Electronic Supplementary Material (ESI) for ChemComm.

Synthesis and characterization of the first neptunium based Metal-Organic Frameworks incorporating $\{Np_6O_8\}$ hexanuclear cluster

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SUPPLEMENTARY MATERIALS

To be submitted to Chem. Comm.
Themed issue "New molecules and materials from the f-block"
Version April 18, 2018

Synthesis.

Caution! *^{237}Np and ^{232}Th precursor is radioactive and chemically toxic reactants, so precautions with suitable equipments and facility for radiation protection are required for handling these substances. The research of ^{237}Np-containing compounds was carried out in the radiological facility belonging to the Institute of Resource Ecology (Helmholtz-Zentrum Dresden-Rossendorf, Germany), which has appropriate equipment for handling such highly radioactive elements.*

The compounds have been solvothermally synthesized under autogenous pressure using 2 mL glass vial with Teflon cap by using the following chemical reactants: neptunium tetrachloride ($NpCl_4$), thorium nitrate ($Th(NO_3)_4 \cdot 5H_2O$, Fluka, 99%), benzoic acid (noted Hbz, Aldrich, ACS reagent ≥ 99.5%) terephthalic acid (H_2bdc, Aldrich, 98%), 2,6-natphalenedicarboxylic acid (H_2ndc, Aldrich, 99%), 4,4'-biphenyldicarboxylic acid (H_2bpdc, Aldrich, 97%), 2-aminobiphenyl-4,4'-dicarboxylic acid (H_2bpdc-NH_2), 2′-amino-p-terphenyl-4,4″-dicarboxylate linker (H_2tpdc-NH_2), N,N-dimethylformamide (DMF, Aldrich, 99.8%) and deoxygenated de-ionized water. Among these chemical reactants Hbz, H_2bdc, H_2ndc, H_2bpdc and DMF are commercially available and have been used without any further purification. The synthesis of $NpCl_4$ was obtained from a protocol using the reaction of hexachloropropene with neptunium oxide $^{237}NpO_2$, from ≈50 mg sample, protocol identical to that used for the production of UCl_4[1] The synthesis of H_2bpdc-NH_2 and H_2tpdc-NH_2 was possible from published procedures.[2] The reactant mixtures concerning the syntheses using $NpCl_4$ have been manipulated and weighted in a glove box under argon atmosphere. They have been then placed in closed glass vials, which are removed from the glove box and then heated in an oven (under ambient atmosphere). For the neptunium-based compounds, only X-ray diffraction analyses have been performed and described in the present work, due to the specific safety constraints for handling such radioactive samples.

Thorium-based compounds were used as model-material for the estimation of the porosity of neptunium-based analogues.

Neptunium MOFs:

$Np_2(bdc)_4(DMF)_4$ (**1**): a mixture of 10 mg (0.026 mmol) $NpCl_4$, 10 mg (0.060 mmol) terephthalic acid and 1 mL (13 mmol) DMF was placed in a closed glass vial and then heated statically at 130°C for 24 hours. The resulting product of **1** (needle-plate like crystals – Figure S1a) was then filtered off, washed with N,N-dimethylformamide (DMF) and dried at room temperature under ambient air. Compound **1** was obtained as a pure phase, as shows the experimental powder X-ray diffraction pattern, compared to the simulated one (Figure S1).

$[Np_6O_4(OH)_4(H_2O)_6(bdc)_6] \cdot x$DMF (**2**): a mixture of 10 mg (0.026 mmol) $NpCl_4$, 10 mg (0.046 mmol) terephthalic acid, 200 mg (1.66 mmol) benzoic acid, 1 mL (13 mmol) DMF and 12 µL (0.66 mmol) H_2O was placed in a closed glass vial and then heated statically at 130°C for 24 hours. The resulting product of **2** (octahedral crystallites) was then filtered off, washed with N,N-dimethylformamide (DMF) and dried at room temperature under ambient air. Compound **2** was obtained as a pure phase, as shows the experimental powder X-ray diffraction pattern, compared to the simulated compound obtained with uranium.[3] (Figure S2). The size of the crystals (10 µm) was too small for single crystals XRD analysis and attempts to get bigger crystals failed.

