Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

The First Actinide Polyiodate: A Complex Multifunctional Compound with Promising X-ray Luminescence Properties and Proton Conductivity

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Section S1: Materials and Methods

1. Synthesis

KIO_3 (0.5 g, 2.4 mmol, Alfa-Aesar 99.0 % min) and $UO_2(NO_3)_2 \cdot 6H_2O$ (0.02 g, 0.04 mmol International Bioanalytical Industries Inc.) were dissolved in 5 ml of deionised water and placed in a 20 ml slow evaporation vessel. Concentrated nitric acid was added to the jar to make up the volume to 20 ml. The jar containing the solution was placed in a fume cupboard and the solution was left to evaporate to dryness where the formation of large green single crystals of UPI-1 were observed and mechanically separated for further analysis.

2. Single Crystal X-ray Diffraction

Suitable quality crystals were selected for analysis and structural refinement using single crystal X-ray diffraction (SC-XRD). Data were recorded with CrysAlisPro software on an Agilent Oxford Diffraction Super Nova diffractometer with a Mo Kα tube at 296 K. Absorption corrections for the raw data were performed using the multiscan method. The unit cell was determined, and background effects were processed by the CrysAlisPro software. The initial structures for **UPI-1** was refined through using SHELXL-2018 within the WinGX (v1.80.05) software,[1] and the ADDSYM algorithm of the PLATON program[2] was used for the checking of possible higher symmetries.

3. Bond Valence Sums

Bond valence sums (BVS) calculations were undertaken for the anions and cations in **UPI-1** using the parameters reported by Burns and co-workers[3] for seven-coordinate U. The parameters provided by Brese and O'Keeffe[4] were used for I, K and O.

4. Powder X-ray Diffraction

Powder X-ray Diffraction (PXRD) measurements were made at room temperature using a Bruker AXS D8 Endeavor diffractometer (40 kV/40 mA) in Bragg−Brentano geometry. The diffractometer has a copper X-ray tube and a primary nickel filter, producing Cu Kα1,2 radiation (λ = 1.541 87 Å). A linear silicon strip LynxEye detector (Bruker-AXS) was used.

Data were collected in the range of 2θ = 10−120° with 10 s/step and a step width of 0.02°. The aperture of the fixed divergence slit was set to 0.2 mm, and the receiving slit was set to 8 mm. The discriminator of the detector was set to an interval of 0.16−0.25 V. Data were analyzed by pattern matching using the program FullProf,[5] where space group and lattice parameter information were obtained from single-crystal X-ray measurements and used as starting parameters.

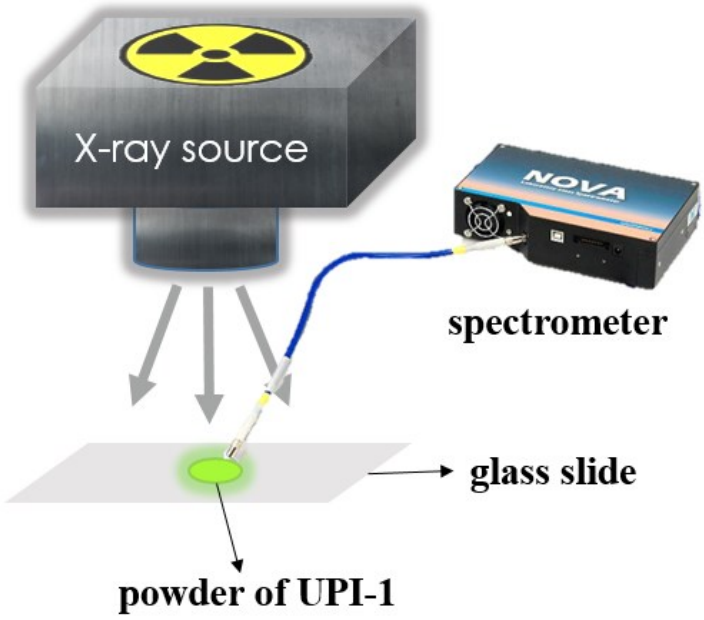
5. Raman Spectroscopy

The unpolarized Raman spectrum was recorded with a Horiba LabRAM HR spectrometer using a Peltier-cooled multichannel CCD detector. An objective lens with 50× magnification was linked to the spectrometer, allowing analysis of samples as small as 2 μm diameter. The samples were in the form of single crystals. The incident radiation was produced by a helium−neon laser line at a power of 17 mW (λ = 632.8 nm). The focal length of the spectrometer was 800 mm, and an 1800 grooves/ mm grating was used. The spectral resolution was approximately 1 cm^{-1} with a slit width of 100 μm. The spectra were recorded in the range of 100−4000 cm^{-1}.

