Supplementary Information for

Luminometric dosimetry of X-ray radiation by a zwitterionic uranium coordination polymer

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S1. Experimental section.

Reagents. $UO_2(NO_3)_2 \cdot 6H_2O$ (99 %), N-(4-carboxybenzyl)-(3,5-dicarboxyl)pyridinium bromide (95 %, Jilin Chinese Academy of Sciences - Yanshen Technology Co., Ltd), acetic acid (99 %, Adamas), and DMF (99.5 %, Adamas) were used as received from commercial suppliers without further purification.

Synthesis. A mixture of $UO_2(NO_3)_2 \cdot 6H_2O$ (0.01 mmol, 0.0050 g), N-(4-carboxybenzyl)-(3,5-dicarboxyl)pyridinium bromide (0.01 mmol, 0.0038g), 50 μL acetic acid, 0.8 mL deionized water, and 0.2 mL DMF were loaded into a 5 mL glass vial. The vial was sealed and heated to 100 °C for 5 hours, followed by cooling to room temperature under ambient conditions. Single crystals of **U-Cbdcp** were isolated after being washed with ethanol and allowed to air-dry at room temperature.

S2. Characterizations.

X-ray crystallography. Single crystal X-ray diffraction measurements were performed using a Bruker D8-Venture single crystal X-ray diffractometer equipped with an IμS 3.0 microfocus X-ray source (Mo–Kα radiation, λ = 0.71073Å) and a CMOS detector at 298 K. The data frames were collected using the program *APEX3* and processed using the program SAINT routine in APEX3.[1] The structures were solved by the direct method and refined on F^2 by full-matrix least-squares methods using *SHELXTL-2018* program.[2] All non-H atoms were refined with anisotropic displacement parameters. During the refinement of **U-Cbdcp,** one fully occupied water molecule can be identified in the difference Fourier map. The rest molecule species are highly disordered and contributions to the scattering from these species were removed using the *SQUEEZE* routine of *PLATON*.[3] Furthermore, electron count per cell for **U-Cbdcp** was found to be 108 e⁻ per unit cell based on *SQUEEZE*, corresponding to 27 e⁻ per molecular formula, which is equivalent to three H_2O molecules. As a consequence, the molecular formula of **U-Cbdcp** was determined to be $UO_2(OH)(H_2Cbdcp)(HCbdcp) \cdot 4H_2O$. Furthermore, thermogravimetric analysis (TGA) study reveals that an initial weight water of 6.9w% occurring before 195 °C, which could be attributed to the departure of the four hydrating water molecules (Fig. S8). Selected crystallographic information is listed in Table S1. Atomic coordinates and additional structural information are provided in the CIFs.

Powder patterns were collected from 5 to 50°, with a step of 0.02° using a Bruker D8 advance X-ray diffractometer with Cu-Kα radiation (λ= 1.54056 Å) equipped with a Lynxeye one-dimensional detector.

Fluorescence Spectroscopy. The solid-state fluorescence spectra were collected on an Edinburgh Instruments FS5 steady state spectrofluorometer from a tablet of **U-Cbdcp** with 365 nm UV excitation.

Fourier Transform Infrared (FTIR) Spectroscopy. The FTIR spectra were recorded on ground samples using a Thermo Nicolet 6700 spectrometer in the range of 400-4000 cm⁻¹, equipped with a diamond attenuated total reflectance (ATR) accessory.

Electron Paramagnetic Resonance (EPR) Study. The EPR spectra for nonirradiated and irradiated samples was recorded on a JEOL-FA200 spectrometer. An X-band spectrometer (JES-FA200) with 100-kHz field modulation was interfaced with a computer to manipulate the spectra and integrate spectral intensity ESR measurements were performed at room temperature and the microwave power used was 1.0 mW.

Radiolytic Stability. The radiation resistance of **U-Cbdcp** were examined by irradiating the powdery sample with X-ray, β-ray, or γ-ray under ambient conditions. X-ray, β-ray and γ-ray radiations were provided by a Cu Kα radiation source (60 kV, 12W), a custom-built electron cyclotron (1.2 MeV), and a ^{60}Co irradiation source (2.22×10^{15} Bq), respectively. **U-Cbdcp** was irradiated with accumulated doses with dose rates of 7.2, 150, and 11.8 kGy/h for X-ray, β-ray, γ-ray, respectively, and the dose rates of radiations were determined by commercialized alanine dosimeters. PXRD study on the irradiated samples were performed to confirm the radiation resistance of **U-Cbdcp**.

