Supporting Information

The first bimetallic Np(V) MOF with $Np_4Cs_2O_8$ structural unit: sorption properties, thermal and radiation stability

Volkov M.A., Parashutin E.D., Fedoseev A.M., Grigoriev M.S., Novikov A.P., Nevolin I.M., Shiryaev A.A., Averin A.A., Abkhalimov E.V.

Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119071 Moscow, Russia; Email: **abkhalimov@ipc.rssi.ru

Experimental

Caution!

Neptunium-237 is a radioactive material that poses a significant health risk if inhaled or ingested. It is an alpha emitter and also releases gamma rays from daughter isotopes (e.g., ^{233}Pa). It must be studied in a facility designed for handling radioactive and toxic heavy metals. All manupulations were performed in a negative pressure radiological glovebox, or in radiochemical fume hoods.

Cesium-137 is extremely γ-radioactive nuclide that poses a significant health risk. All operations must be performed in "hot" cells approved for handling radioactive materials.

Chemicals

N,N,-dimethylformamide (DMF), nitric acid were purchased from Rushim and 1,2,4,5-tetrakis(4-carboxyphenyl) benzene (H_4TCPB) was purchased from Macklin. $^{237}NpO_2$ (isotope pure grade) and $^{137}CsNO_3$ aqueous solution (specific activity 500 MBq/mL) was purchased from Isotope JSC. The reagents were used without further purification.

Synthesis of $Cs_2Np(NO_3)_6$

100 mg of NpO_2 was fully dissolved in 5 mL of 8 M HNO_3 and 1 mL of H_2O_2 (30% wt.) was added. Resulting green solution was mixed up with 500 μL of saturated solution of $CsNO_3$ in 8 M HNO_3 and left overnight. Resulting pale-green residue of $Cs_2Np(NO_3)_6$ was removed from mother liquor via decantation and washed with fresh DMF 3 times. Purity of observed material was controlled by pXRD. (Figure S14). Resulting ^{137}Cs specific activity of the sample was 120 Bq/(mg $Cs_2Np(NO_3)_6$).

Synthesis of NpCs-TCPB

2 mg of $Cs_2Np(NO_3)_6$ was mixed up with 2 mg of H_4TCPB and partially dissolved in 100 μL DMF. Resulting suspension was sealed in glass ampoule and heated in oven for 24 hours at 130 °C. Emerald-green crystals, suitable for SCXRD were produced and removed from mother liquor via decantation with washing by fresh DMF 3 times. The ^{137}Cs-labelled sample possess specific activity of 74 Bq/(mg **NpCs-TCPB** MOF).

SCXRD

The single crystal X-ray diffraction experiment was performed on a Bruker KAPPA APEX II diffractometer. The unit-cell parameters were refined over the entire data set simultaneously with data reduction using the SAINT-Plus software.[1] Absorption corrections were applied using the SADABS program.[2] The structure was solved using the SHELXT-2018/2 program[3] and refined by full-matrix least squares on F2 in the anisotropic approximation for all non-hydrogen atoms in the SHELXL-2018/3 program.[4] The H atoms are located in geometrically calculated positions and refined with isotropic temperature factors equal to 1.2 Ueq(C) for CH and 1.5 Ueq(C) for CH3-groups. The solvent molecules are severely disordered; therefore, their contribution to the diffraction intensities was removed using the SQUEEZE routine implemented in PLATON.[5] The structure was subsequently refined using the modified data set. Crystal data, details of data collection, and refinement parameters are summarized in Table S1. The structure has been deposited with the Cambridge Crystallographic Data Centre[6] (CCDC) under deposition number CCDC 2530557.

pXRD

The pXRD study was performed on a Panalytical Aeris diffractometer, equipped with a Cu-Kα X-ray source (λ = 1.54184 Å) and an X'celerator detector, operating under the following conditions: voltage: 40 kV; current: 40 mA; range: 2°–50°; step size: 0.011°.

Spectroscopy

Spectra in visible-near IR range (380-960 nm) were acquired in transmission mode from individual crystals using MSFU-K (LOMO) microspectrophometer. The aperture size was 30-50 μm depending on the crystal size. Furthermore, the spectrum of the compound in the NaCl matrix was recorded over the range of 400–1300 nm using a Shimadzu UV-3100 UV-vis-NIR spectrophotometer.

IR spectra were collected using iN10 Nicolet microscope in transmission geometry. The aperture size was matching the crystal.

Raman spectra were acquired at inVia Reflex spectrometer (Renishaw) in backscattering geometry using 405 and 633 nm lasers.

Sorption and leaching of ^{137}Cs

A 2 mg of activated **NpCs-TCPB** MOF was placed in a glass vial and filled with 1 ml of a ^{137}Cs-spiked 0.001 M $CsNO_3$ aqueous solution; the specific activity of the solution was 102 Bq/ml. The concentrations of ^{137}Cs and ^{237}Np in the leachates solutions were monitored by γ-spectrometry on a GEM30P4–76 spectrometer (Ortec) using an HPGe detector.

Radiation Resistance

Irradiation experiments have been carried out on a linear electron accelerator LINS 3-350. The energy of electron beam was 3 MeV. Dose rate was 180 Gy/s. Absorbed dose was determined using a film dosimeter. The material for irradiation was divided into three equal parts, each weighing 2 mg. The samples were placed in glass ampoules, purged with argon, evacuated, and sealed.

Thermal analysis

Thermal gravimetry (TG) with simultaneous differential thermal analysis (DTA) was performed using a Netzsch STA Jupiter 449 F3 thermoanalytical complex. The heating rate was set at 10 °C/min, spanning the temperature range from 30 °C to 1000 °C. The experiment utilized Al_2O_3 crucibles, with the atmosphere composed of a synthetic air. The mass of sample was 1.72 mg.

SEM and EDX

Micrographs of the samples were obtained using a Kyky-EM6900 scanning electron microscope at an accelerating voltage of 20 kV in SE and BSE modes. The elemental composition and distribution maps were obtained using an Energy Dispersive X-ray Spectrometer (EDX).

Table S1. Crystal data and structure refinement for **NpCs-TCPB** MOF.

Identification code	**NpCs-TCPB**
Empirical formula	$C_{37}H_{25}Cs_2NNp_2O_{13}$
Formula weight	1431.40
Temperature/K	100(2)
Crystal system	Triclinic
Space group	P-1
a/Å	10.732(2)
b/Å	13.016(3)
c/Å	16.920(4)
α/°	83.593(8)
β/°	75.946(8)
γ/°	88.332(8)
Volume/Å^3	2278.4(9)
Z	2
ρ_{calc}g/cm^3	2.086
μ/mm^{-1}	6.166
F(000)	1308.0
Crystal size/mm^3	0.24 × 0.05 × 0.03
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.57 to 54.998
Index ranges	-13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -21 ≤ l ≤ 21
Reflections collected	34927
Independent reflections	10414 [R_{int} = 0.0619, R_{sigma} = 0.0724]
Data/restraints/parameters	10414/24/498
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0412, wR_2 = 0.0884
Final R indexes [all data]	R_1 = 0.0613, wR_2 = 0.0963
Largest diff. peak/hole / e Å^{-3}	1.42/-2.50

Table S2. Bond Lengths for **NpCs-TCPB.**

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Np1	Np2	3.9743(8)		O10	C3	1.266(9)
Np1	Np2[1]	3.9954(7)		O11	C4	1.273(9)
Np1	Cs1	4.3752(10)		O12	C4	1.259(8)
Np1	Cs2[2]	4.3091(10)		C1	C5	1.500(9)
Np1	O1	1.890(5)		C2	C11	1.498(9)
Np1	O2	1.829(6)		C3	C17	1.495(10)
Np1	O3	2.393(5)		C4	C23	1.482(9)
Np1	O7[3]	2.428(5)		C5	C6	1.387(10)
Np1	O9[4]	2.497(5)		C5	C10	1.390(11)
Np1	O10[4]	2.522(5)		C6	C7	1.388(9)
Np1	O12	2.434(5)		C7	C8	1.391(10)
Np1	C3[4]	2.872(7)		C8	C9	1.409(10)
Np2	Cs2	3.9915(9)		C8	C29	1.475(9)
Np2	Cs2[5]	4.1923(9)		C9	C10	1.393(10)
Np2	O1[1]	2.420(4)		C11	C12	1.394(10)
Np2	O3	1.867(5)		C11	C16	1.399(10)
Np2	O4	1.821(5)		C12	C13	1.387(9)
Np2	O5[6]	2.572(5)		C13	C14	1.403(10)
Np2	O6[6]	2.482(4)		C14	C15	1.397(10)
Np2	O8[3]	2.468(5)		C14	C31	1.489(9)
Np2	O11[1]	2.397(5)		C15	C16	1.396(9)
Np2	C1[6]	2.869(7)		C17	C18	1.381(10)
Cs1	Cs2[2]	5.1177(12)		C17	C22	1.384(11)
Cs1	O3	3.058(5)		C18	C19	1.403(10)
Cs1	O6[6]	3.516(5)		C19	C20	1.383(10)
Cs1	O7[7]	3.367(5)		C20	C21	1.402(10)
Cs1	O10[4]	3.078(5)		C20	C32	1.485(9)
Cs1	O11[1]	3.523(5)		C21	C22	1.384(10)
Cs1	C2[7]	3.702(7)		C23	C24	1.411(10)
Cs1	C11[7]	3.621(7)		C23	C28	1.403(10)
Cs1	C12[7]	3.643(8)		C24	C25	1.394(10)
Cs1	O13	3.126(7)		C25	C26	1.391(10)
Cs2	O1[8]	3.157(5)		C26	C27	1.392(10)
Cs2	O4[5]	3.152(5)		C26	C34	1.492(9)
Cs2	O4	3.124(5)		C27	C28	1.395(9)
Cs2	O5[6]	3.236(5)		C29	C30	1.406(9)
Cs2	O8[3]	3.128(5)		C29	C34	1.416(10)
Cs2	O9[9]	3.168(6)		C30	C31	1.404(10)
Cs2	C3[9]	3.518(8)		C31	C32	1.410(10)
Cs2	O13[8]	3.060(7)		C32	C33	1.408(9)
Cs2	C35[8]	3.832(11)		C33	C34	1.388(10)
O5	C1	1.254(8)		O13	C35	1.264(12)
O6	C1	1.273(9)		N1	C35	1.373(12)
O7	C2	1.275(9)		N1	C36	1.424(14)
O8	C2	1.263(8)		N1	C37	1.440(13)
O9	C3	1.277(8)				

[1]1-X,2-Y,-Z; [2]-1+X,+Y,+Z; [3]1-X,1-Y,1-Z; [4]+X,+Y,-1+Z; [5]2-X,2-Y,-Z; [6]1-X,1-Y,-Z; [7]+X,1+Y,-1+Z; [8]1+X,+Y,+Z; [9]1+X,+Y,-1+Z