$[Np_6O_4(OH)_4(H_2O)_6(bpdc)_6]$ xDMF (**3**): a mixture of 10 mg (0.026 mmol) $NpCl_4$, 10 mg (0.043 mmol) 4,4’-biphenyldicarboxylic acid, 120 mg (1.0 mmol) benzoic acid, 1 mL (13 mmol) DMF and 12 µL (0.66 mmol) H_2O was placed in a closed glass vial and then heated statically at 130°C for 24 hours. The resulting product of **4** (octahedral crystallites) was then filtered off, washed with N,N-dimethylformamide (DMF) and dried at room temperature under ambient air. Compound **4** was obtained as a pure phase, as shows the experimental powder X-ray diffraction pattern, compared to the simulated one (Figure S2).

$[Np_6O_4(OH)_4(H_2O)_6(bpdc\text{-}NH_2)_6]$ xDMF (**4**): a mixture of 10 mg (0.026 mmol) $NpCl_4$, 10 mg (0.038 mmol) 2-aminobiphenyl-4,4’-dicarboxylic acid, 120 mg (1.0 mmol) benzoic acid, 1 mL (13 mmol) DMF and 12 µL (0.66 mmol) H_2O was placed in a closed glass vial and then heated statically at 130°C for 24 hours. The resulting product of **5** (octahedral crystallites) was then filtered off, washed with N,N-dimethylformamide (DMF) and dried at room temperature under ambient air. Compound **5** was obtained as a pure phase, as shows the experimental powder X-ray diffraction pattern, compared to the simulated one (Figure S2).

$[Np_6O_4(OH)_4(H_2O)_6(tpdc\text{-}NH_2)_6]$ xDMF (**5**) : a mixture of 10 mg (0.026 mmol) $NpCl_4$, 10 mg (0.03 mmol) 2′-amino-p-terphenyl-4,4″-dicarboxylate linker, 120 mg (1.0 mmol) benzoic acid, 1 mL (13 mmol) DMF and 30 µL (1.66 mmol) H_2O was placed in a closed glass vial and then heated statically at 130°C for 72 hours. The resulting product of **6** (octahedral crystallites) was then filtered off, washed with N,N-dimethylformamide (DMF) and dried at room temperature under ambient air. Compound **6** was obtained as a pure phase, as shows the experimental powder X-ray diffraction pattern, compared to the simulated one (Figure S2).

Thorium MOFs:

3 and 4 thorium analogues (noted 3’, 4’) were synthesized for the first time in this paper in order to determine the evaluate the porosity of neptunium-based compounds.
2’ and 5’ thorium compounds analogues were not synthesized in this study since their BET surfaces are already reported in the literature.

$[Th_6O_4(OH)_4(H_2O)_6(bpdc)_6]$ xDMF (**3’**): a mixture of 10 mg (0.026 mmol) $NpCl_4$, 10 mg (0.043 mmol) 4,4’-biphenyldicarboxylic acid, 120 mg (1.0 mmol) benzoic acid, 1 mL (13 mmol) DMF and 30 µL (1.66 mmol) H_2O was placed in a closed glass vial and then heated statically at 130°C for 24 hours. The resulting product of **4’** (octahedral crystallites) was then filtered off, washed with N,N-dimethylformamide (DMF) and dried at room temperature under ambient air. Compound **4’** was obtained as a pure phase, as shows the experimental powder X-ray diffraction pattern, compared to the simulated one (Figure S3).

$[Th_6O_4(OH)_4(H_2O)_6(bpdc\text{-}NH_2)_6]$ xDMF (**4’**): a mixture of 10 mg (0.026 mmol) $ThCl_4$, 10 mg (0.038 mmol) 2-aminobiphenyl-4,4’-dicarboxylic acid, 120 mg (1.0 mmol) benzoic acid, 1 mL (13 mmol) DMF and 30 µL (1.66 mmol) H_2O was placed in a closed glass vial and then heated statically at 130°C for 24 hours. The resulting product of **5’** (octahedral crystallites) was then filtered off, washed with N,N-dimethylformamide (DMF) and dried at room temperature under ambient air. Compound **5’** was obtained as a pure phase, as shows the experimental powder X-ray diffraction pattern, compared to the simulated one (Figure S3).

