Supporting Information for

Unexpected Structural Complexity of Thorium Coordination Polymers and Polyoxo Cluster Built from Simple Formate Ligands

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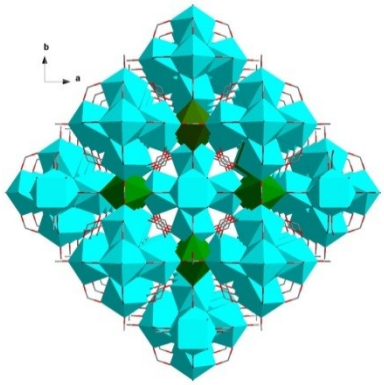

Fig. S1. The polyhedral representation of the **Th-SINAP-1** with the Na^+ cations. Th_6O_8 polyhedral is shown in turquoise while the NaO_8 polyhedra are shown in dark green.

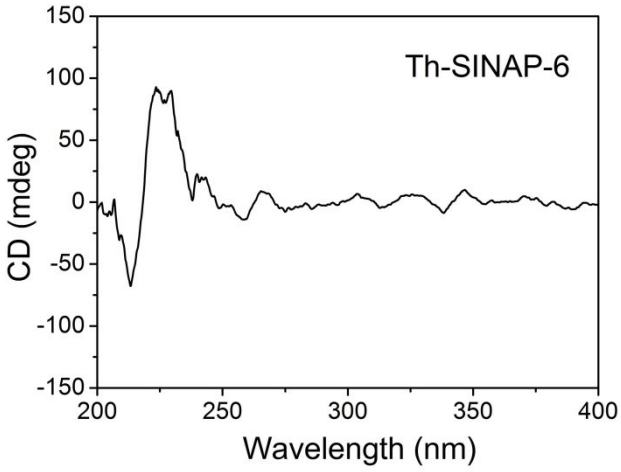

Fig. S2. Solid Circular Dichroism **(**CD) spectra of **Th-SINAP-6**.

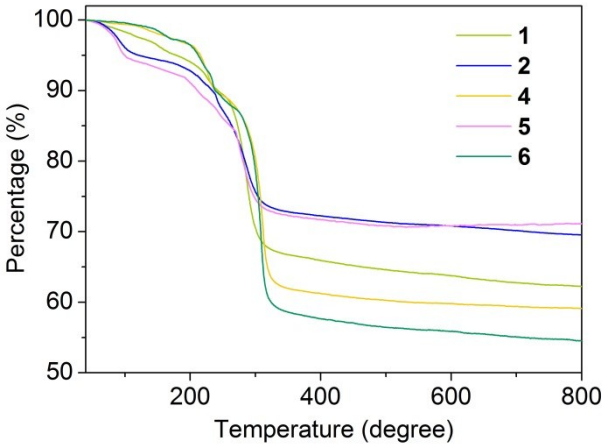

Fig. S3. TGA curves of **Th-SINAP-1**, **Th-SINAP-2**, **Th-SINAP-4**, **Th-SINAP-5**, and **Th-SINAP-6**.

