPF-1	UPF-1(298K)
Formula	C ₁₂ H ₁₆ O ₂₇ P ₄ U ₄	C ₁₂ H ₁₆ O ₂₇ P ₄ U ₄
M	1668.25	1660.18
Crystal system	Tetragonal	Tetragonal
Space group	$\bar{I}4$	$\bar{I}4$
a / Å	21.114(6)	21.287(3)
b / Å	21.114(6)	21.287(3)
c / Å	6.941(2)	6.9924(10)
α / °	90	90
β / °	90	90
γ / °	90	90
V / Å ³	3094(2)	3168.5(10)
Z	4	4
ρ_{calcd} / g cm ⁻³	3.581	3.480
T	100(2)	293
F (000)	2928	2896
(Mo-K α) / mm ⁻¹	2.649	
Goof on F ²	1.077	1.06
R ₁ , wR ₂ [I>2 σ (I)]	0.0351, 0.0786	0.0399, 0.0988
($\Delta\rho$) _{max} , ($\Delta\rho$) _{min} / eÅ ⁻³	1.956, -1.888	2.94, -1.30

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

Table S2. Selected bond distances (Å) and angles (°) for compound **UPF-1**

U1=O9	1.737(8)	U2-O3F	2.289(10)
U1=O10	1.748(9)	U2-O1G	2.363(9)
U1-O2	2.234(8)	U2-O2W	2.448(9)
U1-O5A	2.320(9)	U2-O1W	2.497(11)
U1-O4B	2.330(9)	P1-O3	1.489(11)
U1-O5C	2.477(9)	P1-O1	1.516(10)
U1-O4C	2.512(9)	P1-O2	1.522(8)
U2=O7	1.738(9)	P2-O6	1.473(9)
U2=O8	1.766(9)	P2-O4	1.528(9)
U2-O6	2.266(9)	P2-O5	1.525(10)

Symmetric codes for **UPF-1**: A: $y-1/2, -x+1/2, -z-1/2$; B: $y-1/2, -x+1/2, -z+1/2$; C: $-y, x, -z$; D: $-x-1/2, -y+1/2, z+1/2$; E: $-x-1/2, -y+1/2, z-1/2$; F: $-y+1/2, x+1/2, -z+1/2$; G: $-y+1/2, x+1/2, -z-1/2$.

Table S3. Selected bond distances (Å) and angles (°) for compound **UPF-1(298K)**

U1=O7	1.759(13)	U2-O3B	2.30(2)
U1=O8	1.775(13)	U2-O4G	2.269(13)
U1-O1	2.225(13)	U2-O2W	2.53(3)
U1-O5F	2.329(13)	U2-O1W	2.57(3)
U1-O6G	2.333(13)	P1-O3	1.51(2)
U1-O5I	2.333(13)	P1-O1	1.566(13)
U1-O6I	2.529(15)	P1-O2	1.484(16)
U2=O9	1.744(15)	P2-O6	1.543(15)
U2=O10	1.771(15)	P2-O4	1.485(14)
U2-O2	2.378(14)	P2-O5	1.553(14)

Symmetric codes for **UPF-1(298K)**: A: $x, y, -1+z$; B: $x, y, 1+z$; C: $y, -x, -z$; D: $y, -x, 1-z$; E: $-x, 1-y, z$; F: $-y, x, -z$; G: $-y, x, 1-z$; H: $1/2+x, 1/2+y, -1/2+z$; I: $-1/2+y, 1/2-x, 1/2-z$.

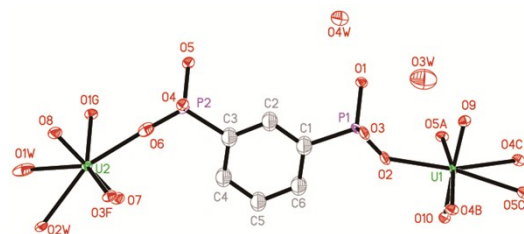


Fig. S1. Building unit of compound **UPF-1** with atomic labeling scheme at 50% probability.