Table S3. Bond Angles for **NpCs-TCPB.**

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
Np2	Np1	Np2^{1}	97.140(18)		O13	Cs1	O11^{1}	153.19(15)
Np2^{1}	Np1	Cs1	88.423(19)		O13	Cs1	C2^{7}	79.07(17)
Np2	Np1	Cs1	60.713(13)		O13	Cs1	C11^{7}	74.62(19)
Np2^{1}	Np1	Cs2^{2}	60.499(14)		O13	Cs1	C12^{7}	91.91(19)
Np2	Np1	Cs2^{2}	128.563(16)		Np2	Cs2	Np1^{8}	160.312(18)
Cs2^{2}	Np1	Cs1	72.210(15)		Np2^{5}	Cs2	Np1^{8}	56.046(12)
O1	Np1	Np2^{1}	25.08(13)		Np2	Cs2	Np2^{5}	109.794(18)
O1	Np1	Np2	98.74(15)		O1^{8}	Cs2	Np1^{8}	23.43(9)
O1	Np1	Cs1	68.20(13)		O1^{8}	Cs2	Np2^{5}	35.00(8)
O1	Np1	Cs2^{2}	41.65(14)		O1^{8}	Cs2	Np2	138.06(9)
O1	Np1	O3	88.20(19)		O1^{8}	Cs2	O5^{6}	159.53(12)
O1	Np1	O7^{3}	98.29(18)		O1^{8}	Cs2	O9^{9}	58.39(13)
O1	Np1	O9^{4}	88.3(2)		O1^{8}	Cs2	C3^{9}	62.75(15)
O1	Np1	O10^{4}	91.51(18)		O1^{8}	Cs2	C35^{8}	101.68(18)
O1	Np1	O12	88.25(19)		O4	Cs2	Np1^{8}	134.14(10)
O1	Np1	C3^{4}	91.9(2)		O4^{5}	Cs2	Np1^{8}	76.07(10)
O2	Np1	Np2^{1}	156.65(16)		O4^{5}	Cs2	Np2^{5}	23.73(9)
O2	Np1	Np2	83.95(18)		O4	Cs2	Np2	26.21(9)
O2	Np1	Cs1	111.92(16)		O4	Cs2	Np2^{5}	90.82(9)
O2	Np1	Cs2^{2}	135.15(17)		O4^{5}	Cs2	Np2	94.20(10)
O2	Np1	O1	176.8(2)		O4^{5}	Cs2	O1^{8}	57.69(13)
O2	Np1	O3	93.9(2)		O4	Cs2	O1^{8}	112.98(13)
O2	Np1	O7^{3}	84.6(2)		O4	Cs2	O4^{5}	82.77(13)
O2	Np1	O9^{4}	88.5(2)		O4^{5}	Cs2	O5^{6}	132.97(13)
O2	Np1	O10^{4}	86.7(2)		O4	Cs2	O5^{6}	59.28(13)
O2	Np1	O12	90.8(2)		O4	Cs2	O8^{3}	56.31(13)
O2	Np1	C3^{4}	85.3(2)		O4^{5}	Cs2	O9^{9}	103.61(13)
O3	Np1	Np2	18.55(11)		O4	Cs2	O9^{9}	160.06(13)
O3	Np1	Np2^{1}	94.03(11)		O4	Cs2	C3^{9}	139.99(15)
O3	Np1	Cs1	42.19(11)		O4^{5}	Cs2	C3^{9}	117.36(15)
O3	Np1	Cs2^{2}	111.29(12)		O4^{5}	Cs2	C35^{8}	127.9(2)
O3	Np1	O7^{3}	76.98(16)		O4	Cs2	C35^{8}	60.9(2)
O3	Np1	O9^{4}	127.89(15)		O5^{6}	Cs2	Np1^{8}	150.46(9)
O3	Np1	O10^{4}	75.81(16)		O5^{6}	Cs2	Np2^{5}	149.45(9)
O3	Np1	O12	155.11(17)		O5^{6}	Cs2	Np2	40.00(9)
O3	Np1	C3^{4}	101.93(19)		O5^{6}	Cs2	C3^{9}	109.64(14)
O7^{3}	Np1	Np2	60.50(11)		O5^{6}	Cs2	C35^{8}	57.85(18)
O7^{3}	Np1	Np2^{1}	75.92(12)		O8^{3}	Cs2	Np1^{8}	147.07(8)
O7^{3}	Np1	Cs1	116.01(12)		O8^{3}	Cs2	Np2^{5}	98.11(9)
O7^{3}	Np1	Cs2^{2}	135.79(12)		O8^{3}	Cs2	Np2	38.18(9)
O7^{3}	Np1	O9^{4}	154.68(16)		O8^{3}	Cs2	O1^{8}	132.74(12)
O7^{3}	Np1	O10^{4}	150.70(17)		O8^{3}	Cs2	O4^{5}	75.06(13)
O7^{3}	Np1	O12	79.19(18)		O8^{3}	Cs2	O5^{6}	61.42(12)
O7^{3}	Np1	C3^{4}	169.7(2)		O8^{3}	Cs2	O9^{9}	143.42(13)
O9^{4}	Np1	Np2^{1}	103.68(13)		O8^{3}	Cs2	C3^{9}	157.28(16)
O9^{4}	Np1	Np2	142.83(11)		O8^{3}	Cs2	C35^{8}	107.65(19)
O9^{4}	Np1	Cs1	89.17(12)		O9^{9}	Cs2	Np1^{8}	34.98(9)
O9^{4}	Np1	Cs2^{2}	46.68(14)		O9^{9}	Cs2	Np2	161.66(9)

O9^{4}	Np1	O10^{4}	52.35(16)		O9^{9}	Cs2	Np2^{5}	88.49(9)
O9^{4}	Np1	C3^{4}	26.36(18)		O9^{9}	Cs2	O5^{6}	121.66(12)
O10^{4}	Np1	Np2	90.82(12)		O9^{9}	Cs2	C3^{9}	21.21(15)
O10^{4}	Np1	Np2^{1}	116.58(13)		O9^{9}	Cs2	C35^{8}	101.6(2)
O10^{4}	Np1	Cs1	43.43(12)		C3^{9}	Cs2	Np1^{8}	41.52(12)
O10^{4}	Np1	Cs2^{2}	65.88(13)		C3^{9}	Cs2	Np2	146.08(11)
O10^{4}	Np1	C3^{4}	26.13(18)		C3^{9}	Cs2	Np2^{5}	97.26(12)
O12	Np1	Np2^{1}	73.19(12)		C3^{9}	Cs2	C35^{8}	80.4(2)
O12	Np1	Np2	139.64(13)		O13^{8}	Cs2	Np1^{8}	85.77(14)
O12	Np1	Cs1	152.97(14)		O13^{8}	Cs2	Np2	86.32(14)
O12	Np1	Cs2^{2}	81.42(14)		O13^{8}	Cs2	Np2^{5}	107.59(14)
O12	Np1	O9^{4}	76.59(17)		O13^{8}	Cs2	O1^{8}	87.28(16)
O12	Np1	O10^{4}	128.91(18)		O13^{8}	Cs2	O4	74.47(17)
O12	Np1	C3^{4}	102.8(2)		O13^{8}	Cs2	O4^{5}	125.87(17)
C3^{4}	Np1	Np2^{1}	114.38(16)		O13^{8}	Cs2	O5^{6}	72.49(16)
C3^{4}	Np1	Np2	116.52(15)		O13^{8}	Cs2	O8^{3}	124.35(16)
C3^{4}	Np1	Cs1	66.47(16)		O13^{8}	Cs2	O9^{9}	86.75(17)
C3^{4}	Np1	Cs2^{2}	54.32(15)		O13^{8}	Cs2	C3^{9}	65.71(19)
Np1	Np2	Np1^{1}	82.860(18)		O13^{8}	Cs2	C35^{8}	16.8(2)
Np1	Np2	Cs2^{5}	121.486(16)		C35^{8}	Cs2	Np1^{8}	102.43(17)
Np1	Np2	Cs2	110.560(19)		C35^{8}	Cs2	Np2	69.83(18)
Np1^{1}	Np2	Cs2^{5}	63.456(16)		C35^{8}	Cs2	Np2^{5}	115.34(17)
Cs2	Np2	Np1^{1}	131.308(15)		Np1	O1	Np2^{1}	135.6(2)
Cs2	Np2	Cs2^{5}	70.205(18)		Np1	O1	Cs2^{2}	114.92(19)
O1^{1}	Np2	Np1^{1}	19.32(11)		Np2^{1}	O1	Cs2^{2}	96.57(16)
O1^{1}	Np2	Np1	85.03(12)		Np1	O3	Cs1	106.10(17)
O1^{1}	Np2	Cs2^{5}	48.43(12)		Np2	O3	Np1	137.4(2)
O1^{1}	Np2	Cs2	112.57(12)		Np2	O3	Cs1	116.43(19)
O1^{1}	Np2	O5^{6}	159.18(16)		Np2	O4	Cs2	104.5(2)
O1^{1}	Np2	O6^{6}	148.81(17)		Np2	O4	Cs2^{5}	112.11(19)
O1^{1}	Np2	O8^{3}	78.95(16)		Cs2	O4	Cs2^{5}	97.23(13)
O1^{1}	Np2	C1^{6}	170.38(18)		Np2^{6}	O5	Cs2^{6}	86.03(13)
O3	Np2	Np1	24.06(14)		C1	O5	Np2^{6}	90.4(4)
O3	Np2	Np1^{1}	79.96(14)		C1	O5	Cs2^{6}	145.9(5)
O3	Np2	Cs2^{5}	135.97(13)		Np2^{6}	O6	Cs1^{6}	88.05(14)
O3	Np2	Cs2	129.88(15)		C1	O6	Np2^{6}	94.1(4)
O3	Np2	O1^{1}	89.78(18)		C1	O6	Cs1^{6}	118.1(4)
O3	Np2	O5^{6}	89.57(19)		Np1^{3}	O7	Cs1^{10}	135.9(2)
O3	Np2	O6^{6}	82.75(18)		C2	O7	Np1^{3}	129.1(4)
O3	Np2	O8^{3}	93.78(18)		C2	O7	Cs1^{10}	95.0(4)
O3	Np2	O11^{1}	90.8(2)		Np2^{3}	O8	Cs2^{3}	90.22(14)
O3	Np2	C1^{6}	81.4(2)		C2	O8	Np2^{3}	123.1(5)
O4	Np2	Np1	155.22(15)		C2	O8	Cs2^{3}	145.7(5)
O4	Np2	Np1^{1}	100.61(15)		Np1^{11}	O9	Cs2^{12}	98.34(18)
O4	Np2	Cs2^{5}	44.15(14)		C3	O9	Np1^{11}	93.4(4)
O4	Np2	Cs2	49.25(16)		C3	O9	Cs2^{12}	95.0(5)
O4	Np2	O1^{1}	90.58(19)		Np1^{11}	O10	Cs1^{11}	102.29(17)
O4	Np2	O3	179.1(2)		C3	O10	Np1^{11}	92.5(4)
O4	Np2	O5^{6}	89.81(19)		C3	O10	Cs1^{11}	143.7(5)
O4	Np2	O6^{6}	97.34(18)		Np2^{1}	O11	Cs1^{1}	89.21(15)

O4	Np2	O8^{3}	85.50(19)		C4	O11	Np2^{1}	145.5(4)
O4	Np2	O11^{1}	90.1(2)		C4	O11	Cs1^{1}	116.5(5)
O4	Np2	C1^{6}	98.3(2)		C4	O12	Np1	123.7(5)
O5^{6}	Np2	Np1	85.92(12)		O5	C1	Np2^{6}	63.7(4)
O5^{6}	Np2	Np1^{1}	168.77(12)		O5	C1	O6	120.7(6)
O5^{6}	Np2	Cs2^{5}	123.91(11)		O5	C1	C5	120.9(7)
O5^{6}	Np2	Cs2	53.97(11)		O6	C1	Np2^{6}	59.6(3)
O5^{6}	Np2	C1^{6}	25.91(18)		O6	C1	C5	118.4(6)
O6^{6}	Np2	Np1^{1}	130.01(12)		C5	C1	Np2^{6}	161.6(5)
O6^{6}	Np2	Np1	98.97(12)		O7	C2	Cs1^{10}	65.0(4)
O6^{6}	Np2	Cs2	95.08(12)		O7	C2	C11	116.3(6)
O6^{6}	Np2	Cs2^{5}	139.48(12)		O8	C2	Cs1^{10}	128.1(5)
O6^{6}	Np2	O5^{6}	51.48(16)		O8	C2	O7	124.6(6)
O6^{6}	Np2	C1^{6}	26.27(18)		O8	C2	C11	119.0(7)
O8^{3}	Np2	Np1^{1}	96.21(12)		C11	C2	Cs1^{10}	75.2(4)
O8^{3}	Np2	Np1	69.72(12)		Np1^{11}	C3	Cs2^{12}	84.16(18)
O8^{3}	Np2	Cs2	51.59(12)		O9	C3	Np1^{11}	60.2(4)
O8^{3}	Np2	Cs2^{5}	68.35(12)		O9	C3	Cs2^{12}	63.8(4)
O8^{3}	Np2	O5^{6}	80.32(16)		O9	C3	C17	118.8(7)
O8^{3}	Np2	O6^{6}	131.58(17)		O10	C3	Np1^{11}	61.3(4)
O8^{3}	Np2	C1^{6}	105.34(19)		O10	C3	Cs2^{12}	103.4(5)
O11^{1}	Np2	Np1^{1}	60.40(11)		O10	C3	O9	121.0(7)
O11^{1}	Np2	Np1	112.38(13)		O10	C3	C17	120.1(6)
O11^{1}	Np2	Cs2	136.74(13)		C17	C3	Np1^{11}	171.9(6)
O11^{1}	Np2	Cs2^{5}	91.54(12)		C17	C3	Cs2^{12}	102.7(5)
O11^{1}	Np2	O1^{1}	76.47(16)		O11	C4	C23	116.9(6)
O11^{1}	Np2	O5^{6}	124.35(15)		O12	C4	O11	124.7(6)
O11^{1}	Np2	O6^{6}	73.41(16)		O12	C4	C23	118.3(7)
O11^{1}	Np2	O8^{3}	154.98(16)		C6	C5	C1	118.6(7)
O11^{1}	Np2	C1^{6}	99.67(18)		C6	C5	C10	118.1(6)
C1^{6}	Np2	Np1^{1}	152.29(15)		C10	C5	C1	123.3(7)
C1^{6}	Np2	Np1	88.41(14)		C5	C6	C7	120.8(7)
C1^{6}	Np2	Cs2^{5}	141.06(14)		C6	C7	C8	121.6(7)
C1^{6}	Np2	Cs2	76.35(15)		C7	C8	C9	117.8(6)
Np1	Cs1	Cs2^{2}	53.297(14)		C7	C8	C29	119.2(7)
Np2	Cs1	Np1	54.956(13)		C9	C8	C29	122.9(7)
Np2	Cs1	Cs2^{2}	105.525(19)		C10	C9	C8	119.9(7)
O3	Cs1	Np1	31.71(9)		C5	C10	C9	121.8(7)
O3	Cs1	Np2	23.26(9)		C2	C11	Cs1^{10}	81.2(4)
O3	Cs1	Cs2^{2}	83.11(9)		C12	C11	Cs1^{10}	79.8(4)
O3	Cs1	O6^{6}	52.01(12)		C12	C11	C2	119.1(6)
O3	Cs1	O7^{7}	62.38(12)		C12	C11	C16	119.2(6)
O3	Cs1	O10^{4}	59.00(13)		C16	C11	Cs1^{10}	108.7(5)
O3	Cs1	O11^{1}	54.83(12)		C16	C11	C2	121.8(7)
O3	Cs1	C2^{7}	78.33(14)		C11	C12	Cs1^{10}	78.1(4)
O3	Cs1	C11^{7}	101.08(13)		C13	C12	Cs1^{10}	108.3(5)
O3	Cs1	C12^{7}	106.38(14)		C13	C12	C11	121.0(7)
O3	Cs1	O13	115.31(16)		C12	C13	C14	120.5(7)
O6^{6}	Cs1	Np1	77.85(8)		C13	C14	C31	119.2(7)
O6^{6}	Cs1	Np2	35.86(7)		C15	C14	C13	118.3(6)