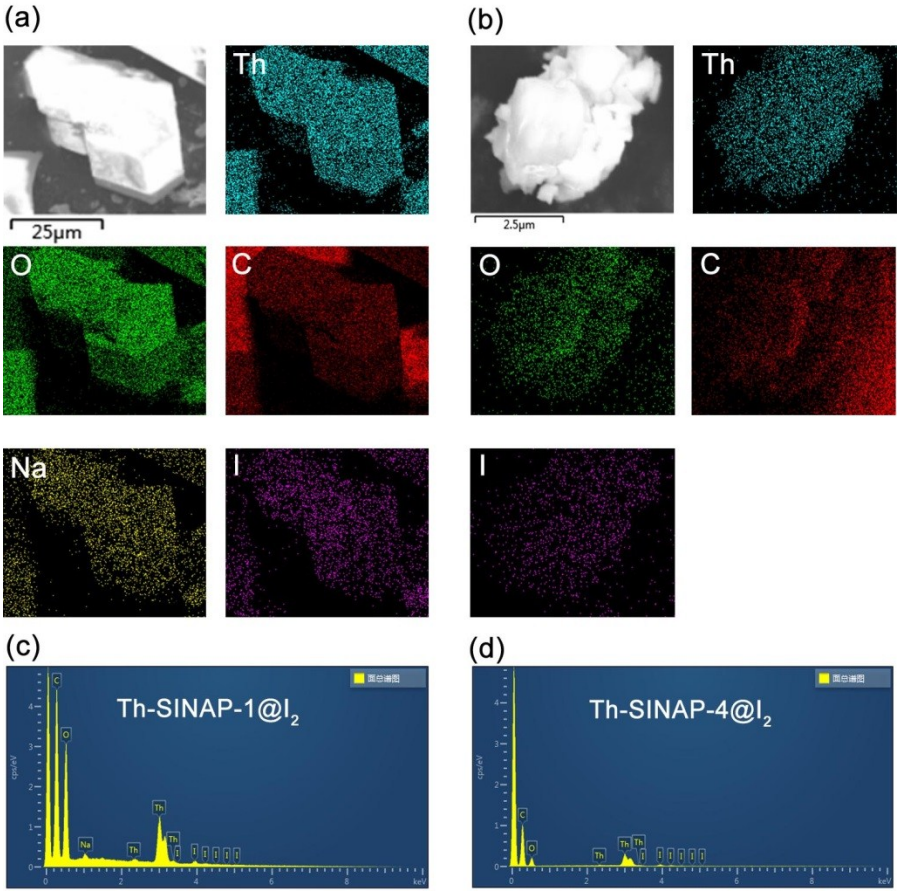

Fig. S4. SEM-EDS mappings and EDS spectra of iodine adsorbed (a, c) **Th-SINAP-1** and (b, d) **Th-SINAP-4**.

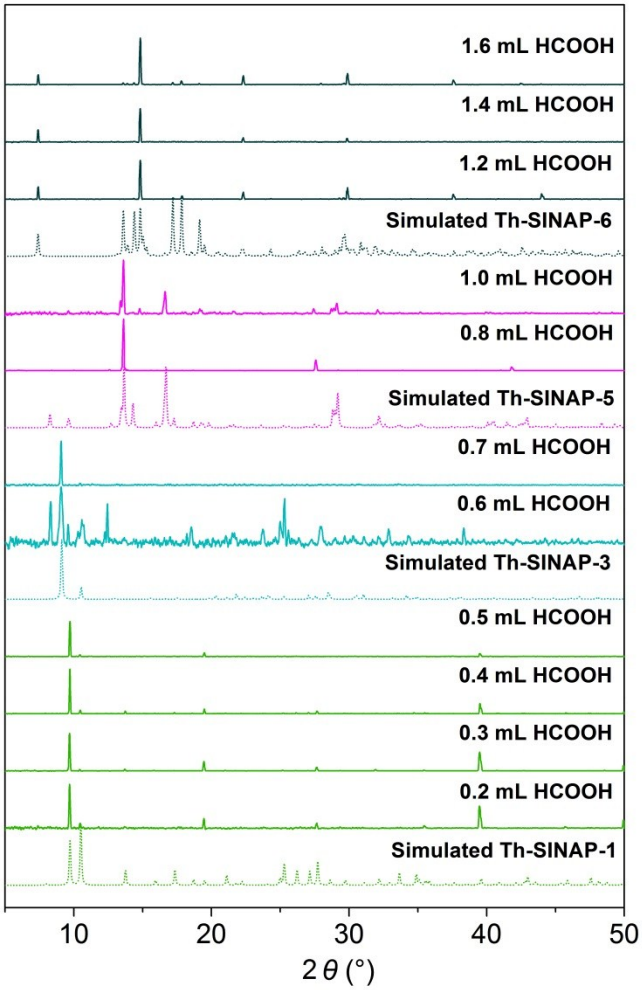

Fig. S5. PXRD patterns of **Th-SINAP-1**, **Th-SINAP-3**, **Th-SINAP-5**, and **Th-SINAP-6**.