Scanning Electron Microscopy and Energy-Dispersive X-ray Spectrometry (SEM-EDS) Analysis. SEM images and EDS data were recorded on a Zeiss Merlin Compact LEO 1530 VP scanning electron microscope. The energy of the electron beam voltage was 5 keV for imaging and 20 keV for quantitative identifications of elements. Samples were attached directly onto carbon conductive tape. The spectra acquisition time was 60 s and all EDS results are provided in Fig. S9.

Calculation of the Detection Limit. The calibration curve was established by plotting the quenching rate $(I_0 - I)/I_0$ (%) as a function of dose at the low dose range (0–30 Gy). The linear domain in low dose range can be fitted as y = 0.71 x + 1.47, where y is the quenching ratio percentage $(I_0 - I)/I_0$ (%) and x is radiation dose (Fig. S2). The standard deviation (σ) is defined as $100 \times (I_{SE}/I_0)$, where I_{SE} is the standard error of the fluorescence intensity measurement, as determined by the baseline measurement of blank samples. If defining three times of the standard deviation as the detectable signal, the detection limit can be projected as 3σ/slope = 3 × 100 × (59.34/270720.44)/0.71 = 0.093 Gy.
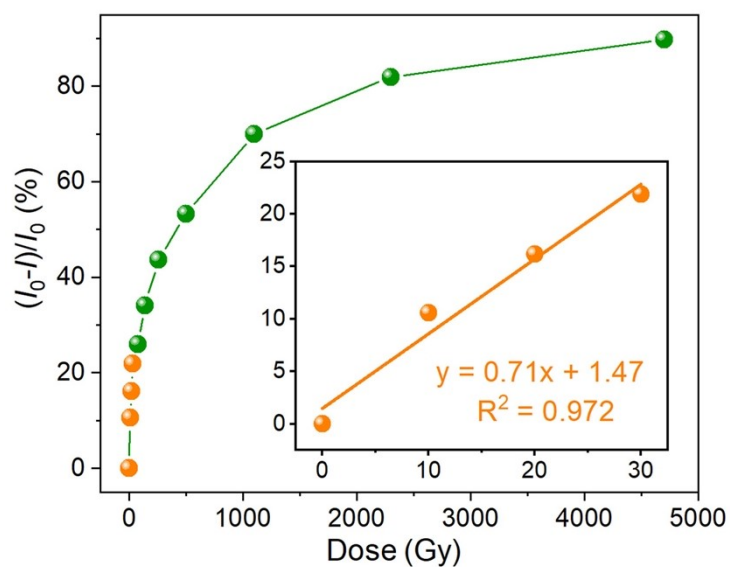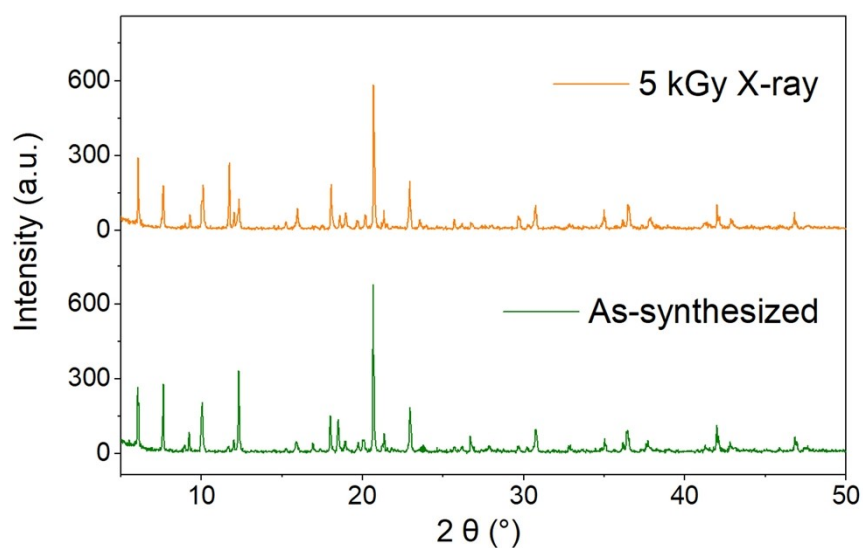
S3. Supplementary Figures.
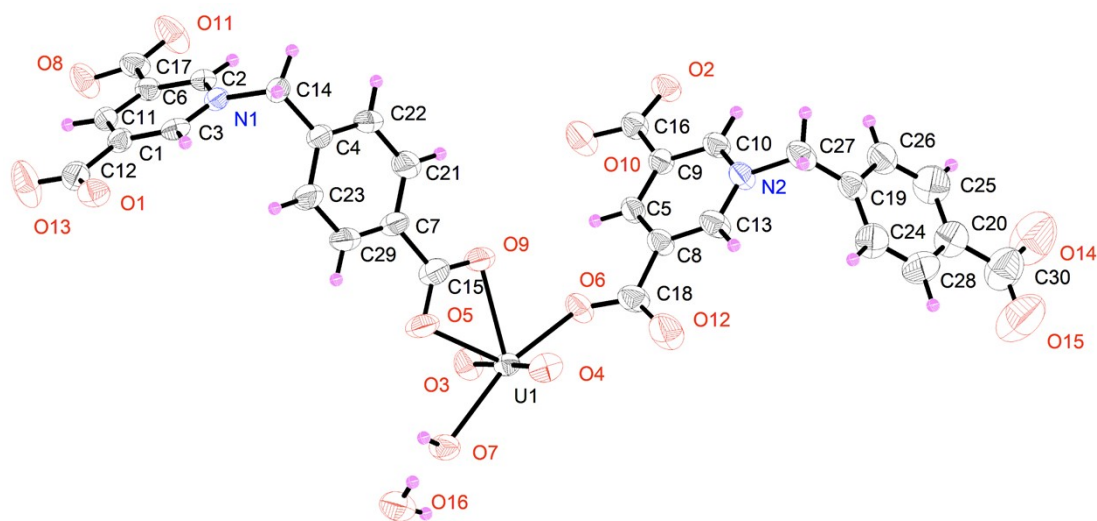
Fig. S1 ORTEP of **U-Cbdcp** with thermal ellipsoids drawn at the 50% probability level.
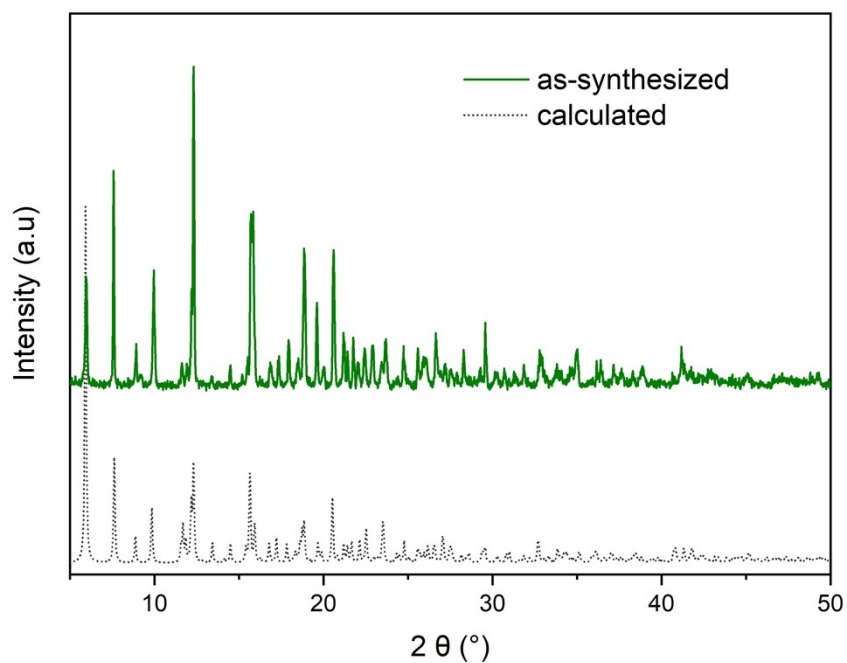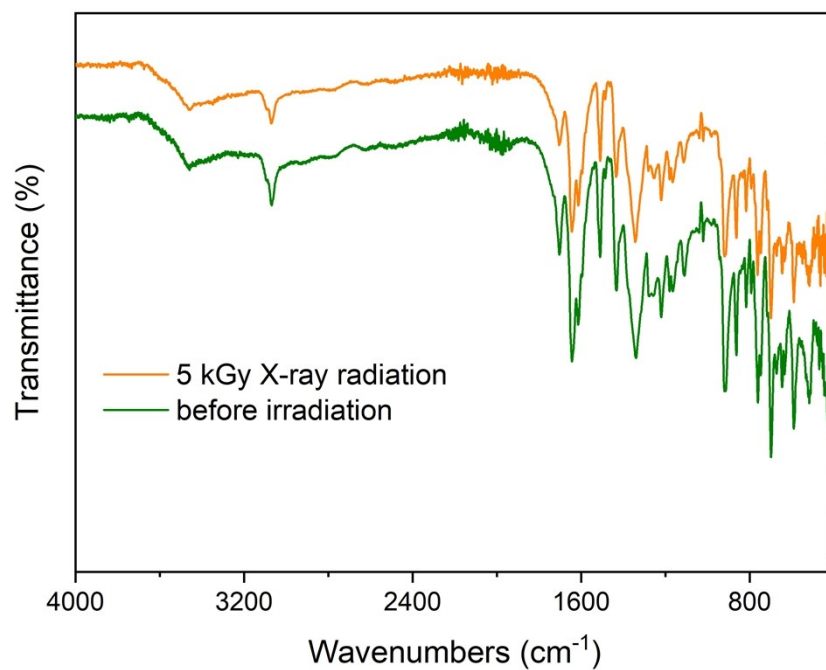