6. UV-Vis and X-ray Excitation Luminescence Spectroscopy

UV-Vis absorption and photoluminescence measurements were performed using a Craic Technologies microspectrophotometer. The crystals were put on the quartz slides and absorption spectra collected from 200 to 800 nm after optimization of the microspectrophotometer. The photoluminescence spectra were recorded by same method with wavelength from 300 to 900 nm.

X-ray excited luminescence (XEL) spectroscopy was recorded by home-made instrument. The illustration of experimental setup is shown in SI Figure 1, a NOVA spectrometer (ideaoptics, China) is collected with a commercial X-ray source (X-RAD SmART system) with radiation shielding system. The sample was fully exposed under incident X-ray photons, and dose rate is calculated to be 26.5 Gy/min.



Supplementary Information Figure 1. Experimental setup for X-ray excition luminescence (XEL).

7. Proton Conductivity Measurements

Alternating current impedance measurements were carried out on a Solartron SI 1260 Impedance/Gain-Phase Analyzer with applied ac voltage amplitude of 1000 mV and a frequency range from 10 MHz to 10 Hz. ZView Software was applied to fit impedance data sets by simulating an equivalent circuit.

All samples are mechanically ground to ensure that the particle size is sufficiently small. A bulk crystalline powder was compressed into a pellet with 0.3 N pressure, the diameter of the pellet is 3 mm, and the thickness is in the range from 1 to 2 mm. The pelletized sample was attached with two gold electrodes and placed in a temperature- and humidity-controlled chamber. All temperature points were calibrated by an external thermocouple. The conductivity was calculated by the following equation

$$\sigma = L/RS$$

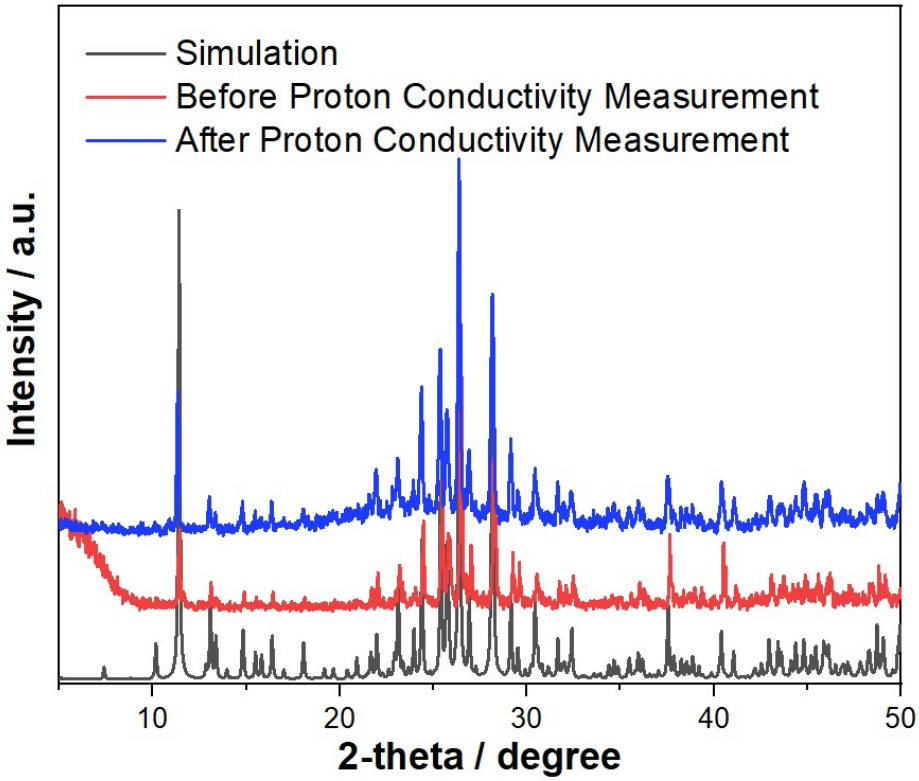
Where S and L are the cross-sectional area and thickness of the pellet, respectively, and R, which was obtained from the impedance plots, is the value of resistance. The activation energy for **UPI-1** was calculated from the following Arrhenius equation:

$$\sigma T = \sigma_0 \, exp(-\frac{E_a}{k_B T})$$

Where σ is the ionic conductivity, k_B is the Boltzmann constant, and σ_0 is the pre-exponential factor, T is the temperature.