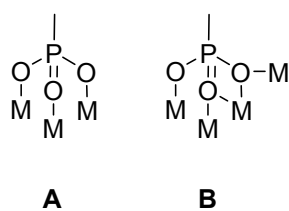


Fig. S2 Coordination modes of phosphonate

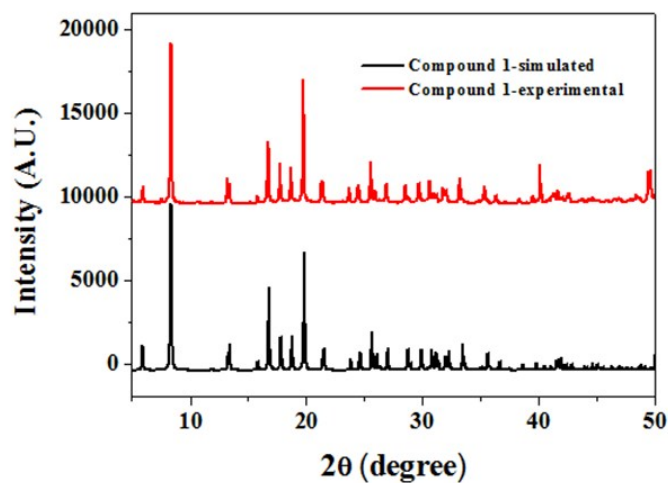


Fig. S3: Experimental X-ray powder pattern (red) and simulated powder pattern (black) obtained from the cif file of **UPF-1** confirm the phase purity.

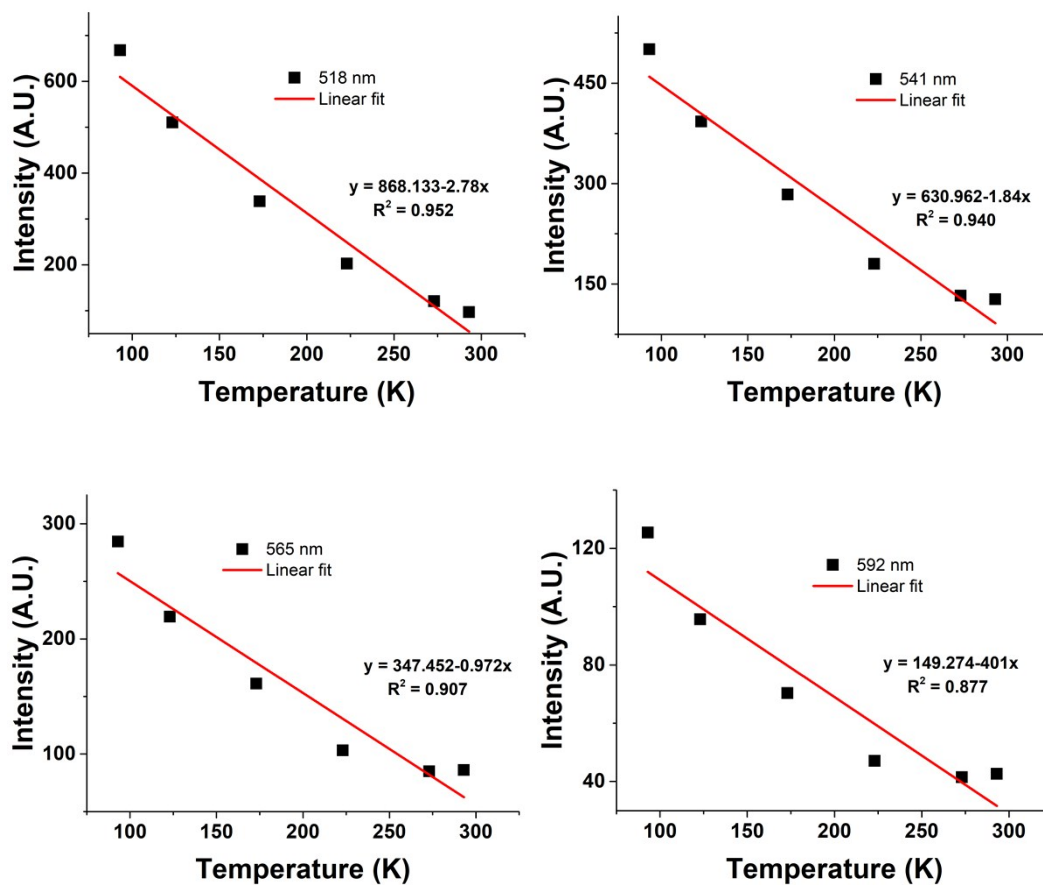


Fig. S4. The plots of intensity vs temperature of peaks in temperature-dependent fluorescence spectra of **UPF-1**