Fig. S2 The as synthesized and calculated PXRD patterns of **U-Cbdcp**.

Fig. S3 The quenching rate of **U-Cbdcp** as a function of radiation dose.

Fig. S4 The PXRD patterns of **U-Cbdcp** before and after 5 kGy X-ray radiation.
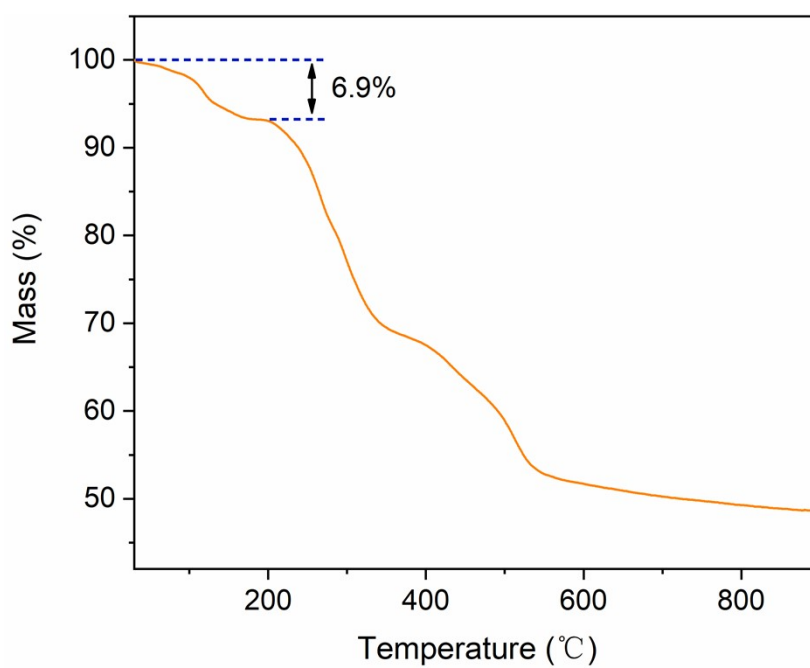
Fig. S5 The FTIR spectra of **U-Cbdcp** before and after 5 kGy X-ray radiation.
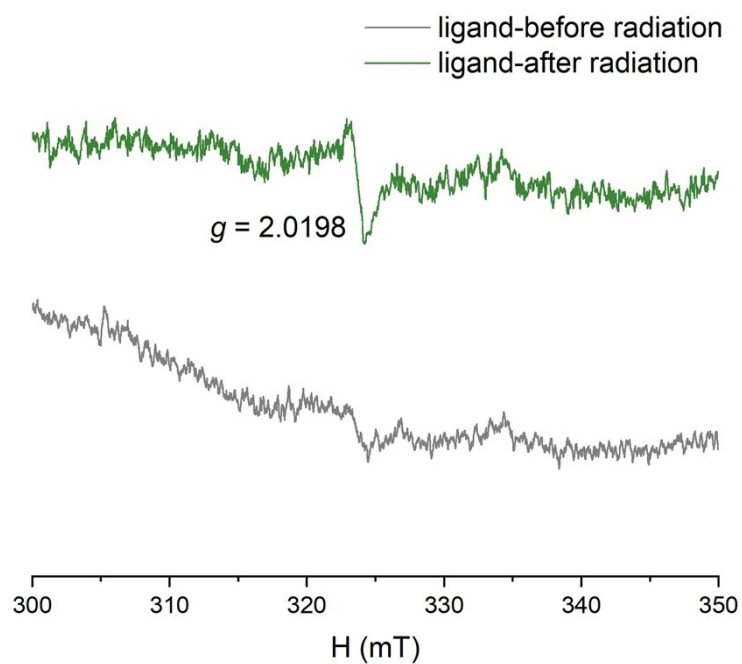
