Supporting Information

Formation Pathways of Metal Organic Frameworks Proceeding Through Partial Dissolution of the Metastable Phase

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S1 Experimental

S1.1 Materials and Characterization Methods

All chemicals were purchased from Sigma Aldrich ($Tb(NO_3)_3 \cdot (H_2O)_6$, H_2DHBDC), and Carl Roth (DMF) and used without further purification. Elemental analyses were performed on a Thermo Scientific Flash 2000 Organic Elemental Analyzer. Infrared spectra were collected on a Perkin Elmer FT-IR/FIR Frontier Spectrometer from 400 to 4000 cm^{-1}. Thermogravimetric analysis (TGA) was performed under N_2 on a TGA Q 500, V20.13 with a balance gas flow of 10 mL/min and a sample gas flow of 25 mL/min. All samples were analyzed with a ramp of 5 ˚C/min. to 950 ˚C followed by an isothermal hold for 15 minutes before cooling down. Powder X-ray diffraction data were collected on a Bruker D8 Advanced using Cu Kα radiation (λ = 1.5418 Å, 50 kW/40mA). Single crystal X-ray diffraction data were collected on a Bruker D8 Venture using Mo Kα (λ = 0.71 Å). Simulated powder X-ray diffraction patterns were generated from the single crystal data using Mercury 3.0. ^1H NMR spectra and *in-situ* experiments were collected on a 400 MHz Bruker NMR. Inductively coupled plasma mass spectrometry was performed on a Perkin Elmer ICPMS nexION 350D spectrometer.

S1.2 Synthesis of SION-1 and SION-2

Synthesis of **SION-2**: H_2DHBDC (20 mg) and $Tb(NO_3)_3 \cdot 6H_2O$ (20 mg) were mixed in a 12 mL vial. 2 mL of DMF was added, and stirred until the entire solution was clear. Following this, 0.5 mL of H_2O was added and the scintillation vial was capped, and shaken to ensure the solution is homogeneous. The vials were placed in an oven and heated at 120˚C, for 24 hrs with a temperature ramp of 2.0˚C, and cooling ramp of 0.2˚C (67 % yield based on Tb(III)). The formula of **SION-2** was determined to be $[Tb_2(DHBDC)_3(DMF)_4] \cdot 2DMF$ on the basis of the combined results of single-crystal X-ray diffraction (SCXRD), thermogravimetric analysis (TGA) and elemental analysis (EA). Anal. Calcd for ($[Tb_2(DHBDC)_3(DMF)_4] \cdot 2DMF$) : C 37.51, H 3.05, N 6.25. Experimental: C 37.27, H 4.14, N 6.20.

Synthesis of **SION-1: SION-1** was synthesized following the same synthetic protocol with that of **SION-2** and the reaction was heated at 120 ^{o}C for 72 hrs (76 % yield based on Tb). The formula of the product was determined to be [Tb_2(DHBDC)(DOBDC)$(DMF)_2$] (DOBDC = 2,5-dioxido-1,4-benzenedicarboxylate) on the basis of the combined results of SCXRD, TGA, and EA. Anal. Calcd for [Tb_2(DHBDC)(DOBDC)$(DMF)_2$] : C 30.93, H 2.36, N 3.28. Experimental: C 28.34, H 2.44, N 3.34.

S1.3 Water loaded SION-1 and SION-2

SION-1 and **SION-2** crystals were immersed in liquid H_2O and their corresponding single crystals were analysed using Synchrotron radiation. The immersion of golden crystals of **SION-2** lead to an immediate color change to dull beige to form **SION-2@H_2O**. Submersion of **SION-1** in H_2O lead to a color change from dark orange crystals to orange crystals to form **SION-1@H_2O**. The formula of **SION-1@H_2O** was determined to be [Tb_2(DHBDC)(DOBDC)$(H_2O)_2$]·$8H_2O$ as confirmed by SCXRD.

S2 Single-crystal X-ray diffraction

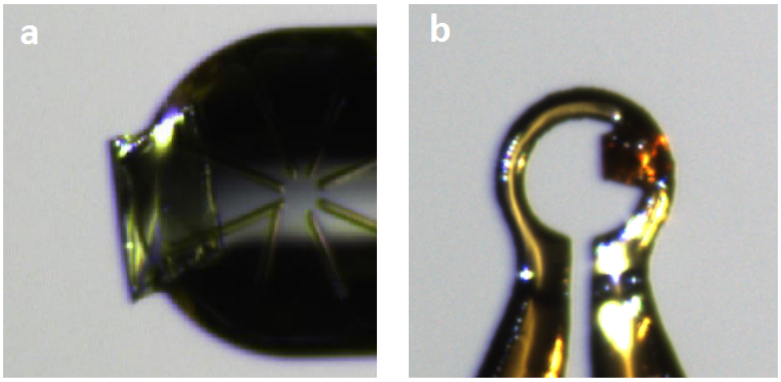

Figure S1: Microscopic images of **SION-2** (a) and **SION-1** (b) single crystals immobilized on polymer loops, ready for the diffraction experiments.

S2.1 Crystal data for SION-2

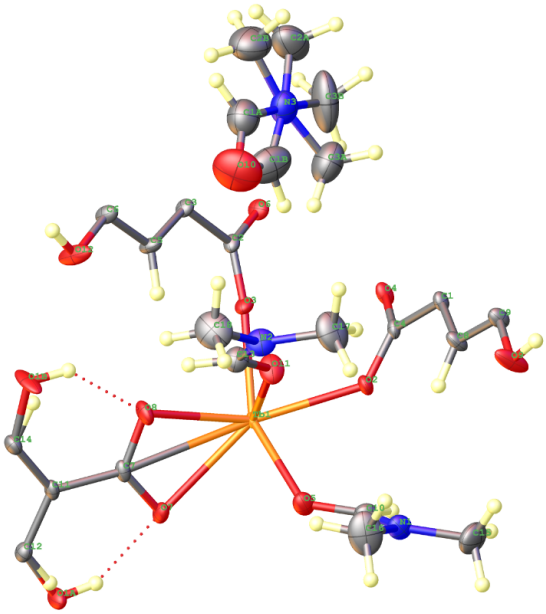

Figure S2: Asymmetric unit of the **SION-2** structure. The atomic displacement ellipsoids are set at a 50% probability level. Color scheme: Orange, Tb; red, O; grey, C; blue, N; yellow, H.

One light yellow single crystal of **SION-2** was isolated from the reaction mixture and mounted on a Bruker D8 Venture diffractometer equipped with a CMOS detector. Raw data were processed with Apex3 program suite,[1] and corrected for absorption with SADABS.[2] Crystal structure was solved with program SHELXS using direct methods and refined with SHELXL refinement package using least-squares minimization, implemented in the Olex2 program suite.[3, 4]

Reflections: –1 0 1, 0 –1 1, and –1 1 0 were excluded from the refinement process due to their intensities disturbed by the beam stop. Atomic positions were found from the difference–Fourier maps and refined anisotropically for all non-H atoms. Positions of aromatic and amide H-atoms were refined using a riding model, while H-atoms in methyl and hydroxy groups were refined as in idealized rotating groups. U_{iso} for H-atoms were set to 1.2 times U_{eq} of neighboring atoms, and 1.5 times U_{eq} of atoms in terminating groups. Atoms C1A, C2A, C3A, and H-atoms bound to them were refined as a disordered group and were set to have the same site-occupancy factor (SOF). The same procedure was applied to the second component of the disorder: atoms C1B, C2B, C3B, and H-atoms bound to them. The sum of SOFs of these two atom groups was set to 1. Disorder over O1A and O1B atoms was refined independently in a similar way. Restraints on U_{ij} were imposed on O1B atom.

Table S1: Crystal data and structure refinement for **SION-2**.

Identification code	**SION-2**
Empirical formula	$C_{21}H_{27}N_3O_{12}Tb$
Formula weight	672.37
Temperature/K	149.72
Crystal system	triclinic
Space group	*P*-1
a/Å	10.4608(8)
b/Å	10.9006(10)
c/Å	12.5293(10)
α/°	104.610(5)
β/°	107.840(4)
γ/°	97.204(4)
Volume/Å^3	1283.78(19)
Z	2
ρ_{calc}g/cm^3	1.739
μ/mm^{-1}	2.821
F(000)	670.0
Crystal size/mm^3	0.221 × 0.146 × 0.059
Radiation	Mo*K*α (λ = 0.71073)
2Θ range for data collection/°	5.84 to 56.644
Index ranges	$-13 \le h \le 13$, $-14 \le k \le 14$, $-16 \le l \le 16$
Reflections collected	38205
Independent reflections	6365 [R_{int} = 0.0389, R_{sigma} = 0.0244]
Data/restraints/parameters	6365/6/383
Goodness-of-fit on F^2	1.080
Final *R* indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0180, wR_2 = 0.0421
Final *R* indexes [all data]	R_1 = 0.0211, wR_2 = 0.0433

Largest diff. peak/hole / e $Å^{-3}$	0.70/-1.06

Table S2: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Sion-2 U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	***x***	***y***	***z***	U_{eq}
Tb1	952.4(2)	5464.8(2)	6825.2(2)	9.36(3)
O2	-352.2(14)	3348.5(13)	5866.9(12)	14.7(3)
O3	1549.2(14)	4861.7(14)	5170.5(13)	16.1(3)
O4	-815.8(15)	2732.9(13)	3917.2(12)	16.1(3)
O5	573.7(16)	4840.6(15)	8409.7(13)	22.1(3)
O6	1299.9(14)	4233.1(14)	3284.5(13)	17.4(3)
O7	1654.1(14)	7630.4(14)	8496.5(12)	18.2(3)
O8	3205.8(15)	6808.0(14)	7864.8(13)	20.3(3)
O9	450(2)	-490.0(16)	7131.4(14)	31.3(4)
O11	2489.6(16)	4054.6(16)	7339.3(15)	26.9(4)
O12	6600.9(16)	6067(2)	7361.8(13)	32.4(4)
N1	-129(2)	3086.0(19)	8918.5(17)	24.8(4)
O1A	2337.5(17)	10053.1(17)	9928.7(16)	22.4(5)
O1B	5955(14)	8009(15)	8823(15)	32(5)
N2	4283(2)	3319(2)	8304.0(18)	27.8(4)
C1	-262(2)	1208.2(18)	4928.7(17)	13.2(4)
C2	2058.8(19)	4626.6(18)	4368.6(18)	13.2(4)
C3	3574.6(19)	4814.4(19)	4679.7(17)	13.5(4)
C4	-494.1(19)	2524.8(18)	4908.6(17)	12.3(4)
C5	4421(2)	5356(2)	5856.6(17)	17.2(4)
C6	5841(2)	5537(2)	6190.7(17)	17.6(4)
C7	2880(2)	7718.4(19)	8507.1(17)	13.9(4)
C8	-30(2)	908.6(19)	5975.5(18)	17.5(4)
C9	234(2)	-282(2)	6068.4(18)	17.3(4)
C10	-313(2)	3876(2)	8273.0(19)	20.7(4)
N3	4760(3)	1523(2)	4537(2)	40.2(5)
C11	3962(2)	8908.4(19)	9280.4(16)	13.7(4)
C12	3636(2)	9983(2)	9948.6(17)	15.5(4)
C13	3703(2)	4229(2)	7954(2)	24.5(5)
C14	5322(2)	8935.6(19)	9338.7(17)	15.8(4)
C15	-1210(3)	1983(3)	8714(3)	40.1(7)
O10	6063(3)	2237(3)	6482(2)	75.6(8)
C16	1145(3)	3282(3)	9884(3)	51.8(8)
C17	3528(3)	2008(3)	7969(3)	47.2(7)
C18	5755(3)	3633(3)	9009(3)	48.7(8)
C1A	5941(6)	1930(5)	5452(5)	50.3(14)
C2A	4693(7)	1129(6)	3336(5)	60.2(17)
C3A	3455(6)	1391(6)	4749(6)	59.2(16)
C1B	4961(13)	2021(12)	5664(11)	63(3)
C2B	5984(13)	1424(12)	4172(11)	68(3)
C3B	3435(13)	1200(12)	3586(12)	85(5)

Table S3: Bond Lengths for **SION-2**.

Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
Tb1	O2	2.3313(14)		N2	C13	1.324(3)

Tb1	O3	2.3084(14)		N2	C17	1.433(4)
Tb1	O4[1]	2.3783(14)		N2	C18	1.467(3)
Tb1	O5	2.3783(15)		C1	C4	1.490(3)
Tb1	O6[1]	2.3869(14)		C1	C8	1.388(3)
Tb1	O7	2.5742(15)		C1	C9[2]	1.405(3)
Tb1	O8	2.3849(14)		C2	Tb1[1]	3.0213(18)
Tb1	O11	2.4183(15)		C2	C3	1.486(2)
Tb1	C2[1]	3.0213(19)		C3	C5	1.392(3)
Tb1	C7	2.8432(19)		C3	C6[3]	1.402(3)
O2	C4	1.258(2)		C5	C6	1.387(3)
O3	C2	1.262(2)		C6	C3[3]	1.402(3)
O4	Tb1[1]	2.3783(14)		C7	C11	1.493(3)
O4	C4	1.270(2)		C8	C9	1.386(3)
O5	C10	1.250(3)		C9	C1[2]	1.405(3)
O6	Tb1[1]	2.3869(14)		N3	C1A	1.332(6)
O6	C2	1.272(2)		N3	C2A	1.434(6)
O7	C7	1.269(2)		N3	C3A	1.466(6)
O8	C7	1.264(2)		N3	C1B	1.317(12)
O9	C9	1.363(2)		N3	C2B	1.493(11)
O11	C13	1.228(3)		N3	C3B	1.456(11)
O12	C6	1.364(2)		C11	C12	1.404(3)
N1	C10	1.316(3)		C11	C14	1.398(3)
N1	C15	1.455(3)		C12	C14[4]	1.387(3)
N1	C16	1.447(3)		C14	C12[4]	1.388(3)
O1A	C12	1.363(2)		O10	C1A	1.211(6)
O1B	C14	1.406(13)		O10	C1B	1.233(13)

[1]-X,1-Y,1-Z; [2]-X,-Y,1-Z; [3]1-X,1-Y,1-Z; [4]1-X,2-Y,2-Z

Table S4: Bond Angles for **SION-2**.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
O2	Tb1	O4[1]	126.69(5)		C10	N1	C16	121.9(2)
O2	Tb1	O5	78.25(5)		C16	N1	C15	116.5(2)
O2	Tb1	O6[1]	78.69(5)		C13	N2	C17	121.9(2)
O2	Tb1	O7	151.35(5)		C13	N2	C18	119.6(2)
O2	Tb1	O8	146.07(5)		C17	N2	C18	118.4(2)
O2	Tb1	O11	74.04(5)		C8	C1	C4	118.65(17)
O2	Tb1	C2[1]	67.36(5)		C8	C1	C9[2]	119.40(18)
O2	Tb1	C7	163.41(5)		C9[2]	C1	C4	121.93(17)
O3	Tb1	O2	77.34(5)		O3	C2	Tb1[1]	73.34(10)
O3	Tb1	O4[1]	75.84(5)		O3	C2	O6	121.36(17)
O3	Tb1	O5	146.03(5)		O3	C2	C3	120.09(18)
O3	Tb1	O6[1]	122.28(5)		O6	C2	Tb1[1]	48.94(9)
O3	Tb1	O7	131.17(5)		O6	C2	C3	118.55(17)
O3	Tb1	O8	88.77(5)		C3	C2	Tb1[1]	163.65(14)
O3	Tb1	O11	78.29(6)		C5	C3	C2	119.03(17)
O3	Tb1	C2[1]	98.80(5)		C5	C3	C6[3]	119.84(17)
O3	Tb1	C7	109.95(5)		C6[3]	C3	C2	121.13(17)
O4[1]	Tb1	O5	138.11(5)		O2	C4	O4	124.76(18)
O4[1]	Tb1	O6[1]	78.15(5)		O2	C4	C1	118.14(17)
O4[1]	Tb1	O7	68.30(5)		O4	C4	C1	117.10(17)
O4[1]	Tb1	O8	77.78(5)		C6	C5	C3	121.10(18)
O4[1]	Tb1	O11	140.94(5)		O12	C6	C3[3]	123.29(17)
O4[1]	Tb1	C2[1]	72.38(5)		O12	C6	C5	117.65(18)
O4[1]	Tb1	C7	69.90(5)		C5	C6	C3[3]	119.06(18)
O5	Tb1	O6[1]	74.90(5)		O7	C7	Tb1	64.84(10)
O5	Tb1	O7	76.54(5)		O7	C7	C11	120.23(17)
O5	Tb1	O8	98.67(5)		O8	C7	Tb1	56.25(10)
O5	Tb1	O11	72.51(6)		O8	C7	O7	120.90(17)
O5	Tb1	C2[1]	93.19(5)		O8	C7	C11	118.87(17)
O5	Tb1	C7	88.57(5)		C11	C7	Tb1	173.24(14)
O6[1]	Tb1	O7	81.79(5)		C9	C8	C1	121.81(18)
O6[1]	Tb1	O11	140.88(5)		O9	C9	C1[2]	123.48(18)
O6[1]	Tb1	C2[1]	23.70(5)		O9	C9	C8	117.72(18)
O6[1]	Tb1	C7	107.78(5)		C8	C9	C1[2]	118.80(18)
O7	Tb1	C2[1]	100.65(5)		O5	C10	N1	124.5(2)
O7	Tb1	C7	26.51(5)		C1A	N3	C2A	123.1(4)
O8	Tb1	O6[1]	133.70(5)		C1A	N3	C3A	119.4(4)
O8	Tb1	O7	52.61(5)		C2A	N3	C3A	117.4(4)
O8	Tb1	O11	72.88(5)		C1B	N3	C2B	118.6(8)
O8	Tb1	C2[1]	146.22(5)		C1B	N3	C3B	124.9(9)
O8	Tb1	C7	26.16(5)		C3B	N3	C2B	116.0(9)
O11	Tb1	O7	110.52(5)		C12	C11	C7	121.15(17)
O11	Tb1	C2[1]	140.87(5)		C14	C11	C7	118.81(17)
O11	Tb1	C7	92.51(6)		C14	C11	C12	120.04(17)
C7	Tb1	C2[1]	124.09(5)		O1A	C12	C11	124.08(18)
C4	O2	Tb1	132.76(12)		O1A	C12	C14[4]	116.80(18)
C2	O3	Tb1	171.24(13)		C14[4]	C12	C11	119.11(18)
C4	O4	Tb1[1]	138.29(12)		O11	C13	N2	124.5(2)

C10	O5	Tb1	123.76(14)		C11	C14	O1B	132.7(6)
C2	O6	Tb1[1]	107.36(12)		C12[4]	C14	O1B	106.4(6)
C7	O7	Tb1	88.65(11)		C12[4]	C14	C11	120.85(18)
C7	O8	Tb1	97.59(12)		O10	C1A	N3	126.2(5)
C13	O11	Tb1	134.70(15)		O10	C1B	N3	125.6(9)
C10	N1	C15	121.6(2)					

[1]-X,1-Y,1-Z; [2]-X,-Y,1-Z; [3]1-X,1-Y,1-Z; [4]1-X,2-Y,2-Z

Table S5: Atomic Occupancy for **SION-2**.

Atom	***Occupancy***		**Atom**	***Occupancy***		**Atom**	***Occupancy***
O1A	0.890(5)		H1A	0.890(5)		O1B	0.110(5)
H1B	0.110(5)		H12A	0.110(5)		H14	0.890(5)
C1A	0.649(6)		H1AA	0.649(6)		C2A	0.649(6)
H2AA	0.649(6)		H2AB	0.649(6)		H2AC	0.649(6)
C3A	0.649(6)		H3AA	0.649(6)		H3AB	0.649(6)
H3AC	0.649(6)		C1B	0.351(6)		H1BA	0.351(6)
C2B	0.351(6)		H2BA	0.351(6)		H2BB	0.351(6)
H2BC	0.351(6)		C3B	0.351(6)		H3BA	0.351(6)
H3BB	0.351(6)		H3BC	0.351(6)			

S2.2 Crystal data for SION-1

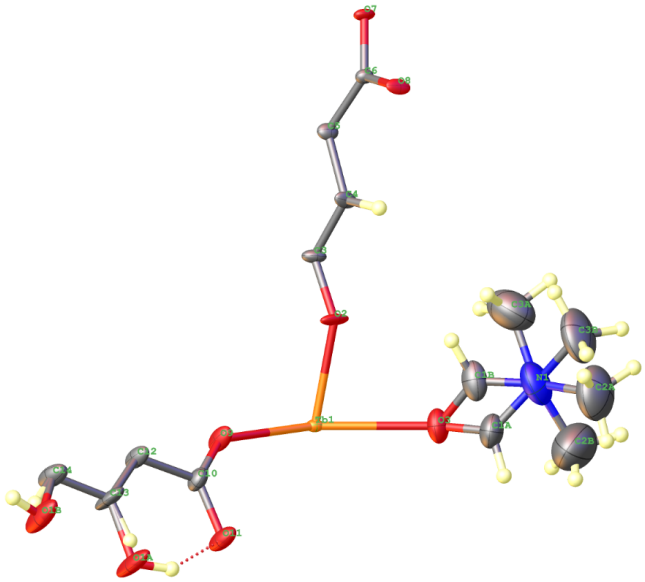

Figure S3: Asymmetric unit of the **SION-1** structure. The atomic displacement ellipsoids are set at a 50% probability level. Color scheme: Orange, Tb; red, O; grey, C; blue, N; yellow, H.

One red single crystal of **SION-1** was isolated from the reaction mixture, immobilized on a polymer loop, and mounded on a Bruker D8 Venture diffractometer equipped with a CMOS detector. Raw data treatment, structure solution, and refinement were performed using the same software as in case of **SION-2**.

Atomic positions were found from the difference–Fourier maps and refined anisotropically for all non-H atoms. H-atom positions were found and their x, y, z, and U_{iso} refined in the same way as in the structure of **SION-2**. Atoms: (C1A, C2A, C3A) and (C1B, C2B, C3B), together with the H-atoms bound to them, were refined as two components of a disorder in a similar way to the one used in the structure of **SION-2**. Same method was applied to independently refine the disorder over O1A and O1B atoms. On the atoms C1A, C2A, C3A, N1, belonging to the disordered DMF molecule, were imposed restraints for interatomic distances, planarity, and atomic displacement parameters. Same restraints were applied for C1B, C2B, C3B, N1 atoms.

