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ARTICLE

Centrosymmetric and Chiral Porous Thorium Organic Frameworks Exhibiting Uncommon Thorium Coordination Environments

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Solvothermal reaction of thorium nitrate and tris-(4-carboxylphenyl)phosphineoxide in DMF affords a centrosymmetric porous thorium organic framework compound [Th(TPO)(OH)(H₂O)]·8H₂O (**1**). In contrast, ionothermal reaction of the same reagents in the ionic liquid 1-butyl-2,3-dimethylimidazolium chloride results in the formation of a rare example of a chiral and porous thorium organic framework compound, [C₉H₁₇N₂][Th(TPO)Cl₂]·18H₂O (**2**), which is derived solely from achiral starting materials. The geometries of the Th(IV) centers in compounds **1** and **2** are both atypical for low valent actinides, which can be best described as ten-coordinate spherical sphenocorona and irregular muffin, respectively. Large cavity of 17.5 Å (max. face to face) × 8 Å (min. face to face) with a BET surface area of 623 m²/g in compound **2** is observed. The poor stability indicated by thermalgravimetric analysis and water-resistance test for compound **2** may be originated from the unique anisotropic coordination geometry for thorium. Temperature-dependent luminescence studies for both compounds indicate the trends in intensity vary as Th–Th distance and the coordination environments of Th(IV) centers changes.

Introduction

The synthesis and characterization of metal-organic frameworks (MOFs) has attracted increasing interest in the field of chemical, material, and environmental sciences owing to their structure diversity and the potential applications in luminescence, molecular recognition, gas storage, catalysis, etc.^{1–3} Most of the research attention of MOFs has been paid to the MOFs based on transition metals and lanthanides.^{4, 5} Generally, the metal–ligand bonds in carboxylate based MOFs are predominately ionic and the bond strength that influences the stability of MOFs is strongly associated with the charge density of metal cations (i.e. the formal valence of the metal cations), which is clearly evident for the fact that the high valent metal based MOFs often exhibit elevated thermal stability and water resistance. For example, one of the earliest reported and most studied MOFs, MOF-5, constructed from divalent Zn ion and 1,4-benzenedicarboxylate, can retain its

structure only below 300 °C, in addition, the water resistance of MOF-5 is quite poor, rendering many practical applications not realistic.⁶ The trivalent Eu ion containing MOFs exhibit a higher thermal stability at nearly 450 °C as well as enhanced water resistance compared to most divalent based carboxylate compounds;⁷ While the UiO-66, based on tetravalent Zr ion, possesses superior thermal stability up to 500 °C that can completely retain the structure even after soaked in aqueous solutions under a wide range of pHs.⁸ Up to now, a series of Zr(IV) based MOFs have been synthesized with the majority showing remarkably high stability.⁸

Over the past two decades, significant effort has been focused on the crystal chemistry of actinide elements which is heavily dominated by the linear uranyl ion (UO₂)²⁺ with an emphasis on its critical role in the traditional nuclear fuel cycle.^{9, 10} In comparison, thorium is relatively less explored, mostly probably due to two reasons: first, thorium is not relevant to uranium based nuclear fuel cycle; second, the chemistry of thorium is not as rich as uranium since only tetravalent state of thorium dominates under normal conditions, despite that there is renewed interest on Th-232 as nuclear fuel in the molten salt reactor in several countries, which may push further understanding on the solid state chemistry of thorium.^{11–14} Furthermore, recent development on the redox chemistry of thorium shown that the chemistry of thorium can be indeed as rich as uranium.¹⁵ Similar to Zr(IV), tetravalent thorium cation has an effective charge of 4+, making it a good candidate for constructing metal organic framework materials with high stability, though much less work in this respect has been performed. Compared with

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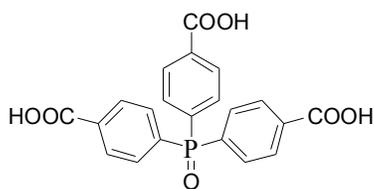
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Zr(IV), Th(IV) is significantly larger in ionic radius (0.75 Å for Zr(IV) and 1.1 Å for Th(IV)), in fact, Th(IV) is the largest tetravalent cation occurring naturally, with the largest known coordination number of 15 in a solid state compound.¹⁶ Although the charge density of Th(IV) is not as large as Zr(IV), assumably leading to poorer stability of Th(IV) MOFs, the better involvement in bonding for 5f and 6d orbitals in thorium compounds may add covalent character to the corresponding Th-O bonds, potentially compensating the stability compared with the Zr(IV) analogue. A direct evidence is the melting point of ThO₂ is 675 K higher than the ZrO₂ analogue.^{17,18} Tetravalent thorium typically displays a spherical coordination environment, which avoids the formation of both one-dimensional chains and two-dimensional sheets.^{19, 20} Only a few 3D MOFs of Th(IV) have been documented up to date^{13, 19-25} with the majority constructed from the carboxylic acids based on either nitrogencyclic ring or benzene ring^{13, 19, 20, 22, 24, 25} and several built by organic/inorganic acids of simple small molecules.²¹⁻²³