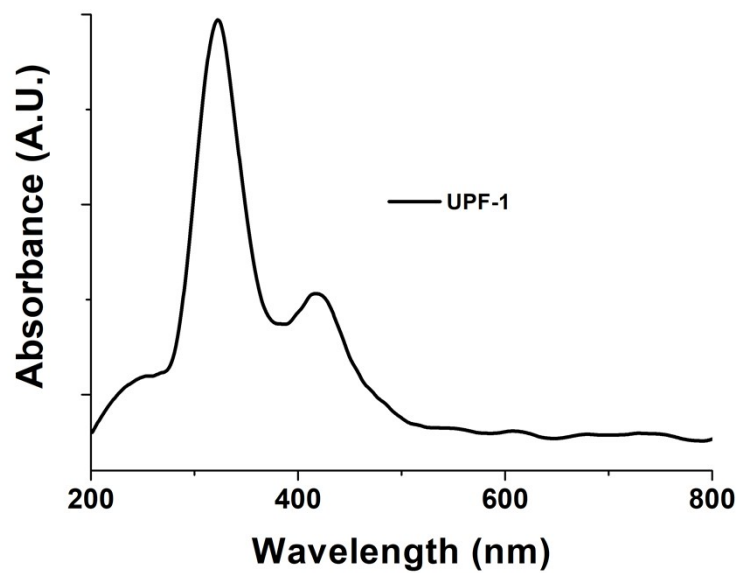


Fig. S5. UV-Vis spectra of compound UPF

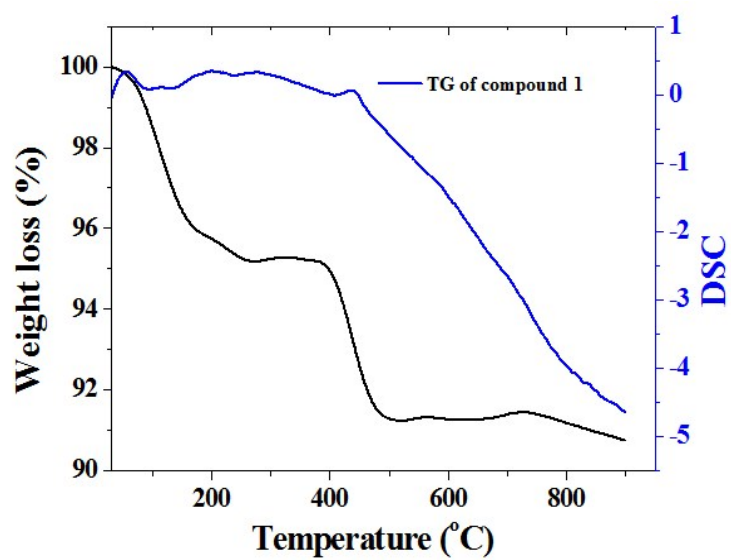


Fig. S6: the TGA and DSC plot of the compound UPF-1.

-1.

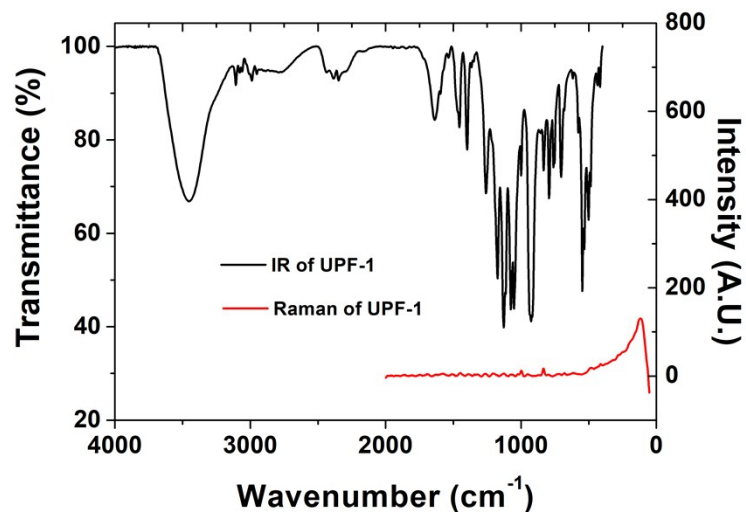


Fig. S7. IR and Raman spectra of UPF-1.

References

1. (a) S. S. Iremonger, J. Liang, R. Vaidhyanathan and G. K. Shimizu, *Chem. Commun.*, 2011, **47**, 4430-4432; (b) T. Zheng, Y. Gao, D. Gui, L. Chen, D. Sheng, J. Diwu, Z. Chai, T. E. Albrecht-Schmitt and S. Wang, *Dalton Trans.*, 2016, **45**, 9031-9035.
2. G. Sheldrick, *Acta Crystallogr. C*, 2015, **71**, 3-8.