O6[6]	Cs1	Cs2[2]	130.42(8)		C15	C14	C31	122.4(7)
O6[6]	Cs1	O11[1]	48.96(12)		C16	C15	C14	121.3(7)
O6[6]	Cs1	C2[7]	118.49(13)		C15	C16	C11	119.7(7)
O6[6]	Cs1	C11[7]	131.65(14)		C18	C17	C3	120.3(7)
O6[6]	Cs1	C12[7]	117.82(15)		C18	C17	C22	121.1(7)
O7[7]	Cs1	Np1	68.09(8)		C22	C17	C3	118.6(6)
O7[7]	Cs1	Np2	64.84(9)		C17	C18	C19	119.4(7)
O7[7]	Cs1	Cs2[2]	73.00(9)		C20	C19	C18	120.0(6)
O7[7]	Cs1	O6[6]	98.44(12)		C19	C20	C21	119.7(7)
O7[7]	Cs1	O11[1]	55.98(12)		C19	C20	C32	120.4(6)
O7[7]	Cs1	C2[7]	20.06(13)		C21	C20	C32	119.8(7)
O7[7]	Cs1	C11[7]	39.24(13)		C22	C21	C20	120.2(7)
O7[7]	Cs1	C12[7]	46.47(13)		C21	C22	C17	119.5(7)
O10[4]	Cs1	Np1	34.29(9)		C24	C23	C4	120.1(6)
O10[4]	Cs1	Np2	79.04(10)		C28	C23	C4	120.5(7)
O10[4]	Cs1	Cs2[2]	51.49(10)		C28	C23	C24	119.4(6)
O10[4]	Cs1	O6[6]	84.17(13)		C25	C24	C23	120.1(6)
O10[4]	Cs1	O7[7]	100.17(12)		C26	C25	C24	120.5(7)
O10[4]	Cs1	O11[1]	113.24(13)		C25	C26	C27	119.4(6)
O10[4]	Cs1	C2[7]	100.69(15)		C25	C26	C34	120.6(6)
O10[4]	Cs1	C11[7]	118.27(15)		C27	C26	C34	119.7(6)
O10[4]	Cs1	C12[7]	139.63(15)		C26	C27	C28	121.3(6)
O10[4]	Cs1	O13	67.21(18)		C27	C28	C23	119.4(7)
O11[1]	Cs1	Np1	84.87(8)		C30	C29	C8	117.9(7)
O11[1]	Cs1	Np2	34.48(8)		C30	C29	C34	117.7(6)
O11[1]	Cs1	Cs2[2]	123.90(8)		C34	C29	C8	124.4(6)
O11[1]	Cs1	C2[7]	74.51(14)		C31	C30	C29	122.8(7)
O11[1]	Cs1	C11[7]	82.80(14)		C30	C31	C14	119.4(7)
O11[1]	Cs1	C12[7]	70.51(15)		C30	C31	C32	119.0(6)
C2[7]	Cs1	Np1	74.66(11)		C32	C31	C14	121.4(6)
C2[7]	Cs1	Np2	84.37(11)		C31	C32	C20	123.6(6)
C2[7]	Cs1	Cs2[2]	60.69(11)		C33	C32	C20	118.4(7)
C11[7]	Cs1	Np1	97.28(10)		C33	C32	C31	117.9(6)
C11[7]	Cs1	Np2	102.86(11)		C34	C33	C32	123.1(7)
C11[7]	Cs1	Cs2[2]	69.69(12)		C29	C34	C26	125.0(6)
C11[7]	Cs1	C2[7]	23.58(15)		C33	C34	C26	115.4(6)
C11[7]	Cs1	C12[7]	22.13(16)		C33	C34	C29	119.4(6)
C12[7]	Cs1	Np1	113.33(11)		Cs2[2]	O13	Cs1	111.7(2)
C12[7]	Cs1	Np2	99.15(12)		C35	O13	Cs1	121.5(7)
C12[7]	Cs1	Cs2[2]	91.75(12)		C35	O13	Cs2[2]	118.8(6)
C12[7]	Cs1	C2[7]	39.69(16)		C35	N1	C36	122.3(10)
O13	Cs1	Np1	83.86(13)		C35	N1	C37	117.7(10)
O13	Cs1	Np2	138.46(13)		C36	N1	C37	119.8(9)
O13	Cs1	Cs2[2]	33.76(12)		O13	C35	Cs2[2]	44.4(5)
O13	Cs1	O6[6]	149.37(17)		O13	C35	N1	121.6(11)
O13	Cs1	O7[7]	97.21(16)		N1	C35	Cs2[2]	133.4(7)

[1]1-X,2-Y,-Z; [2]-1+X,+Y,+Z; [3]1-X,1-Y,1-Z; [4]+X,+Y,-1+Z; [5]2-X,2-Y,-Z; [6]1-X,1-Y,-Z; [7]+X,1+Y,-1+Z; [8]1+X,+Y,+Z; [9]1+X,+Y,-1+Z; [10]+X,-1+Y,1+Z; [11]+X,+Y,1+Z; [12]-1+X,+Y,1+Z

Table S4. Torsion Angles for **NpCs-TCPB**.

A	B	C	D	Angle/°		A	B	C	D	Angle/°
Np1[1]	Np2	O3	Np1	-95.0(3)		O9[9]	Np1	O1	Cs2[7]	-2.40(18)
Np1	Np2	O3	Cs1	-176.1(5)		O9	C3	C17	C18	-160.5(8)
Np1[1]	Np2	O3	Cs1	88.91(17)		O9	C3	C17	C22	16.5(12)
Np1	Np2	O4	Cs2	40.5(4)		O10[9]	Np1	O1	Np2[1]	-179.2(3)
Np1[1]	Np2	O4	Cs2[2]	32.25(18)		O10[9]	Np1	O1	Cs2[7]	49.9(2)
Np1[1]	Np2	O4	Cs2	136.47(10)		O10	C3	C17	C18	18.7(12)
Np1	Np2	O4	Cs2[2]	-63.7(4)		O10	C3	C17	C22	-164.3(8)
Np1[3]	O7	C2	Cs1[4]	179.7(5)		O11[1]	Np2	O3	Np1	-154.7(3)
Np1[3]	O7	C2	O8	-60.0(9)		O11[1]	Np2	O3	Cs1	29.2(2)
Np1[3]	O7	C2	C11	122.8(5)		O11[1]	Np2	O4	Cs2[2]	92.1(2)
Np1[5]	O9	C3	Cs2[6]	-98.7(2)		O11[1]	Np2	O4	Cs2	-163.68(16)
Np1[5]	O9	C3	O10	-8.4(8)		O11	C4	C23	C24	-158.1(7)
Np1[5]	O9	C3	C17	170.8(6)		O11	C4	C23	C28	19.6(10)
Np1[5]	O10	C3	Cs2[6]	75.5(3)		O12	Np1	O1	Np2[1]	51.9(3)
Np1[5]	O10	C3	O9	8.3(8)		O12	Np1	O1	Cs2[7]	-79.0(2)
Np1[5]	O10	C3	C17	-170.8(7)		O12	C4	C23	C24	18.8(11)
Np1	O12	C4	O11	16.6(11)		O12	C4	C23	C28	-163.5(7)
Np1	O12	C4	C23	-160.0(5)		C1[8]	Np2	O3	Np1	105.6(4)
Np2	Np1	O1	Np2[1]	-88.2(3)		C1[8]	Np2	O3	Cs1	-70.5(2)
Np2[1]	Np1	O1	Cs2[7]	-130.9(4)		C1[8]	Np2	O4	Cs2[2]	-168.1(2)
Np2	Np1	O1	Cs2[7]	140.92(14)		C1[8]	Np2	O4	Cs2	-63.89(19)
Np2[8]	O5	C1	O6	-18.1(7)		C1	C5	C6	C7	174.3(7)
Np2[8]	O5	C1	C5	159.7(6)		C1	C5	C10	C9	-176.3(7)
Np2[8]	O6	C1	O5	18.9(7)		C2	C11	C12	Cs1[4]	73.9(6)
Np2[8]	O6	C1	C5	-159.0(6)		C2	C11	C12	C13	178.2(7)
Np2[3]	O8	C2	Cs1[4]	77.6(6)		C2	C11	C16	C15	-176.7(7)
Np2[3]	O8	C2	O7	-5.9(10)		C3[9]	Np1	O1	Np2[1]	154.6(3)
Np2[3]	O8	C2	C11	171.2(4)		C3[9]	Np1	O1	Cs2[7]	23.7(2)
Np2[1]	O11	C4	O12	32.3(14)		C3	C17	C18	C19	175.7(7)
Np2[1]	O11	C4	C23	-151.1(6)		C3	C17	C22	C21	-175.6(8)
Np2[8]	C1	C5	C6	-56.8(19)		C4	C23	C24	C25	176.4(7)
Np2[8]	C1	C5	C10	119.9(15)		C4	C23	C28	C27	-177.0(7)
Cs1	Np1	O1	Np2[1]	-141.7(4)		C5	C6	C7	C8	3.0(12)
Cs1	Np1	O1	Cs2[7]	87.40(15)		C6	C5	C10	C9	0.4(11)
Cs1[8]	O6	C1	Np2[8]	90.0(3)		C6	C7	C8	C9	-1.3(11)
Cs1[8]	O6	C1	O5	108.9(7)		C6	C7	C8	C29	-177.9(7)
Cs1[8]	O6	C1	C5	-69.0(7)		C7	C8	C9	C10	-0.8(10)
Cs1[4]	O7	C2	O8	120.3(7)		C7	C8	C29	C30	-44.9(10)
Cs1[4]	O7	C2	C11	-56.9(6)		C7	C8	C29	C34	131.5(8)
Cs1[5]	O10	C3	Np1[5]	-114.8(7)		C8	C9	C10	C5	1.3(11)
Cs1[5]	O10	C3	Cs2[6]	-39.3(8)		C8	C29	C30	C31	175.4(7)
Cs1[5]	O10	C3	O9	-106.5(8)		C8	C29	C34	C26	-2.3(12)
Cs1[5]	O10	C3	C17	74.3(10)		C8	C29	C34	C33	-177.0(7)
Cs1[1]	O11	C4	O12	-101.9(7)		C9	C8	C29	C30	138.7(7)
Cs1[1]	O11	C4	C23	74.7(7)		C9	C8	C29	C34	-45.0(11)
Cs1[4]	C2	C11	C12	-73.1(6)		C10	C5	C6	C7	-2.5(11)
Cs1[4]	C2	C11	C16	106.7(7)		C11	C12	C13	C14	0.5(11)
Cs1[4]	C11	C12	C13	104.3(7)		C12	C11	C16	C15	3.1(11)

