Electronic Supplementary Material (ESI) for Dalton Transactions.

Design and Synthesis of a Chiral Uranium based Microporous Metal Organic Framework with High SHG Efficiency and Sequestration Potential towards Low-Valent Actinides

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Contents

S1. Materials and instrumentations. All reagents and solvents were used as received from commercial suppliers without further purification. The infrared spectra of KBr pellets were recorded in the range of 4000-450 cm^{-1} on a Thermo Nicolet 6700 spectrometer. Elemental analyses (C, H, and N) were performed with a Vario EL CHNOS elemental analyzer. Powder X-ray diffraction (PXRD) data were collected from 5 to 50° with a step of 0.02° and the time for data collection was 0.5 s on a Bruker D8 Advance diffractometer with Cu Kα radiation (λ=1.54056 Å) and a Lynxeye one-Dimensional detector. Thermalgravimetric analysis was carried out on a NETZSCH STA 449F3 instrument in the range of 30-900 °C under a nitrogen flow at a heating rate of 10 °C/ min. The solid-state luminescence and UV-vis-NIR spectra were recorded on a Craic Technologoes microspectrophotometer, crystals were placed on quartz slides under Krytox oil, and data was collected after optimization of microspectro-photometer. Scanning electron microscopy/energy-dispersive spectroscopy (SEM/EDS) images and data were collected using FEI Quanta 200FEG. The energy of the electron beam was 30 kV, and the spectrum acquisition time was 100 s. Laser-ablation inductively coupled plasma mass spectrometry (LA-ICPMS) measurements on single crystals were conducted using a ThermoFisher Element2 ICP-MS instrument coupled to a UP213 Nd:YAG laser ablation system (New Wave Research). Second Harmonic Generation (SHG) experiments were executed by Kurtz-Perry powder SHG test using an Nd:YAG laser (1064 nm) with input pulse of 350 mV. The values of the nonlinear optical coefficients for SHG have been determined by comparison with a KDP reference.

S2. Synthetic methods.

Synthesis of tris-(4-carboxylphenyl)phosphineoxide (H_3TPO). H_3TPO was synthesized according to literature reported methods,[1] white powder of H_3TPO was collected.

S3. X-ray crystallography. Data collection was performed on a Bruker D8-Venture diffractometer with a Turbo X-ray Source (Mo–Kα radiation, λ = 0.71073 Å) adopting the direct-drive rotating anode technique and a CMOS detector at room temperature. The data frames were collected using the program APEX2 and processed using the program SAINT routine in APEX2. The structures were solved by direct methods and refined by the full-matrix least squares on F^2

using the SHELXTL-97 program.[2] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were placed in geometrically idealized positions and included as riding atoms (C-H bond fixed at 0.97 Å). Crystallographic and refinement details are summarized in Table **S1**. Selected bond lengths and angles for **SCU-3** is listed in Tables **S2**. For **SCU-3**, the solvent molecules in the structure are highly disordered and impossible to refine using conventional discrete-atom models. To resolve this issue, the contribution of solvent-electron density was removed using the SQUEEZE routine in PLATON[3], thereby producing a set of solvent-free diffraction intensities. The final formulas were calculated from the SQUEEZE results in combination with those of elemental analyses and TGA. Two A-level alerts are present for the checkcif file, the first one is due to the partial lacking of intense high angle data (which is possible for a crystal with large unit cell) while the second one is common for a open framework structure solution after SQUEEZE operation.

