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SCU-3 is a two-fold interpenetrated homochiral microporous uranyl organic framework exhibiting the highest void volume (68.8%) and second-harmonic generation (SHG) efficiency (1.54 KDP) among all actinide compounds reported to date, which is also able to capture large amounts of Th(IV) to form a new type of heterobimetallic 5f/5f compounds.
Design and Synthesis of a Chiral Uranium-based Microporous Metal Organic Framework with High SHG Efficiency and Sequestration Potential for Low-Valent Actinides

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The solvothermal reaction of tris-(4-carboxylphenyl)phosphineoxide [H₃TPO] with UO₂(NO₃)₂·6H₂O in DMF affords a uranium-based chiral, microporous, metal-organic framework compound [{(HO)₃NH₂}{UO₂(TPO)}·4DMF·12.5H₂O (SCU-3)] that exhibits the highest void volume (68.8%) and second-harmonic generation (SHG) efficiency (1.54 KDP) for an actinide compound reported to date. The combination of large channels and the coordination capabilities of P=O moieties in the structure enables SCU-3 to capture large amounts of Th(IV) from aqueous solutions, providing a new strategy for preparing heterobimetallic Sr/Sr compounds, and may lead to applications in nuclear waste management.

Introduction

The construction of actinide based metal–organic hybrid compounds has recently attracted increasing amount of attention owing to their structural diversity but also for their unique properties. Among numerous actinide coordination polymers reported to date, major efforts have been made on hexavalent uranyl(VI) cations as building units. These exhibit significant structural diversity with multiple coordination geometries of square bipyramidal, pentagonal bipyramidal, and hexagonal bipyramidal. The structural topologies of uranyl(VI) coordination polymers can vary from clusters to one-dimensional (1D) chains to two-dimensional (2D) layers to three-dimensional (3D) frameworks. Layered structures dominates owing to the inert nature of axial oxo atoms in the (UO₂)₁₁⁺ unit. However, the majority of actinide coordination polymers have only been structurally characterized while the physical properties of these compounds remains underexplored. In fact, the limited investigations that have taken place show that uranyl(VI) coordination polymers can exhibit versatile properties, such as gas adsorption, nonlinear optics, photochemical catalysis, and photoelectronic effects. For instance, O’Hare et al. reported a porous thorium framework TOF-2 by self-assembly of trimesic acid with thorium salt, which shows high adsorption capacity for N₂ and other gases; Lii et al. found a uranyl silicate crystal [K₂C₁₂O₁₂[(UO₂)₃(Si₂O₇)₃]] exhibiting superior second-harmonic generation (SHG) efficiency; Chen et al. reported a series of uranyl(VI) coordination polymers displaying either photoelectronic or photocatalysis properties. We recently reported a microporous polyacatenated 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 remove cesium from aqueous solutions without structural degradation. Generally, coordination polymers containing organic moieties do not possess intrinsic advantages in terms of long-term chemical stability when compared with purely inorganic materials, therefore, actinide-based, metal-organic frameworks may not be practical waste forms for geological disposal. However, the “soft” nature of these compounds may provide additional α-radiation resistance, and may find useful applications in some short-term manipulations of radionuclides such as intermediate waste forms or fuel precursors.

In this work, we chose a low symmetry tris-(4-carboxylphenyl)phosphineoxide (H₃TPO) as a ligand for constructing coordination polymers with U(VI). This ligand contains a neutral P=O group that shows selectivity for the extraction of trivalent, tetravalent, and hexavalent actinides from highly acidic waste solutions. This is confirmed by Chen and co-workers, leading to the well-known "TRPO" (TRPO= trialkyl phosphate oxide) process for effective separations of actinides from high-level waste solutions. In contrast, uranyl(VI) is known to show an exceptional affinity for
carboxylate groups under a variety of environmental and synthetic conditions. Therefore, it should be possible to assemble a porous material by ligating U(VI) with a carboxylate group from a multifunctional ligand that also incorporates P=O moieties that do not bind the original U(VI) centers, and can therefore be utilized to sequester actinide cations present in solution. A material of this type has potential applications in waste partitioning and the remediation of contaminated sites.

Results and discussion

Synthesis of [(CH$_3$)$_2$NH$_2$][UO$_2$(TPO)-4DMF-12.5H$_2$O (SCU-3). H$_2$TPO (40.0 mg, 0.1 mmol) and UO$_2$(NO$_3$)$_2$·6H$_2$O (50.2 mg, 0.1 mmol) were dissolved in a mixture of 3 mL DMF and 2 mL H$_2$O. The resulting solution was sealed in a 20 mL glass vial and heated at 90 °C for 3 days. The reaction system was cooled slowly to room temperature. After filtration and washing with DMF, ethanol, light yellow plate like crystals suitable for X-ray structural analysis were collected. Yield: ca. 48.5% (based on UO$_2$(NO$_3$)$_2$·6H$_2$O). Anal. Calcd for C$_{33}$H$_{55}$O$_{35}$N$_{20}$PU: C, 34.09; H, 5.97; N, 5.69; Found: C, 33.77; H, 4.68; N, 5.70.