XRD powder patterns

For the neptunium-based compounds, powder XRD patterns were collected at room temperature on a Rigaku MiniFlex 600 with Bragg−Brentano geometry (θ−2θ mode), Cu Kα source (40 kV and 15 mA for X-ray generation), and a D/Tex Ultra Si strip detector.
For the gas sorption thorium-based reference material, powder XRD patterns were collected at room temperature with a D8 Advance A25 Bruker apparatus with Bragg−Brentano geometry (θ−2θ mode). The D8 diffractometer is equipped with a LynxEye detector with Cu Kα radiation.

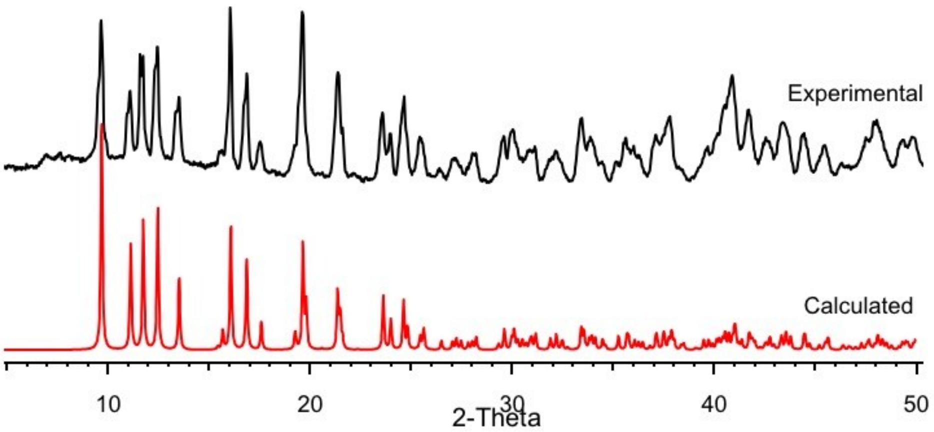

Figure S1 : Calculated and experimental Powder X-ray diffraction patterns of **1**.