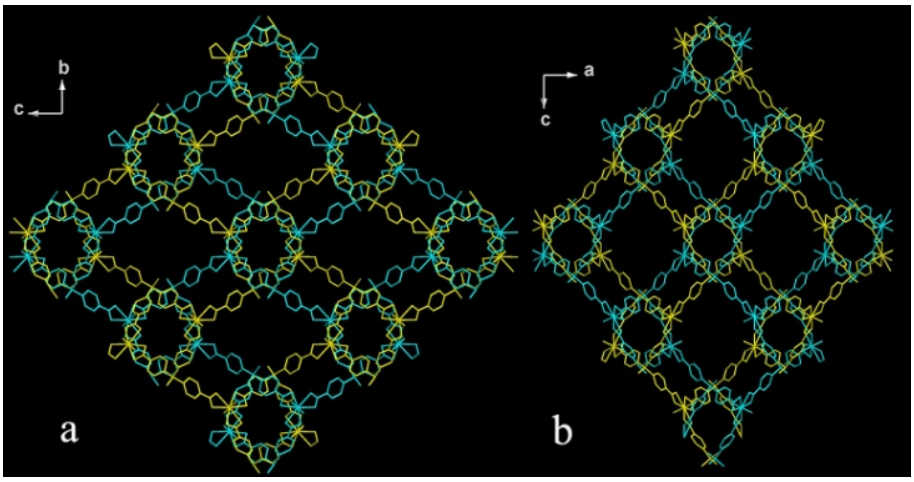


Fig. S1. The 3D frameworks of **SCU-3**: (a) viewing along *a* axis direction; (b) viewing along *b* axis direction.

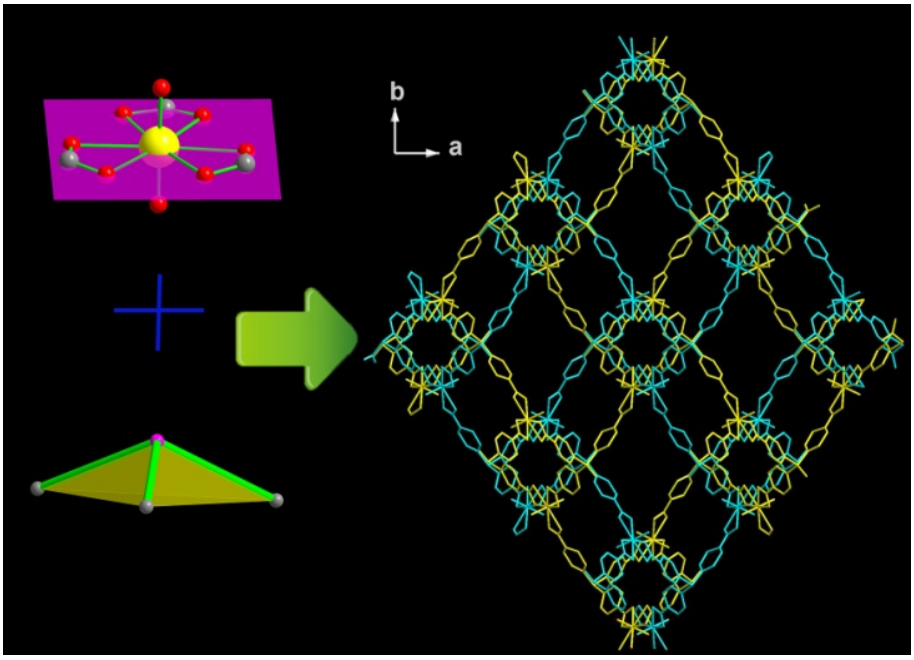


Fig. S2. The construction of 3D framework in **SCU-3**.