$Cs1^{4}$	C11	C16	C15	-85.5(7)		C12	C13	C14	C15	-1.0(11)
$Cs1^{4}$	C12	C13	C14	87.3(7)		C12	C13	C14	C31	-179.2(7)
Cs1	O13	C35	$Cs2^{7}$	-146.2(9)		C13	C14	C15	C16	2.5(11)
Cs1	O13	C35	N1	92.3(11)		C13	C14	C31	C30	121.9(8)
$Cs2^{7}$	Np1	O1	$Np2^{1}$	130.9(4)		C13	C14	C31	C32	-54.1(10)
Cs2	Np2	O3	Np1	41.5(4)		C14	C15	C16	C11	-3.6(11)
$Cs2^{2}$	Np2	O3	Np1	-61.7(4)		C14	C31	C32	C20	-3.6(12)
Cs2	Np2	O3	Cs1	-134.57(12)		C14	C31	C32	C33	173.7(7)
$Cs2^{2}$	Np2	O3	Cs1	122.17(14)		C15	C14	C31	C30	-56.3(10)
$Cs2^{2}$	Np2	O4	Cs2	104.2(2)		C15	C14	C31	C32	127.7(8)
Cs2	Np2	O4	$Cs2^{2}$	-104.2(2)		C16	C11	C12	$Cs1^{4}$	-105.9(6)
$Cs2^{8}$	O5	C1	$Np2^{8}$	83.5(7)		C16	C11	C12	C13	-1.6(11)
$Cs2^{8}$	O5	C1	O6	65.4(11)		C17	C18	C19	C20	0.3(12)
$Cs2^{8}$	O5	C1	C5	-116.8(8)		C18	C17	C22	C21	1.4(13)
$Cs2^{3}$	O8	C2	$Cs1^{4}$	-117.8(7)		C18	C19	C20	C21	0.6(12)
$Cs2^{3}$	O8	C2	O7	158.7(5)		C18	C19	C20	C32	-177.0(7)
$Cs2^{3}$	O8	C2	C11	-24.2(11)		C19	C20	C21	C22	-0.5(12)
$Cs2^{6}$	O9	C3	$Np1^{5}$	98.7(2)		C19	C20	C32	C31	125.1(8)
$Cs2^{6}$	O9	C3	O10	90.3(7)		C19	C20	C32	C33	-52.2(11)
$Cs2^{6}$	O9	C3	C17	-90.5(7)		C20	C21	C22	C17	-0.5(13)
$Cs2^{6}$	C3	C17	C18	132.6(7)		C20	C32	C33	C34	178.0(7)
$Cs2^{6}$	C3	C17	C22	-50.3(8)		C21	C20	C32	C31	-52.5(11)
$Cs2^{7}$	O13	C35	N1	-121.6(9)		C21	C20	C32	C33	130.2(8)
$O1^{1}$	Np2	O3	Np1	-78.3(3)		C22	C17	C18	C19	-1.3(13)
$O1^{1}$	Np2	O3	Cs1	105.6(2)		C23	C24	C25	C26	0.4(11)
$O1^{1}$	Np2	O4	$Cs2^{2}$	15.6(2)		C24	C23	C28	C27	0.7(11)
$O1^{1}$	Np2	O4	Cs2	119.85(16)		C24	C25	C26	C27	1.2(11)
O3	Np1	O1	$Np2^{1}$	-103.5(3)		C24	C25	C26	C34	-172.2(7)
O3	Np1	O1	$Cs2^{7}$	125.60(19)		C25	C26	C27	C28	-1.9(11)
$O5^{8}$	Np2	O3	Np1	80.9(3)		C25	C26	C34	C29	-49.6(11)
$O5^{8}$	Np2	O3	Cs1	-95.2(2)		C25	C26	C34	C33	125.3(8)
$O5^{8}$	Np2	O4	Cs2	-39.32(16)		C26	C27	C28	C23	0.9(11)
$O5^{8}$	Np2	O4	$Cs2^{2}$	-143.55(19)		C27	C26	C34	C29	137.1(8)
O5	C1	C5	C6	-156.1(7)		C27	C26	C34	C33	-48.0(10)
O5	C1	C5	C10	20.6(11)		C28	C23	C24	C25	-1.4(11)
$O6^{8}$	Np2	O3	Np1	132.1(4)		C29	C8	C9	C10	175.7(7)
$O6^{8}$	Np2	O3	Cs1	-44.0(2)		C29	C30	C31	C14	-173.4(7)
$O6^{8}$	Np2	O4	Cs2	-90.39(17)		C29	C30	C31	C32	2.7(11)
$O6^{8}$	Np2	O4	$Cs2^{2}$	165.38(18)		C30	C29	C34	C26	174.1(7)
O6	C1	C5	C6	21.8(10)		C30	C29	C34	C33	-0.6(11)
O6	C1	C5	C10	-161.6(7)		C30	C31	C32	C20	-179.6(7)
$O7^{3}$	Np1	O1	$Np2^{1}$	-26.9(4)		C30	C31	C32	C33	-2.3(11)
$O7^{3}$	Np1	O1	$Cs2^{7}$	-157.83(17)		C31	C14	C15	C16	-179.3(7)
O7	C2	C11	$Cs1^{4}$	51.7(6)		C31	C32	C33	C34	0.6(12)
O7	C2	C11	C12	-21.4(10)		C32	C20	C21	C22	177.1(8)
O7	C2	C11	C16	158.4(7)		C32	C33	C34	C26	-174.2(7)
$O8^{3}$	Np2	O3	Np1	0.7(3)		C32	C33	C34	C29	0.9(12)
$O8^{3}$	Np2	O3	Cs1	-175.4(2)		C34	C26	C27	C28	171.6(7)
$O8^{3}$	Np2	O4	Cs2	40.98(16)		C34	C29	C30	C31	-1.2(11)
$O8^{3}$	Np2	O4	$Cs2^{2}$	-63.24(19)		C36	N1	C35	$Cs2^{7}$	-54.4(15)

O8	C2	C11	Cs1[4]	-125.7(6)		C36	N1	C35	O13	0.7(17)
O8	C2	C11	C12	161.2(7)		C37	N1	C35	Cs2[7]	130.4(9)
O8	C2	C11	C16	-19.0(10)		C37	N1	C35	O13	-174.5(10)
O9[9]	Np1	O1	Np2[1]	128.5(3)						

[1]1-X,2-Y,-Z; [2]2-X,2-Y,-Z; [3]1-X,1-Y,1-Z; [4]+X,-1+Y,1+Z; [5]+X,+Y,1+Z; [6]-1+X,+Y,1+Z; [7]-1+X,+Y,+Z; [8]1-X,1-Y,-Z; [9]+X,+Y,-1+Z

Table S5. Parameters of pores and cavities in **NpCs-TCPB** MOF.

Parameter	Result	Unit
System Volume	2278.445	$Å^3$
System Mass	2862.999	g/mol
System Density	2.087	g/cm^3
Total surface area	3.11	$Å^2$
Total surface area per volume	13.66	m^2/cm^3
Total surface area per mass	6.55	m^2/g
Network-accessible surface area	0.00	$Å^2$
Network-accessible surface area per volume	0.00	m^2/cm^3
Network-accessible surface area per mass	0.00	m^2/g
Total helium volume	451.382	$Å^3$
Total helium volume	0.095	cm^3/g
Total geometric volume	901.931	$Å^3$
Total geometric volume	0.190	cm^3/g
Network-accessible helium volume	451.382	$Å^3$
Network-accessible helium volume	0.095	cm^3/g
Network-accessible geometric volume	901.360	$Å^3$
Network-accessible geometric volume	0.190	cm^3/g
Pore limiting diameter	2.69	Å
Maximum pore diameter	4.22	Å
Number of percolated dimensions	1	-

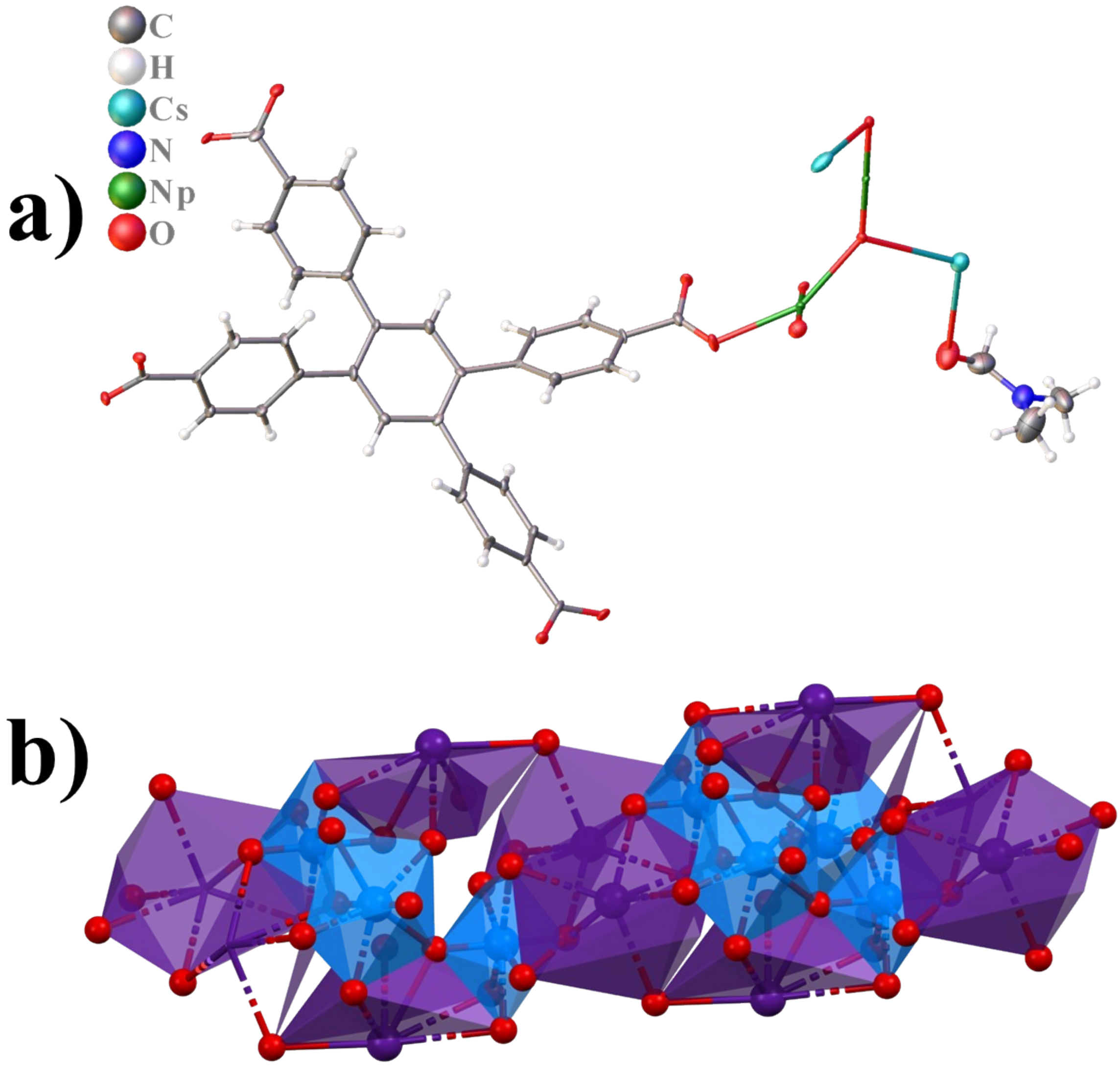


Figure S1. a) Asymmetric unit of structure **NpCs-TCPB**; b) coordination polyhedra of neptunium and cesium atoms in **NpCs-TCPB** MOF.