Fig. 1 (a) The hexagonal bipyramidal coordination of uranyl units in SCU-3; (b) coordination between TPO ligand and uranyl units in SCU-3; (c) an overview of the 3D framework structure of SCU-3; (d) two-fold interpenetration present in SCU-3.

Structures of SCU-3. The solvothermal reaction of H$_2$TPO with UO$_2$(NO$_3$)$_2$·6H$_2$O in DMF affords bulk crystalline products of [(CH$_3$)$_2$NH$_2$][UO$_2$(TPO)-4DMF-12.5H$_2$O (SCU-3, SCU = Soochow University). The chemical constituents of SCU-3 was derived using a combination of thermogravimetric (TGA) measurements and CHN elemental analysis. Single crystal X-ray diffraction analysis reveals that SCU-3 exhibits a 3D framework and crystallizes in the chiral orthorhombic space group of I$_2$2$_1$2$_1$. The asymmetric unit of SCU-3 is composed of one uranyl unit and one TPO ligand with the uranyl unit displaying the common coordination geometry of a hexagonal bipyramid (Fig. 1a). The coordination sphere of each uranyl unit is provided by three carboxylate groups from three different tetrakis-semi-rigid TPO ligands in bidentate mode. This coordination mode is observed within a variety of uranyl(VI) carboxylate structures and often yields traditional 2D, flat configurations. Notably, the monodentate P=O group in TPO ligand remains terminal and is available to coordinate additional metal centers as a result of losing the coordination competition with the chelating carboxylate units towards uranyl(VI) ions during the formation of SCU-3. In fact, uncoordinated P=O group is extremely rare among the reported TPO ligand based MOFs owing to its ability to coordinate f-element ions under a variety of conditions. All carboxylate groups in SCU-3 bind to uranyl(VI) centers, hence, the TPO ligand bridges three neighbouring uranyl ions in a distorted trigonal configuration (Fig. S2) affording a three dimensional microporous [3,3] connecting framework with large channels of 8 × 20 Å$^2$ (Fig. 1b) along three directions. Moreover, two-fold interpenetrated structure is formed along c axis, as a result, the effective pore size of SCU-3 shrinks to three smaller channels of 8 × 8, 8 × 6, and 8 × 6 Å$^2$. However, 3D channels are still found even with the interpenetration (Fig. 1c and 1d). Other channels also exist in SCU-3, where the largest effective pore size are 9 × 9 and 10 × 10 Å$^2$ along a and b axis, respectively (Fig. S1). The simplified topology of SCU-3 is shown in Fig. S3. The bond length of linear O=U=O is 1.749(7) Å and 1.771(8) Å (Table S2), which is comparable to the value reported in the literature.

Fig. 2 Double helical chains in the 3D structure of SCU-3.

To further understand the chiral nature of SCU-3, helical chains were disclosed around the small channels when viewing along c axis (Fig. 2). Interestingly, “DNA-like” right-handed double helical structure with 2$_1$ symmetry is built from two-fold interpenetrated framework interwoven with each other. The helical chains are all in the right-handed manner which is...
clearly different from reported structures containing alternate arrangement of both left- and right-handed enantiomers giving rise to the racemic mixture.\textsuperscript{12} The homochiral nature of SCU-3 is also confirmed by the flack number of 0.020 given in the crystal structure solution file. Inspired by the homochiral architecture of SCU-3, second-order nonlinear optical (NLO) effects were also measured on polycrystalline samples under irradiation with 1064 nm light to evaluate its potential application as new NLO material. As shown in Fig. 3, SCU-3 is a nonlinear active material displaying SHG efficiency of approximately 1.54 times of that of potassium dihydrogen phosphate (KDP). To the best of our knowledge, this value is approximately 1.54 times of that of potassium dihydrogen phosphate (KDP). To the best of our knowledge, this value is the highest among all previously tested actinide-containing materials.\textsuperscript{8a, 8d, 11}

![Fig. 3](image1)