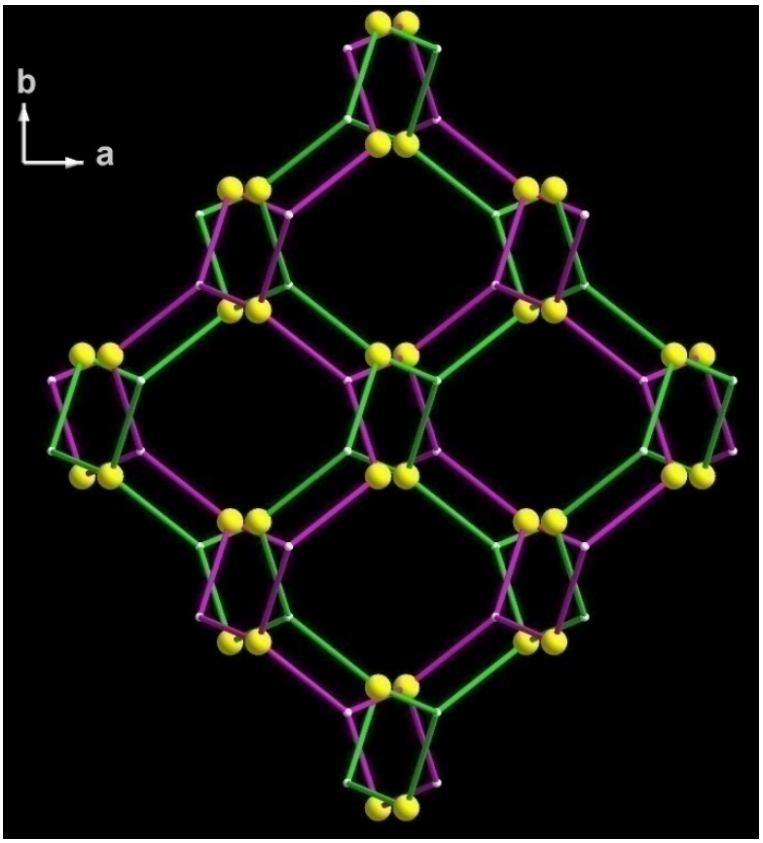


Fig. S3. Topological representation of **SCU-3**.

Table S1. Crystallographic data for **SCU-3**

Sample	**SCU-3**
Formula	$C_{35}H_{72}O_{25}N_5PU$
*M*r[g mol^{-1}]	1231.96
Crystal system	orthorhombic
Space group	*I*212121
a (Å)	19.552(3)
b (Å)	21.898(4)
c (Å)	25.297(4)
α	90
β	90
γ	90
V (Å^3)	10930(3)
Z	8
D_c (g cm^{-3})	0.842
μ (mm^{-1})	3.048
F (000)	2574
T(K)	273(2)
GOF on F^2	0.987
R1,[a] wR2[b] ($I>2\sigma(I)$)	0.0471,0.0585
R1,[a] wR2[b] (all data)	0.1260,0.1350

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

Table S2. Selected bond lengths (Å) and angles (°) for compound **1**

Selected Bond Lengths (Å)			
U1-O9	1.749(7)	U1-O4	1.771 (8)
U1-O7	2.419 (9)	U1-O8	2.441 (9)
U1-O6	2.448 (9)	U1-O1	2.454 (8)
U1-O5	2.454 (9)	U1-O2	2.459 (9)
Selected Bond Angles (°)			
O9-U1-O4	179.0 (4)	O9-U1-O7	90.3 (4)
O4-U1-O7	90.7 (4)	O9-U1-O8	91.0 (4)
O4-U1-O8	89.4 (4)	O9-U1-O6	91.8 (4)
O4-U1-O6	88.8 (4)	O9-U1-O1	89.4 (4)
O4-U1-O3	89.9 (3)		

S4. Thermogravimetric analysis. The as-synthesized dried samples were heated at a constant rate 10 K/min in nitrogen from 30 to 900 ºC. Only one weight loss step is observed in **SCU-3** (found. 45.1 %, cal. 45.4 %), which can be attributed to the lost of free water, DMF and protonated dimethylamine cation.