Supporting Information Table 1. Experimental parameters and calculated conductivity for **UPI-1**.

T/K	RH	R	L/mm	D/mm	δ
363	95%	7.68E+04	1	1.45	1.97E-05
343	95%	2.17E+05	1	1.45	6.98E-06
323	95%	4.83E+05	1	1.45	3.14E-06
303	95%	9.90E+05	1	1.45	1.53E-06



Supplementary Information Figure 2. PXRD data collected on UPI-1 prior and post proton conductivity measurement.

Section S2: Crystallographic Details

Supplementary Information Table 2. Crystallographic data for UP-1

Compound	*UPI-1*
Formula	$K_4[(UO_2)_2(IO_3)_6(I_4O_{11})]\cdot(HIO_3)_4(H_2O)_6$
Formula weight	3225.06
Crystal system	Orthorhombic
Space group	*Pna*21
a (Å)	16.406(3)
b (Å)	25.363(6)
c (Å)	23.926(12)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	9956(6)
Z / μ (mm^{-1})	4
F(000)	11280.0
d_{calcd} (g cm^{-3})	4.303
GOF	1.059
Absolute Structure Parameter	0.493(4)
Final R_1 [a] [$I > 2\sigma(I)$]	0.0547
Final wR_2 [b] [$I > 2\sigma(I)$]	0.1317

Section S3: Bond Valence Sums Calculations for UPI-1

Supplementary Information Table 3. UPI-1 Cation BVS Calculations

U cations in UO_7		I cations in IO_3		I cations in I_4O_{11}		K cations	
Atom	**BVS**	**Atom**	**BVS**	**Atom**	**BVS**	**Atom**	**BVS**
U(1)	**6.03**	I(2)	**4.56**	I(1)	**5.26**	K(1)	**1.18**
U(2)	**6.28**	I(3)	**5.06**	I(7)	**5.01**	K(2)	**1.13**
U(3)	**5.95**	I(4)	**4.90**	I(8)	**4.76**	K(3)	**0.85**
U(4)	**5.92**	I(5)	**4.85**	I(9)	**4.91**	K(4)	**1.11**
-	-	I(6)	**5.06**	I(10)	**4.85**	K(5)	**0.85**
-	-	I(11)	**4.76**	I(13)	**5.19**	K(6)	**1.07**
-	-	I(12)	**4.97**	I(26)	**5.21**	K(7)	**0.86**
-	-	I(14)	**5.33**	I(27)	**4.89**	K(8)	**0.82**
-	-	I(15)	**5.29**	-	-	-	-
-	-	I(16)	**5.47**	-	-	-	-
-	-	I(17)	**5.14**	-	-	-	-
-	-	I(18)	**5.12**	-	-	-	-
-	-	I(19)	**4.66**	-	-	-	-
-	-	I(20)	**5.08**	-	-	-	-
-	-	I(21)	**4.85**	-	-	-	-
-	-	I(22)	**5.09**	-	-	-	-

U cations in UO_7		I cations in IO_3		I cations in I_4O_{11}		K cations	
Atom	**BVS**	**Atom**	**BVS**	**Atom**	**BVS**	**Atom**	**BVS**
-	-	I(23)	**5.19**	-	-	-	-
-	-	I(24)	**4.94**	-	-	-	-
-	-	I(25)	**4.87**	-	-	-	-
-	-	I(28)	**5.08**	-	-	-	-