We recently reported a microporous polycatenated uranyl(VI) organic framework structure with high β and γ radiation-resistance and chemical stability in aqueous solutions within a wide pH range from 3 to 12. More importantly, this material is able to selectively capture cesium from aqueous solutions without structural degradation²⁶. As further development in the field of three-dimensional Th(IV) organic hybrid materials, the synthesis and crystal structures of two 3D Th(IV) frameworks with tris-(4-carboxylphenyl)phosphineoxide (denoted as H₃TPO, as shown in **Scheme 1**) are reported herein. Solvothermal and/or ionothermal conditions are selected in this work to prevent the hydrolysis of Th(IV) ions. Solvothermal reaction of H₃TPO with Th(NO₃)₄ affords [Th(TPO)(OH)(H₂O)]·8H₂O (**1**) and [C₉H₁₇N₂][Th(TPO)Cl₂]·18H₂O (**2**) is synthesized under ionothermal condition. One of the key features of the two compounds is the extremely rare coordination geometries for low-valent actinides. Moreover, compound **2** exhibits a surprisingly low stability indicated by thermogravimetric analysis and water-resistance test, which is likely originated from the irregular coordination of thorium. The spectroscopic characterizations are also conducted, establishing structure-property relationships in this system.



Scheme 1. The structure of H₃TPO: (tris-(4-carboxylphenyl)phosphineoxide)

EXPERIMENTAL SECTION

Materials and Instrumentations. H₃TPO was synthesized according to the procedure in the literature.²⁷ All other reagents and solvents were used as received from commercial

suppliers without further purification. Powder X-ray diffraction patterns were collected from 5° to 50° using Bruker D8 advance X-ray diffractometer with Cu-K α ($\lambda=1.54056$ Å) radiation. A Quantachrome Autosorb Gas Sorption analyzer IQ2 was used to perform N₂ adsorption measurements (details are shown in supporting information S4). Thermogravimetric analyses were accomplished on a NETZSCH STA 449F3 instrument with temperature from 30 to 900 °C under a nitrogen flow at 10 °C/min. Luminescence and UV-vis absorption spectra were obtained using a Craic Technologies UV-vis-NIR microspectrophotometer.

Synthesis of [Th(TPO)(OH)(H₂O)]·8H₂O, (1**).** Th(NO₃)₄·6H₂O (58.8 mg, 0.1 mmol), H₃TPO (43.9 mg, 0.1 mmol), DMF (5 mL), and 3 drops of concentrated nitric acid were placed in a 23 mL PTFE-lined autoclave and heated at 160 °C for 3 days before it was allowed to cool to 25 °C in 2 days. Colorless block crystals appeared in an extremely low yield (ca. < 5%). Attempts aiming at improving the yield by changing the reaction parameters such as temperature, time, and concentration were not successful. In addition, some unidentified amorphous solids are always present, making the actual yield determination impossible. Therefore, conventional characterizations such as PXRD, IR, and EA are therefore not accomplishable.

Synthesis of [C₉H₁₇N₂][Th(TPO)Cl₂]·18H₂O, (2**).** Th(NO₃)₄·6H₂O (58.8 mg, 0.1 mmol), H₃TPO (43.9 mg, 0.1 mmol), and ionic liquid of 1-butyl-2,3-dimethylimidazolium chloride (283 mg, 1.5 mmol) were placed in a 20 mL closed glass vial and allowed to heated at 140 °C for 3 days. Colorless long strips single crystals appeared together with large quantities of ionic liquid and were collected in ca. 60% yield based on thorium followed by being washed with ethanol ultrasonically. The phase purity of compound **2** was confirmed by the experimental PXRD (**Figure S2**). Elemental analysis results : C calculated, 30.30 %; found, 29.90 %; N calculated, 2.30 %; found, 1.94 %; H calculated, 5.40 %; found, 2.93 %.