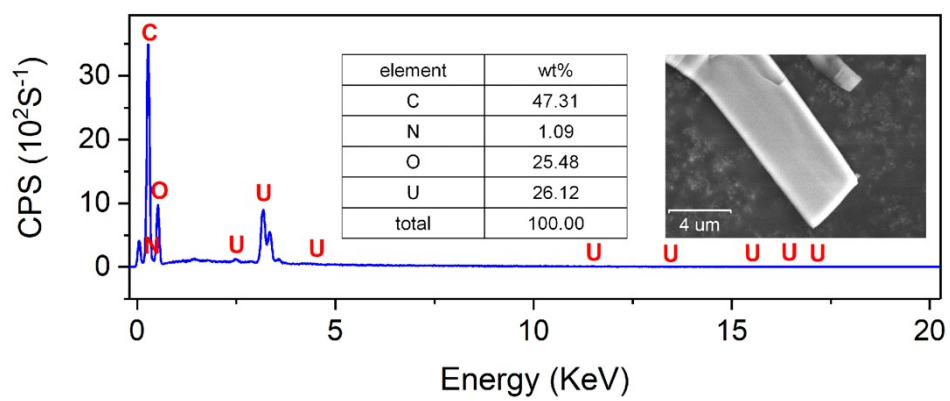**Fig. S6** EPR spectra of $H_3CbdcpBr$ ligand before and after 5 kGy X-ray radiation.
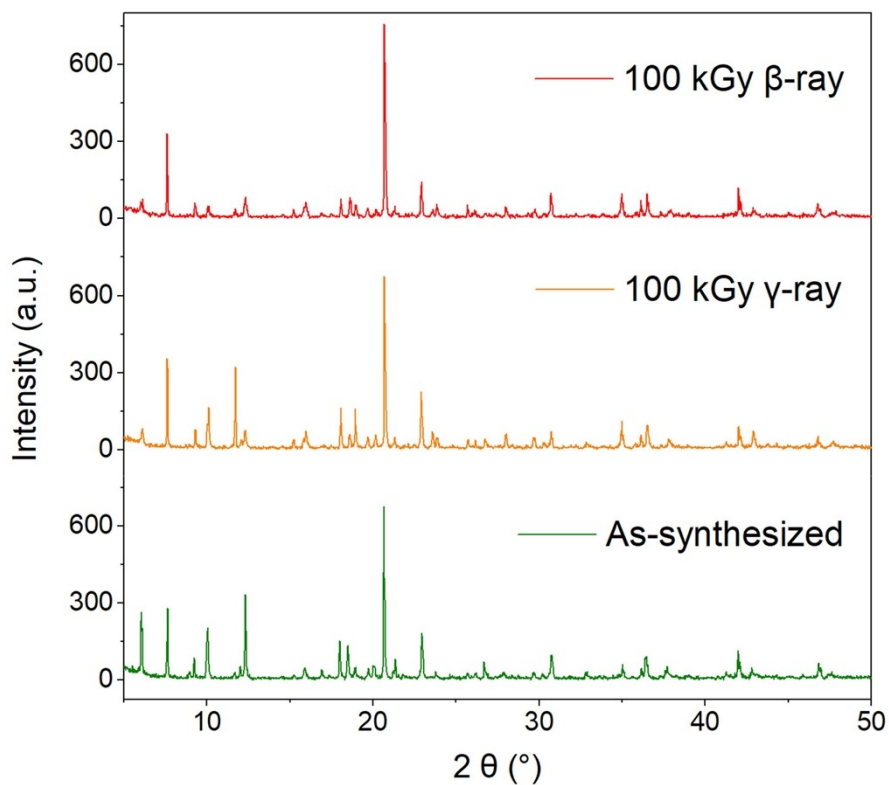
Fig. S7 The PXRD patterns of **U–Cbdcp** before and after 100 kGy β-ray and γ-ray radiations.

Fig. S8. The TGA plot of **U–Cbdcp**.

Fig. S9 SEM images and EDS spectra of **U-Cbdcp**.

S4. Supplementary Tables.

Table S1. Selected crystallographic data for **U-Cbdcp** before and after radiation.