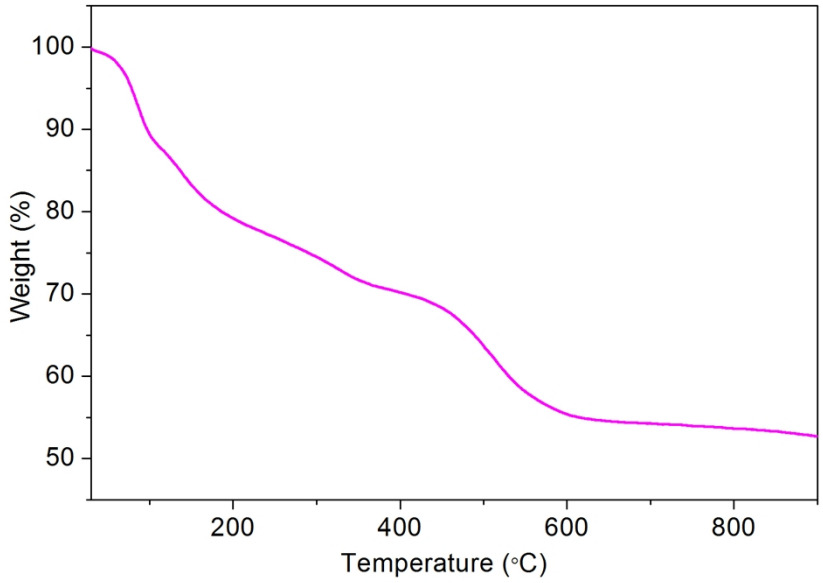


Fig. S4. The TGA curve for **SCU-3**.

S5. Water-stability Measurements. Water-stability measurements for **SCU-3** was studied by soaking the samples in water and shaked vigorously on an oscillator for 3 days. The PXRD results demonstrate that **SCU-3** is stable in water.

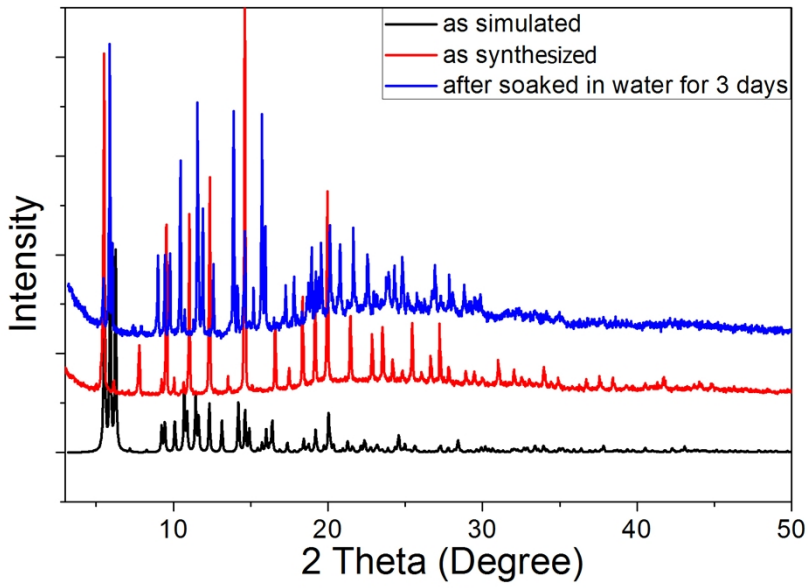
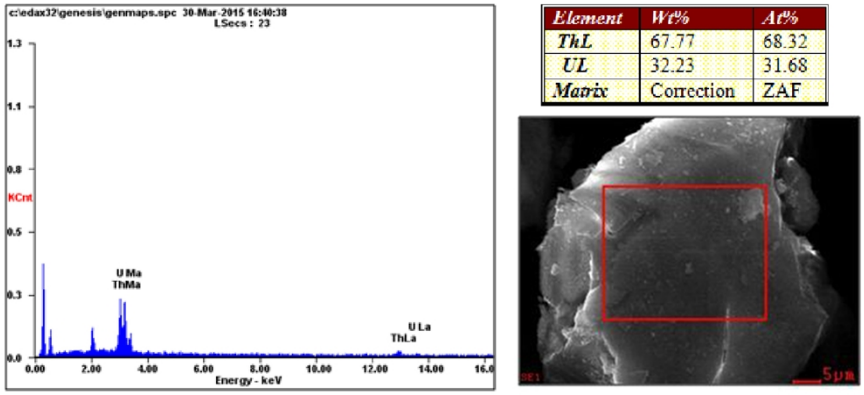


Fig. S5. The PXRD data for **SCU-3** after soaked in water for 3 days.