Crystallography. The diffraction data were collected at room temperature (293 K) using Bruker D8-Venture single crystal X-ray diffractometer. The diffractometer is equipped with a brilliant Turbo X-ray Source with Mo K α ($\lambda = 0.71073$ Å) radiation and a CMOS detector. The data collection, data integration, and absorption correction were accomplished using APEXII, SAINT, and SADABS software, respectively. All structures were solved incompletely using direct method and the refinement was carried out by SHELX-97²⁸. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions. Detailed information of structures of compounds **1** and **2** is presented in **Table 1**.

Table 1. Crystallographic data for complexes **1** and **2**.

	Compound 1	Compound 2
Formula	[Th(TPO)(OH)(H ₂ O)]·8H ₂ O	[C ₉ H ₁₇ N ₂][Th(TPO)Cl ₂]·18H ₂ O
F _w	818.48	1187.76
CCDC No.	1421126	1421127
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$

<i>a</i> / Å	11.797(2)	21.735(2)
<i>b</i> / Å	12.889(2)	23.205(2)
<i>c</i> / Å	14.037(3)	10.5286(10)
α / °	66.065(4)	90
β / °	78.731(4)	90
γ / °	69.924(4)	90
<i>V</i> / Å ³	1828.3(6)	5310.4(9)
<i>Z</i>	2	4
ρ_{calcd} / g cm ⁻³	1.452	0.888
<i>F</i> (000)	758	1332
(<i>Mo</i> - <i>K</i>) / mm ⁻¹	4.180	2.956
Goof on <i>F</i> ²	1.058	1.095
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0653	0.0632
	0.2289	0.1810
<i>R</i> ₁ , <i>wR</i> ₂ (all data) ^a	0.0695	0.0793
($\Delta\rho$) _{max}	0.2353	0.1956
($\Delta\rho$) _{min} / e ⁻ Å ⁻³	6.978	2.341
($\Delta\rho$) _{min} / e ⁻ Å ⁻³	-3.449	-2.641

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$$

Table 2. Selected bond distances (Å) for compounds **1** and **2**.

Bond	Distance(Å)	Bond	Distance(Å)
Compound 1			
Th1-O8	2.339(7)	Th1-O8 ^a	2.382(7)
Th1-O1	2.362(8)	Th1-O5 ^b	2.448(8)
Th1-O4 ^c	2.454(8)	Th1-O3 ^d	2.479(9)
Th1-O7 ^e	2.552(9)	Th1-O9	2.590(10)
Th1-O6 ^e	2.614(8)	Th1-O2 ^d	2.695(9)
Compound 2			
Th1-O1	2.371(7)	Th1-O5 ^f	2.472(7)
Th1-O6 ^g	2.499(6)	Th1-O3 ^h	2.509(8)
Th1-O2 ^h	2.509(8)	Th1-O7 ^g	2.532(8)
Th1-O4 ^f	2.568(7)	Th1-Cl1	2.754(4)
Th1-Cl2	2.744(4)		

Symmetry codes: a = -x+1, -y+1, -z+1; b = -x+2, -y+1, -z+1; c = x-1, y, z; d = -x+1, -y+2, -z+1; e = -x+1, -y+1, -z+2; f = x, y, z+1; g = x+1/2, -y+1/2, -z+2; h = -x, -y+1, z.

RESULTS AND DISCUSSION

Crystal Structure of [Th(TPO)(OH)(H₂O)]·8H₂O (1). Compound **1** crystallizes in the centrosymmetric triclinic space group of *P* $\bar{1}$ and exhibits a three-dimensional framework structure constructed of dimers of thorium-oxygen subunit of [Th₂O₁₈], as depicted in **Figure 1b**. The asymmetric unit of compound **1** contains one crystallographically independent Th(IV) ion, two μ_2 -bridging oxygen atoms (two O8 with the Th–O lengths of 2.38 and 2.34 Å, respectively) from two bridging hydroxyl groups, two oxygen atoms (O5 and O4, with both Th–O distances of 2.45 Å) from two bidentate bridging carboxylate groups, four oxygen atoms (O2, O3, O6 and O7, with the Th–O length from 2.48 to 2.69 Å) from two chelating carboxylate groups, one phosphine oxygen atom (O1, with Th–O distance of 2.36 Å), and one terminal oxygen atom (O9, with Th–O distance of 2.59 Å) as a water molecule, affording a thorium coordination number of 10 in comparison with the other six thorium organic frameworks containing the 10-coordinate Th(IV) center^{13, 24, 25, 29, 30} (**Figure 1a**). The coordination