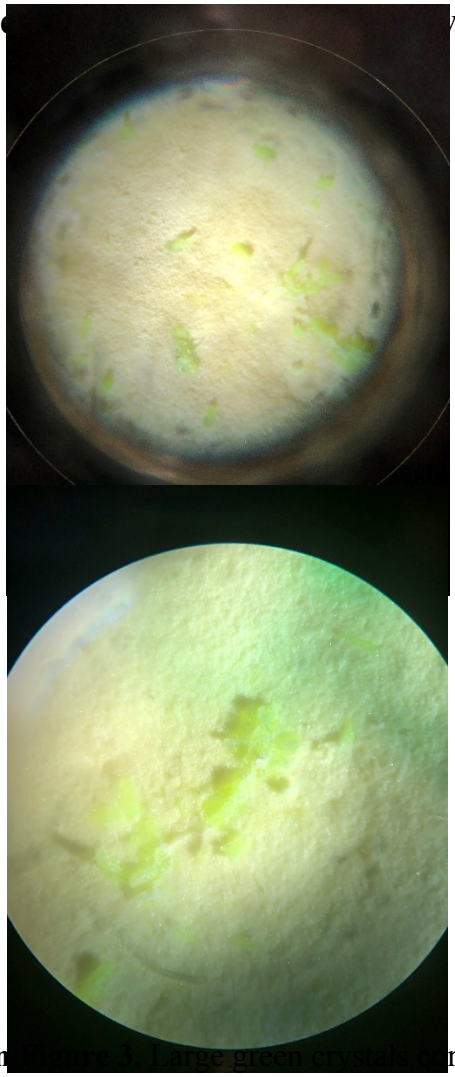
Supplementary Information Table 4. UPI-1 O BVS Calculations

O atom	BVS	Assignment	O atom	BVS	Assignment	O atom	BVS	Assignment
1	**1.83**	O^{2-}	35	**1.36**	HIO_3	69	**1.94**	O^{2-}
2	**1.82**	O^{2-}	36	**1.89**	O^{2-}	70	**2.20**	O^{2-}
3	**1.82**	O^{2-}	37	**1.64**	O^{2-}	71	**2.20**	O^{2-}
4	**1.61**	O^{2-}	38	**2.33**	O^{2-}	72	**1.92**	O^{2-}
5	**1.92**	O^{2-}	39	**2.14**	O^{2-}	73	**1.99**	O^{2-}
6	**2.12**	O^{2-}	40	**1.98**	O^{2-}	74	**2.19**	O^{2-}
7	**1.65**	O^{2-}	41	**1.66**	O^{2-}	75	**2.27**	O^{2-}
8	**1.59**	O^{2-}	42	**1.34**	HIO_3	76	**2.35**	O^{2-}
9	**2.18**	O^{2-}	43	**1.71**	O^{2-}	77	**0.12**	H_2O
10	**1.84**	O^{2-}	44	**1.77**	O^{2-}	78	**2.09**	O^{2-}

O atom	BVS	Assignment	O atom	BVS	Assignment	O atom	BVS	Assignment
11	**1.71**	HIO_3	45	**1.96**	O^{2-}	79	**2.05**	O^{2-}
12	**2.21**	O^{2-}	46	**2.05**	O^{2-}	80	**0.13**	H_2O
13	**2.03**	O^{2-}	47	**1.87**	O^{2-}	81	**1.69**	O^{2-}
14	**1.55**	O^{2-}	48	**1.39**	HIO_3	82	**2.37**	O^{2-}
15	**2.09**	O^{2-}	49	**2.11**	O^{2-}	83	**1.90**	O^{2-}
16	**0.10**	H_2O	50	**1.45**	HIO_3	84	**1.76**	O^{2-}
17	**1.79**	O^{2-}	51	**0.09**	H_2O	85	**1.83**	O^{2-}
18	**2.22**	O^{2-}	52	**1.56**	O^{2-}	86	**1.76**	O^{2-}
19	**2.21**	O^{2-}	53	**2.01**	O^{2-}	87	**1.89**	O^{2-}
20	**2.19**	O^{2-}	54	**1.53**	HIO_3	88	**0.15**	H_2O
21	**2.15**	O^{2-}	55	**2.33**	O^{2-}	89	**1.88**	O^{2-}
22	**2.18**	O^{2-}	56	**2.25**	O^{2-}	90	**1.71**	HIO_3
23	**2.13**	O^{2-}	57	**0.11**	H_2O	91	**2.02**	O^{2-}
24	**2.10**	O^{2-}	58	**1.91**	O^{2-}	92	**0.11**	H_2O
25	**1.80**	O^{2-}	59	**1.84**	O^{2-}	93	**1.89**	O^{2-}
26	**1.69**	HIO_3	60	**1.89**	O^{2-}	94	**1.87**	O^{2-}
27	**2.13**	O^{2-}	61	**2.03**	O^{2-}	95	**0.09**	H_2O
28	**1.97**	O^{2-}	62	**1.68**	O^{2-}	96	**0.14**	H_2O

