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Supporting Information

Topological modulation of the porous structure of a coordination polymer constructed from a flexible building block *via* framework–guest interaction during self-assembly

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Contents

1. Experimental Details

2. Additional Data

1. Experimental Details

Materials. Samarium (III) nitrate hexahydrate [$Sm(NO_3)_3\cdot 6H_2O$] was purchased from Kanto Chemical Co., Inc. Tris(2-aminoethyl)amine (tren) and 5-methylsalicylaldehyde (5-MeSal) were purchased from Tokyo Chemical Industry Co., Ltd. All reagents were used without further purification.

Synthesis of the coordination polymer 1. A solution of tren (0.0728 g, 0.5 mmol) dissolved in methanol (2 mL) was added to a hot solution of $Sm(NO_3)_3\cdot 6H_2O$ (0.2278 g, 0.5 mmol) dissolved in methanol (13 mL) and stirred for 10 min at 60 ºC. Then, a solution of 5-MeSal (0.2185 g, 1.5 mmol) dissolved in methanol (2 mL) was added and stirred for 5 min at 60 ºC. After the solution was cooled at room temperature for 2 h, a yellow product was obtained. Recrystallization from DMF afforded single crystals. Yield: 0.273 g, 60.2 %.

[$Sm(H_3L)(NO_3)_3\cdot DMF\cdot 1/6H_2O]_n$ (1). Anal. Calc. for $C_{33}H_{43.33}N_8O_{13.17}Sm$: C 43.40, H 4.78, N 12.27. Found: C 43.40, H 4.64, N 12.03. IR (cm^{-1}): 2918(m), 2859(m), 1677(m), 1649(s), 1535(m), 1485(s), 1440(m), 1383(m), 1335(m), 1273(s), 1225(m), 1210(s), 1160(s), 1140(m), 1093(w), 1066(m), 1024(s), 939(w), 921(m), 890(w), 870(m), 826(m), 800(s), 735(m), 705(w), 660(m).

Synthesis of the coordination polymer 2. A solution of tren (0.7360 g, 5 mmol) dissolved in methanol (20 mL) was added to a hot solution of $Sm(NO_3)_3\cdot 6H_2O$ (2.2747 g, 5 mmol) dissolved in methanol (130 mL) and stirred for 10 min at 60 ºC. Then, a solution of 5-MeSal (2.050 g, 15 mmol) dissolved in methanol (20 mL) was added and stirred for 5 min at 60 ºC. After the solution was cooled at room temperature for 2 h, a yellow product was obtained. Recrystallization by diffusion of methanol vapor into DMF solution afforded single crystals. Yield: 3.021 g, 71.1 %.

[$Sm(H_3L)(NO_3)_3\cdot 1/3MeOH\cdot 1/6H_2O]_n$ (2). Anal. Calc. for $C_{30.17}H_{36}N_7O_{12.5}Sm$: C 42.83, H 4.46, N 11.53. Found: C 43.04, H 4.59, N 11.78. IR (cm^{-1}): 2919(m), 2857(m), 1677(m), 1648(s), 1535(m), 1485(s), 1383(m), 1335(m), 1271(s), 1225(m), 1210(s), 1160(s), 1140(m), 1065(m), 1025(s), 939(w), 922(m), 890(w), 867(m), 835(m), 800(s), 734(m), 705(w), 660(w).

Physical measurements. Elemental analysis was performed with a J-Science Lab NM-11. IR spectra were recorded with a Nicolet 6700 FT-IR spectrometer in the 4000–650 cm^{-1} region employing attenuated total reflectance mode. Powder X-ray diffraction (PXRD) was recorded using RINT-2200VHF (Rigaku). Simulation of X-ray diffraction patterns with the CIF files of the corresponding single-crystal X-ray diffraction data were conducted with CrystalDiffract. Thermogravimetric analysis (TGA) was performed by TG/DTA 6200 (Seiko Instruments Inc.). The powders of **1** and **2** were treated at 120 ºC under reduced pressure for 12 h for gas adsorption study. N_2 adsorption isotherms of **1** and **2** were measured by NOVA-4200e (Quantachrome Instruments).