geometry of Th(IV) ion can be described as a spherical sphenocorona³¹ with two planes: a square plane defined by O1, O2, O3, and O6 atoms and a pentagonal plane composed of O4, O5, O7, O8 and O9 atoms, respectively (avg. deviations of 0.11 and 0.07 Å and dihedral angle of 6.5°), as well as O8 atom in the capping position. Therefore the overall coordination polyhedron contains twenty-two edges and fourteen faces of twelve triangles and two squares, respectively (**Figure 1c**). As shown in **Table 2**, the bond distance of Th–O ranges from 2.34 to 2.69 Å and the single Th–O bonds with the carboxylate moieties (with Th–O from 2.45 to 2.69 Å) are significantly longer than the Th–O bond with the phosphine unit (2.36 Å), while the latter is close to the corresponding values of Th–O phosphor distances of 2.27 and 2.31 Å, respectively.²² The two adjacent Th(IV) ions are linked by two μ_2 -bridging hydroxyl oxygen atoms and two bidentate carboxylate oxygen atoms to form a bimetallic thorium-oxygen subunit of [Th₂O₁₈] with the shared edge of O8–O6 with the distance between two Th(IV) ions of 3.9 Å (**Figure 1b**). Each TPO unit links to five Th(IV) ions from different directions which belong to four [Th₂O₁₈] subunits. Each dimer of [Th₂O₁₈] unit is double-linked by two TPO units with neighboring four [Th₂O₁₈] units in [*ac*] plane and four [Th₂O₁₈] dimers in [*bc*] plane, resulting in a 4-node three-dimensional framework, as shown in **Figure 2**. Quadrilateral channels are observed in the planes [*ac*] and [*ab*] with the size of 6.9 and 7.6 Å, respectively. The total void volume of the framework (after removal of all solvent molecules) reaches 55.3% calculated by PLATON, making this compound one of most porous actinide based compounds in the literature.^{13, 20}

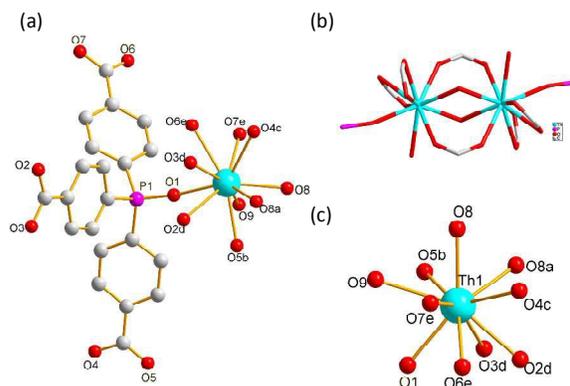


Figure 1. (a) The asymmetric unit of compound **1**; (b) The subunit dimer of thorium-oxygen, [Th₂O₁₈], in compound **1**; (c) The spherical sphenocorona coordination geometry of thorium center in compound **1**.

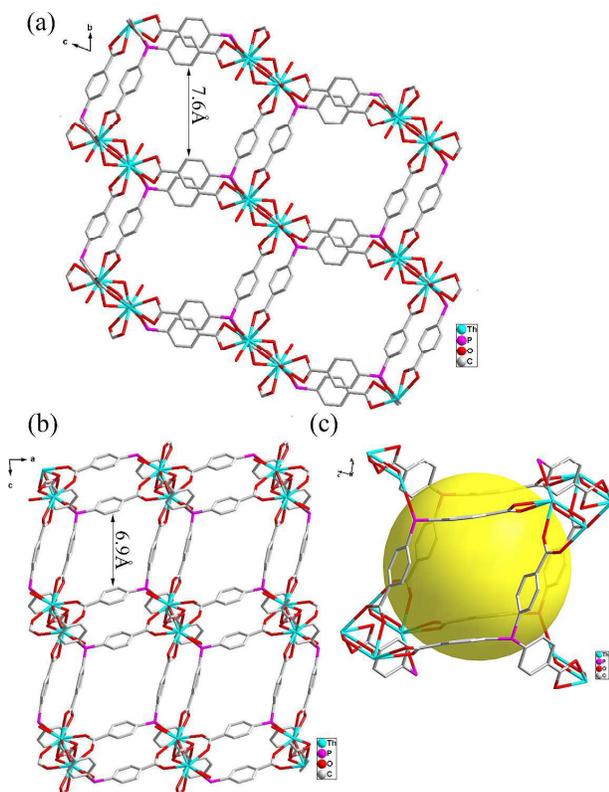


Figure 2. (a) View of **1** along *b* axis; (b) View of **1** along *c* axis; and (c) the porous structure of **1** with a yellow ball placed in the structure for clarity, showing the void space in the framework.