O atom	BVS	Assignment	O atom	BVS	Assignment	O atom	BVS	Assignment
29	**1.93**	O^{2-}	63	**1.80**	O^{2-}	97	**0.14**	H_2O
30	**2.34**	O^{2-}	64	**0.15**	H_2O	98	**2.21**	O^{2-}
31	**1.83**	O^{2-}	65	**1.65**	O^{2-}	99	**2.04**	O^{2-}
32	**1.96**	O^{2-}	66	**1.87**	O^{2-}	100	**0.13**	H_2O
33	**1.95**	O^{2-}	67	**1.90**	O^{2-}	101	**1.68**	O^{2-}
34	**1.82**	O^{2-}	68	**1.83**	O^{2-}	102	**1.84**	O^{2-}

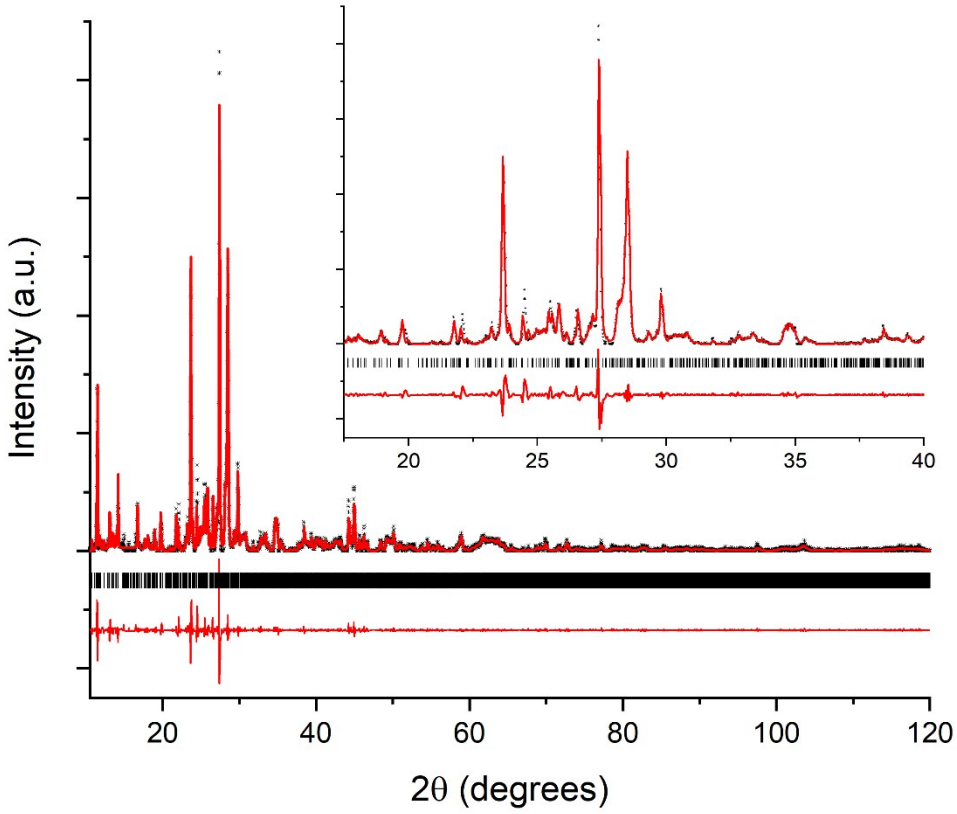
Section S4: Optical Image[illegible]vaporation vessel



Supplementary Information Figure 3. Large green crystals correspond to UPI-1 within flux matrix of partial amorphous and crystalline uranyl iodate by-product.