X-ray crystallographic data collection and refinement of the structure. Single-crystal X-ray diffraction data were collected on a Bruker AXS II CCD diffractometer using MoKα radiation (λ = 0.71073 Å) and employing a Bruker Helios multilayered confocal mirror as a monochromator and Bruker TXS fine-focus rotating anode as a radiation source. The data were integrated and reduced using SAINT and XPREP, and absorption corrections were made using the semi-empirical method with SADABS.[1] The structure was solved by the direct method using SHELXS-97[2] and refined using least-squares methods on F^2 with SHELXL-97. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms bound to carbon atoms were placed at the calculated positions. Hydrogen atoms bound to the nitrogen atoms were found as follows. The final difference Fourier map showed peaks in the expected positions for hydrogen atoms with an identical N–H distance; however, they did not converge into the expected N–H distances upon refinement with the isotropic temperature factors. Thus, the positions were fixed in the amide geometry (N–H = 0.88 Å), and only the temperature factors were refined, proving the existence of the hydrogen atom located at the nitrogen atom. The structures of **1** and **2** contained disordered moieties. In the crystal structures of **1**, there was disordered nitrate anion of which occupancies was refined with free variables. In the crystal structures of compounds **2**, there were disordered nitrate anion and aromatic ring of H_3L of which occupancies were refined with free variables, and there was disordered methanol molecule. Solvent-accessible void volume was calculated using Olex2.[3] The crystallographic data are summarized in Table S4.

References

1. (a) *SMART, SAINT, and XPREP, Area Detector Control and Data Integration and Reduction Software*, Bruker Analytical X-ray Instruments Inc., Madison, WI, 1995. (b) Sheldrick, G. M. *SADABS*, *Empirical Absorption Correction Program for Area Detector Data*, University of Göttingen, Germany, 1996.
2. Sheldrick, G. M. *SHELX-97*, *Program for Crystal Structure Analysis*, University of Göttingen, Germany, 1998.

3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339.