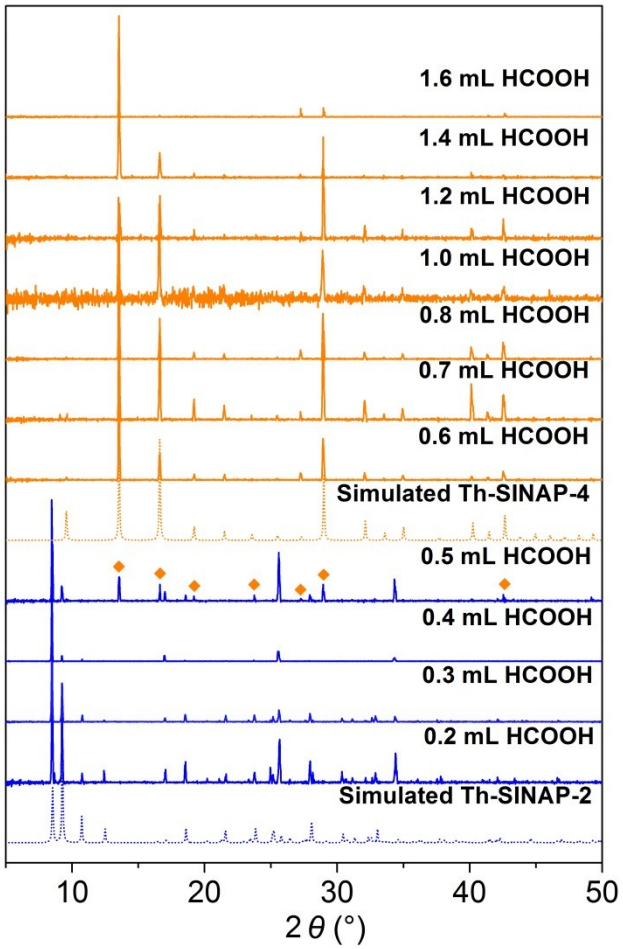

Fig. S6. PXRD patterns of **Th-SINAP-2** and **Th-SINAP-4**. For the reaction with 0.5 mL HCOOH, a coformation of **Th-SINAP-2** and **Th-SINAP-4** was observed.

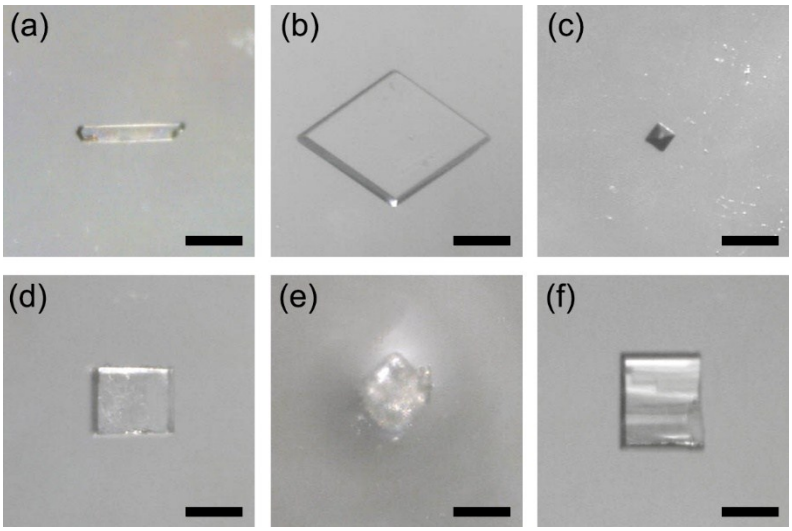

Fig. S7. Crystal images of **Th-SINAP-1**, **Th-SINAP-2**, **Th-SINAP-3**, **Th-SINAP-4**, **Th-SINAP-5**, and **Th-SINAP-6**. The scale bars represent length of 100 μm.