Section S5: Powder X-ray Diffraction Measurement and Analysis

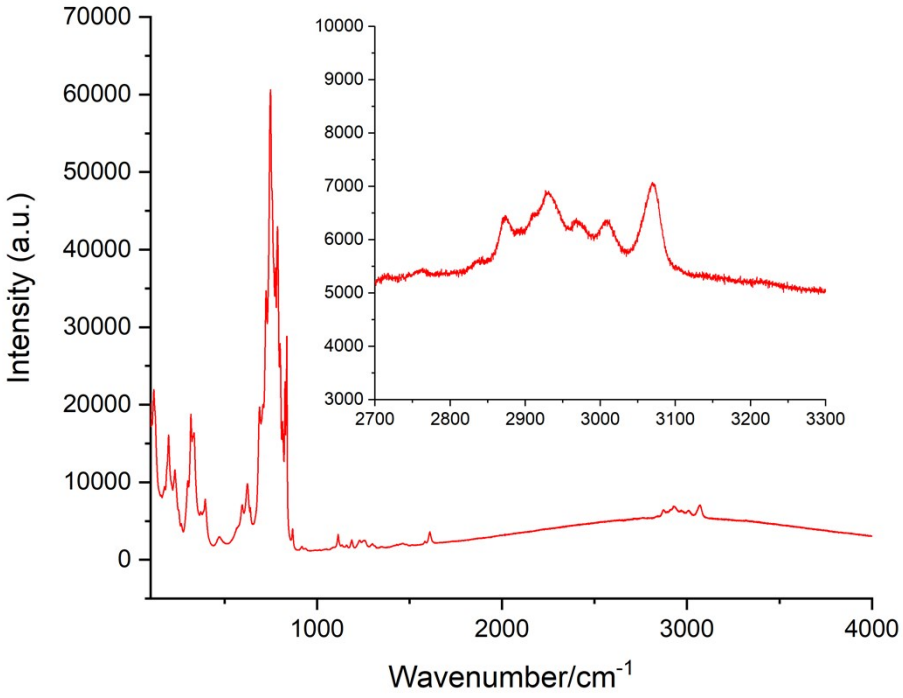
PXRD data collected against a sample of UPI-1 was analysed using profile matching in the program Fullprof.[5] A starting model using the lattice parameters determined from the SC-XRD measurements given previously was used and refined with the zero point, peak shape (pseudo-Voigt function) and instrument parameters against the collected data. The refinement profile is given in SI Figure 4 where lattice parameters of a = 16.406(2) Å b = 25.363(2) Å c = 23.926(3) Å and $\alpha = 90^{o}$ $\beta = 90^{o}$ $\gamma = 90^{o}$ and V = 9955.74(2) Å^3 were determined and consistent with that of UPI-1 identified from SC-XRD measurements, indicating its pure phase acquisition.



Supplementary Information Figure 4. PXRD and profile matching analysis for UPI-1 where R_p = 8.35 %, wR_p = 5.02 %.

Section S6: Raman Spectroscopy

Raman spectra were collected for single crystals of UPI-1 in the range 4000 – 100 cm^{-1} and the spectra is presented in SI Figure 5. Raman modes indicative of the uranyl group could be observed at around 190 to 300 cm^{-1} corresponding to the bending mode (v_2), at around 800 and 870 cm^{1-} corresponding to the symmetric vibration (v_1) and 930 to 980 corresponding to the antisymmetric stretching mode (v_3).[6] Bands around 3000 cm^{-1} typical symmetric bending and stretching modes (v_1 and v_2) for H_2O can also observed. Iodate related Raman modes can be observed at around 320 , 400, 677 and 810 cm^{-1} corresponding to the $v_{4,}$ $v_{2,}$ v_1 and v_2 respectively.[7]



Supplementary Information Figure 5. Raman spectra for UPI-1 in the range of 4000 – 100 cm^{-1}.

Section S7: Supplementary Information References

1. G. Sheldrick, *Acta Crystallographica Section A*, 2008, **64**, 112-122.
2. A. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7-13.
3. P. C. Burns, R. C. Ewing and F. C. Hawthorne, *Can. Mineral.*, 1997, **35**, 1551-1570.
4. N. E. Brese and M. O'Keeffe, *Acta Crystallographica Section B*, 1991, **47**, 192-197.
5. J. Rodríguez-Carvajal, *Physica B: Condensed Matter*, 1993, **192**, 55-69.
6. Y. Hao, G. L. Murphy, D. Bosbach, G. Modolo, T. E. Albrecht-Schmitt and E. V. Alekseev, *Inorg. Chem.*, 2017, **56**, 9311-9320.
7. Y. Wang, Y. Wang, L. Zhang, L. Chen, Z. Liu, X. Yin, D. Sheng, J. Diwu, J. Wang, N. Liu, Z. Chai and S. Wang, *Inorg. Chem.*, 2017, **56**, 3702-3708.