Table S6: Crystal data and structure refinement for **SION-1**.	
Identification code	**SION -1**
Empirical formula	$C_{11}H_{10}NO_7Tb$
Formula weight	427.12
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.388(3)
b/Å	6.6366(12)
c/Å	15.567(2)
α/°	90
β/°	98.599(14)
γ/°	90
Volume/Å^3	1367.6(4)
Z	4
ρ_{calc}g/cm^3	2.074
μ/mm^{-1}	5.200
F(000)	816.0
Crystal size/mm^3	0.062 × 0.059 × 0.024
Radiation	Mo$K\alpha$ (λ = 0.71073)
2Θ range for data collection/°	5.294 to 61.078
Index ranges	$-18 \le h \le 19$, $-9 \le k \le 9$, $-22 \le l \le 21$
Reflections collected	15156
Independent reflections	4070 [R_{int} = 0.0666, R_{sigma} = 0.0711]
Data/restraints/parameters	4070/40/225
Goodness-of-fit on F^2	1.055
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0369, wR_2 = 0.0495
Final R indexes [all data]	R_1 = 0.0681, wR_2 = 0.0552
Largest diff. peak/hole / e Å^{-3}	0.91/-1.00

Table S7: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for SION -1. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	***x***	***y***	***z***	U_{eq}
Tb1	3313.4(2)	5786.6(3)	2875.2(2)	9.76(5)
O7	7130(2)	10908(4)	6763.9(17)	13.9(6)
O8	6800(2)	7698(4)	6735.1(18)	16.5(7)
O9	1919(2)	5440(4)	3591(2)	25.1(8)
O2	4346(2)	6658(4)	4018(2)	23.7(8)
O11	1029(3)	2666(5)	3188(2)	31.0(8)
O3	4814(3)	4197(5)	2546(2)	35.2(8)
C6	6587(3)	9429(6)	6425(2)	11.0(8)
C4	5407(3)	8102(5)	5198(3)	16.3(9)
C5	5772(3)	9765(6)	5706(3)	14.3(9)
C10	1231(3)	4214(7)	3667(3)	21.5(9)
C3	4640(3)	8286(6)	4484(3)	16.0(9)
C12	592(4)	4583(6)	4355(3)	22.7(11)

O1A	-445(4)	1572(7)	4010(3)	47.9(16)
O1B	-1333(19)	2030(30)	5311(17)	52(8)
C14	-757(4)	3673(7)	5147(3)	30.6(12)
C13	-176(4)	3255(7)	4504(3)	32.4(13)
N1	6245(4)	2571(9)	3116(4)	62.7(16)
C1B	5554(8)	3786(16)	3138(8)	42(3)
C3B	7057(10)	1960(20)	3789(10)	91(5)
C2B	6243(13)	1450(20)	2281(10)	136(8)
C1A	5361(12)	2790(20)	2633(11)	44(4)
C3A	6552(15)	4310(30)	3730(12)	91(7)
C2A	6791(17)	700(30)	3289(16)	97(8)

Table S8: Bond Lengths for **SION-1**.

Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
Tb1	O7[1]	2.362(3)		O3	C1A	1.180(14)
Tb1	O7[2]	2.439(3)		C6	Tb1[5]	2.983(4)
Tb1	O8[3]	2.401(3)		C6	C5	1.460(5)
Tb1	O8[2]	2.682(3)		C4	C5	1.401(5)
Tb1	O9	2.324(3)		C4	C3	1.401(6)
Tb1	O2	2.162(3)		C5	C3[1]	1.420(5)
Tb1	O11[4]	2.346(3)		C10	C12	1.487(6)
Tb1	O3	2.391(3)		C3	C5[1]	1.420(5)
Tb1	C6[2]	2.983(4)		C12	C14[7]	1.392(6)
O7	Tb1[5]	2.439(3)		C12	C13	1.400(6)
O7	Tb1[1]	2.362(3)		O1A	C13	1.374(5)
O7	C6	1.287(4)		O1B	C14	1.38(2)
O8	Tb1[3]	2.401(3)		C14	C12[7]	1.392(6)
O8	Tb1[5]	2.682(3)		C14	C13	1.384(6)
O8	C6	1.262(4)		N1	C1B	1.231(11)
O9	C10	1.248(5)		N1	C3B	1.451(12)
O2	C3	1.328(4)		N1	C2B	1.498(13)
O11	Tb1[6]	2.346(3)		N1	C1A	1.312(17)
O11	C10	1.275(5)		N1	C3A	1.516(16)
O3	C1B	1.278(11)		N1	C2A	1.444(16)

[1]1-X,2-Y,1-Z; [2]-1/2+X,3/2-Y,-1/2+Z; [3]1-X,1-Y,1-Z; [4]1/2-X,1/2+Y,1/2-Z; [5]1/2+X,3/2-Y,1/2+Z;

[6]1/2-X,-1/2+Y,1/2-Z; [7]-X,1-Y,1-Z

Table S9: Bond Angles for **SION-1**.

Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Atom**	**Angle/°**
O7[1]	Tb1	O7[2]	115.93(6)		C6	O8	Tb1[5]	90.9(2)
O7[1]	Tb1	O8[2]	67.49(8)		C6	O8	Tb1[3]	162.6(3)
O7[1]	Tb1	O8[3]	143.76(10)		C10	O9	Tb1	140.1(3)
O7[2]	Tb1	O8[2]	50.00(8)		C3	O2	Tb1	140.2(3)
O7[1]	Tb1	O3	135.22(11)		C10	O11	Tb1[6]	140.5(3)
O7[1]	Tb1	C6[2]	91.75(9)		C1B	O3	Tb1	121.7(6)

O7[2]	Tb1	C6[2]	24.97(9)		C1A	O3	Tb1	148.3(8)
O8[3]	Tb1	O7[2]	71.11(9)		O7	C6	Tb1[5]	53.15(19)
O8[3]	Tb1	O8[2]	117.28(7)		O7	C6	C5	120.6(3)
O8[3]	Tb1	C6[2]	94.24(9)		O8	C6	Tb1[5]	64.0(2)
O8[2]	Tb1	C6[2]	25.02(9)		O8	C6	O7	117.2(3)
O9	Tb1	O7[2]	79.11(10)		O8	C6	C5	122.2(3)
O9	Tb1	O7[1]	74.30(10)		C5	C6	Tb1[5]	173.7(3)
O9	Tb1	O8[3]	72.43(10)		C3	C4	C5	122.1(4)
O9	Tb1	O8[2]	76.85(11)		C4	C5	C6	118.0(3)
O9	Tb1	O11[4]	143.48(11)		C4	C5	C3[1]	120.6(4)
O9	Tb1	O3	145.05(11)		C3[1]	C5	C6	121.4(3)
O9	Tb1	C6[2]	76.74(11)		O9	C10	O11	124.4(4)
O2	Tb1	O7[1]	73.04(9)		O9	C10	C12	118.3(4)
O2	Tb1	O7[2]	167.05(10)		O11	C10	C12	117.4(4)
O2	Tb1	O8[2]	140.45(9)		O2	C3	C4	119.0(4)
O2	Tb1	O8[3]	96.11(9)		O2	C3	C5[1]	123.6(4)
O2	Tb1	O9	95.33(12)		C4	C3	C5[1]	117.4(3)
O2	Tb1	O11[4]	100.20(13)		C14[7]	C12	C10	118.5(4)
O2	Tb1	O3	80.79(12)		C14[7]	C12	C13	119.3(4)
O2	Tb1	C6[2]	164.40(10)		C13	C12	C10	122.1(4)
O11[4]	Tb1	O7[2]	90.98(11)		O1B	C14	C12[7]	126.8(10)
O11[4]	Tb1	O7[1]	78.96(10)		O1B	C14	C13	111.4(9)
O11[4]	Tb1	O8[2]	70.12(11)		C13	C14	C12[7]	120.6(4)
O11[4]	Tb1	O8[3]	137.27(11)		O1A	C13	C12	123.8(4)
O11[4]	Tb1	O3	70.60(11)		O1A	C13	C14	116.0(4)
O11[4]	Tb1	C6[2]	79.73(12)		C14	C13	C12	120.0(4)
O3	Tb1	O7[2]	97.01(11)		C1B	N1	C3B	130.3(11)
O3	Tb1	O8[2]	126.85(11)		C1B	N1	C2B	116.5(10)
O3	Tb1	O8[3]	73.49(11)		C3B	N1	C2B	113.1(10)
O3	Tb1	C6[2]	113.43(11)		C1A	N1	C3A	114.3(11)
Tb1[1]	O7	Tb1[5]	114.79(10)		C1A	N1	C2A	126.3(14)
C6	O7	Tb1[5]	101.9(2)		C2A	N1	C3A	117.0(13)
C6	O7	Tb1[1]	131.2(2)		N1	C1B	O3	128.6(12)
Tb1[3]	O8	Tb1[5]	105.30(9)		O3	C1A	N1	130.2(16)

[1]1-X,2-Y,1-Z; [2]-1/2+X,3/2-Y,-1/2+Z; [3]1-X,1-Y,1-Z; [4]1/2-X,1/2+Y,1/2-Z; [5]1/2+X,3/2-Y,1/2+Z;

[6]1/2-X,-1/2+Y,1/2-Z; [7]-X,1-Y,1-Z

Table S10: Atomic Occupancy for **SION-1**.

Atom	***Occupancy***		**Atom**	***Occupancy***		**Atom**	***Occupancy***
O1A	0.830(7)		H1A	0.830(7)		O1B	0.170(7)
H1B	0.170(7)		H14	0.830(7)		H13	0.170(7)
C1B	0.589(11)		H1BA	0.589(11)		C3B	0.589(11)
H3BA	0.589(11)		H3BB	0.589(11)		H3BC	0.589(11)
C2B	0.589(11)		H2BA	0.589(11)		H2BB	0.589(11)
H2BC	0.589(11)		C1A	0.411(11)		H1AA	0.411(11)
C3A	0.411(11)		H3AA	0.411(11)		H3AB	0.411(11)
H3AC	0.411(11)		C2A	0.411(11)		H2AA	0.411(11)

H2AB	0.411(11)		H2AC	0.411(11)			

S2.3 Crystal data for SION-2@H_2O

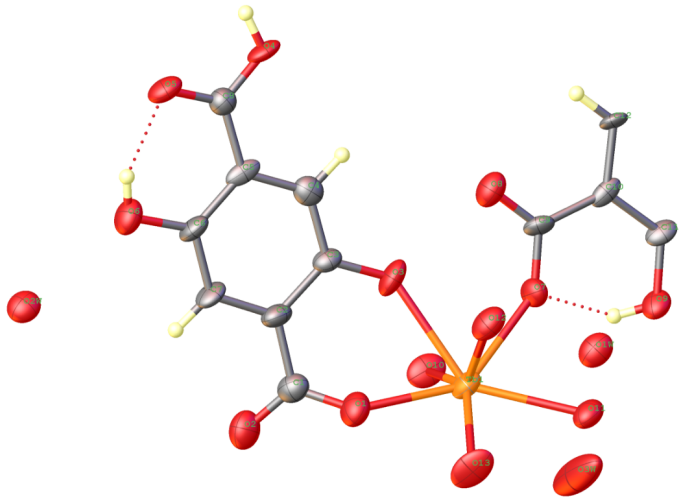

Figure S4: Asymmetric unit of the **SION-2@H_2O** structure. The atomic displacement ellipsoids are set at a 50% probability level. Color scheme: Orange, Tb; red, O; grey, C; blue, N; yellow, H.

Single crystals of **SION-2@H_2O** were isolated from the reaction vessel. A suitable crystal was selected and mounted onto the diffractometer at the BM01 Beamline of the European Synchrotron Radiation Facility. The crystal was kept at 100.0 K during data collection. Using Olex2,[3] the structure was solved with the ShelXT[4] structure solution program using Intrinsic Phasing and refined with the ShelXT[4] refinement package using Least Squares minimization. Atomic positions were found from the difference–Fourier maps and refined anisotropically for all non-H atoms. Positions of aromatic and amide H-atoms were refined using a riding model, while H-atoms in methyl and hydroxy groups were refined as in idealized rotating groups. U_{iso} for H-atoms were set to 1.2 times U_{eq} of neighboring atoms, and 1.5 times U_{eq} of atoms in terminating groups. O-atoms belonging to coordinated (O10, O11, O12, O13) as well as free water solvent molecules (O1W, O2W, O3W) have been found from the difference–Fourier maps, however H-atoms attached to them were not localized due to the lack of chemical information or distinctive electron density maxima.