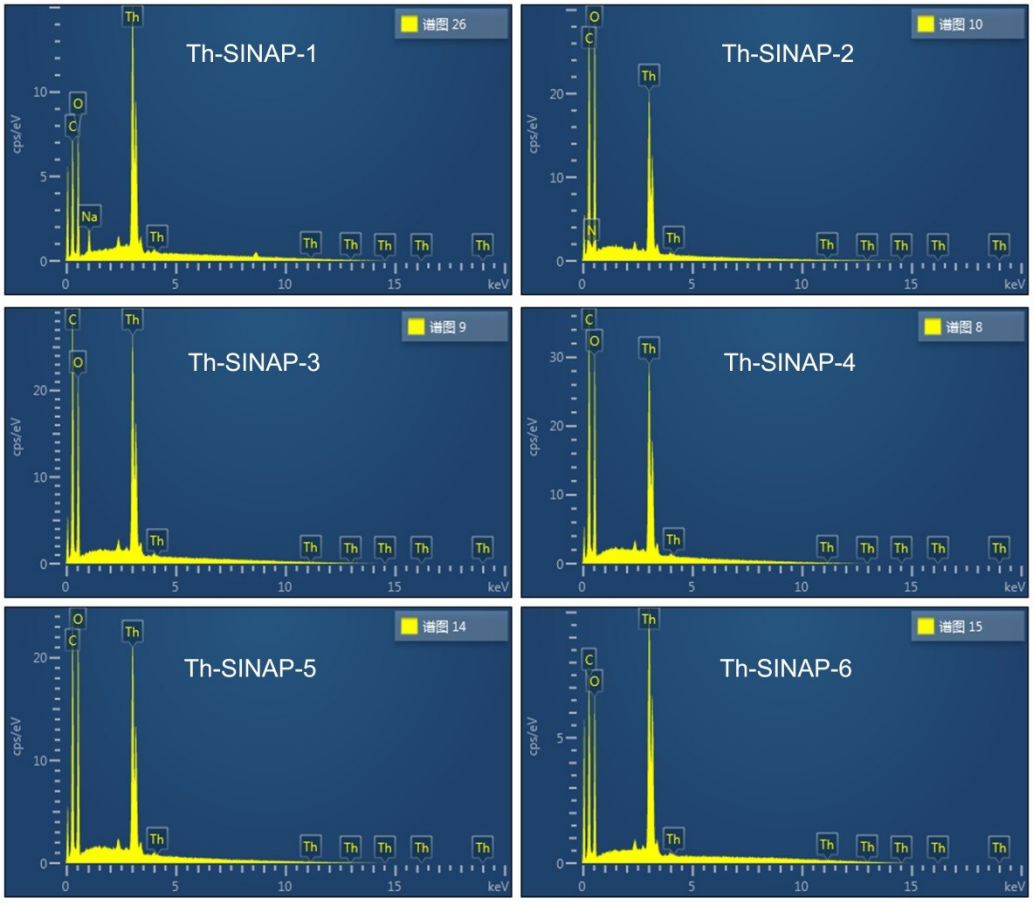

Fig. S8. SEM-EDS spectra of **Th-SINAP-1**, **Th-SINAP-2**, **Th-SINAP-3**, **Th-SINAP-4**, **Th-SINAP-5**, and **Th-SINAP-6**.

Table S1. Crystallographic Data for **Th-SINAP-1**, **Th-SINAP-2**, **Th-SINAP-3**, **Th-SINAP-4**, **Th-SINAP-5**, and **Th-SINAP-6**.