2. Additional Data

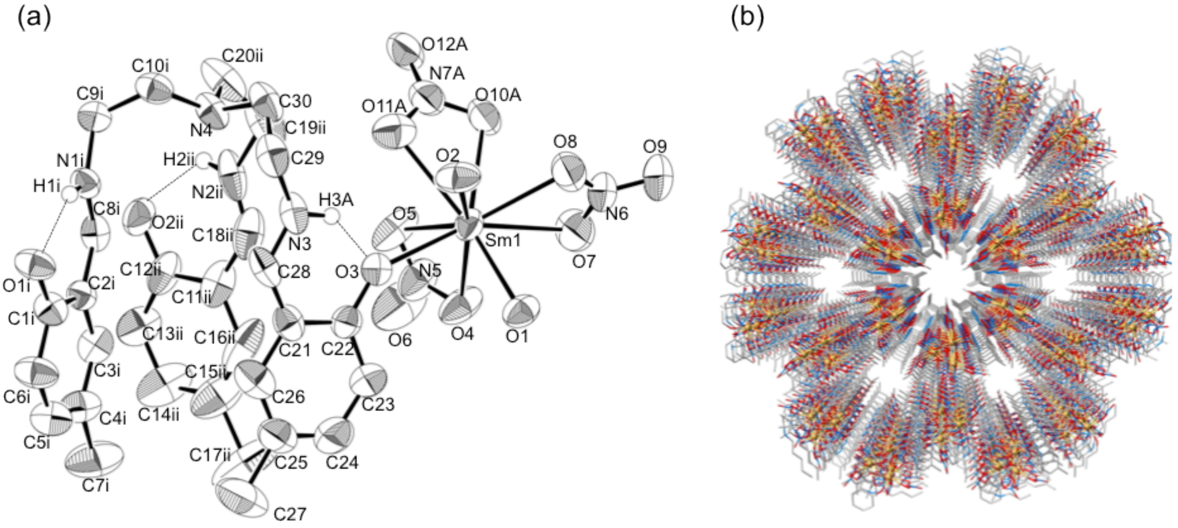

Fig. S1 (a) ORTEP diagram of **1** with numbering, showing only the atoms O10A, N7A, O11A, and O12A of the disordered nitrate anion, and the atoms C15A, C16A, and C17A of the disordered aromatic ring. Symmetry codes: i: 4/3-y, 2/3+x-y, -1/3+z, ii: 1/3+x-y, -1/3+x, 5/3-z. Open circles represent imino proton. All other hydrogen atoms and crystal solvents are omitted for clarity. (b) View along *c* axis for 3D framework of **1**. Orange balls represent Sm(III) ions. Gray, blue, and red sticks represent bonds from carbon, nitrogen, and oxygen atoms, respectively. Hydrogen atoms and crystal solvents are omitted for clarity.

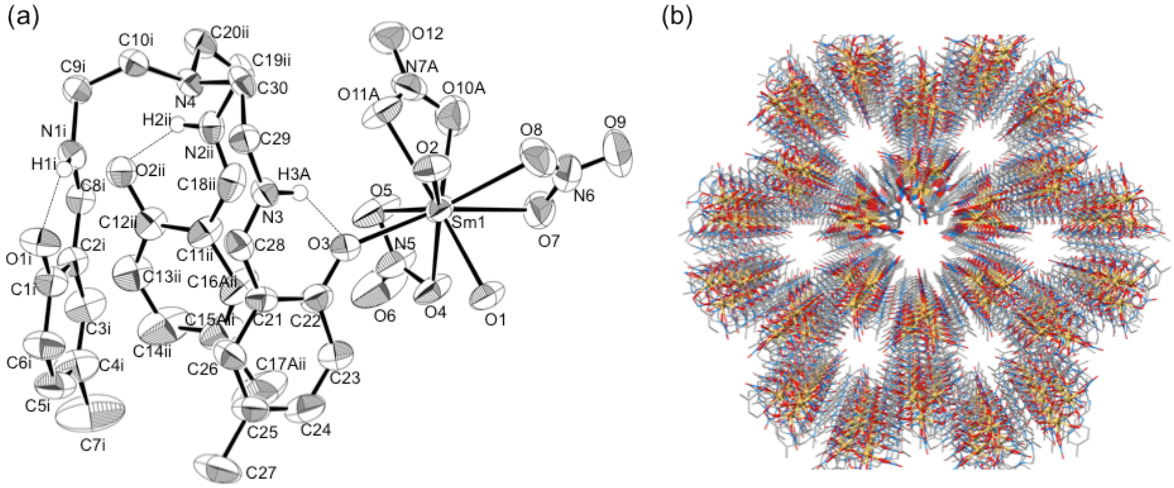

Fig. S2 (a) ORTEP diagram of **2** with numbering, showing only the atoms O10A, N7A, O11A, and O12A of the disordered nitrate anion, and the atoms C15A, C16A, and C17A of the disordered aromatic ring. Symmetry codes: i: 1/3-y, 2/3+x-y, -1/3+z, ii: +x-y, +x, -z. Open circles represent imino proton. All other hydrogen atoms and crystal solvents are omitted for clarity. (b) View along *c* axis for 3D framework of **2**. Orange balls represent Sm(III) ions. Gray, blue, and red sticks represent bonds from carbon, nitrogen, and oxygen atoms, respectively. Hydrogen atoms and crystal solvents are omitted for clarity.

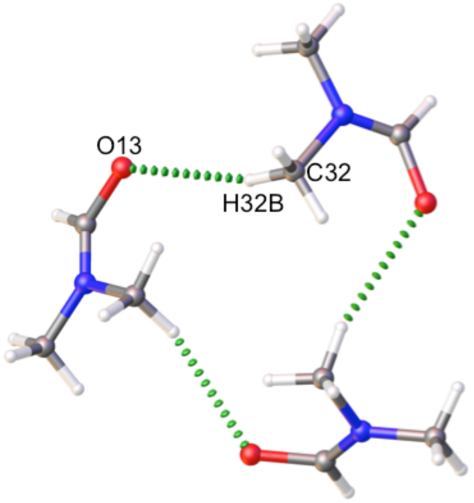

Fig. S3 Relative orientation of the DMF guests in **1**. View along *c* axis. Green dotted line represents CH···O hydrogen bond.