S6. Th $^{4+}$ uptake experiments. Th^{4+} uptake measurement of **SCU-3** was studied by soaking 10 mg of **SCU-3** in 10 mL of water solutions of $Th(NO_3)_4$ (298 K, pH = 2.87, 2000 ppm Th^{4+}) for 1 day. EDS data was collected to determine the amount of thorium and uranium. LA-ICP-MS results for crystals of **SCU-3** was collected by soaking **SCU-3** in water solutions with 2000 ppm of Th^{4+}. The precise Th and U ratio in **SCU-3-Th** was measured by ICP-MS on dissolved solution of Th-incorporated crystals in concentrated nitric acid. The final result shows that Th:U ratio is 0.9:1 (Th: 96 ppb, U: 106 ppb).



Element	Wt%	At%
ThL	67.77	68.32
UL	32.23	31.68
Matrix	Correction	ZAF

Fig. S6. The EDS results for crystals of **SCU-3** soaked in solutions of Th^{4+} (2000 ppm) for 1 days.

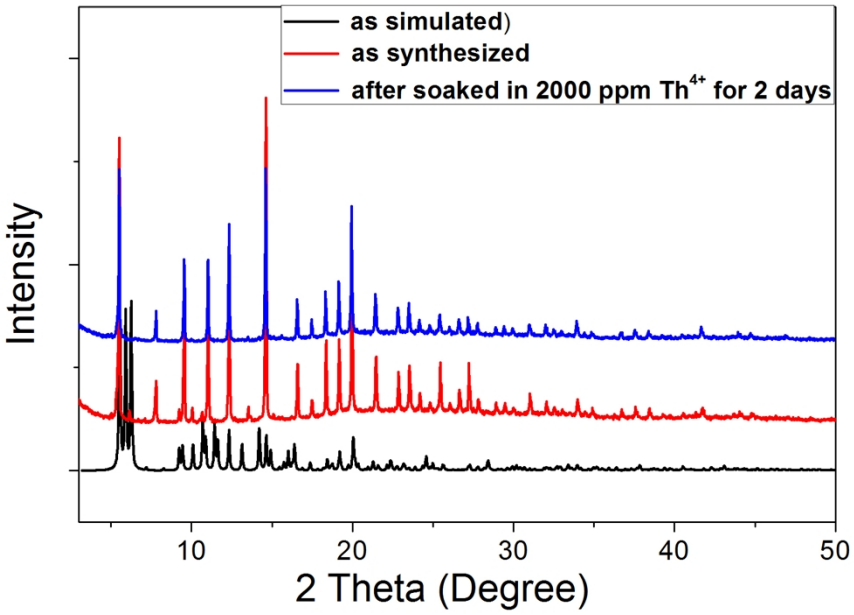


Fig. S7. The PXRD for **SCU-3** after soaked in 2000 ppm Th^{4+} for 2 days.