Code	1	2	3	4	5	6
CCDC number	1934856	1934859	1934860	1934855	1934858	1934857
Formula	$C_{14}NaO_{39}Th_6H_{18}$	$C_9NO_{17}Th_3H_4$	$C_{12}O_{46}Th_6H_{24}$	$C_9H_9O_{18}Th_2$	$C_{18}H_{11}O_{36}Th_4$	$C_{11}H_{17}NO_{18}Th_2$
Mass	2221.48	1094.25	2296.55	869.24	1731.43	915.33
Habit	Prism	Rhombohedra	Octahedra	Tablet	Tablet	Tablet
Space Group	*P*4/*nmm*	*Fmmm*	*Fd*-3*c*	*I*-43*m*	*Cmcm*	$P2_12_12_1$
a (Å)	12.8712(7)	16.4914(5)	33.5889(6)	13.0671(6)	18.354(2)	6.76770(10)
b (Å)	12.8712(7)	20.7320(5)	33.5889(6)	13.0671(6)	13.1655(14)	12.7311(2)
c (Å)	11.1211(6)	14.1668(4)	33.5889(6)	13.0671(6)	18.3476(18)	23.8922(5)
V (Å^3)	1842.4(2)	4843.6(2)	37895.5(12)	2231.2(3)	4433.6(8)	2058.56(6)
Z	2	8	32	4	4	4
T (K)	120.0	139.0	128.0	120.0	301.0	120.0
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Max. 2θ (°)	55.09	54.982	54.924	54.764	55.05	55.056
ρ_{calcd} (g cm^{-3})	4.004	3.001	3.220	2.588	2.594	2.953
μ (mm^{-1})	24.267	18.445	18.885	13.391	13.477	14.523
Flack factor	N/A	N/A	N/A	N/A	N/A	0.347(6)
GoF on F^2	1.195	1.094	1.176	1.157	1.173	1.047
R_1, wR_2 [I > 2σ(I)]	0.0241, 0.0496	0.0133, 0.0322	0.0297, 0.0689	0.0382, 0.0992	0.0437, 0.1166	0.0191, 0.0427
R_1, wR_2 (all data)	0.0324, 0.0540	0.0148, 0.0329	0.0451, 0.0805	0.0436, 0.1049	0.0481, 0.1199	0.0206, 0.0435
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$/e (Å^{-3})	1.21, −1.67	0.547, −0.963	1.68, −1.20	2.73, −1.40	3.81, −3.43	0.557, −0.712

Table S2. Selected bond distances for **Th-SINAP-1**, **Th-SINAP-2**, **Th-SINAP-3**, **Th-SINAP-4**, **Th-SINAP-5**, and **Th-SINAP-6.**

Th-SINAP-1	**(Å)**	**Th-SINAP-2**	**(Å)**	**Th-SINAP-3**	**(Å)**	**Th-SINAP-4**	**(Å)**	**Th-SINAP-5**	**(Å)**	**Th-SINAP-6**	**(Å)**
Th(1)-O(3)×4	2.454(6)	Th(1)-O(1)×2	2.469(4)	Th(1)-O(1)	2.679(6)	Th(1)-O(1)×3	2.44(2)	Th(1)-O(9) ×2	2.395(8)	Th(1)-O(6)#1	2.454(6)
Th(1)-O(1)×4	2.299(14)	Th(1)-O(3)×2	2.404(4)	Th(1)-O(2)	2.508(7)	Th(1)-O(2)×3	2.478(19)	Th(1)-O(1)	2.338(12)	Th(1)-O(3)	2.510(6)
Th(1)-O(1A)×4	2.510(19)	Th(1)-O(9)×3	2.464(5)	Th(1)-O(3)#2	2.564(6)	Th(1)-O(3)×3	2.344(18)	Th(1)-O(6)×2	2.422(9)	Th(1)-O(4)#2	2.368(5)
Th(1)-O(10)	2.858(17)	Th(1)-O(9A)×4	2.291(4)	Th(1)-O(4)	2.381(7)			Th(1)-O(5)	2.411(9)	Th(1)-O(1)	2.417(5)
				Th(1)-O(5)#1	2.397(8)			Th(1)-O(3) ×2	2.504(10)	Th(1)-O(5)	2.464(5)
Th(2)-O(5)	2.490(7)	Th(2)-O(4)×2	2.425(3)	Th(1)-O(5)#3	2.369(8)			Th(1)-O(2)#7	2.498(12)	Th(1)-O(12)#3	2.547(5)
Th(2)-O(8)×2	2.470(5)	Th(2)-O(5)×2	2.461(3)	Th(1)-O(5)	2.348(8)					Th(1)-O(7)	2.431(6)
Th(2)-O(1)×2	2.339(8)	Th(2)-O(9)×4	2.480(5)	Th(1)-O(6)	2.476(7)			Th(2)-O(4) ×2	2.430(11)	Th(1)-O(18)	2.470(6)
Th(2)-O(2A)×2	2.516(9)	Th(2)-O(9A)×4	2.266(4)	Th(1)-O(7)#1	2.471(7)			Th(2)-O(8) ×2	2.409(8)	Th(1)-O(9)	2.443(6)
Th(2)-O(1A)×2	2.519(15)							Th(2)-O(11)	2.466(13)		
		Th(3)-O(6)×2	2.498(3)					Th(2)-O(12)	2.394(11)	Th(2)-O(2)#4	2.480(6)
Th(3)-O(6)×4	2.473(7)	Th(3)-O(2)×2	2.504(4)					Th(2)-O(7) ×2	2.487(8)	Th(2)-O(11)	2.441(5)
Th(3)-O(2)×4	2.309(15)	Th(3)-O(7)	2.481(5)					Th(2)-O(10)	2.468(12)	Th(2)-O(15)	2.452(6)
Th(3)-O(2A)×4	2.489(14)	Th(3)-O(9)×3	2.558(5)							Th(2)-O(14)#5	2.436(6)
Th(3)-O(10)	2.745(17)	Th(3)-O(9A)×4	2.316(5)							Th(2)-O(13)	2.448(5)
										Th(2)-O(17)	2.535(6)
										Th(2)-O(8)#3	2.444(5)
										Th(2)-O(10)	2.454(5)
										Th(2)-O(16)#6	2.444(6)