Table S11: Crystal data and structure refinement for **SION-2@H_2O**.	
Identification code	**SION-2@H2O**
Empirical formula	$C_{12}H_{12}O_{16}Tb$
Formula weight	571.14
Temperature/K	100.0
Crystal system	triclinic
Space group	*P*-1
a/Å	9.5715(9)
b/Å	10.1208(10)
c/Å	11.6980(13)
α/°	113.409(10)
β/°	101.145(9)
γ/°	105.464(8)
Volume/Å^3	943.19(18)
Z	2
ρ_{calc}g/cm^3	2.011
μ/mm^{-1}	3.885
F(000)	554.0
Crystal size/mm^3	0.565 × 0.173 × 0.071
Radiation	synchrotron (λ = 0.7153)
2Θ range for data collection/°	4.058 to 51.322
Index ranges	$-10 \le h \le 11$, $-12 \le k \le 11$, $-13 \le l \le 8$
Reflections collected	6544
Independent reflections	2780 [R_{int} = 0.0645, R_{sigma} = 0.0890]
Data/restraints/parameters	2780/42/264
Goodness-of-fit on F^2	1.063
Final *R* indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0770, wR_2 = 0.1941
Final *R* indexes [all data]	R_1 = 0.1008, wR_2 = 0.2210
Largest diff. peak/hole / e Å^{-3}	1.82/-4.96

Table S12: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **SION-2@H_2O**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Tb1	6380.4(8)	5891.8(8)	8688.4(8)	31.4(4)
O1	4082(12)	5066(14)	8896(13)	43(3)
O2	2245(13)	3443(13)	9129(13)	47(3)
O3	4407(11)	3784(12)	6543(12)	41(3)
O4	280(12)	490(11)	1973(11)	32(3)
O5	-1894(12)	267(12)	2429(11)	36(3)
O6	-1920(12)	1016(14)	4763(13)	42(3)
O7	7689(11)	5130(12)	7160(11)	35(3)
O8	6070(12)	3893(12)	5096(13)	40(3)
O9	10591(12)	6148(13)	7687(12)	36(3)
O10	6567(14)	3532(12)	8548(13)	41(3)
O11	8821(12)	7976(13)	9431(12)	39(3)
O12	5604(12)	7025(13)	7399(13)	42(3)
O13	6069(14)	8218(12)	10103(14)	51(3)

C1	2838(18)	3896(18)	8402(18)	35(4)
C2	2049(18)	3084(17)	6992(16)	33(4)
C3	2850(17)	3046(16)	6062(16)	26(3)
C4	2019(18)	2259(17)	4704(17)	32(4)
C5	437(17)	1538(15)	4206(16)	29(4)
C6	-341(17)	1621(17)	5146(17)	31(4)
C7	448(17)	2327(17)	6446(17)	32(4)
C8	-432(17)	719(17)	2808(17)	29(3)
C9	7395(17)	4580(16)	5901(15)	27(4)
C10	8758(16)	4771(15)	5441(16)	27(4)
C11	10272(17)	5560(16)	6341(16)	28(3)
C12	8501(16)	4220(15)	4103(14)	24(3)
O3W	6818(16)	11880(20)	10150(18)	119(9)
O1W	7078(13)	9960(13)	7942(12)	41(3)
O2W	-3804(12)	1020(13)	6207(12)	40(3)

Table S13: Bond Lengths for **SION-2@H_2O**.

Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
Tb1	O1	2.232(11)		O8	C9	1.236(18)
Tb1	O2[1]	2.359(14)		O9	C11	1.378(19)
Tb1	O3	2.486(11)		C1	C2	1.44(2)
Tb1	O7	2.375(10)		C2	C3	1.44(2)
Tb1	O10	2.385(10)		C2	C7	1.40(2)
Tb1	O11	2.407(10)		C3	C4	1.40(2)
Tb1	O12	2.353(13)		C4	C5	1.38(2)
Tb1	O13	2.417(10)		C5	C6	1.43(2)
O1	C1	1.262(19)		C5	C8	1.44(2)
O2	Tb1[1]	2.359(13)		C6	C7	1.34(2)
O2	C1	1.27(2)		C9	C10	1.50(2)
O3	C3	1.358(17)		C10	C11	1.40(2)
O4	C8	1.278(18)		C10	C12	1.38(2)
O5	C8	1.274(18)		C11	C12[2]	1.37(2)
O6	C6	1.373(18)		C12	C11[2]	1.37(2)
O7	C9	1.290(18)				

[1]1-X,1-Y,2-Z; [2]2-X,1-Y,1-Z

Table S14: Bond Angles for **SION-2@H_2O**.

Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Atom**	**Angle/°**
O1	Tb1	O2[1]	93.7(4)		C9	O7	Tb1	137.3(9)
O1	Tb1	O3	68.3(4)		O1	C1	O2	121.1(16)
O1	Tb1	O7	139.9(4)		O1	C1	C2	119.6(15)
O1	Tb1	O10	86.8(4)		O2	C1	C2	119.2(14)
O1	Tb1	O11	148.6(4)		C1	C2	C3	122.4(14)
O1	Tb1	O12	94.4(4)		C7	C2	C1	121.8(15)
O1	Tb1	O13	74.5(4)		C7	C2	C3	115.8(15)
O2[1]	Tb1	O3	145.5(4)		O3	C3	C2	118.2(14)
O2[1]	Tb1	O7	114.1(4)		O3	C3	C4	121.9(14)
O2[1]	Tb1	O10	75.2(4)		C4	C3	C2	119.8(14)

O2[1]	Tb1	O11	71.5(4)		C5	C4	C3	122.5(15)
O2[1]	Tb1	O13	74.3(4)		C4	C5	C6	116.9(15)
O7	Tb1	O3	72.7(4)		C4	C5	C8	123.0(15)
O7	Tb1	O10	74.2(4)		C6	C5	C8	120.1(13)
O7	Tb1	O11	70.8(4)		O6	C6	C5	121.7(15)
O7	Tb1	O13	138.8(4)		C7	C6	O6	117.2(15)
O10	Tb1	O3	74.6(4)		C7	C6	C5	121.1(14)
O10	Tb1	O11	114.4(4)		C6	C7	C2	123.9(16)
O10	Tb1	O13	142.8(5)		O4	C8	C5	119.5(13)
O11	Tb1	O3	137.5(4)		O5	C8	O4	121.2(15)
O11	Tb1	O13	74.9(4)		O5	C8	C5	119.3(14)
O12	Tb1	O2[1]	141.3(4)		O7	C9	C10	116.5(13)
O12	Tb1	O3	71.6(4)		O8	C9	O7	122.8(14)
O12	Tb1	O7	81.7(4)		O8	C9	C10	120.7(14)
O12	Tb1	O10	142.9(4)		C11	C10	C9	121.5(15)
O12	Tb1	O11	82.4(4)		C12	C10	C9	118.6(13)
O12	Tb1	O13	71.6(4)		C12	C10	C11	119.8(14)
O13	Tb1	O3	124.3(4)		O9	C11	C10	122.2(14)
C1	O1	Tb1	142.7(11)		C12[2]	C11	O9	117.5(13)
C1	O2	Tb1[1]	124.1(11)		C12[2]	C11	C10	120.3(15)
C3	O3	Tb1	136.5(10)		C11[2]	C12	C10	119.8(14)

[1]1-X,1-Y,2-Z; [2]2-X,1-Y,1-Z

S2.4 Crystal data for SION-1@H_2O

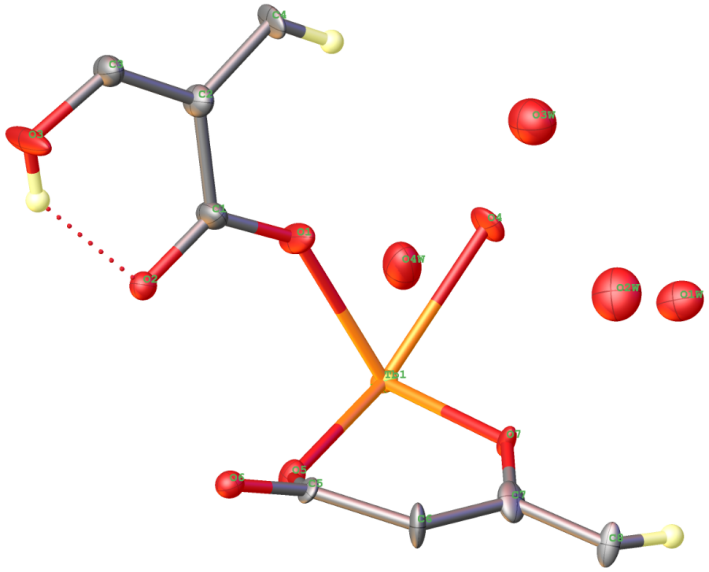

Figure S5: Asymmetric unit of the **SION-1@H_2O** structure. The atomic displacement ellipsoids are set at a 50% probability level. Color scheme: Orange, Tb; red, O; grey, C; blue, N; yellow, H.

Single crystals of **SION-1@H_2O** were isolated from the reaction vessel. A suitable crystal was selected and mounted onto the 3-circle diffractometer at the 11.3.1 beamline of the Advance Light Source synchrotron facility. Only one out of many attempts to probe this compound with X-rays turned out to be successful. The crystal, however, was characterized by strong mosaicity and gave broad reflections. The crystal was kept at 100(2) K during data collection. Using Olex2,[3] the structure was solved with the ShelXT[4] structure solution program using Intrinsic Phasing and refined with the ShelXL[4] refinement package using Least Squares minimization.

Atomic positions were found from the difference–Fourier maps and refined anisotropically for all non-H atoms. H-atoms were refined as a riding model. O-atoms belonging to coordinated (O4) as well as free water solvent molecules (O1W, O2W, O3W, O4W) have been found from the difference–Fourier maps, however H-atoms attached to them were not localized due to the lack of chemical information or distinctive electron density maxima. Upon the final refinement some significant electron density maxima have been recognized, most of them about Tb-atom, but no atoms are expected in their positions. Several electron density peaks and holes in the proximity of

the Tb-atom can be explained as artifact (finite Fourier sum truncation), whereas those in the channels are probably coming from unresolved disorder of free solvent molecules unaccounted for by the model.