Crystal Structure of $[\text{C}_9\text{H}_{17}\text{N}_2][\text{Th}(\text{TPO})\text{Cl}_2] \cdot 18\text{H}_2\text{O}$ (2**).** Compound **2** is obtained under ionothermal condition using ionic liquid of 1-butyl-2,3-dimethylimidazolium chloride as the solvent. It crystallizes in the chiral orthorhombic space group $P2_12_12_1$, with the flack number refined in the structural solution close to 0.5, indicating both enantiomers are equally present. The asymmetric unit in compound **2** consists of one Th(IV) center, one 1-butyl-2,3-dimethylimidazolium cation, one TPO unit, and two terminal chloride atoms as depicted in **Figure 3a**. The thorium center is 9-coordinate with six oxygen atoms from three chelating carboxylate groups, one phosphine oxygen atom (O1), and two terminal chloride atoms (Cl1 and Cl2) (**Figure 3b**). It should be noted that the thorium ion coordinated by three chelating carboxylate groups is rarely observed. Among the reported thorium carboxylate complexes, only two examples exhibit coordination environment of Th(IV) chelated by mono-carboxylate group²⁹ and all the other thorium carboxylate complexes contain either monodentate²⁴ or bridging (bidentate)³⁰ carboxylate groups, though it is easy to form the five-member-ring chelation by nitrogen and oxygen atoms from nitrogen heterocyclic carboxylic acids.^{24,25} The bond distance of Th–O ranges from 2.371 Å to 2.568(7) Å (**Table 2**), comparable to the average 2.5 Å in similar thorium compounds.^{24,29,30} The environment of 9-coordinate thorium center in compound **2** can be best described as an irregular

muffin shape with the vertices arrangement of 1:5:3.³² This 9-coordinate polyhedron is often observed in the lanthanide complexes but is very rare for actinides. In fact, the most prevalent coordination geometries for 9-coordinate thorium compounds reported are tricapped trigonal prismatic and bicapped square antiprismatic polyhedron.^{29,32} Two adjacent Th(IV) in [*ab*] plane are double-bridged by two TPO units with the coordination sites of chelating carboxylate oxygen atoms and phosphine oxygen atom affording a $[\text{Th}_2]$ binuclear subunit. Each $[\text{Th}_2]$ unit connects to four neighboring $[\text{Th}_2]$ units to form (4, 4) layer in [*ab*] plane. The TPO bridges further link between the layers to form a three-dimensional framework with an average Th–Th distance of ca. 10 Å. Impressively, hexagonal and quadrilateral channels are observed in this thorium organic framework with size of ca. 17.5 Å (maximum face to face) \times 8 Å (minimum face to face) for hexagonal channel along *c* axis and with size of ca. 6 Å \times 6 Å (face to face) for quadrilateral channels along *b* axis, as shown in **Figure 4**. Further study on this chiral structure shows two neighboring Th(IV) centers are linked by the bridging TPO units, forming two different 1D helix chains along *a* and *b* axis, respectively, as depicted in **Figure 5**. As indicated in **Table S1**, nitrogen has been confirmed by elemental analysis though we are unable to identify nitrogen in the electron density map, indicating the 1-butyl-2,3-dimethylimidazolium cation is highly disordered in the cavities. When removing all guests and solvent molecules, the total accessible void volume of the framework reaches 66.9% calculated using PLATON, significantly more porous than compound **1** as well as other reported thorium based hybrid compounds.^{13,20} Nitrogen adsorption experiment at 77 K was carried out to confirm the porosity of **2**. The adsorption measurements for **2** exhibits type I isotherm with a N_2 uptake of $130 \text{ m}^3 \cdot \text{g}^{-1}$ and a high surface area of $623 \text{ m}^2 \cdot \text{g}^{-1}$ calculated using the BET theory (**Figure 6**), which is higher than one of the earliest reported thorium frameworks TOF-2 (CO_2 : $273 \text{ m}^2 \cdot \text{g}^{-1}$) and comparable to the Th based UiO-66 structure (N_2 : $730 \text{ m}^2 \cdot \text{g}^{-1}$).^{13,20}

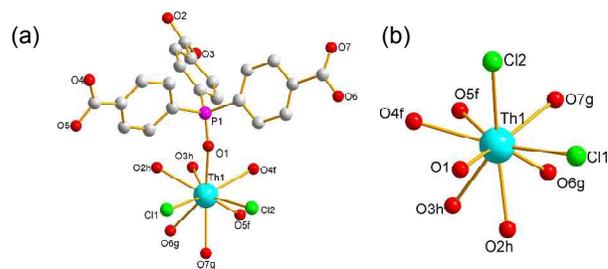


Figure 3. Coordination configuration of compound **2**: (a) the asymmetric unit of compound **2**; (b) The irregular muffin coordination geometry of Th(IV) center in **2**.