Table S3. Synthesis details for **Th-SINAP-1**, **Th-SINAP-2**, **Th-SINAP-3**, **Th-SINAP-4**, **Th-SINAP-5**, and **Th-SINAP-6**.

Entry	Product	$Th(NO_3)_4 \cdot 6H_2O$ (g)	[HCOOH] (mL)	[HCOOH]/[Th(IV)]	Water (mL)	pH value before crystallization	pH value after crystallization
1	**Th-SINAP-1**	0.047	0.2	66	0.44	1.97	6.42
2			0.3	99		1.86	6.31
3			0.4	133		1.71	6.22
4			0.5	166		1.61	6.10
5	**Th-SINAP-3**		0.6	199		1.50	5.96
6			0.7	232		1.41	5.87
7	**Th-SINAP-5**		0.8	265		1.28	5.38
8			1.0	331		1.03	4.61
9	**Th-SINAP-6**		1.2	398		0.92	3.37
10			1.4	464		0.80	3.32
11			1.6	530		0.67	3.27
12	**Th-SINAP-2**		0.2	66	0	2.25	5.78
13			0.3	99		2.09	5.49
14			0.4	133		2.01	5.32
15	**Th-SINAP-2/4**		0.5	166		1.96	5.15
16	**Th-SINAP-4**		0.6	199		1.85	4.99
17			0.7	232		1.78	4.93
18			0.8	265		1.74	4.82
19			1.0	331		1.68	4.61
20			1.2	398		1.60	4.40
21			1.4	464		1.45	4.19

22	1.6	530		1.32	3.98

Table S4. The effect of acidity on the metal-ligand complexation.

entry	$Th(NO_3)_4 \cdot 6H_2O$ (mmol)	HCOOH (mL)	Conc. HCl (mL)	DMF (mL)	H_2O (mL)	result
1	0.08	0.2	0.1	1.99	0.44	amorphous product
2	0.08	0.2	0.2	1.99	0.44	amorphous product
3	0.08	0.2	0.3	1.99	0.44	amorphous product
4	0.08	0.2	0.4	1.99	0.44	amorphous product
5	0.08	0.2	0.55	1.99	0.44	amorphous product
6	0.08	0.2	0.7	1.99	0.44	amorphous product
7	0.08	0.2	0.85	1.99	0.44	amorphous product
8	0.08	0.2	1.0	1.99	0.44	amorphous product
9	0.08	0.2	1.3	1.99	0.44	amorphous product
10	0.08	0.2	1.6	1.99	0.44	amorphous product
11	0.08	0.2	0.1	4	0	**Th-SINAP-2**
12	0.08	0.2	0.2	4	0	**Th-SINAP-2**
13	0.08	0.2	0.3	4	0	**Th-SINAP-2**
14	0.08	0.2	0.4	4	0	clear solution
15	0.08	0.2	0.55	4	0	clear solution
16	0.08	0.2	0.7	4	0	clear solution
17	0.08	0.2	0.85	4	0	clear solution
18	0.08	0.2	1.0	4	0	clear solution
19	0.08	0.2	1.3	4	0	clear solution
20	0.08	0.2	1.6	4	0	clear solution