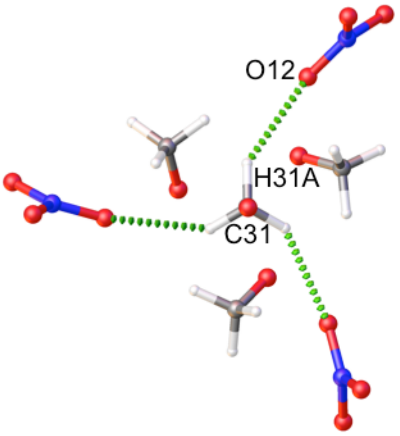

Fig. S4 Interaction between the nitrate anions of framework and the methanol guest in **2**. View along *c* axis. Green dotted line represents CH···O hydrogen bond. The methanol molecule shows locational disorder.

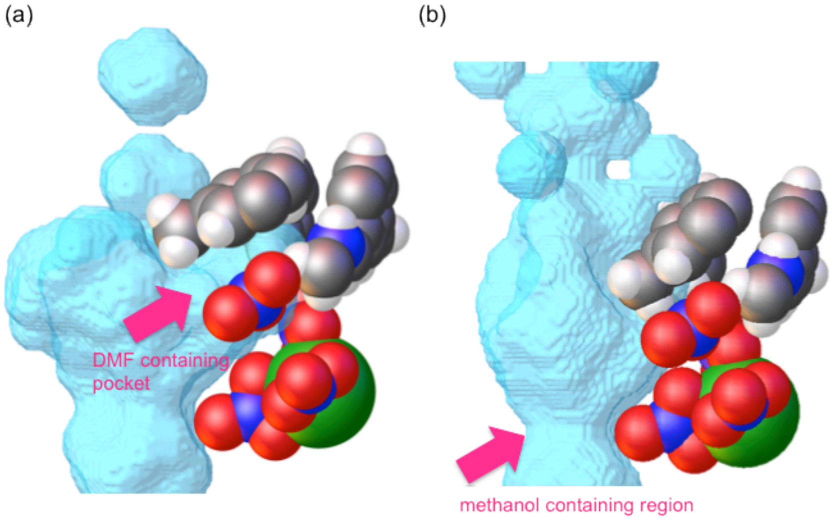

Fig. S5 Depiction of hydrophobic and hydrophilic voids. (a) Voids surface in the vicinity of the DMF containing pocket for **1**. (b) Voids surface for **2**, showing that the space corresponding to the pocket observed in **1** is packed by the methyl group of H_3L and nitrate anion to prevent the solvent from accessing. The surface of the void is shown in light blue. H: white, C: gray, O: red, N: blue, Sm: green.

