

Electronic Supplementary Information for:

A porous Sm(III) coordination nanotube with hydrophobic and hydrophilic channels

Nazario Lopez,^a Hanhua Zhao,^a Dan Zhao,^b Hong-Cai Zhou,^a Joseph P. Riebenspies^a and Kim R. Dunbar^{a*}

^a Texas A&M University, Department of Chemistry, College Station, TX, 77842, United States

^b National University of Singapore, Department of Chemical and Biomolecular Engineering,
Singapore 117576

*To whom correspondence should be addressed. K.R.D. (dunbar@chem.tamu.edu).

Procedures and Methods

General. All manipulations were performed using standard Schlenk-line techniques. All reagents were purchased from Aldrich. Methanol was of HPLC grade. Thermogravimetry analyses (TGA) were performed under N₂ on a SHIMADZU TGA-50 Thermogravimetric Analyzer, with a heating rate of 5 °C min⁻¹. Particle size data were obtained on a Micromeritics Saturn DigiSizer 5200.

Crystallography. X-ray diffraction data of microcrystalline samples were collected on a Bruker-AXS D8 Advanced Bragg-Brentano X-ray Powder Diffractometer. Low-temperature diffraction data of single crystals were collected on a three-circle diffractometer coupled to a Bruker-AXS Smart Apex charged-coupled device (CCD) detector with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) for both structures. The structures were solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-97¹ using established methods.² All non-hydrogen atoms were refined anisotropically.

Low-pressure gas sorption measurements. Low pressure (< 800 torr) gas sorption isotherms were measured using a Micromeritics ASAP 2020 surface area and pore size analyzer. Pore size distribution data were calculated from the N₂ sorption isotherms based on the DFT model in the Micromeritics ASAP 2020 software package (assuming slit pore geometry). Prior to the measurements, the samples were degassed for 10 h at 120 °C. UHP grade gases were used for all measurements. Oil-free vacuum pumps and oil-free pressure regulators were used for all measurements to prevent contamination of the samples during the degassing process and isotherm measurement.

¹ G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112.

² P. Müller, *Cryst. Rev.* 2009, **15**, 57.

Synthesis of Single Crystals of $[\text{Sm}(\text{tptz})(\text{HCOO})_3]\cdot 2.5\text{H}_2\text{O}$ ∞: To a solution of $\text{Sm}(\text{Otf})_3\cdot 6\text{H}_2\text{O}$ (0.5 mmol) in methanol (5 mL) was added dropwise, with stirring, a solution of 2,4,6-tri(2-pyridyl)-1,3,5-triazine (tptz) (0.5 mmol) in methanol (5 mL) and the mixture was stirred for 20 minutes. Methanol (4 mL) was added to the top of the resulting light purple solution to slow down the diffusion and then a solution of $[\text{NH}_4][\text{HCOO}]$ (95 mg, 1.5 mmol) in methanol (6 mL) was layered on top. Colorless single crystals were collected on a medium frit after 1 week and washed three times with aliquots of methanol (10 mL). The volatiles were removed under dynamic vacuum for 1 h. Yield 213 mg (66%). CCDC 895843

Bulk Synthesis of $[\text{Sm}(\text{tptz})(\text{HCOO})_3]\cdot 2.5\text{H}_2\text{O}$ ∞: To a solution of $\text{Sm}(\text{Otf})_3\cdot 6\text{H}_2\text{O}$ (352 mg, 0.5 mmol) in methanol (5 mL) was added dropwise, with stirring, a solution of 2,4,6-tri(2-pyridyl)-1,3,5-triazine (tptz) (156 mg, 0.5 mmol) in methanol (4 mL) and stirring was kept for 20 minutes. The resulting light purple solution was stirred with a solution of $[\text{NH}_4][\text{HCOO}]$ (95 mg, 1.5 mmol) in methanol (3 mL). White microcrystalline material was collected on a medium frit after 30 minutes and washed three times with aliquots of methanol (10 mL). The volatiles were removed under dynamic vacuum for 1 h. Yield 222 mg (69%). Anal. Calcd (Found) for $[\text{Sm}(\text{tptz})(\text{HCOO})_3]\cdot 3\text{H}_2\text{O}$ ∞, $\text{C}_{21}\text{H}_{21}\text{N}_6\text{O}_9\text{Sm}$: C, 38.70 (38.62); H, 3.25 (2.67); N, 12.89 (12.78).