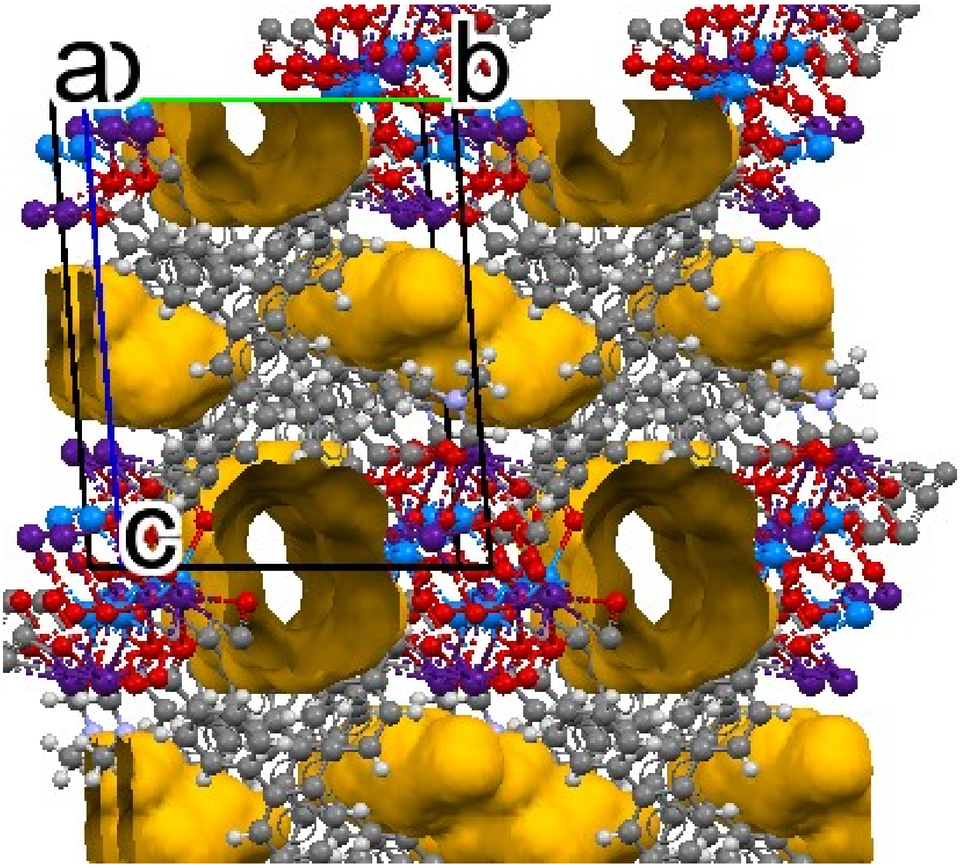


Figure S2. View showing the pores in **NpCs-TCPB**.

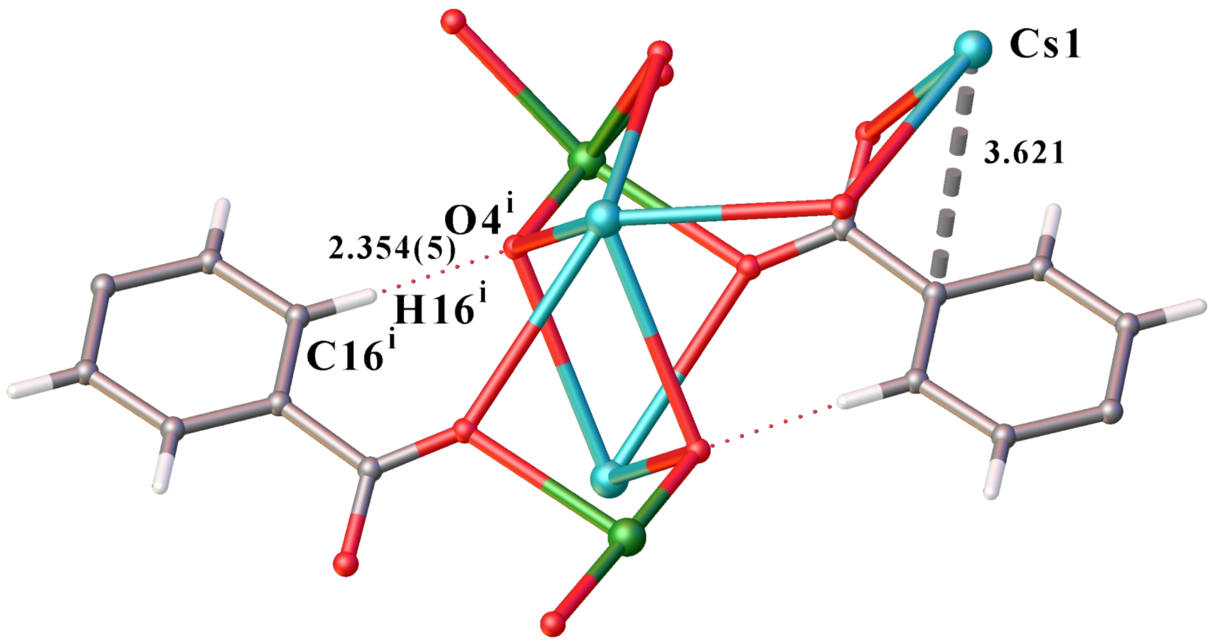


Figure S3. View showing cation-π interactions and hydrogen bonds in the **NpCs-TCPB** MOF.

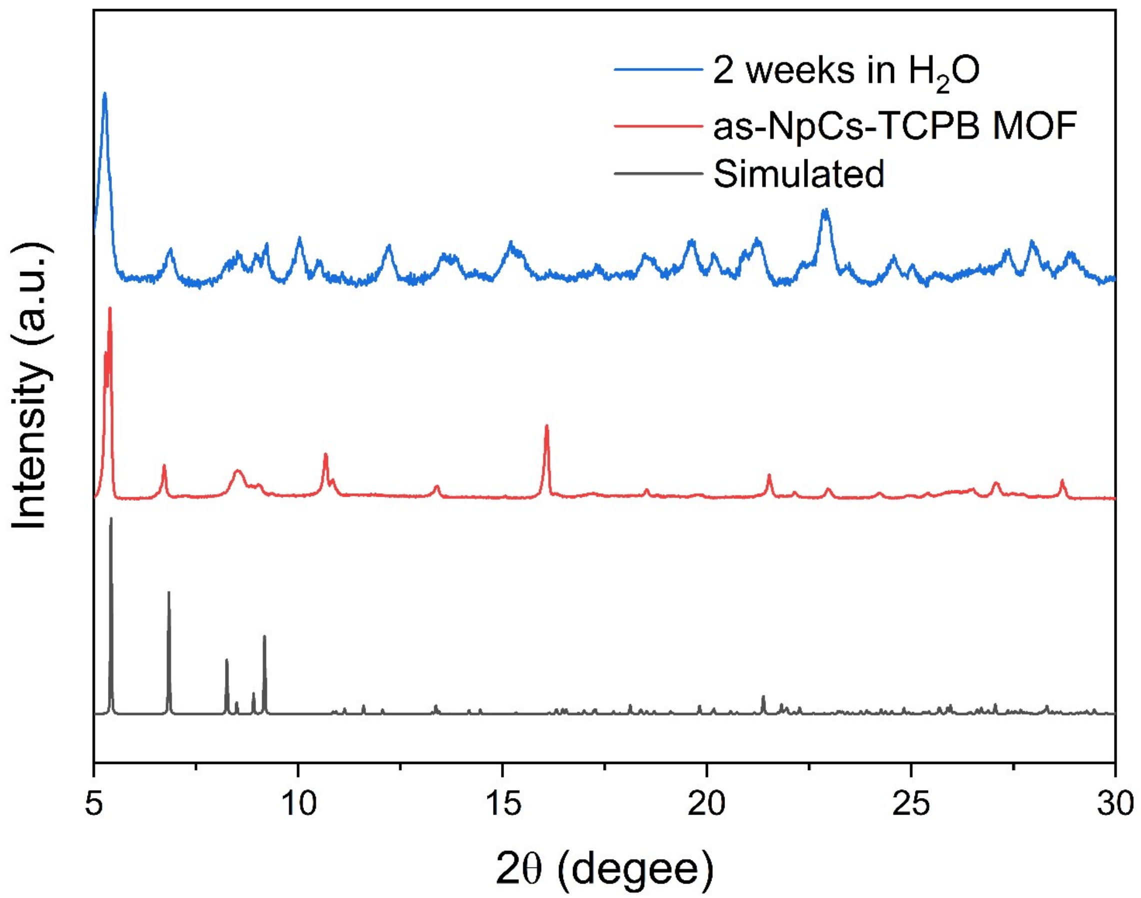


Figure S4. Comparison of **NpCs-TCPB** MOF XRD patterns of simulated, as-synthesized and aged in water for 2 weeks.

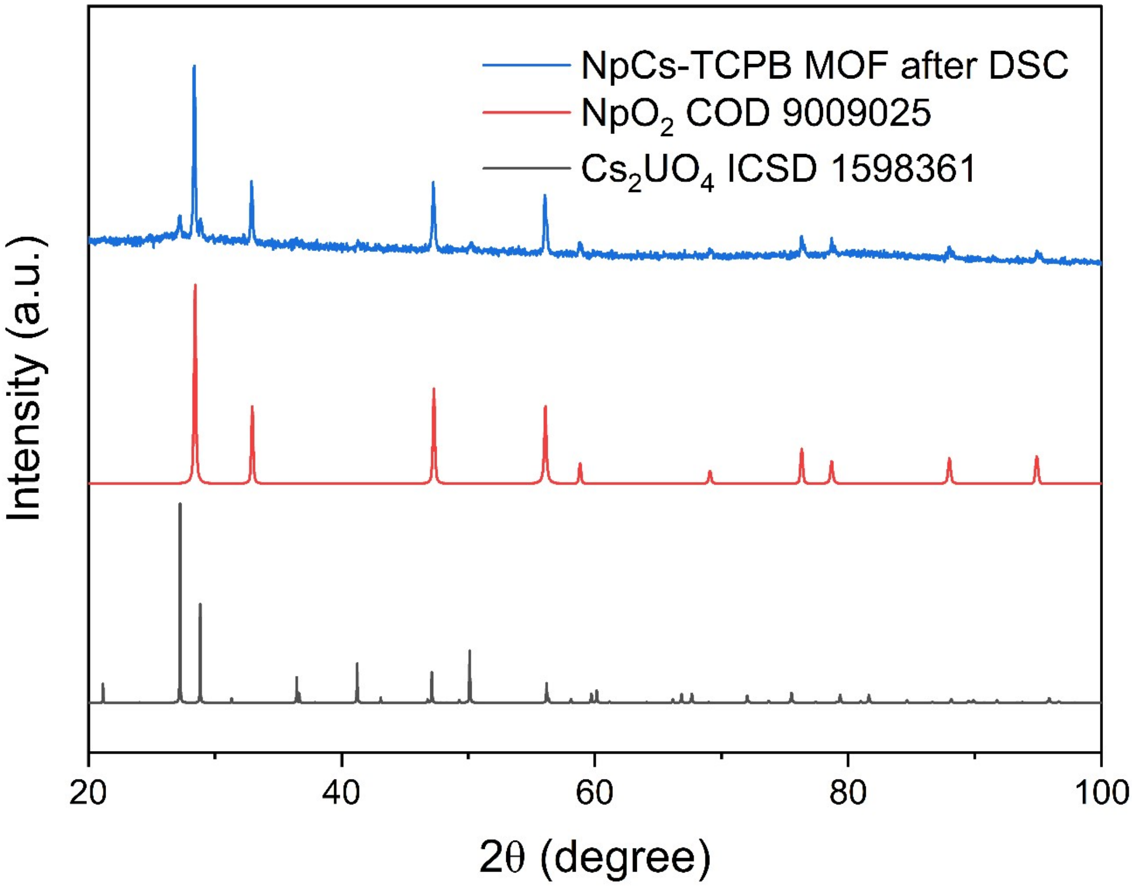


Figure S5. XRD patterns of thermolysis products of **NpCs-TCPB** MOF.