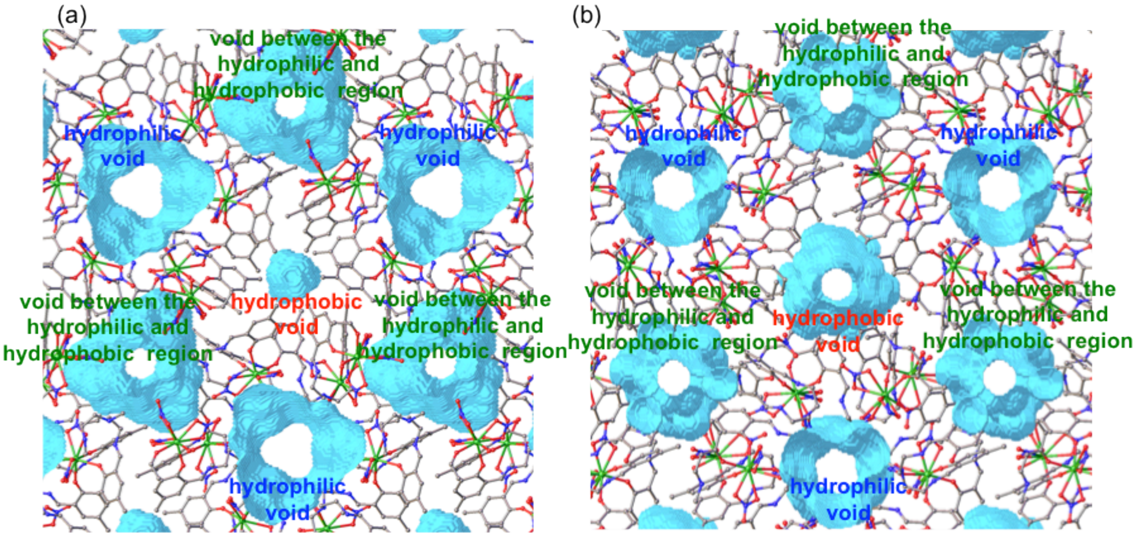

Fig. S6 Spatial arrangement of the hydrophobic and hydrophilic voids in *ab* plane for (a) **1** and (b) **2**. The surface of the void is shown in light blue.

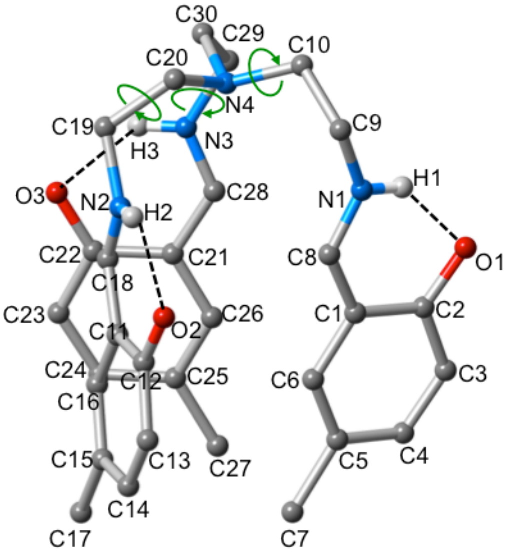

Fig. S7 Schematic drawing of twist in H_3L.

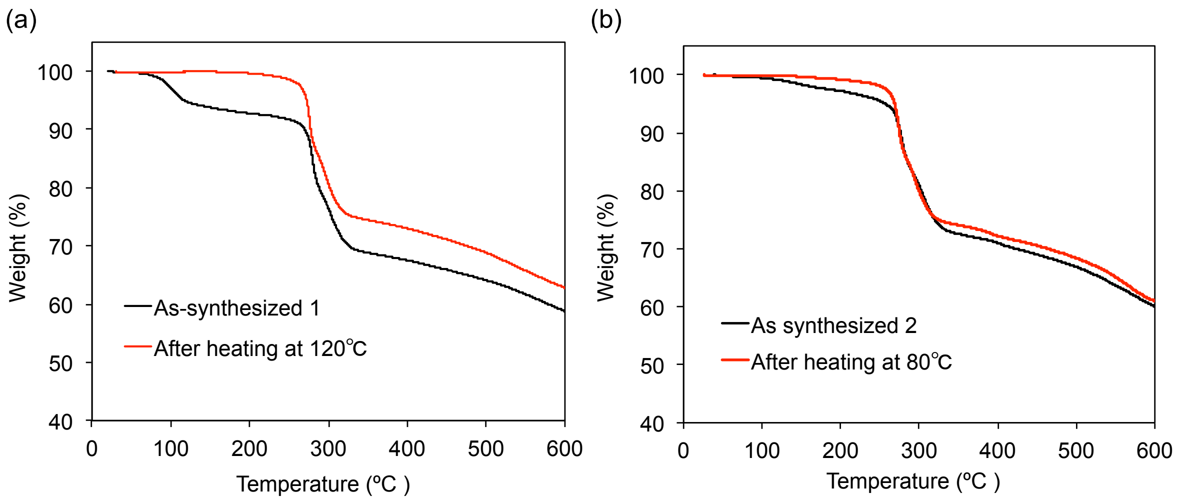

Fig. S8 TGA profiles for (a) **1** and (b) **2**. (black line: as-synthesized sample, red line: dried sample that is prepared by heating at 120 °C for **1** and 80 °C for **2** for 3 hr.)