Table S15: Crystal data and structure refinement for **SION-1@H_2O**.	
Identification code	**SION-1@H2O**
Empirical formula	$C_8H_{11}O_{11}Tb$
Formula weight	442.08
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.3720(10)
b/Å	6.5373(4)
c/Å	16.4809(12)
α/°	90
β/°	99.121(5)
γ/°	90
Volume/Å^3	1316.11(17)
Z	4
ρ_{calc}g/cm^3	2.231
μ/mm^{-1}	6.762
F(000)	848.0
Crystal size/mm^3	0.02 × 0.015 × 0.01
Radiation	synchrotron (λ = 0.7749)
2Θ range for data collection/°	4.88 to 57.922
Index ranges	$-15 \le h \le 15$, $-8 \le k \le 8$, $-20 \le l \le 20$
Reflections collected	15766
Independent reflections	2673 [R_{int} = 0.0874, R_{sigma} = 0.0605]
Data/restraints/parameters	2673/36/182
Goodness-of-fit on F^2	1.166
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.1081, wR_2 = 0.2569
Final R indexes [all data]	R_1 = 0.1247, wR_2 = 0.2649
Largest diff. peak/hole / e Å^{-3}	8.27/-10.67

Table S16: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **SION-1@H_2O**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Tb1	6573.4(9)	820.6(17)	2173.3(6)	9.6(3)
O1	6056(17)	2630(30)	3262(11)	27(4)
O2	6991(13)	5540(30)	3556(9)	13(3)
O3	6600(20)	7800(30)	4763(14)	43(6)
O4	5172(15)	-1020(30)	2656(11)	23(4)
O5	7068(13)	4050(30)	1823(9)	15(3)
O6	6747(13)	7270(30)	1795(9)	14(3)
O7	5410(14)	1710(20)	1069(9)	13(3)
C1	6270(20)	4280(40)	3693(14)	19(5)
C2	5620(20)	4650(40)	4366(15)	17(5)
C3	5810(20)	6400(40)	4850(15)	19(5)

C4	4830(20)	3290(40)	4536(16)	20(5)
C5	6492(17)	5640(40)	1495(12)	10(4)
C6	5710(20)	5260(40)	731(16)	18(5)
C7	5240(20)	3260(40)	546(17)	20(5)
C8	4560(20)	3080(40)	-215(15)	16(5)
O3W	3383(19)	1350(30)	2732(14)	37(5)
O4W	4339(18)	5260(30)	2256(13)	35(5)
O1W	3233(17)	410(30)	1014(12)	29(5)
O2W	2546(18)	4580(30)	974(14)	37(5)

Table S17: Bond Lengths for **SION-1@H_2O**.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Tb1	O1	2.321(17)		O6	Tb1[3]	2.645(16)
Tb1	O2[1]	2.304(15)		O6	Tb1[4]	2.420(17)
Tb1	O4	2.350(17)		O6	C5	1.20(3)
Tb1	O5[1]	2.455(16)		O7	C7	1.33(3)
Tb1	O5	2.296(18)		C1	C2	1.49(3)
Tb1	O6[2]	2.420(17)		C2	C3	1.40(3)
Tb1	O6[1]	2.645(16)		C2	C4	1.38(3)
Tb1	O7	2.211(15)		C3	C4[5]	1.40(3)
Tb1	C5[1]	2.98(2)		C4	C3[5]	1.40(3)
O1	C1	1.29(3)		C5	Tb1[3]	2.98(2)
O2	Tb1[3]	2.304(15)		C5	C6	1.48(3)
O2	C1	1.26(3)		C6	C7	1.44(3)
O3	C3	1.36(3)		C6	C8[6]	1.39(3)
O5	Tb1[3]	2.455(16)		C7	C8	1.40(3)
O5	C5	1.33(3)		C8	C6[6]	1.39(3)

[1]3/2-X,-1/2+Y,1/2-Z; [2]+X,-1+Y,+Z; [3]3/2-X,1/2+Y,1/2-Z; [4]+X,1+Y,+Z; [5]1-X,1-Y,1-Z; [6]1-X,1-Y,-Z

Table S18: Bond Angles for **SION-1@H_2O**.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
O1	Tb1	O4	71.9(6)		O7	Tb1	O6[1]	141.0(5)
O1	Tb1	O5[1]	87.9(7)		O7	Tb1	C5[1]	163.3(6)
O1	Tb1	O6[1]	66.7(6)		C1	O1	Tb1	142.3(16)
O1	Tb1	O6[2]	137.2(6)		C1	O2	Tb1[3]	140.4(16)
O1	Tb1	C5[1]	74.9(7)		Tb1	O5	Tb1[3]	116.5(6)
O2[1]	Tb1	O1	140.6(6)		C5	O5	Tb1	132.5(14)
O2[1]	Tb1	O4	143.8(6)		C5	O5	Tb1[3]	99.9(13)
O2[1]	Tb1	O5[1]	79.2(5)		Tb1[4]	O6	Tb1[3]	105.7(6)
O2[1]	Tb1	O6[2]	71.5(6)		C5	O6	Tb1[4]	158.9(15)
O2[1]	Tb1	O6[1]	76.8(5)		C5	O6	Tb1[3]	94.2(14)
O2[1]	Tb1	C5[1]	77.6(5)		C7	O7	Tb1	138.8(15)
O4	Tb1	O5[1]	89.6(6)		O1	C1	C2	117(2)
O4	Tb1	O6[1]	120.8(6)		O2	C1	O1	122(2)
O4	Tb1	O6[2]	72.4(6)		O2	C1	C2	120(2)
O4	Tb1	C5[1]	106.2(6)		C3	C2	C1	120(2)
O5	Tb1	O1	81.0(6)		C4	C2	C1	122(2)
O5	Tb1	O2[1]	71.5(6)		C4	C2	C3	118(2)

O5	Tb1	O4	142.7(6)		O3	C3	C2	123(2)
O5	Tb1	O5[1]	115.0(4)		O3	C3	C4[5]	119(2)
O5	Tb1	O6[1]	67.6(5)		C2	C3	C4[5]	118(2)
O5	Tb1	O6[2]	141.0(5)		C2	C4	C3[5]	124(2)
O5[1]	Tb1	O6[1]	49.6(5)		O5	C5	Tb1[3]	54.2(10)
O5	Tb1	C5[1]	90.4(6)		O5	C5	C6	116.8(19)
O5[1]	Tb1	C5[1]	26.0(6)		O6	C5	Tb1[3]	62.2(12)
O6[2]	Tb1	O5[1]	69.0(6)		O6	C5	O5	116.2(19)
O6[2]	Tb1	O6[1]	114.7(4)		O6	C5	C6	126(2)
O6[2]	Tb1	C5[1]	93.3(6)		C6	C5	Tb1[3]	166.4(16)
O6[1]	Tb1	C5[1]	23.6(6)		C7	C6	C5	121(2)
O7	Tb1	O1	106.2(7)		C8[6]	C6	C5	117(2)
O7	Tb1	O2[1]	92.7(6)		C8[6]	C6	C7	122(2)
O7	Tb1	O4	89.7(6)		O7	C7	C6	122(2)
O7	Tb1	O5[1]	164.9(6)		O7	C7	C8	122(2)
O7	Tb1	O5	73.5(6)		C8	C7	C6	116(2)
O7	Tb1	O6[2]	96.5(6)		C6[6]	C8	C7	122(2)

[1]3/2-X,-1/2+Y,1/2-Z; [2]+X,-1+Y,+Z; [3]3/2-X,1/2+Y,1/2-Z; [4]+X,1+Y,+Z; [5]1-X,1-Y,1-Z; [6]1-X,1-Y,-Z

S3 Structural Topologies of SION-2 and SION-1

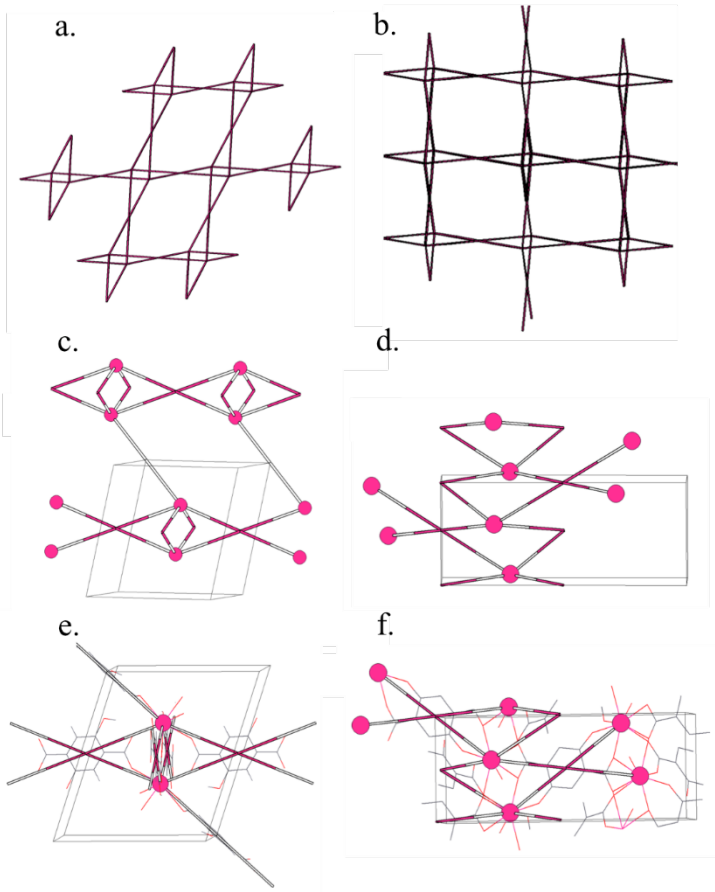

Figure S6: Network topologies of a. ***lvt*** of **SION-1**, b. ***xah*** of **SION-2** along the *c*-axis., c. projection of the xah net approximately along the *a*-axis, d. projection of the lvt net approximately along the a-axis. e. the xah net with **SION-2** superposed in the background. f. the lvt net with **SION-1** superposed in the background. Tb(III) ions are represented as purple balls, while the organic ligands are represented as purple and white lines**.**

S4 Solid State Characterization

S4.1 Phase purity

The phase purity of **SION-1**, **SION-2, SION-1@H_2O** and **SION-2@H_2O** was confirmed by the comparison of the experimental PXRD pattern with the simulated generated from the single crystal structure. **SION-1** and **SION-2**and it is found that are stable over a period of 6 months at ambient temperature while stored in a vial.

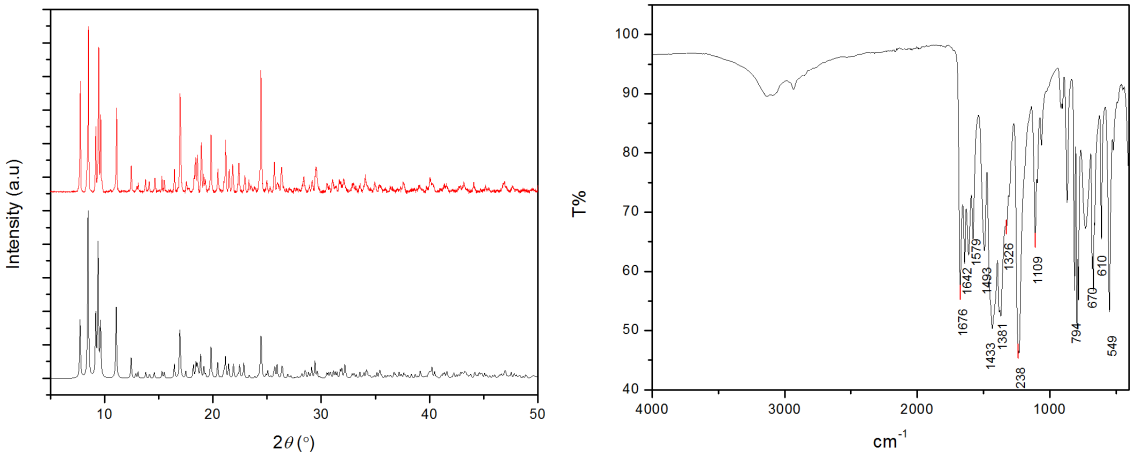

Figure S7: Left, PXRD of **SION-2**, color scheme: black, theory; red, experimental. Right, IR of **SION-2**. Both spectrum were obtained after conventional heating experiments.