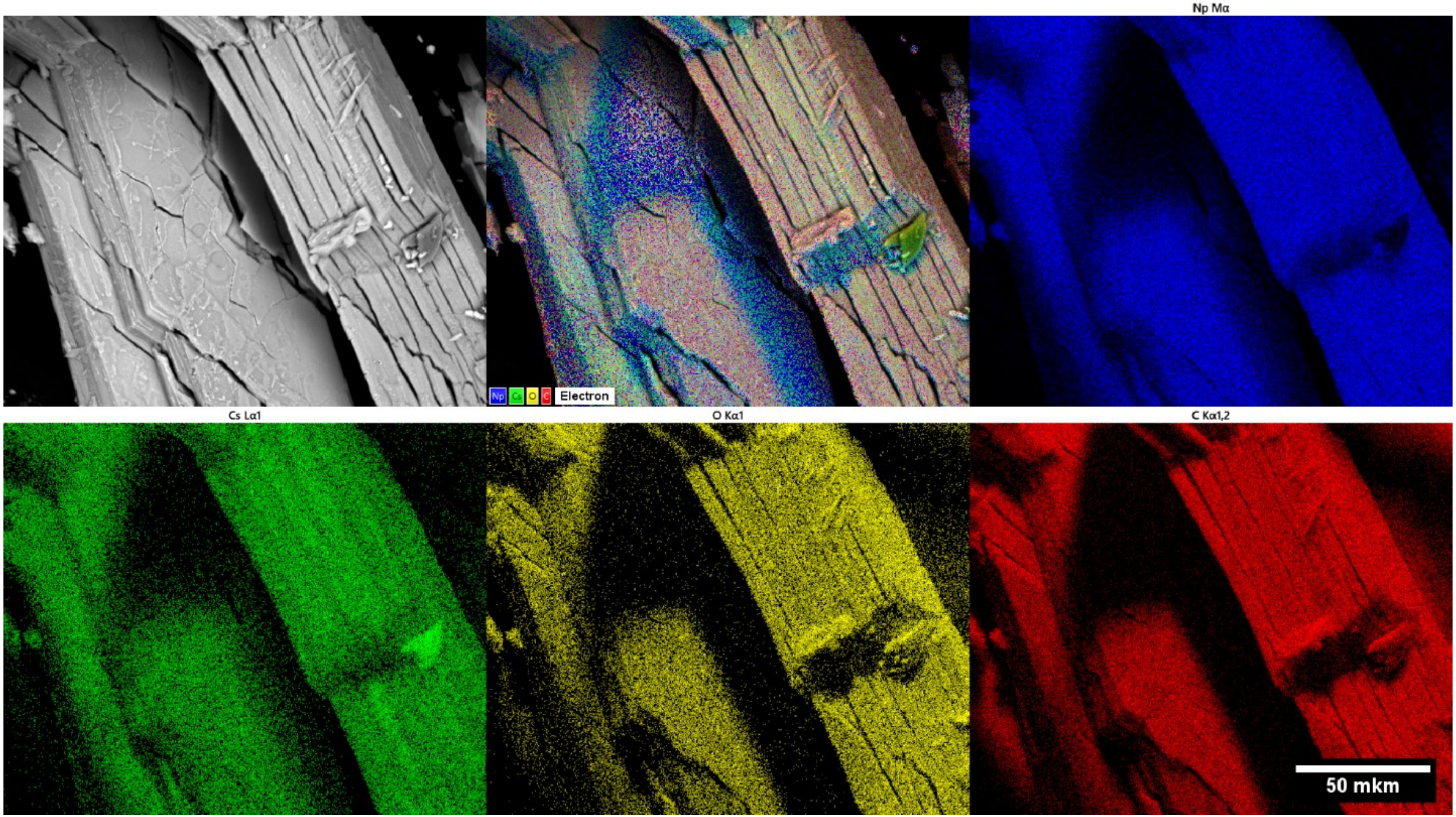


Figure S6. BSE SEM image, multilayer elements map, and Np, Cs, O and C distribution of **NpCs-TCPB** MOF.

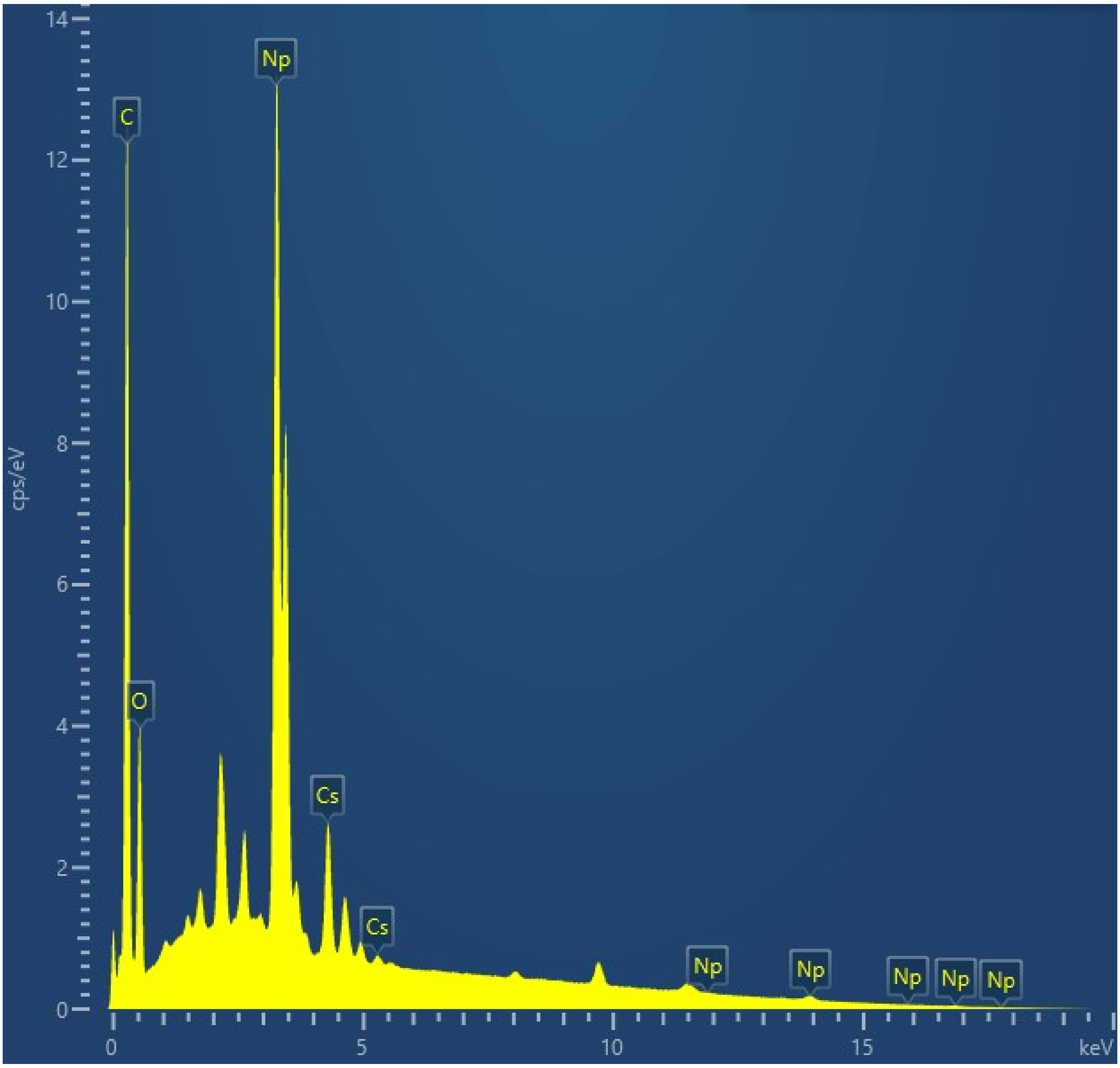


Figure S7. EDX spectrum of **NpCs-TCPB** MOF.

Table S6. EDX analysis of **NpCs-TCPB** MOF.

Element	At.%	Wt%	σ
C	73.88	38.00	0.07
O	20.08	13.77	0.07
Np	3.10	31.49	0.06
Cs	2.94	16.74	0.07

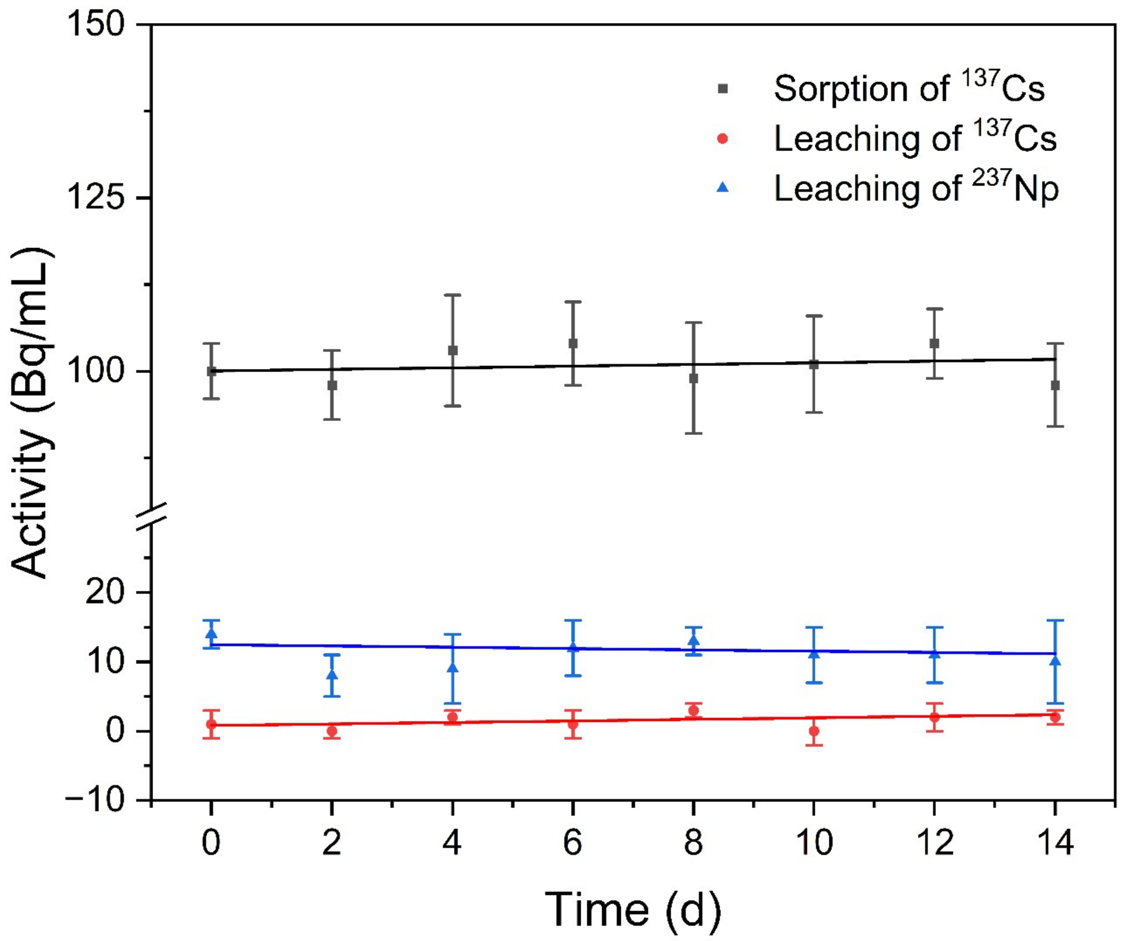


Figure S8. Sorption and leaching curves of ^{137}Cs and ^{237}Np in water for **NpCs-TCPB** MOF. Instrumental error 5%.