**Fig. 3** Oscilloscope traces of the SHG signals of SCU-3 and KDP.

Porosity and stability. The free void volume of SCU-3 was calculated using PLATON on the basis of the dynamics diameter of N\textsubscript{2}. Calculation result shows that SCU-3 exhibits the highest void volume of 68.8 % among all actinide compounds reported so far, in particular, SCU-3 is significantly more porous than other well known and most porous actinide based materials, for instance, the void volumes for a thorium organic framework compound ((TOF-2))\textsuperscript{8a}, a chiral uranyl phosphonate compound\textsuperscript{14}, and a cationic thorium borate framework compound (NDTB-1)\textsuperscript{1b} are 41%, 55%, and 43%, respectively. More importantly, the structure of SCU-3 is retained even after shaking vigorously in water for three days as indicated by the powder X-ray diffractions data (Fig. S5). In addition, thermogravimetric analysis (TGA) measurements reveal that this compound is stable up to 450 °C (Fig. S4), showing a clear advance in thermal stability over the majority of MOF materials. However, reliable BET surface area measurements are not possible because SCU-3 is not stable under vacuum.

**Fig. 4** The emission spectra for SCU-3 and SCU-3-Th at 298 K under excitation at 365 nm's light.

**Th\textsuperscript{4+} uptake and luminescence experiments.** The porous and stable architecture of SCU-3 equipped with coordinating-available P=O groups is well suited for the capture and separation of heavy metal cations especially the long-term radiotoxicity-contributing actinide cations in nuclear waste such as plutonium and americium. Owing to the current operational limitation on the transuranic materials at Soochow University, Th\textsuperscript{4+} was selected as an analog for Pu\textsuperscript{4+}.\textsuperscript{15} The Th\textsuperscript{4+} cation uptake experiment was performed by soaking the crystals of SCU-3 in aqueous solutions containing 2000 ppm of Th\textsuperscript{4+}. After separated by filtration, ICP-MS measurements were used to measure the content of actinides sorbed into the crystals (supporting information). It was found that the molar ratio of U:Th is ca. 1:0.9, that is, about 72 % of P=O groups in SCU-3 are coordinating Th\textsuperscript{4+}, assuming 0.25 equivalence of Th\textsuperscript{4+} is sorbed through ion-exchange process with [(CH\textsubscript{3})\textsubscript{2}NH\textsubscript{2}]\textsuperscript{4+}, giving rise to a new type of 5f/5f heterobimetallic compound SCU-3-Th synthesized through post-metallation of the uranyl metal organic framework. Importantly, the framework structure of SCU-3 remains unchanged after thorium metallation as demonstrated by the PXRD data (Fig. S7). To investigate the depth distribution of Th\textsuperscript{4+} in the crystals of SCU-3, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was adopted giving concomitant time-resolved signals for both uranium and thorium, confirming that thorium is incorporated into the whole crystal of SCU-3 instead of being absorbed on the surface (Fig. S8). Furthermore, Raman spectra of the original SCU-3 and SCU-3-Th samples clearly indicate that the metallation the thorium is achieved via P=O coordination (ca. 1130 cm\textsuperscript{-1} for P=O in SCU-3, 1122 cm\textsuperscript{-1} for P=O in SCU-3-Th) (Fig. S9). The coordination of P=O can be further confirmed by the red shift of peak from 1168 to 1160 cm\textsuperscript{-1} in the IR spectra, which is characteristic for P=O for SCU-3 and SCU-3-Th, respectively (Fig. S11). Finally, emission spectroscopy of SCU-3 and SCU-3-Th were conducted at room temperature under excitation at 365 nm. As shown in Fig. 4, the emission spectra of the two samples exhibit well-defined vibronically-coupled charge-transfer features between 450 and 600 nm, which are...
characteristic for uranyl compounds. However, after metallation of thorium, a significant enhancement of the intensity and a blue shift are observed in the spectra. It is well-known that the emission spectra of uranyl compounds are highly sensitive to the coordination environments. The obvious change of emission spectra before and after Th uptake corresponds to change of ligand field for uranyl induced by incorporation of thorium, which is supportive for the statement that Th$^{4+}$ is sorbed by SCU-3 not only through simple ion exchange process.

Conclusions

In conclusion, a new chiral uranium based microporous MOF, SCU-3, with the highest void volume among known actinide compounds to date was designed and prepared. The framework displays two-fold interpenetration and “DNA-like” chiral double helix structure. SCU-3 is a nonlinear active material displaying SHG efficiency of approximately 1.54 times that of KDP, which is also the highest among current known actinide-containing materials. In addition, the uncoordinated P=O groups and large void volume in SCU-3 ensure excellent sequestrations ability towards tetravalent actinides such as Th$^{4+}$, providing a new strategy for making heterobimetallic 5f/5f compounds, which may find potential applications during nuclear waste management processes.

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Notes and references