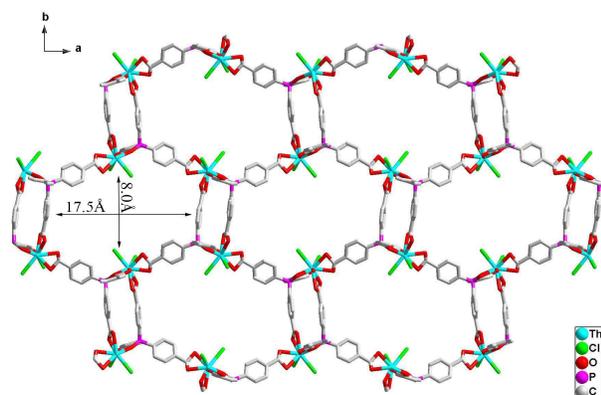


Figure 4. The hexagonal channels in compound **2** along *c* axis with a size of 17.5 Å (max. face to face) × 8 Å (min. face to face).

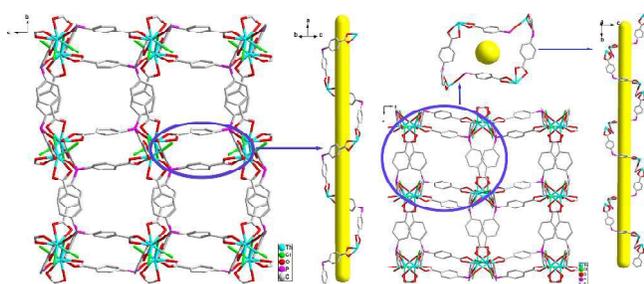


Figure 5. Two helix chains in compound **2**: (a) 1D helix chain along *a* direction; (b) 1D helix chain along *b* axis.

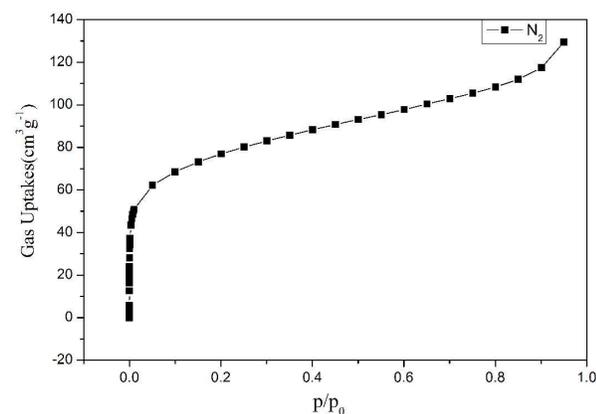
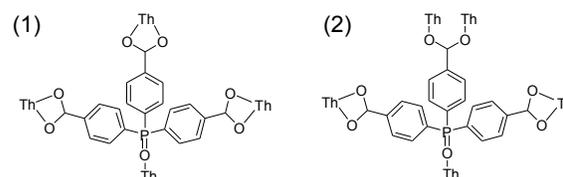


Figure 6. The N₂ adsorption isotherm for compound **2** at 77 K.

Discussion

Compounds **1** and **2** are synthesized under mild solvothermal/ionothermal conditions and it is clear that the reaction media is crucial for this system. The decomposition of DMF gives the product **1** while the same starting reagents with ionic liquid 1-butyl-2,3-dimethylimidazolium chloride produces product **2**, giving a further uncommon example of chiral

complexes generated from all achiral starting materials under the ionothermal conditions.²⁴ However, optimization on the synthesis of compound **1** failed and the yield can't be increased, making characterizations on bulk materials of **1** quite difficult. For structural analyses, both chelating and bidentate coordination fashions are observed in two compounds. Three carboxylate groups in each TPO ligand coordinate to thorium center either with two chelate and one bidentate or all three chelate fashions (**Scheme 2**). The phosphine oxygen atoms are very active to be involved in the coordination of thorium in both compounds, which is reasonable since P=O group is known to show selective extraction of trivalent, tetravalent, and hexavalent actinides from highly acidic waste solutions.²² Three carboxylate groups in TPO units connect to either four or three metal centers to make the TPO units a five-bridging ligand in compound **1** and four-bridging in compound **2**. Furthermore, the pore size found in compound **2** is larger than compound **1** (approximately 16.6 Å × 7.2 Å), likely owing to templating effect of the ionic liquid.