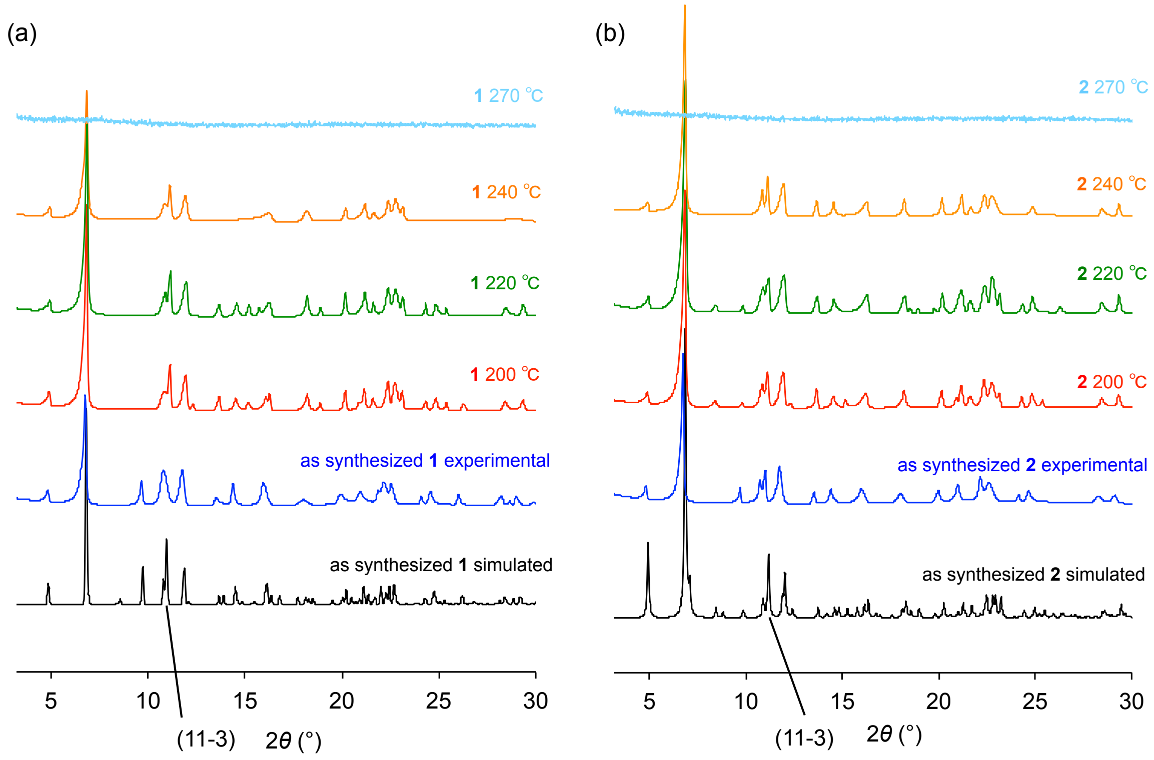

Fig. S9 Experimental and simulated PXRD patterns of (a) **1** and (b) **2**. (black line: simulated pattern from single-crystal X-ray data, blue line: as-synthesized sample, red, green, orange, pale blue, and pink line: dried sample that is prepared by heating at 200, 220, 240 and 270 °C for 15 min.)