Compound	U-Cbdcp-before radiation	U-Cbdcp-after radiation
CCDC number	2141552	2141553
formula	$C_{30}N_2O_{16}UH_{21}(+ O_3H_6)$	$C_{30}N_2O_{16}UH_{21}(+ O_3H_6)$
formula weight	957.57	957.57
space Group	$P2_1/n$	$P2_1/n$
a (Å)	8.0892(6)	8.0842(2)
b (Å)	23.3482(17)	23.3422(5)
c (Å)	19.1156(12)	19.1627(4)
α (deg)	90	90
β (deg)	95.277(3)	95.2160(10)
γ (deg)	90	90
V (Å^3)	3595.0(4)	3601.09(14)
Z	4	4
λ (Å)	0.71073	0.71073
Max. 2θ (°)	55.21	55.11
ρ_{calcd} Mg/m^3	1.769	1.766
μ (mm^{-1})	4.586	4.578
GoF on F^2	1.014	1.034
R_1,	0.0380	0.0353
wR_2 [I > 2σ(I)]	0.0873	0.0816
R_1,	0.0596	0.0554
wR_2 (all data)	0.0952	0.0889
$(\Delta\rho)_{max}$,	0.726	0.640
$(\Delta\rho)_{min}$/e (Å^{-3})	-1.587	-1.185

Table S2. Selected bond distances and angles for **U-Cbdcp** before and after radiation.

	Compound	U-Cbdcp-before radiation	U-Cbdcp-after radiation
bond distance (Å)	U(1)-O(1)	2.335(3)	2.335(3)
	U(1)-O(3)	1.757(3)	1.756(3)
	U(1)-O(4)	1.756(3)	1.758(3)
	U(1)-O(5)#1	2.422(3)	2.428(3)
	U(1)-O(6)	2.336(3)	2.340(3)
	U(1)-O(7)	2.413(3)	2.413(3)
	U(1)-O(9)#1	2.456(3)	2.457(3)
bond angle (°)	O(1)-U(1)-O(5)#1	149.98(12)	150.21(11)
	O(1)-U(1)-O(6)	83.81(12)	83.85(11)
	O(1)-U(1)-O(7)	78.62(11)	78.88(11)
	O(1)-U(1)-O(9)#1	156.82(11)	156.69(11)
	O(1)-U(1)-C(15)#1	176.63(14)	176.79(13)
	O(3)-U(1)-O(1)	89.32(15)	89.37(14)
	O(3)-U(1)-O(4)	178.08(15)	178.33(14)
	O(3)-U(1)-O(5)#1	92.90(15)	92.90(14)
	O(3)-U(1)-O(6)	86.42(14)	86.67(13)
	O(3)-U(1)-O(7)	87.24(14)	87.06(13)
	O(3)-U(1)-O(9)#1	88.30(15)	88.45(14)
	O(3)-U(1)-C(15)#1	90.48(17)	90.40(15)
	O(4)-U(1)-O(1)	88.94(14)	89.14(13)
	O(4)-U(1)-O(5)#1	88.21(15)	88.01(14)
	O(4)-U(1)-O(6)	94.20(15)	93.93(14)
	O(4)-U(1)-O(7)	91.62(15)	91.91(14)
	O(4)-U(1)-O(9)#1	93.62(15)	93.21(14)
	O(4)-U(1)-C(15)#1	91.21(16)	91.04(15)
	O(5)#1-U(1)-O(9)#1	53.19(11)	53.10(10)
	O(5)#1-U(1)-C(15)#1	26.69(13)	26.62(13)
	O(6)-U(1)-O(5)#1	126.20(12)	125.93(11)
	O(6)-U(1)-O(7)	161.37(12)	161.67(11)
	O(6)-U(1)-O(9)#1	73.03(12)	72.86(11)
	O(6)-U(1)-C(15)#1	99.53(14)	99.34(13)
	O(7)-U(1)-O(5)#1	71.60(11)	71.59(11)
	O(7)-U(1)-O(9)#1	124.26(11)	124.15(11)
	O(7)#1-U(1)-C(15)#1	98.02(13)	97.91(13)
	O(9)#1-U(1)-C(15)#1	26.51(12)	26.48(11)

S5. Reference

1. *Bruker APEX3 Software Suite; Bruker AXS Inc.: Madison, WI, 2016.*
2. G. M. Sheldrick, *Acta Crystallogr. Sect. C: Struct. Chem.*, 2015, **71**, 3.
3. A. L. Spek, *Acta Crystallogr. Sect. C: Struct. Chem.*, 2015, **71**, 9.