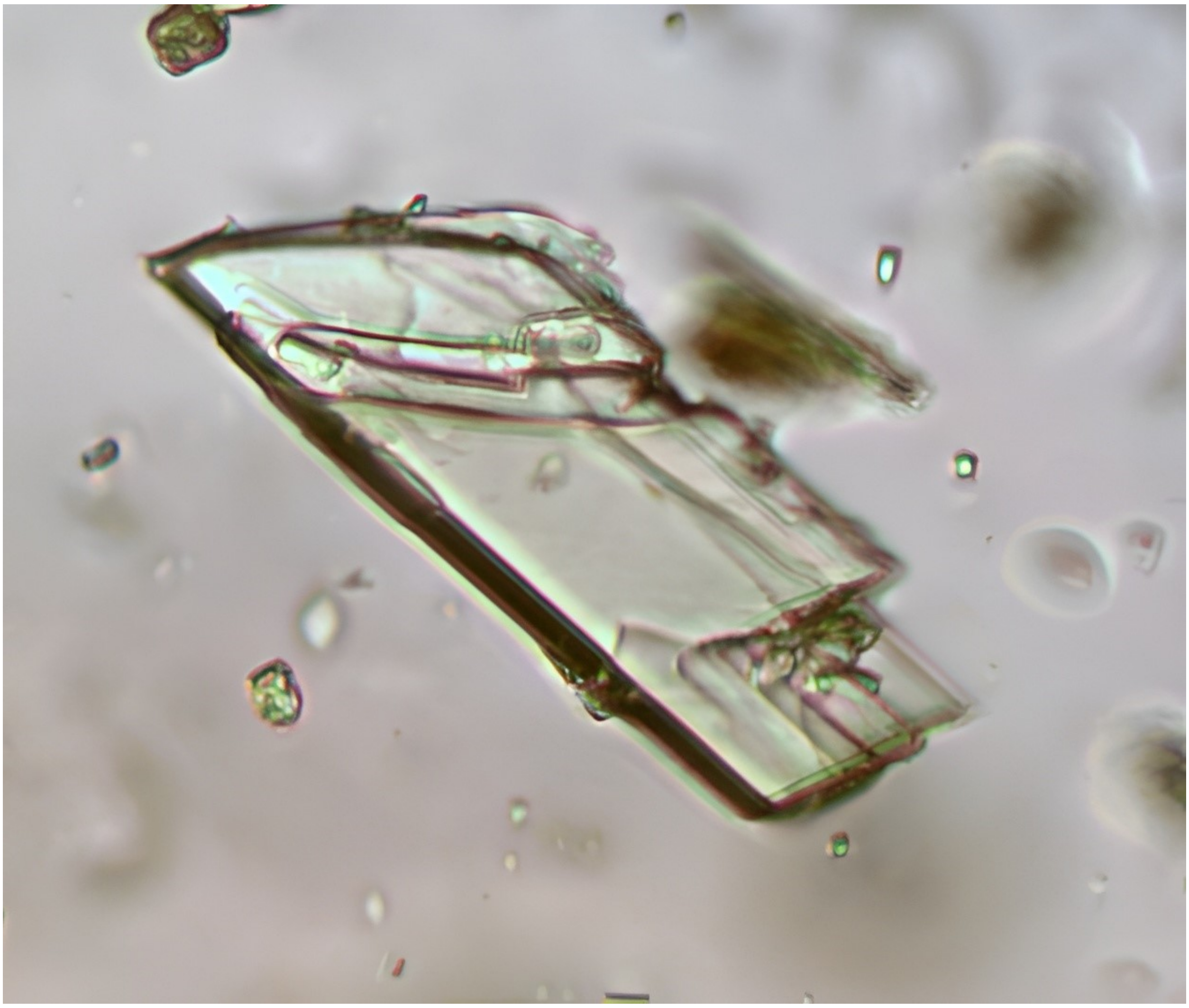


Figure S9. Optical photograph of **NpCs-TCPB** MOF crystal.

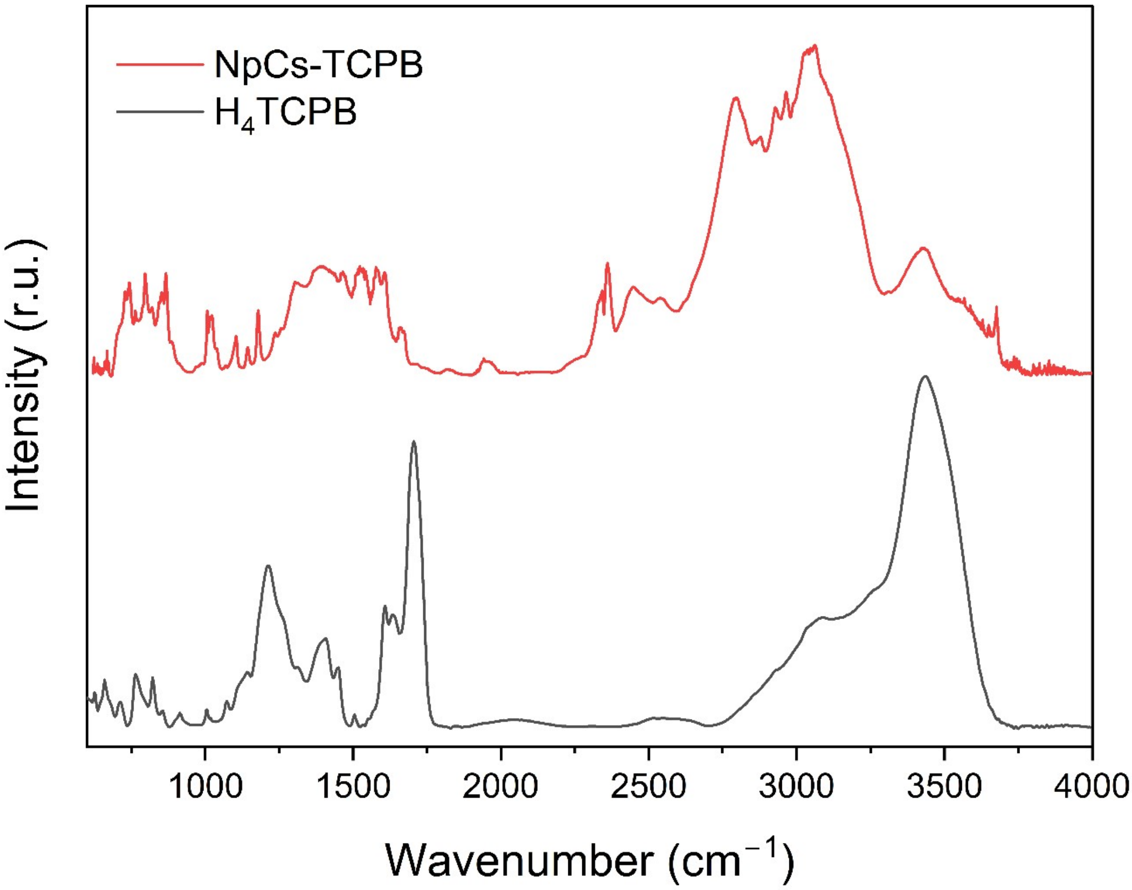


Figure S10. IR spectra of **NpCs-TCPB** MOF and H_4TCPB.

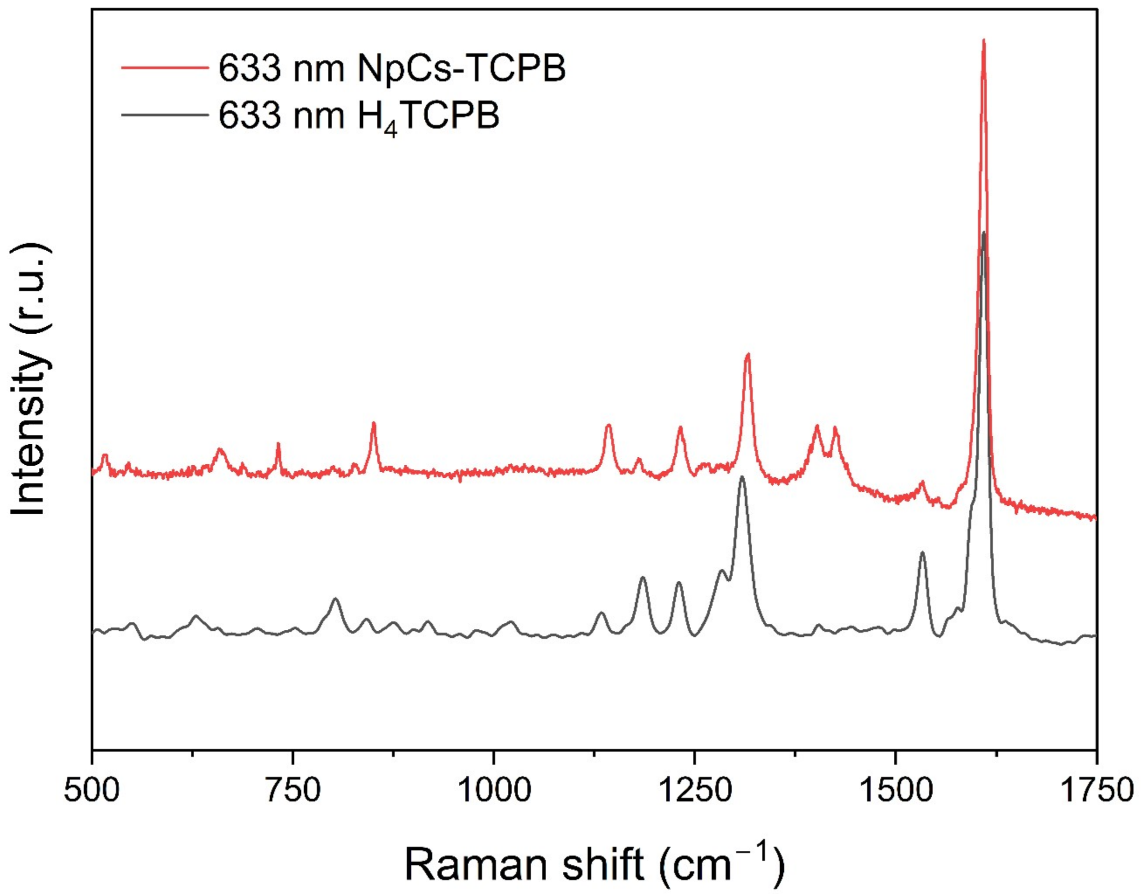


Figure S11. Raman spectra of **NpCs-TCPB** MOF and H_4TCPB.

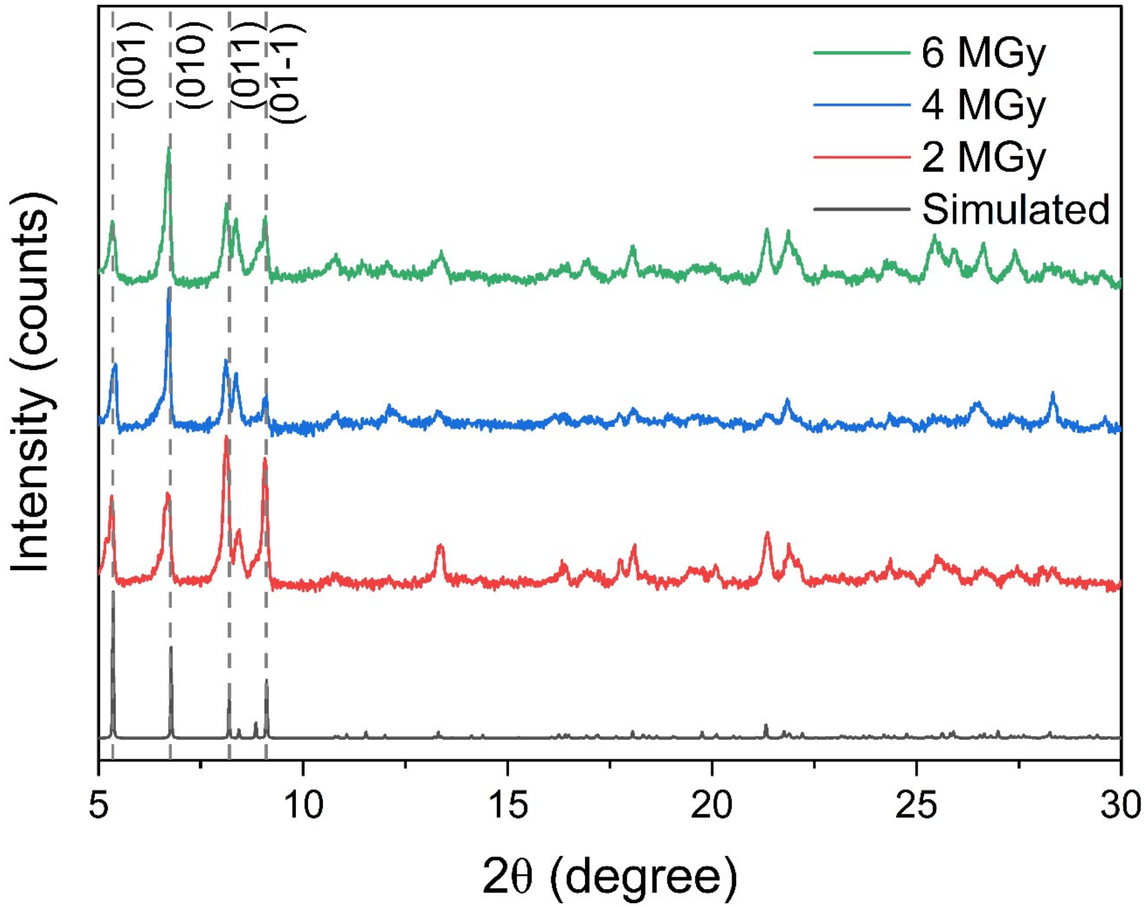


Figure S12. pXRD patterns of MOF after irradiated various dose.