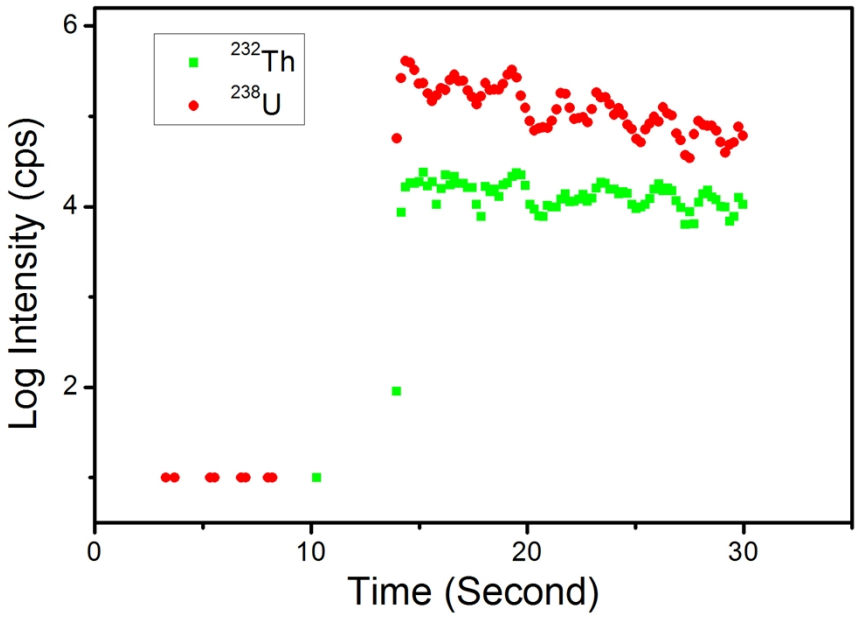


Fig. S8. The LA-ICP-MS results for crystals of **SCU-3** soaked in solutions of Th^{4+} (2000 ppm) for 2 days (**t**he initial 10 s background with the laster shutter in place followed by the 20 s ablation measurement). The background signal measurements show that background ions counts are in range of 0-2 cps, while both uranium and thorium signal exhibits an enhanced counts when laser-ablation was performed on the crystal. The thorium signal is concomitant with signal for uranium indicating that Th^{4+} ions are incorporated into the whole crystals of **SCU-3** instead of being absorbed on the surface.

S8. Spectroscopic characterizations.