Table S1. Crystallographic data and structural refinement parameters for isostructural $\{[\text{Pr}(\text{tptz})(\text{HCOO})_3] \cdot 2.5\text{H}_2\text{O}\}_\infty$ (**Pr-tube**) and $\{[\text{Sm}(\text{tptz})(\text{HCOO})_3] \cdot 2.5\text{H}_2\text{O}\}_\infty$ (**Sm-tube**) compounds.

	Pr-tube	Sm-tube
Formula	$\text{C}_{21}\text{H}_{20}\text{N}_6\text{O}_{8.5}\text{Pr}$	$\text{C}_{21}\text{H}_{20}\text{N}_6\text{O}_{8.5}\text{Sm}$
Formula weight	633.33	642.78
Space group	<i>P63/mcm</i>	<i>P63/mcm</i>
<i>T</i> (K)	110	110
<i>a</i> (Å)	25.213(4)	25.158(4)
<i>b</i> (Å)	25.213(4)	25.158(4)
<i>c</i> (Å)	6.752(1)	6.704(1)
α (°)	90	90
β (°)	90	90
γ (°)	120	120
<i>V</i> (Å ³)	3717(1)	3674(1)
<i>Z</i>	6	6
Crystal description, color	light green	colorless
Crystal size (mm ³)	0.19 × 0.11 × 0.05	0.19 × 0.11 × 0.11
λ (Å)	0.71073	0.71073
<i>D</i> _{calc} (g cm ⁻³)	1.499	1.629
μ (cm ⁻¹)	2.001	2.444
<i>F</i> (000)	1656	1788
Reflections collected	23457	32365
Independent reflections	3023	3098
	[<i>R</i> (int) = 0.0116]	[<i>R</i> (int) = 0.0960]
Observed data [<i>I</i> > 2σ(<i>I</i>)]	1165	1060
Data/parameters/restraints	3023/113/132	3098/118/138
<i>R</i> ^a , <i>wR</i> ^b (all data)	0.0625, 0.1474	0.0725, 0.1766
<i>R</i> ^a , <i>wR</i> ^b (<i>I</i> > 2σ(<i>I</i>))	0.0620, 0.1470	0.0654, 0.1703
Goodness-of-fit ^c on <i>F</i> ²	1.119	1.006
Largest diff. peak and hole (e Å ⁻³)	2.142, -0.968	1.777, -1.032

$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum w(F_o^2)^2} \right\}^{1/2}$$