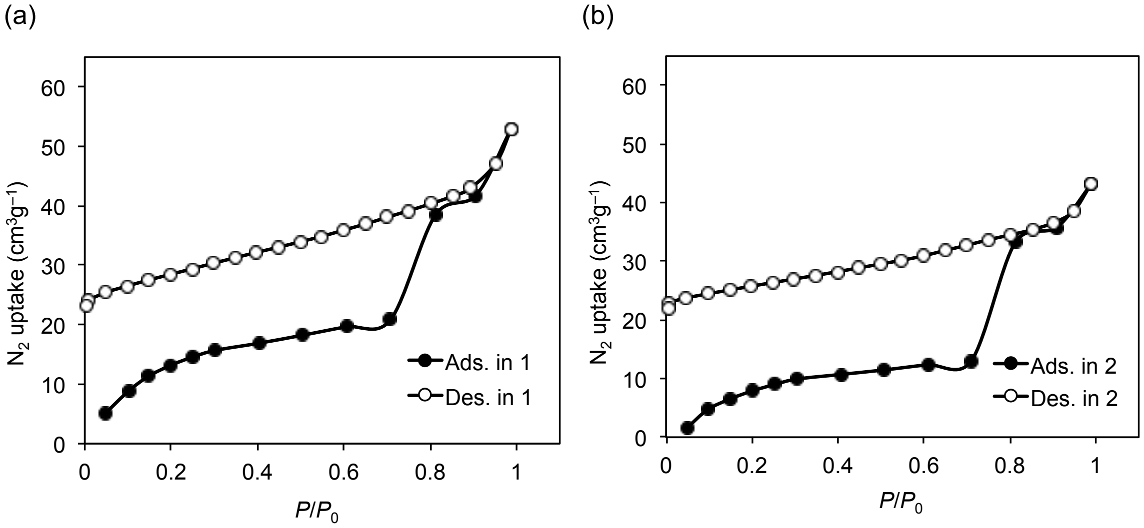

Fig. S10 N$_2$ adsorption and desorption isotherms of (a) **1** and (b) **2** at 77 K.

Table S1. CH···O hydrogen bond between the framework and the guest solvents and classical NH···O hydrogen bonds for compounds **1** and **2**.

Compound	H-bond	H···A	D···A	D–H···A
		CH···O		
1	C9–H9A···O13	2.57	3.316(15)	132
1	C17–H17···O13	2.71	3.411(17)	129
1	C32–H32A···O10A	2.81	3.44(4)	123
1	C32–H32A···O12A	3.00	3.88(5)	152
1	C31–H31···O6	2.81	3.053(17)	94
1	C31–H31A···O6	2.81	3.053(17)	94
1	C31–H31B···O6	3.00	3.053(17)	83
1	C32–H32B···O13	2.71	3.67(3)	170
2	C31–H31A···O12	2.69	3.54(2)	145
		NH···O		
1	N1–H1···O1	1.90(5)	2.648(7)	143(7)
1	N2–H2···O2	2.02(6)	2.606(8)	123(6)
1	N3–H3A···O3	1.90(4)	2.625(8)	140(6)
1	N1–H1···O4	2.41(6)	3.029(8)	128(6)
1	N2–H2···O11A	2.35(7)	3.15(6)	140(6)
2	N1–H1···O1	1.89(3)	2.630(6)	141(4)
2	N2–H2···O2	1.87(3)	2.615(6)	142(4)
2	N3–H3A···O3	1.94(5)	2.672(6)	140(6)
2	N1–H1···O4	2.32(4)	3.005(6)	135(4)
2	N2–H2···O11A	2.35(4)	2.975(19)	129(4)

Table S2. Selected bond distances (Å) for compounds **1** and **2**.

	1	**2**
Sm1–O1	2.307(5)	2.313(4)
Sm1–O2	2.337(5)	2.334(4)
Sm1–O3	2.328(5)	2.354(4)
Sm1–O4	2.483(5)	2.477(4)
Sm1–O5	2.574(6)	2.545(4)
Sm1–O7	2.548(6)	2.523(4)
Sm1–O8	2.450(6)	2.490(4)
Sm1–O10A	2.58(2)	2.639(16)
Sm1–O11A	2.56(6)	2.464(16)

Table S3. Selected bond angles (deg) for compounds **1** and **2**.