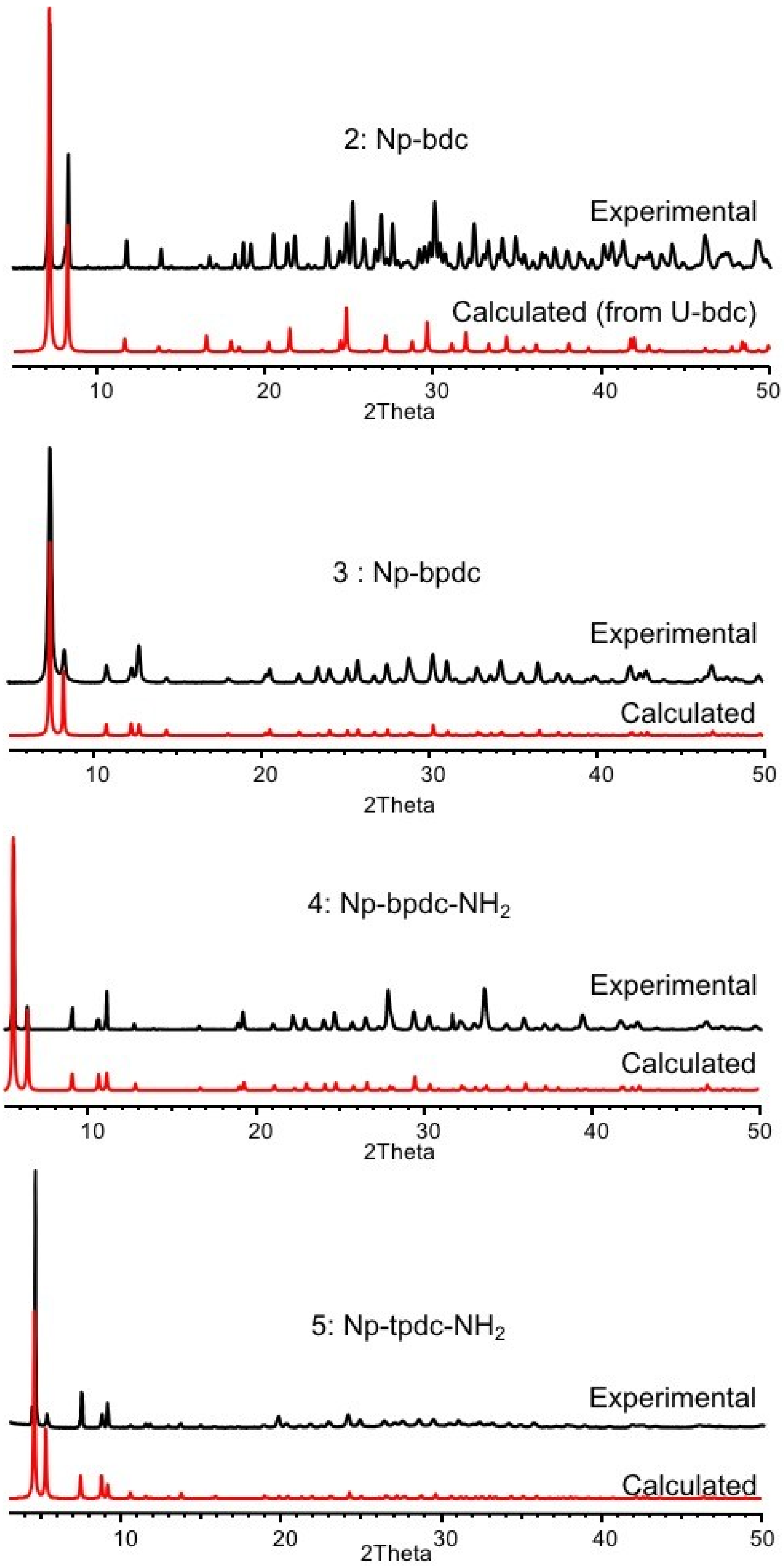

Figure S2 : Calculated and experimental Powder X-ray diffraction patterns of Np-based MOFs (**2-5**).

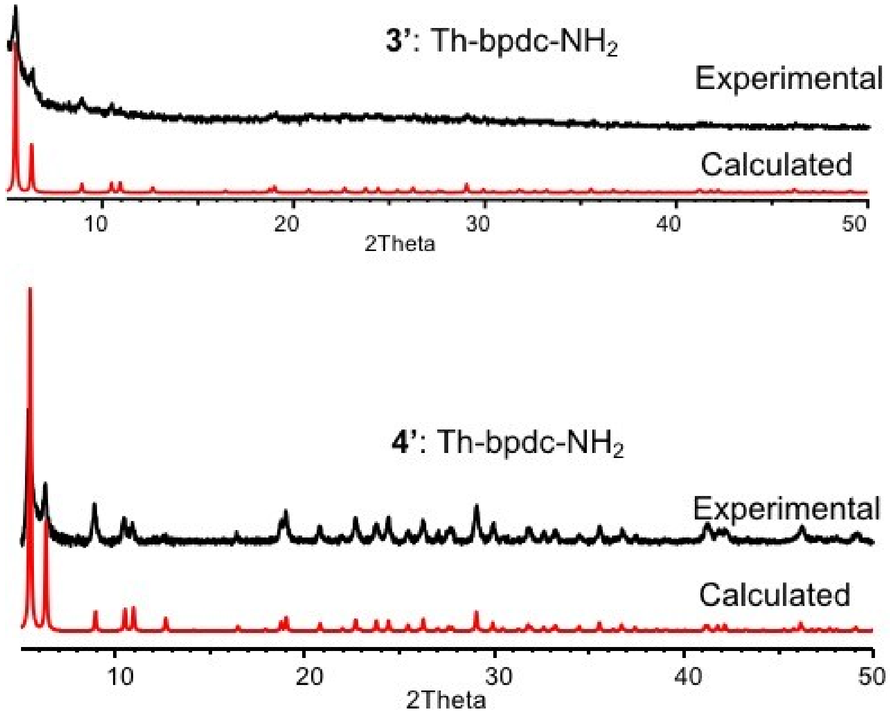

Figure S3 : Calculated and experimental Powder X-ray diffraction patterns of Th-based MOFs (3'-4') synthesized in this study.