Scheme 2. The coordination modes of H₃TPO unit in both compounds.

As shown in **Figure S3**, the thermogravimetric curve of compound **2** suggests that the framework loses water molecules (exp. 25.1 % and cal. 27.3 %) below 200 °C and then the 1-butyl-2,3-dimethylimidazolium departs. The subsequent structure collapses at above 460 °C. Surprisingly, both compounds are not stable in water, probably originated from the atypical coordination geometry of the thorium(IV) center in the compounds, which contrast sharply with the stable Th-bdc compounds containing either ten-coordinate Th(IV) ion or the nine-coordinate Th(IV) center with a monocapped square antiprismatic geometry.¹³ The nine-coordinate tricapped trigonal prism is thought to be the most common and isotropic geometry for thorium(IV) ions.³²

UV-vis absorptions for both compounds have been investigated as shown in **Figure S4**. The spectra for compounds **1** and **2** show similar absorption features at around 282.8 nm and 263.4 nm, likely stem from the ligand to metal charge transfer process and/or the π - π^* electronic transitions within the ligands.^{33, 34} It is well known that Th(IV) ion does not possess any intrinsic photoluminescence properties thus the fluorescent properties of the thorium complexes have not yet been well studied.³³ Most emission of thorium compounds may be originated from luminophores other than the Th(IV) centers, as reported recently.³⁴ And the study further concluded that the luminescence emission of thorium

compounds may originate from the cooperative phenomena between Th(IV) centers thus the intensity of luminescence peaks of the complexes could be greatly affected by the distance of two Th(IV) centers.³⁵ Herein, the solid state of luminescent studies of Th(IV) based compounds **1**, **2** and the ligand have been investigated. The fluorescence spectra have been collected for the compounds **1** and **2** with an excitation at 365 nm and recorded from 93 K to 293 K. As shown in **Figure 7**, the luminescence spectra of compound **1** show intense vibrationally coupled emission peaks at 430 nm, 450 nm, 470 nm, and 620 nm, respectively. The temperature dependent luminescence spectra indicate that the four peaks show different temperature versus intensity-variation in two temperature ranges: 213 K to 293 K and 93 K to 213 K, respectively. The intensities of four peaks firstly decrease fast as the temperature decreases (with the temperature range from 213 K to 293 K) and then increase as the temperature continues to decrease (with temperature ranging from 93 K to 213 K). As depicted in **Figure 8**, the broad peak ranging from 420 nm to 800 nm is observed in the temperature dependent fluorescence emission spectra for compound **2** with no vibrational features. The monotonic decrease in intensity is observed with the increase of temperature for compound **2**. Owing to the fact that the non-radiative emission of phonon is promoted as elevated temperature, it is common the fluorescence intensity increases while temperature decreases.³³ Compared to compound **2**, the luminescence of compound **1** shows an obvious different trend of intensity variation versus temperature. Given that the strong emission of the TPO ligand under the excitation of 365 nm, the fluorescence emission of both compounds mainly originate from the TPO unit and the variation in these emission phenomenon may probably be attributed to the coordination of the Th(IV) centers to the TPO units. Referring to Brittain et al.'s work, the distance between thorium centers greatly affected the intensity of fluorescence, we consider that the local coordination environment of thorium may greatly affect its corresponding fluorescence property. Comparing the structures of two compounds, the significant deviation includes the much shorter Th–Th distance of ca. 4 Å in compound **1** and the coordination environments. The water molecules bonded to thorium center in **1** may generate the deviation in the emission energy range and the temperature dependent intensity alteration since the hydration is one of the key features in the study of the fluorescence lifetime of lanthanide complexes.³⁶ To fully understand the mechanism of the thorium fluorescence, detailed comparison experiment together with theoretical calculation must be involved before pronounced conclusion can be reached.