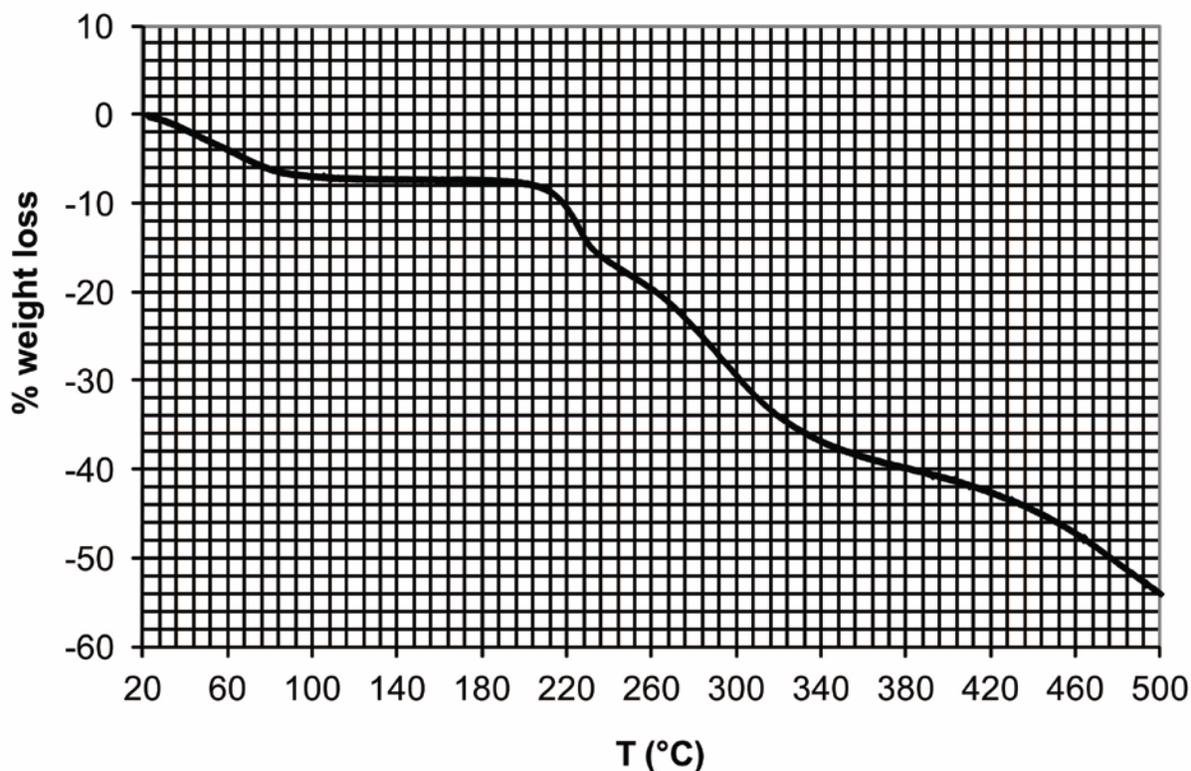


Figure S1. TGA profile of $\{[\text{Sm}(\text{tptz})(\text{HCOO})_3] \cdot 2.5\text{H}_2\text{O}\}_\infty$ prepared by the bulk synthesis method. The plateau at 7.3% weight loss from 120 °C to 190 °C corresponds to the loss of 2.5 water molecules per Sm ion.

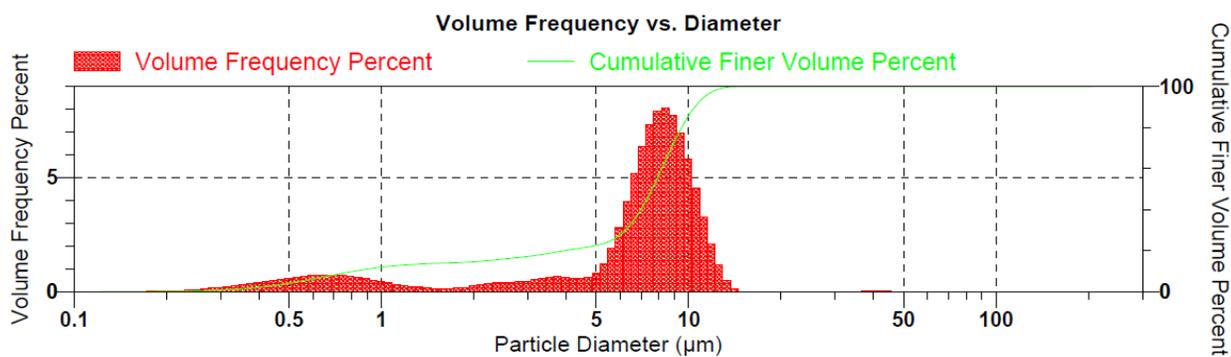


Figure S2. Particle size distribution of a representative sample of $\{[\text{Sm}(\text{tptz})(\text{HCOO})_3] \cdot 2.5\text{H}_2\text{O}\}_\infty$, which was used for gas sorption studies and was prepared by the bulk synthesis method.