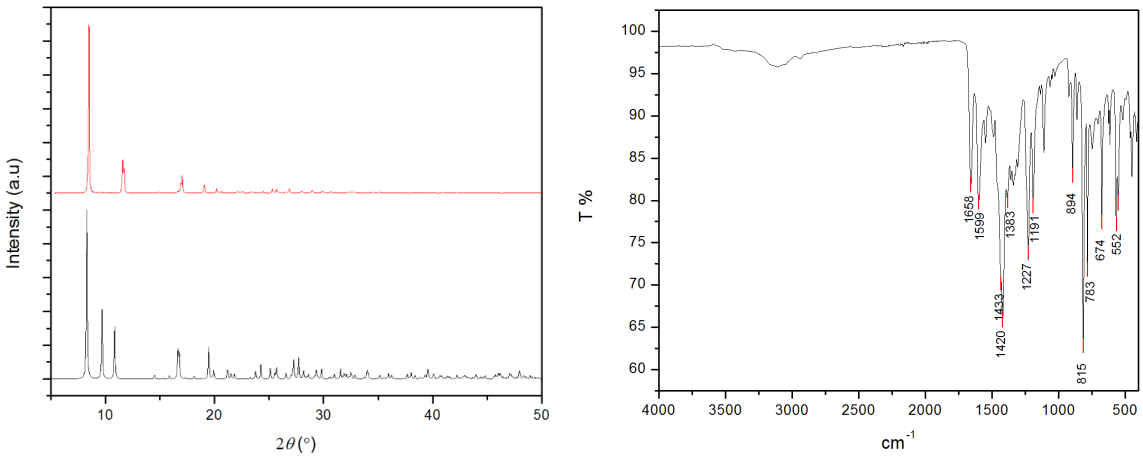

Figure S8: Left, PXRD of **SION-1**, color scheme: black, theory; red, experimental. Right, IR of **SION-1**. Both spectra were obtained after conventional heating experiments.

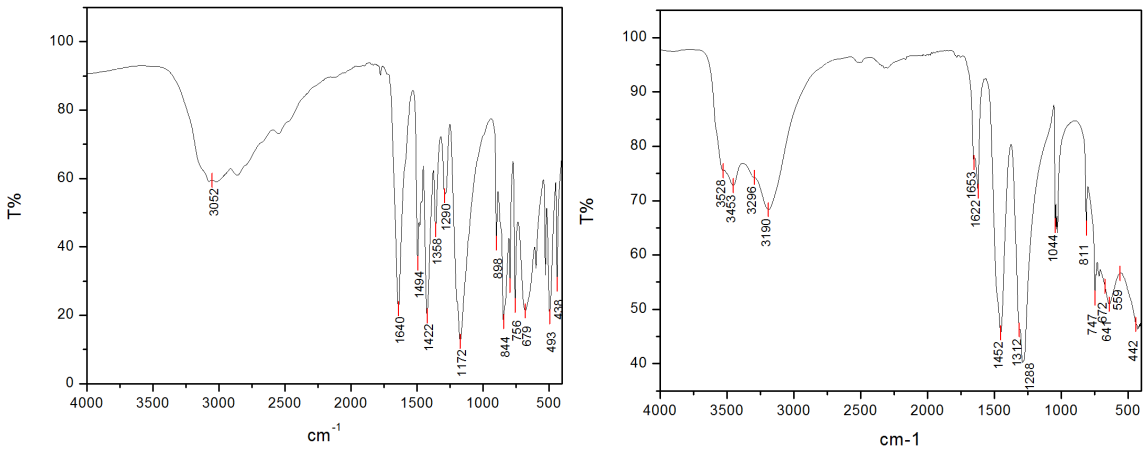

Figure S9: Left: IR of the ligand, DHBDC; Right: IR of the metal salt $Tb(NO_3)_3 \cdot 6H_2O$

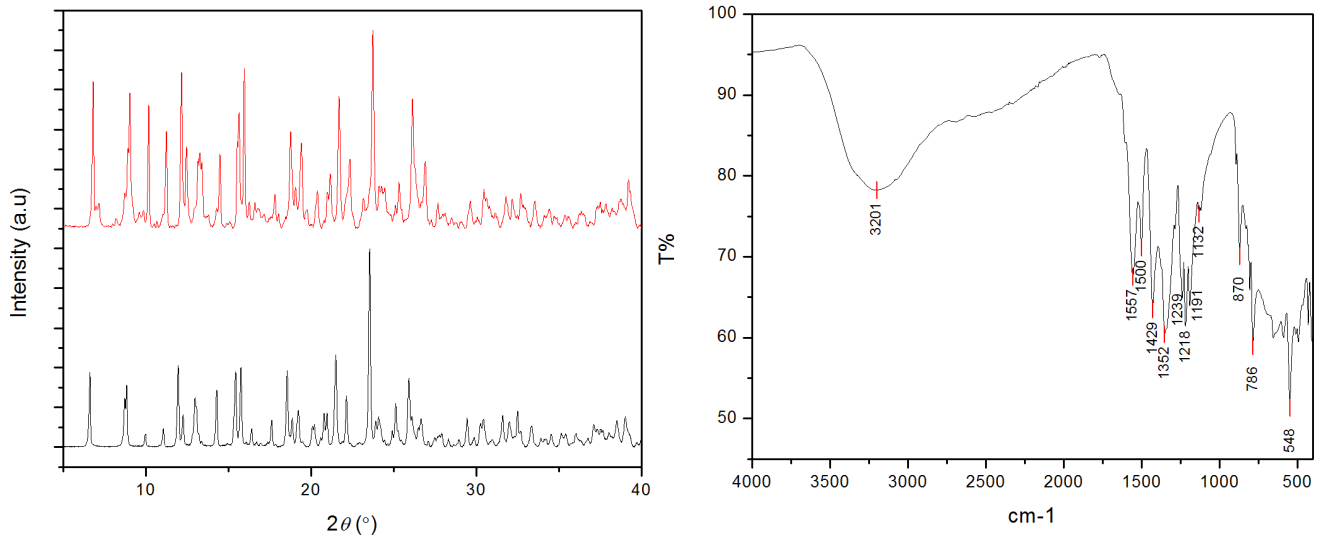

Figure S10: PXRD of **SION-2@H_2O** after **SION-2** has been immersed in H_2O for 72 hrs (left) and the respective IR of **SION-2@H_2O** (right). Color scheme for PXRD: black, **SION-2@H_2O** theory; red, experimental.

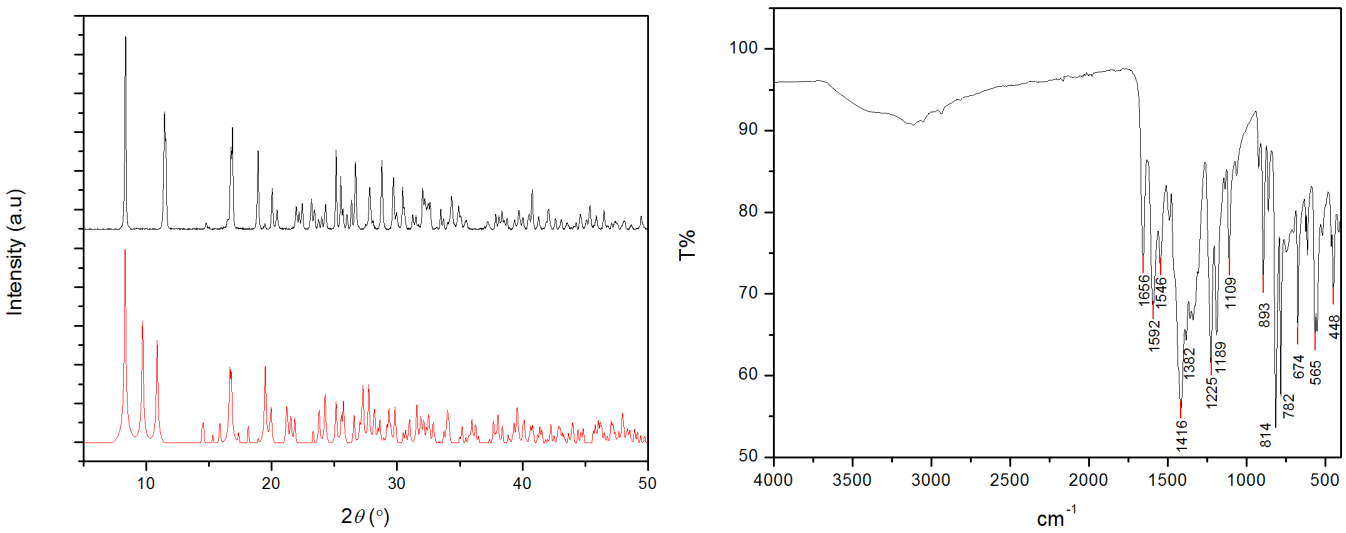

Figure S11: PXRD of **SION-1@H_2O** after **SION-1** has been immersed in H_2O for 72 hrs, color scheme: theoretical red; experimental, black. The respective IR of **SION-1@H_2O** is on the right.

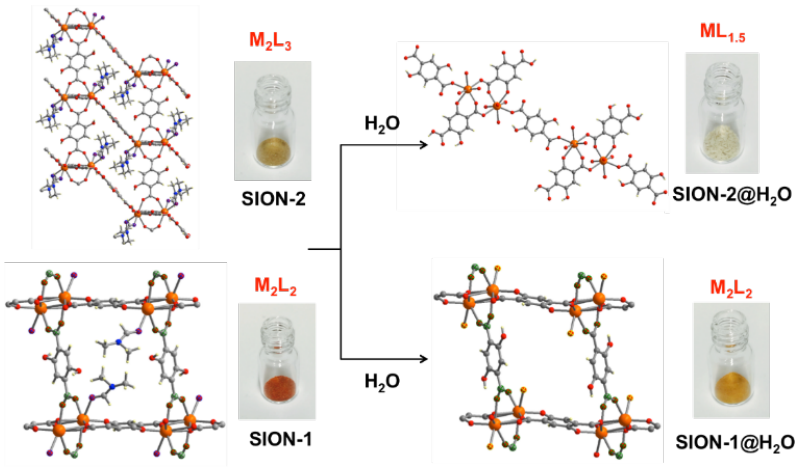

Figure S12. Schematic illustration showing how the structures of **SION-1** and **SION-2** are affected when are immersed in water. The 3-dimensional structure of **SION-2** collapses into 1-dimensional chains of **SION-2@H_2O**. The structure of **SION-1** retains its structural integrity when is immersed in H_2O, but H_2O molecules displace the coordinated guest DMF molecules. Atom colours: orange, Tb; red, O; blue, N; grey, C; pale yellow, H. In **SION-1** and **SION-1@H_2O**, red and grey with green cross, carboxylate C and O of DHBDC; red with blue cross, O of DMF and red with yellow cross, O of H_2O.

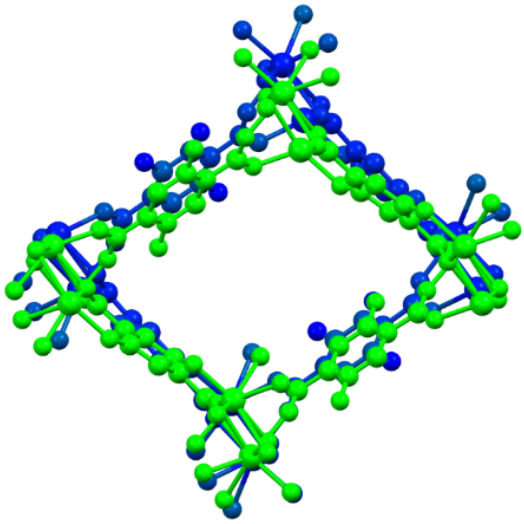

Figure S13: Pore shrinkage from **SION-1** to **SION-1 @ H_2O.** Here, blue represents **SION-1** while green is **SION-1@H_2O**.