Single-crystal X-ray diffraction

Crystal of Np-based compounds (**1**, **3−6**) were selected under polarizing optical microscope and glued on a glass fiber for single-crystal X-ray diffraction experiments. X-ray intensity data were collected and analyzed on a Bruker D8 VENTURE diffractometer with a PHOTON 100 CMOS detector using microfocused Mo Kα radiation (λ = 0.71073 Å) with an optical fiber as collimator. Several sets of narrow data frames (20 s per frame) were collected at different values of θ for two initial values of ϕ and ω, respectively, using 0.5° increments of ϕ or ω. Data reduction was accomplished using SAINT V7.53a.[4] The substantial redundancy in data allowed a semiempirical absorption correction (SADABS V2.10[5]) to be applied, on the basis of multiple measurements of equivalent reflections. The structure was solved by direct methods, developed by successive difference Fourier syntheses, and refined by full-matrix least-squares on all F2 data using SHELX program suite[6] and OLEX2 software[7]. Hydrogen atoms of the benzene ring and DMF molecule were included in calculated positions and allowed to ride on their parent atoms. Crystals of compound **3** were systematically twinned. Therefore, the twinning treatment was performed by using JANA software.[8] The final refinements include anisotropic thermal parameters of all non-hydrogen atoms. The crystal data are given in Table S1.

Table S1: Crystal data and structure refinements for the Np-based solids

Compound	**1**	**3**	**4**	**5**
Empirical formula	$NpC_{22}H_{22}N_2O_{10}$	$C_{336}Np_{24}O_{184}$	$C_{168}Np_{12}O_{86}$	$C_{192}Np_{12}O_{76}$
Formula weight	711.41	12668.37	6237.68	6365.92
Temperature/K	297.31	100.25	100.0	100.0
Crystal system	monoclinic	cubic	cubic	cubic
Space group	*C2/c*	*Fm*-3*m*	*Fm*-3*m*	*Fm*-3*m*
a/Å	15.3450(7)	27.6042(12)	27.5467(12)	33.3917(9)
b/Å	11.4621(4)	27.6042(12)	27.5467(12)	33.3917(9)
c/Å	13.3406(6)	27.6042(12)	27.5467(12)	33.3917(9)
α/°	90	90	90	90
β/°	101.4300(10)	90	90	90
γ/°	90	90	90	90
Volume/Å^3	2299.89(17)	21034(3)	20903(3)	37232(3)
Z	4	1	2	2
ρ_{calc}g/cm^3	2.055	1.000	0.991	0.568
μ/mm^{-1}	4.580	2.979	2.996	1.682
F(000)	1364.0	5721.0	5624.0	5752.0
Crystal size/mm^3	0.037 × 0.02 × 0.017	0.328 × 0.242 × 0.233	0.273 × 0.203 × 0.196	0.254 × 0.136 × 0.124
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.746 to 50.05	4.894 to 61.014	4.182 to 52.706	4.88 to 52.71
Index ranges	$-18 \le h \le 18$ $-13 \le k \le 13$ $-15 \le l \le 15$	$-38 \le h \le 38$ $-35 \le k \le 38$ $-39 \le l \le 34$	$-33 \le h \le 34$ $-34 \le k \le 27$ $-34 \le l \le 34$	$-41 \le h \le 27$ $-41 \le k \le 41$ $-33 \le l \le 41$
Reflections collected	13623	59776	47337	32772
Independent reflections	2029 [R_{int} = 0.0667]	1642 [R_{int} = 0.0291]	1127 [R_{int} = 0.0360]	1929 [R_{int} = 0.0688]
Parameters	164	45	39	30
Goodness-of-fit on F^2	1.130	1.248	1.259	1.074
Final R indexes [I>=2σ (I)]	R_1 = 0.0329, wR_2 = 0.0507	R_1 = 0.0321, wR_2 = 0.1081	R_1 = 0.0352, wR_2 = 0.1178	R_1 = 0.0643, wR_2 = 0.1864
Final R indexes [all data]	R_1 = 0.0435, wR_2 = 0.0525	R_1 = 0.0348, wR_2 = 0.1114	R_1 = 0.0380, wR_2 = 0.1212	R_1 = 0.0840, wR_2 = 0.2113
Largest diff. peak/hole / e Å^{-3}	1.11/-1.79	2.47/-1.72	1.63/-1.75	2.13/-2.19