	1	**2**		**1**	**2**
O1-Sm1-O2	92.67(18)	90.73(14)	O3-Sm1-O8	145.7(2)	148.05(16)
O1-Sm1-O3	86.53(18)	88.97(14)	O3-Sm1-O10A	129.1(5)	124.8(5)
O1-Sm1-O4	76.03(17)	72.83(13)	O3-Sm1-O11A	90.1(7)	83.0(4)
O1-Sm1-O5	123.68(18)	122.17(14)	O4-Sm1-O5	49.82(17)	50.37(13)
O1-Sm1-O7	73.7(2)	77.76(16)	O4-Sm1-O7	71.9(2)	72.21(16)
O1-Sm1-O8	82.4(2)	84.51(16)	O4-Sm1-O8	122.3(2)	121.93(16)
O1-Sm1-O10A	139.3(5)	144.3(3)	O4-Sm1-O10A	86.5(8)	96.4(7)
O1-Sm1-O11A	162.1(10)	162.4(4)	O4-Sm1-O11A	121.3(9)	121.8(4)
O2-Sm1-O3	76.29(18)	77.00(14)	O5-Sm1-O7	99.0(2)	92.72(17)
O2-Sm1-O4	159.4(2)	156.16(15)	O5-Sm1-O8	135.8(2)	131.39(18)
O2-Sm1-O5	132.33(19)	137.71(14)	O5-Sm1-O10A	60.6(7)	62.9(8)
O2-Sm1-O7	122.0(2)	121.99(16)	O5-Sm1-O11A	72.3(9)	71.4(4)
O2-Sm1-O8	72.0(2)	71.86(16)	O7-Sm1-O8	50.7(2)	50.71(16)
O2-Sm1-O10A	112.6(8)	106.8(7)	O7-Sm1-O10A	65.9(5)	66.5(3)
O2-Sm1-O11A	68.8(14)	72.2(4)	O7-Sm1-O11A	114.3(8)	114.7(3)
O3-Sm1-O4	85.7(2)	85.37(14)	O8-Sm1-O10A	76.4(6)	72.4(7)
O3-Sm1-O5	76.5(2)	77.83(16)	O8-Sm1-O11A	90.7(7)	94.0(4)
O3-Sm1-O7	152.9(2)	156.43(15)	O10A-Sm1-O11A	53.0(9)	48.7(5)

Table S4. Crystallographic data and structure refinement details.

Complexes	**1**	**2**
Empirical formula	$C_{33}H_{43}N_8O_{13.17}Sm$	$C_{30.33}H_{36.53}N_7O_{12.50}Sm$
Formula weight	912.82	849.54
Crystal system	Trigonal	Trigonal
Space group	$R\overline{3}$	$R\overline{3}$
a / Å	25.917(3)	25.758(4)
b / Å	25.917(3)	25.758(4)
c / Å	30.915(4)	30.055(4)
α / °	90	90
β / °	90	90
γ / °	120	120
Volume / $Å^3$	17984(4)	17269(4)
Z	18	18
Density (calculated) / $g \cdot cm^{-3}$	1.517	1.470
Absorption coefficient / mm^{-1}	1.540	1.596
$F(000)$	8358	7732
Crystal size / mm	0.10 × 0.04 × 0.02	0.06 × 0.02 × 0.01
Crystal color	Yellow	Yellow
Reflections included in the refinement (total)	25854	33105
Independent reflections	6060 [R(int) = 0.0641]	8782 [R(int) = 0.1044]
Reflections with [$I > 2\sigma(I)$]	4329 [R(int) = 0.0569]	4602 [R(int) = 0.1164]
Completeness to θ_{max} / %	100	99.5
Refined parameters	552	551
Final R indices [all data]	$R_1 = 0.0790$ $wR_2 = 0.1380$	$R_1 = 0.1306$ $wR_2 = 0.1239$
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0496$ $wR_2 = 0.1197$	$R_1 = 0.0502$ $wR_2 = 0.0925$
GOF on F^2	1.049	1.003
r (max, min) / $e \cdot Å^{-3}$	1.017, –0.775	0.780, –0.882