S4.2 Thermogravimetric Analysis

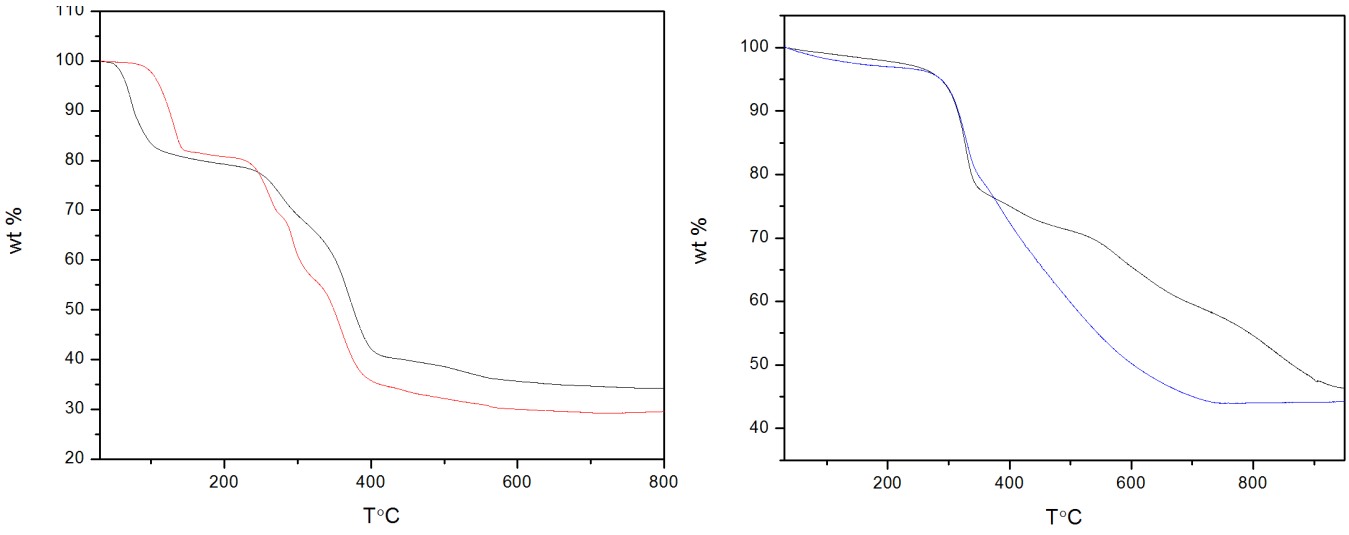

Figure S14: TGA analysis of **SION-2@H_2O**, and **SION-2** (left) as well as **SION-1@H_2O** and **SION-1** (right). Color scheme: **SION-2**, red; **SION-2@H_2O**, black (left). **SION-1**, black; **SION-1@H_2O**, blue (right).

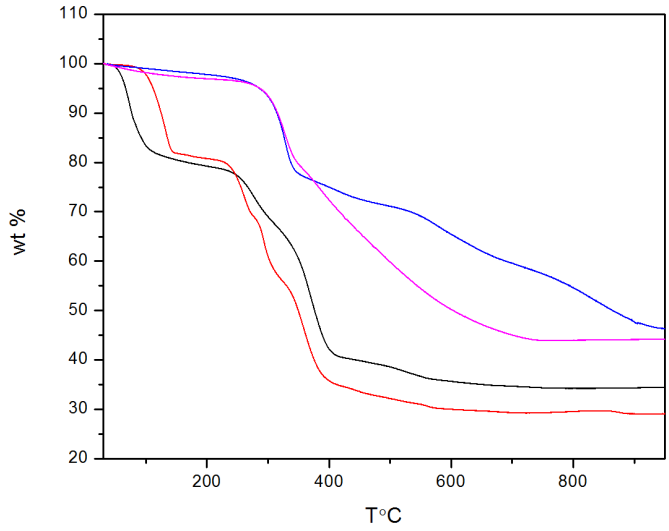

Figure S15: Combined TGA of the SION family, color scheme: **SION-2**, red; **SION-2@H_2O**, black; **SION-1**, blue; **SION-1@H_2O**, pink.

TGA shows that **SION-2@H_2O** is less thermally stable compared to **SION-2**, with an initial weight loss of 18% at 60˚C corresponding to the loss of H_2O, followed by total decomposition of the material at 250 ˚C. The TGA profile of **SION-1@H_2O** is very comparable to that of **SION-1**, with an initial weight loss of 4 % corresponding to H_2O at 313 ˚C, followed by the slow decomposition of the material at 343 ˚C

S4.3 Effects of concentration on formation of SION-2 and SION-1

Following the conditions described above for the synthesis of **SION-1** using conventional solvothermal synthesis, with the exception of the volume of DMF added which ranged from 1.0 to 2.2 mL of DMF in 0.1 mL increments. Vials were capped, and placed in the oven using the same temperature and ramping scheme for 72 hrs. Once the vials were removed, the material was filtered, washed with fresh DMF, and allowed to dry in air.

S4.4 Effects of Time on the Formation of SION-2 and SION-1

Following the conditions described above for the synthesis of **SION-1** using conventional solvothermal synthesis, vials were capped, and placed in the oven using the same temperature and

ramping scheme for their allotted times of 12, 24, 48, 52, 62, and 65 hrs. Once the vials were removed, the material was filtered, washed with fresh DMF, and allowed to dry in air.

S4.5 SION-2 to SION-1 (direct, 72 hrs)

Following the conditions described above for the synthesis of **SION-2** using conventional solvothermal synthesis, vials were capped, and placed in the oven using the same temperature and ramping scheme for 24 hrs to form fresh **SION-2**. After formation, the material was washed with fresh DMF. Finally, 2 mL of DMF and 0.5 mL H_2O was added to the vial, capped, and placed in an oven using the same ramping conditions described above. Original golden colored crystal emerged bright orange.

S4.6 Single-crystal to Single-Crystal transformation test: Wet vs Dry SION-2

To test to see if the transformation between **SION-2** and **SION-1** was single-crystal to single-crystal, fresh **SION-2** (previously made via conventional heating conditions previously described) was dried overnight on a filter paper and placed in a vial, thus affording dry crystals. In a separate vial, fresh **SION-2** was made, and washed with DMF until clear. Any solvent present in the vial was removed with a pipette, this leaving behind "wet" crystals. Both vials were capped, and placed in the oven for 72 hrs using the same ramping and cooling process described in the conventional heating section.

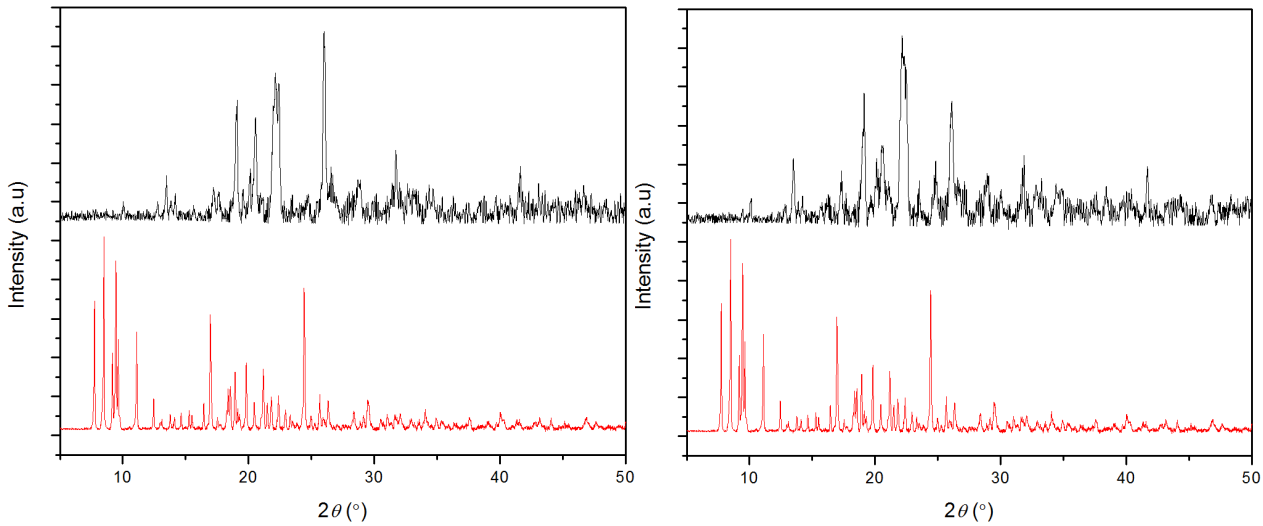

Figure S16: In order to rule out single-crystal to single-crystal transformation in air from **SION-2** to **SION-1** using material that had been previously dried (left) and material that had been just removed from solvent ("wet") but not dried (right). Color scheme: **SION-2** Theory, red; dry/wet material after heating, black.

S5 *In-situ* ^{1}H NMR experiments

Approximately 12 mg of newly synthesized **SION-2** was washed 3 times with a total of 0.5 mL of $_{d}$-DMF. The solid was transferred into a standard NMR tube with 0.5 mL of $_{d}$-DMF, 0.125 mL of D_2O, and 10 μL of *p*-xylenes (internal standard). The NMR tube was flame sealed to ensure no evaporation of liquids, and placed into a 400 MHz Bruker NMR. The internal NMR temperature was set to 120 ^{o}C and allowed to stabilize until no more movement was observed by the hydroxide peaks present in the spectrum. Subsequently a ^{1}H NMR spectrum was taken every 15 minutes for approximately 65 hrs. Using an algorithm/script through Mestrenova (see section 8 of the SI), the movement of peaks, as well as their concentration were calculated.

General calculations for the percentage of ligand lost were performed by using the formula to determine the overall percentage of ligand found in **SION-2** that could be lost (2.7×10^{-5} mols, average ~12 mg **SION-2** used). This percentage represents the total dissolution of the MOF during the transformation process. Through algorithm/script generated from Mestrenova, a maximum concentration of ligand released is calculated using the known (10 μL) volume of *p*-xylenes added. From that concentration (0.043 mol/l for 2.7×10^{-5} mols), and the known volume inside the NMR tube (0.626 mL), the moles of ligand is found. Finally, compared to the total amount that could be released 1.0×10^{-5} mols, or 37 % of the total amount of ligand was found in solution, representing a partial dissolution.

S5.1 SION-2 to SION-1 transformation for NMR comparison

Following the NMR experiments, **SION-2** was made through MW synthesis and washed with DMF until the solvent was clear. The material was placed in a vial, along with 2 mL of DMF and 0.5 mL of H_2O. The vials were placed in the oven using the conditions described above for their allotted times (1, 5, 10, 14, 18, 20, 24, and 48 hrs). Once the vials were removed, the material was filtered, washed with fresh DMF, and allowed to dry in air. PXRD was performed on each sample to determine what was happening during the NMR experiments.