As explained in the paper compounds **3-6** are highly porous with the presence of two type of cavities resulting in a ALERT A in the checkcif procedure. Some DMF or water molecule are probably trapped in the pores but the electronic densities are too diffuse to reveal the nature and the location of such molecules.

One can also note the aromatic rings of the dicarboxylate ligands are statistically disordered (Figure S4) on two (compounds **4** and **5**) or three positions (compound **3**).

Due to this disorder we were not able to attribute an occupancy of 1 for C atoms close to the central aromatic ring. C5 and C6 were arbitrary refined with a 0.5 occupancy. C7 and C8 simulate disorder of this ring and are refined with an occupancy of 0.29 and 0.21 respectively.

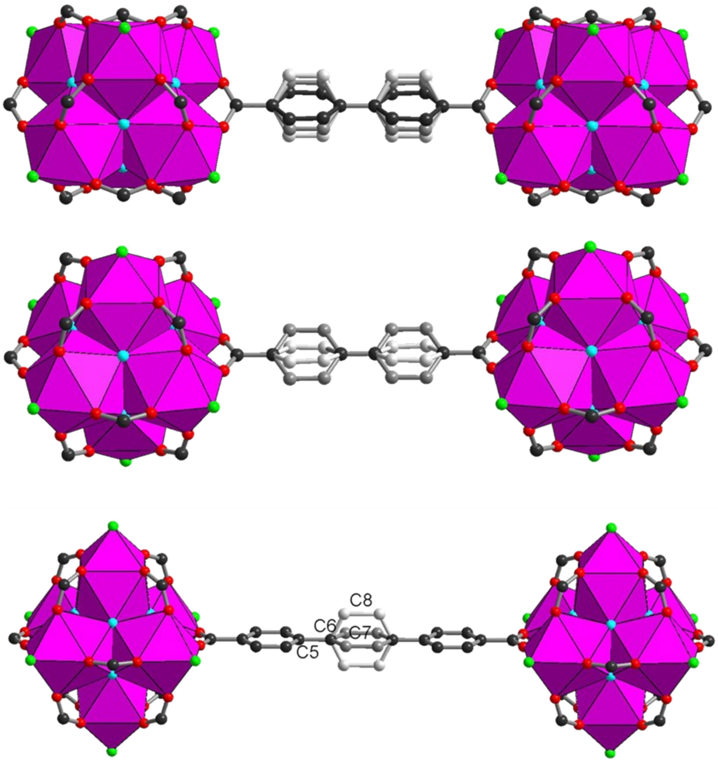

Figure S4 : View of the organic dicarboxylate ligand connecting two adjacent $Np_6O_4(OH)_4(H_2O)_6(L)_6$ building blocks, and showing the statistical disorder of the carbon atoms (light to dark grey) belonging to the aromatic ring. (top) compound **3** with L = 4,4’-biphenyldicarboxylate; (middle) compound **4** with L = 2-aminobiphenyl-4,4’-dicarboxylate; (bottom) compound **5** with L = 2′-amino-p-terphenyl-4,4′′-dicarboxylate.