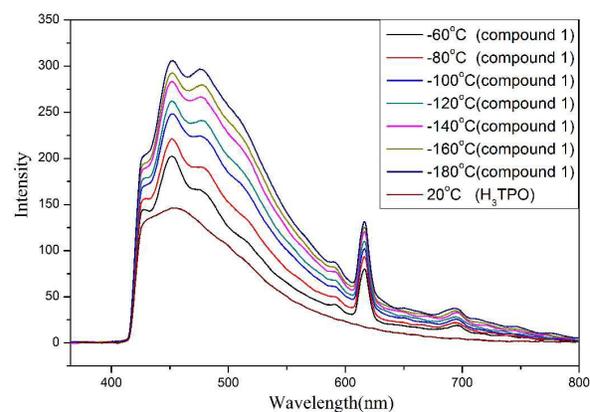
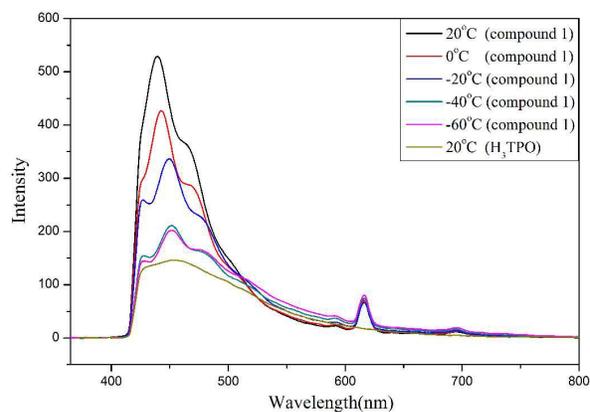


Figure 7. Temperature-dependent luminescence spectra for compound **1** under excitation at 365 nm.

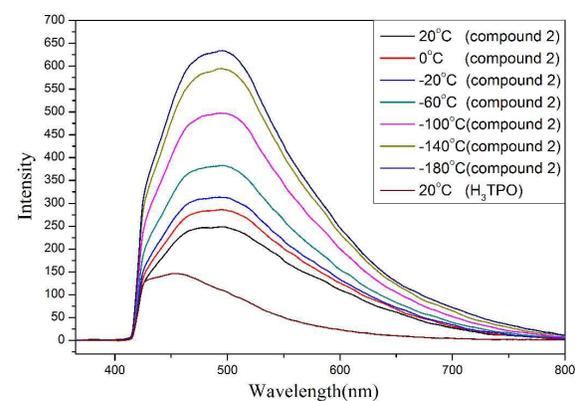


Figure 8. Temperature-dependent luminescent spectra for compound **2** and H₃TPO.

CONCLUSIONS

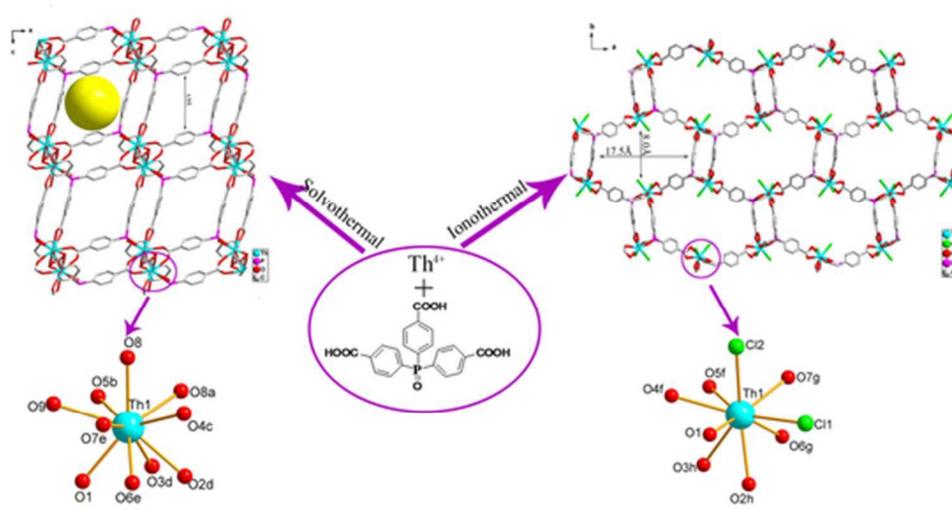
In summary, two new 3D thorium organic frameworks: [Th(TPO)(OH)(H₂O)]·8H₂O (**1**), and [C₉H₁₇N₂][Th(TPO)Cl₂]·18H₂O (**2**), have been synthesized under solvothermal or ionothermal conditions. The coordination environments for Th(IV) ions exhibit interesting features, varying from ten-coordinate spherical sphenocorona for **1** to 9-coordinate muffin mode for **2**. The Th(IV) center in compound **2** is a rare case of being chelated by three different carboxylate groups. The low thermal and water stabilities for compound **2** may stem from the unique anisotropic coordination geometry of the central thorium ion of compound **2**. Large cavity of 17.5 Å (max. face to face) × 8 Å (min. face to face) with a BET surface area of 623 m²/g is observed in compound **2**. Both compounds exhibit strong luminescence emission and the temperature-dependent intensity variation show different trends as the coordination environments deviate. Further investigations aiming at extremely robust thorium based hybrid materials are on the way.

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