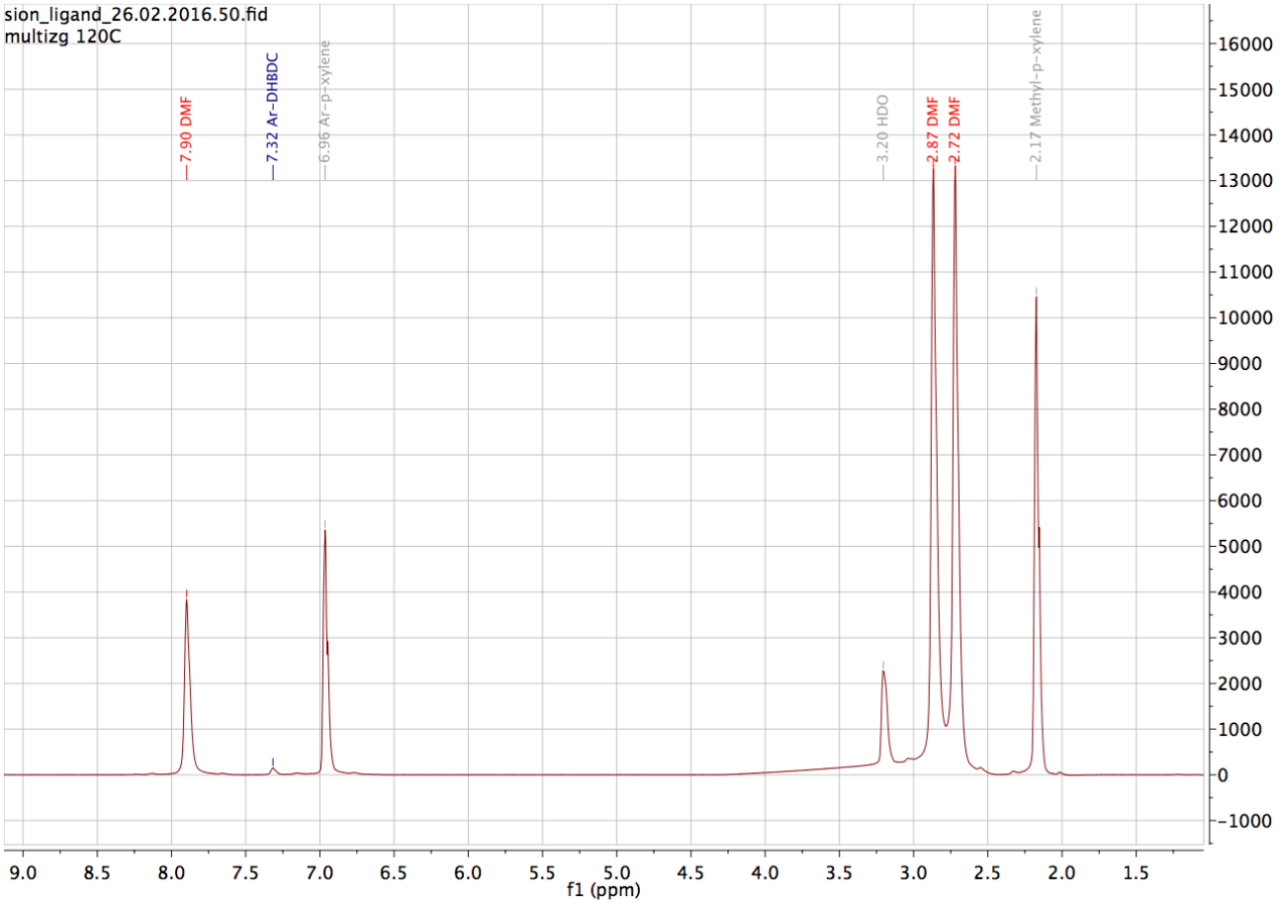

Figure S17: Initial scan of DHBDC in $_d$-DMF/D_2O at 120˚C.

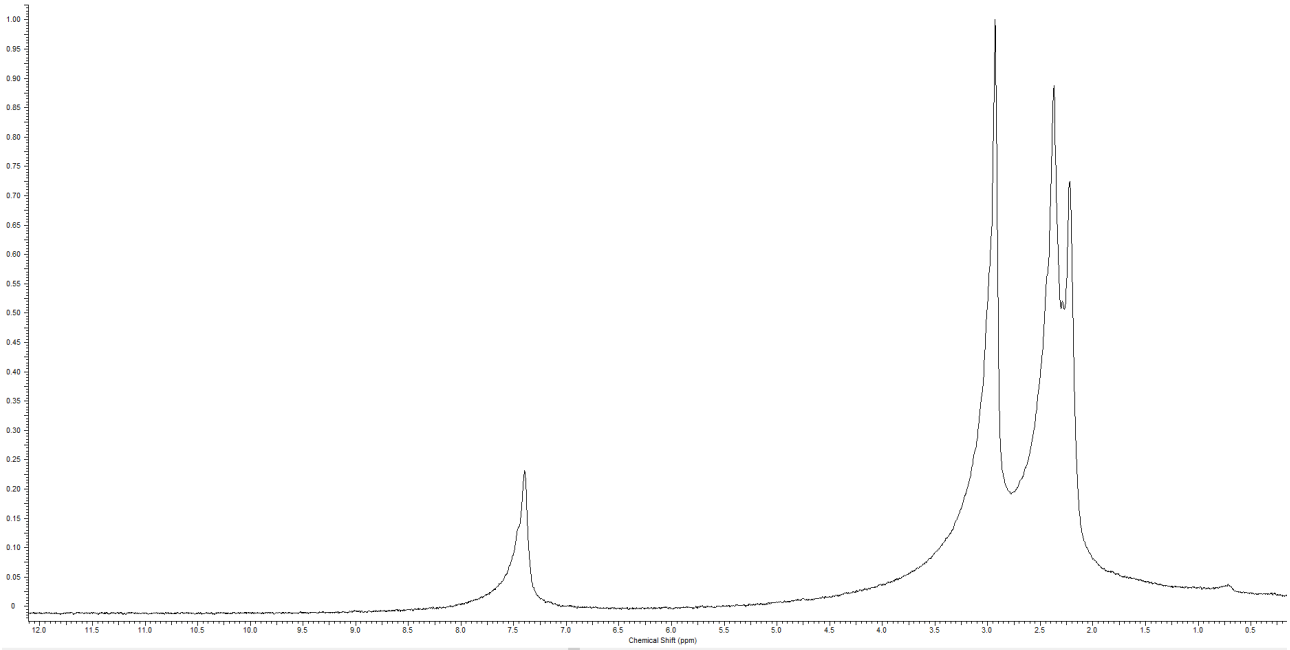

Figure S18: Initial scans of **SION-2** (only) at 120°C. The peaks here correspond to $_d$-DMF (~7.5 ppm and ~2.0-2.5 ppm) and H_2O/D_2O (~ 3.0 ppm).

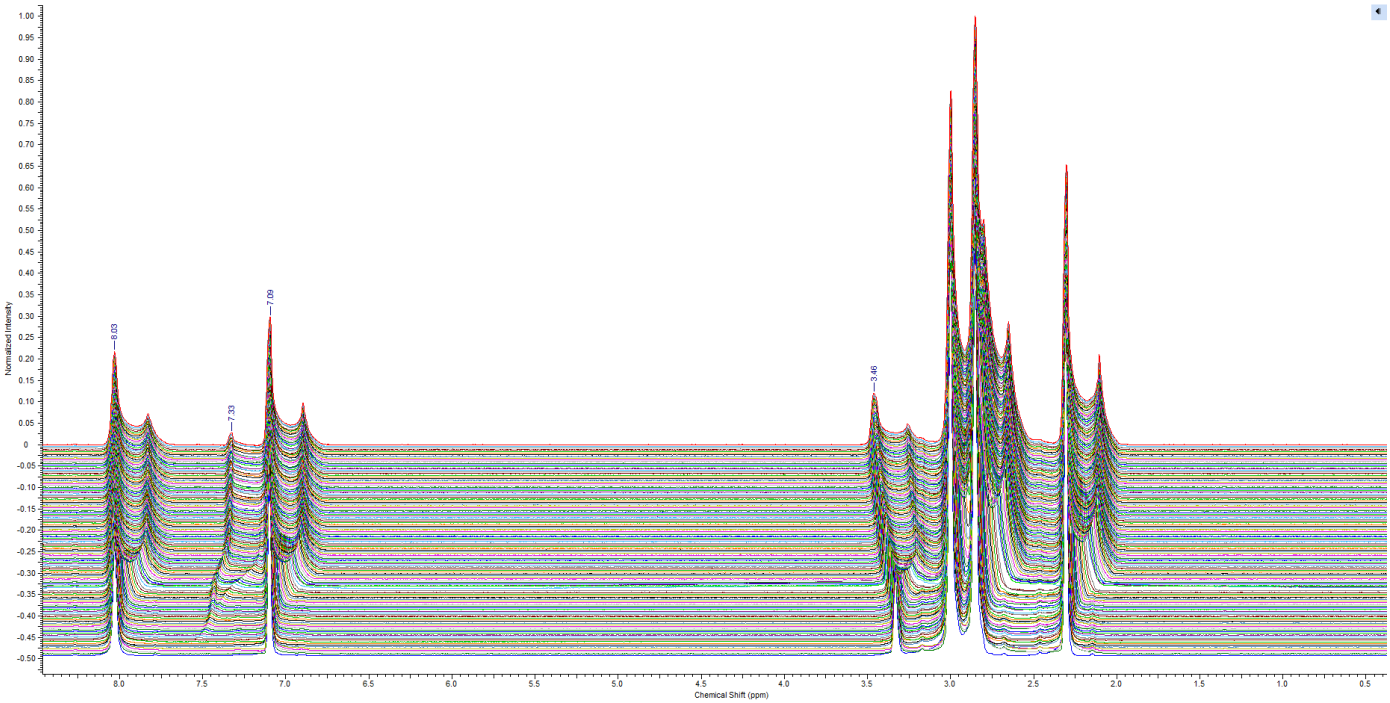

Figure S19: 30 minute interval ^{1}H NMR scans of **SION-2** at 120˚C. Starting from the bottom (-0.50, y axis) is time 0, following through to the top (0.0, y axis) for 62 hrs. Peaks at 8.03 ppm and 2.5-3.0 ppm correspond to $_{d}$-DMF, while peaks at 7.09 ppm and between 2.0-2.4 ppm correspond to the *p*-xylene internal standard added in (10 µL). The peak at 3.46 represents H_2O/D_2O, while the one that starts at approximately 7.60-7.33 represents the evolution of DHBDC from the framework **SION-2** into the solvent while the framework changes to **SION-1**.

S6 ICPMS

The ICPMS experiments were performed under the assumption that the pathway occurs through a partial dissolution mechanism. Using a Tb standard (TraceCERT, 1000 mg/L Tb in HNO_3 purchased from Sigma Aldrich), a calibration curve with 200 µg/L, 50 µg/L, 20 µg/L, 18 µg/L, 10 µg/L, 2 µg/L, and 0.2 µg/L values was initially constructed.

Samples of freshly prepared **SION-2** (MW synthesis) were washed with fresh DMF until the solution was clear, and 2.0 mL of DMF and 0.5 mL of H_2O were added with an Eppendorf pipette. These samples were placed in the oven for 5, 10, 14, 16, 18, 24, 35, 48 and 72 hrs. Following the allotted reaction time, 6.41 µL of solvent was removed from the reactions, and placed in a 100 mL volumetric flask and diluted and immediately analyzed on the ICPMS.

S7 In-situ PXRD study

In-situ Synchrotron X-ray powder diffraction was performed at the Swiss Norwegian Beamlines SNBL of ESRF (European Synchrotron Radiation Facility), at beamline BM31. Preformed **SION-2** crystals were ground in a DMF/H_2O mixture and loaded into a 0.8 mm quartz capillary, which was heated with a hot air blower (ramp of 2 ˚C /min to 120 ˚C). Data were collected at 60s exposure time with a mar345 area detector, using a wavelength of 0.5008 Å and after having performed a previous calibration of the setup with a Lab6 standard. Data integration was performed with Bubble. Lattice parameters were then extracted by means of profile fits (Le Bail) using the Topas software.

S8 Computational Methods

The relative energies of **SION-1** and **SION-2** were calculated subtracting the sum of the energy of each individual atom ($nE_{Tb} + nE_C + nE_{O2} + nE_{H2} + nE_{N2}$) from the total energies of the pure crystal structure (E_{AB}); the energy of each atom was obtained dividing the total energy of its standard state (i.e. Tb (s, hcp phase), C (s, hcp phase), $O_2(g)$, $H_2(g)$, $N_2(g)$) by the number of atoms in the respective unit cell (Tb=2, C=4, O=2, H=2, N=2).

Electronic structure calculations were performed out on the periodic crystals in the VASP (Vienna ab-initio Simulation Program) code at GGA DFT level of theory using the PBEsol functional.[5] Projector-augmented wave (PAW) potentials were used for modeling the interactions between core and shell of the atoms, projector-augmented wave. The geometries were optimized at Γ-point relaxing both the atomic positions and the cell parameters converging the forces to 0.005 eV/Å and the electronic structure to 10^{-7} eV. The bonding energies were calculated removing one ligand from the crystal and subtracting the total energy the crystal fragment (E_A^{x+}) and of the removed ligand (E_B^{x-}) from the one of the pure crystal (E_{AB}).

S9 References

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