Table S2: Crystal data and structure refinements for the Th-based solids

Compound	**3’**	**4’**
Empirical formula	$C_{168}O_{70}Th_{12}$	$C_{168}O_{70}Th_{12}$
Formula weight	5922.16	5922.16
Temperature/K	296.15	299.18
Crystal system	cubic	cubic
Space group	*Fm*-3*m*	*Fm*-3*m*
a/Å	27.9879(11)	27.9960(15)
b/Å	27.9879(11)	27.9960(15)
c/Å	27.9879(11)	27.9960(15)
α/°	90	90
β/°	90	90
γ/°	90	90
Volume/$Å^3$	21924(3)	21943(4)
Z	2	2
$\rho_{calc}g/cm^3$	0.897	0.896
μ/mm^{-1}	4.089	4.085
F(000)	5296.0	5296.0
Crystal size/mm^3	0.094 × 0.092 × 0.055	0.162 × 0.158 × 0.141
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.52 to 52.654	2.52 to 60.858
Index ranges	$-12 \leq h \leq 34$ $-31 \leq k \leq 21$ $-11 \leq l \leq 34$	$-33 \leq h \leq 39$ $-39 \leq k \leq 30$ $-27 \leq l \leq 39$
Reflections collected	11372	40250
Independent reflections	1177 [R_{int} = 0.1213, R_{sigma} = 0.0577]	1704 [R_{int} = 0.0686, R_{sigma} = 0.0233]
Parameters	42	41
Goodness-of-fit on F^2	1.255	1.302
Final R indexes [I>=2σ (I)]	R_1 = 0.0623, wR_2 = 0.1955	R_1 = 0.0445, wR_2 = 0.1371
Final R indexes [all data]	R_1 = 0.0902, wR_2 = 0.2100	R_1 = 0.0611, wR_2 = 0.1508
Largest diff. peak/hole / e $Å^{-3}$	1.74/-1.84	2.45/-1.68

Gas sorption

The porosity of compound 3'and 4' was estimated by gas sorption isotherm experiment in liquid nitrogen using the Micromeritics ASAP2020 apparatus (for BET surface area calculations, p/p_0 range: 0.02−0.2).

Table S3 : BET specific surfaces of thorium-based MOFs.

Compound	BET surface (m^2/g)	Reference
2'	730	[9]
3'	791	This work
4'	342	This work
5'	880	[10]

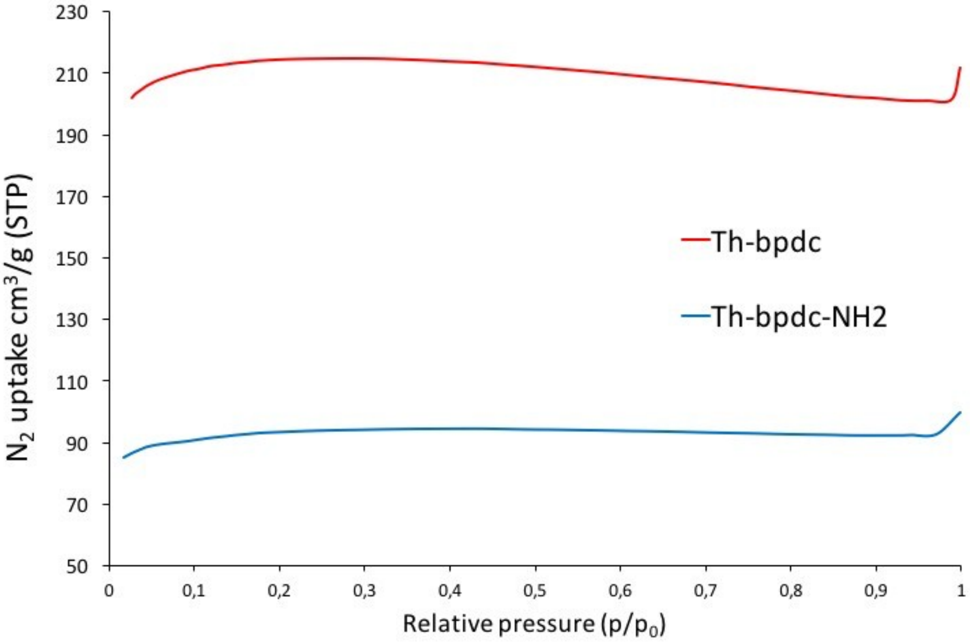

Figure S5 : Experimental adsorption isotherms of thorium-based compounds 3' and 4'.

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