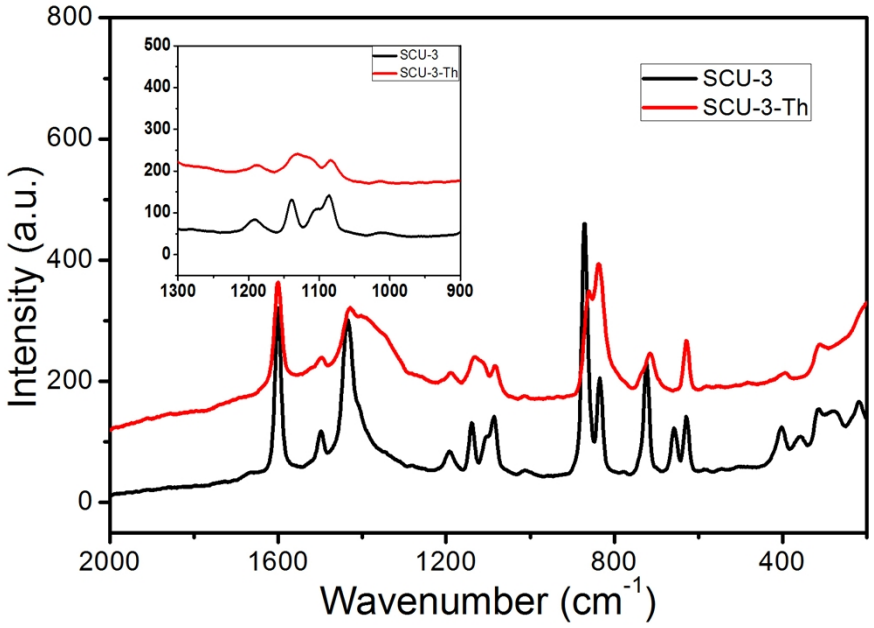


Fig. S9. The Raman spectra for **SCU-3** and **SCU-3-Th** measured at 298 K**.**

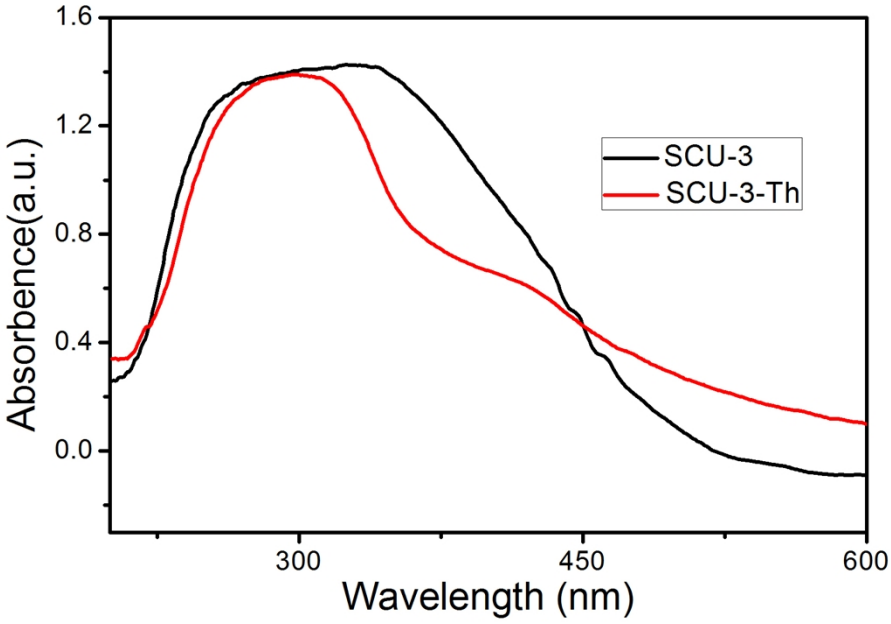


Fig. S10. The UV-vis absorption spectra for **SCU-3** and **SCU-3-Th** measured at 298 K.

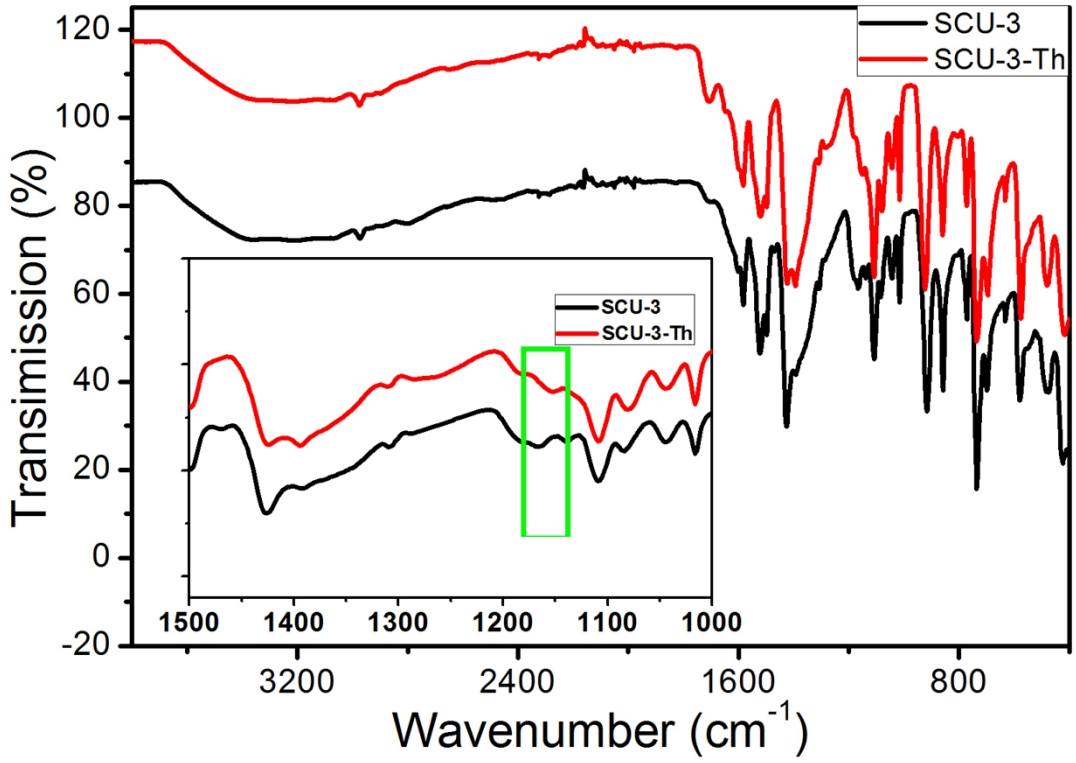


Fig. S11. The IR spectra for **SCU-3** and **SCU-3-Th** measured at 298 K**.**

Reference:

[ ] R. Amengual, E. Genin, V. Michlet, M. Savignac and J.-P. Genêt, Adv. Synth. Catal., **2002**, 344, 393.

[2] SHELXTL, version 5.10; Siemens Analytical X-ray Instruments Inc.: Madison, WI, **1994**.

[3] O. Hübner, A. Glöss, M. Fichtner,W. Klopper, *J. Phys. Chem. A* **2004**, *108*, 3019-3023.