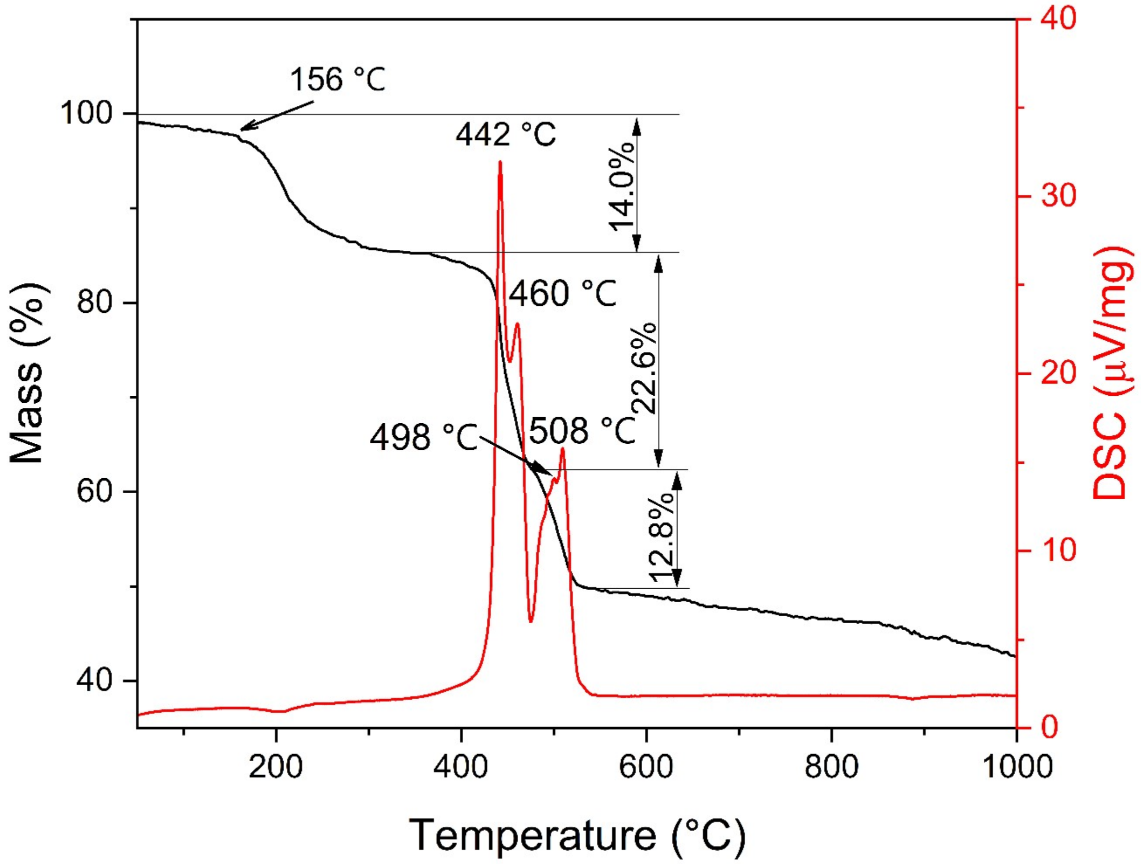


Figure S13. TGA and DSC analysis of NpCs-TCPB.

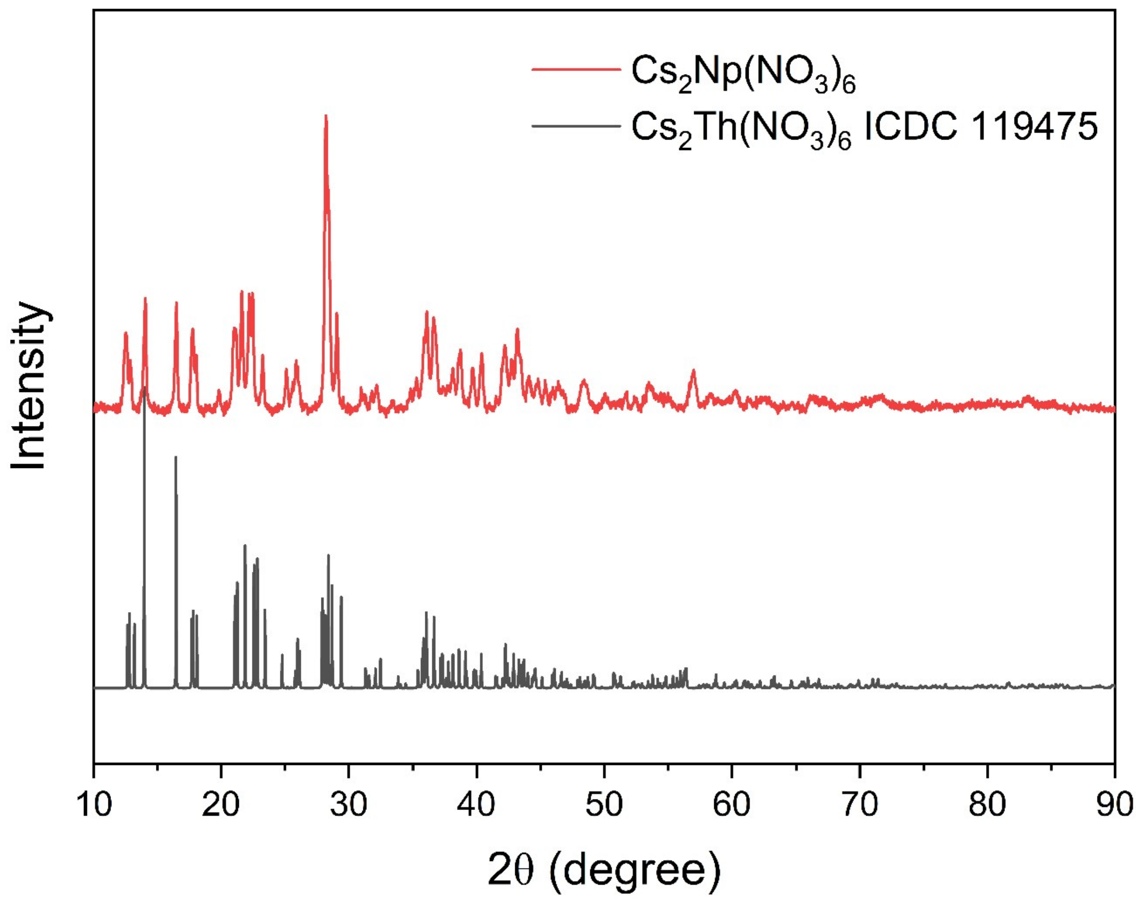
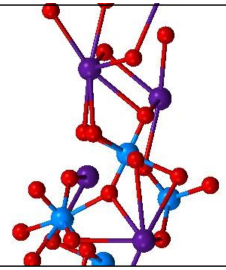
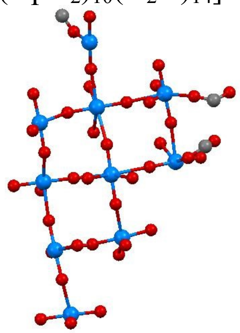
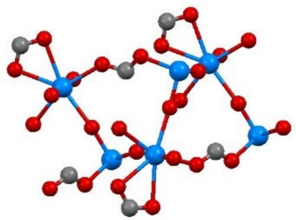
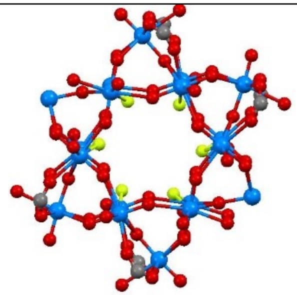
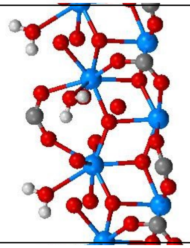
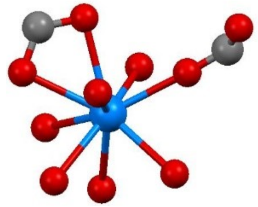
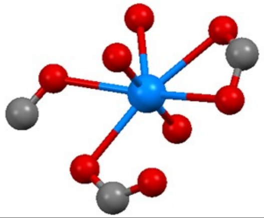
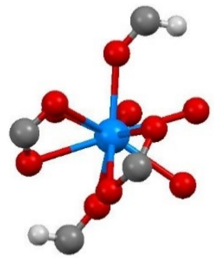
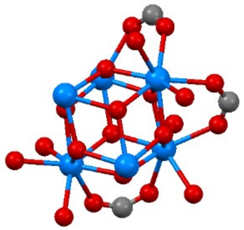


Figure S14. Experimental pXRD $Cs_2Np(NO_3)_6$ and simulated patterns for $Cs_2Th(NO_3)_6$.

Table S7. Some properties of known Np consist SBU MOFs

CCDC, name	SBU/BU	Pore diameter, limiting/ maximum, Å	Radiological stability, MGy	Thermal stability, °C	Ref.
NpCs-TCPB		2.69/4.22	>6	400	This work
1509607	$[(NpO_2)_{10}(H_2O)_{14}]^{12+}$ 	0.83/2.36	n/a	n/a	[7]
2103779 **NSM**	$(NpO_2)_4$ 	6.12/6.60	3	100	[8]
1944580 **NNS1**	$(NpO_2)_{18}$	5.19/10.06		200	
1944581 **NNS2**		5.31/10.01			
			n/a		[9]

NNS3					
1509605 **$[(NpO_2)_{10}(H_2O)_{14}(Hmel)_2]$ $\cdot 12H_2O$**		1.18/2.35	n/a	n/a	[7]
2194874 **Np-1β**	NpO_3^- 	0.72/2.04	n/a	n/a	[10]
2194873 **Np-1α**		0.82/1.64			
1845094 **NRCP1**	NpO_3^- 	1.61/3.21	n/a	n/a	[11]
1837987 **TRU-MOF1**	NpO_3	1.28/1.81	n/a	n/a	[12]

					
1837814 **TRU-MOF2**	$[Np_6O_4(OH)_4(H_2O)_6]^{12+}$ 	n/a			
1837816 **TRU-MOF3**					

References

1 Bruker AXS Inc., *SAINT, V8.40B*, Madison, WI, USA, 2020.

2 L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr.*, 2015, **48**, 3–10.

3 G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Adv.*, 2015, **71**, 3–8.

4 G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.*, 2015, **71**, 3–8.

5 A. L. Spek, *Acta Crystallogr. Sect. C Struct. Chem.*, 2015, **71**, 9–18.

6 C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, *Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater.*, 2016, **72**, 171–179.

7 N. P. Martin, J. März, C. Volkringer, N. Henry, C. Hennig, A. Ikeda-Ohno and T. Loiseau, *Inorg. Chem.*, 2017, **56**, 2902–2913.

8 S. E. Gilson, M. Fairley, S. L. Hanna, J. E. S. Szymanowski, P. Julien, Z. Chen, O. K. Farha, J. A. LaVerne and P. C. Burns, *J. Am. Chem. Soc.*, 2021, **143**, 17354–17359.

9 S. E. Gilson, P. Li, J. E. S. Szymanowski, J. White, D. Ray, L. Gagliardi, O. K. Farha and P. C. Burns, *J. Am. Chem. Soc.*, 2019, **141**, 11842–11846.

10 N. B. Beck, Z. Bai, J. P. Brannon, D. G. Martinez, D. Grödler, B. N. Long, T. N. Poe, B. M. Rotermund, T. E. Albrecht-Schönzart and J. M. Sperling, *Inorg. Chem.*, 2022, **61**, 17730–17737.

11 L. Mei, C. Xu, Q. Wu, K. Hu, L. Yuan, J. Chen, C. Xiao, S. Wang, Z. Chai and W. Shi, *Chem. Commun.*, 2018, **54**, 8645–8648.

12 N. P. Martin, J. März, H. Feuchter, S. Duval, P. Roussel, N. Henry, A. Ikeda-Ohno, T. Loiseau and C. Volkringer, *Chem. Commun.*, 2018, **54**, 6979–6982.