Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information

Hexacoordinate Germanate Metal-Organic Frameworks for the Detection of Pb^{2+} ions in Aqueous Solution

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Materials and general methods

All chemicals are commercially available, unless specified, were used without further purification. Anhydrous solvent was obtained under a nitrogen atmosphere from a PuresSolv multiple dispensing solvent drying system. All "water" or "H_2O" refer to deionized water. Linker synthesis reactions were performed under N_2 using standard Schlenk line techniques, and all glasswares were dried in a 120 °C oven overnight before use. NMR spectra were recorded on a Bruker 400 MHz spectrometer and all chemical shifts are reported in . Infrared (IR) spectra were recorded on an Agilent Cary 630 FTIR Spectrometer. Powder X-ray diffraction (PXRD) results were collected on a Bruker 2D Phaser machine with Cu-K_α radiation (1.51184 Å) between 5° and 50° (2θ). Single crystal X-ray diffraction (SCXRD) results were collected on an Oxford Diffraction Xcalibur 3 diffractometer ($[Et_3NH]_2[H_3$**L-Si**]), a Rigaku FR-E+ diffractometer (**IMP-33-Sc**) and a Rigaku 007HF diffractometer (**IMP-34-Y** and **IMP-34-Dy**). Thermogravimetric analysis (TGA) was carried out on a Perkin Elmer TGA 8000 instrument under a N_2 flow (50 mL/min) over the range of 30-600 °C at a heating rate of 10 °C/min. Photoluminescence (PL) spectrum was recorded on a Cary Eclipse Fluorescence Spectrophotometer and the slit width of both the source and detector for the excitation and the emission were kept at 5 nm to maintain consistency. PL quantum yield was measured using Edinburgh Instruments FLS1000 spectrometer with an integrating sphere. UV-vis spectrum was recorded on a Cary 5000 UV-Vis-NIR Spectrophotometer.

Crystal growth

Single crystals of $[Et_3NH]_2[H_3$**L-Si**] were obtained through vapour diffusion method.[1] 16 mg compound was dissolved in 0.5 mL hot DMF and placed in a 3.5 mL glass vial, and this vial was placed in a 14 mL glass vial containing 2.5 mL diethyl ether. Colourless tablet crystals were obtained in the small vial after 3 days.

MOF synthesis

IMP-RE series MOFs were synthesized through hydrothermal method. A mixture of metal nitrate (Sc, Y, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu, all trivalent, 0.1 mmol) and $[Et_3NH]_2[H_3$**L-Ge**] (0.05 mmol) were placed in a 7 mL glass vial followed by adding water (3 mL) and MeCN (1 mL). The glass vial was then sonicated for 5 mins to ensure the reagent completely dissolved, before heating at 80 ℃ for 24 h to afford blade-shaped crystals (**IMP-33-Sc** was in prism shape). **IMP-34-Ho** and **IMP-34-Er** exhibited light orange and pink colours respectively, while other crystals were colourless.

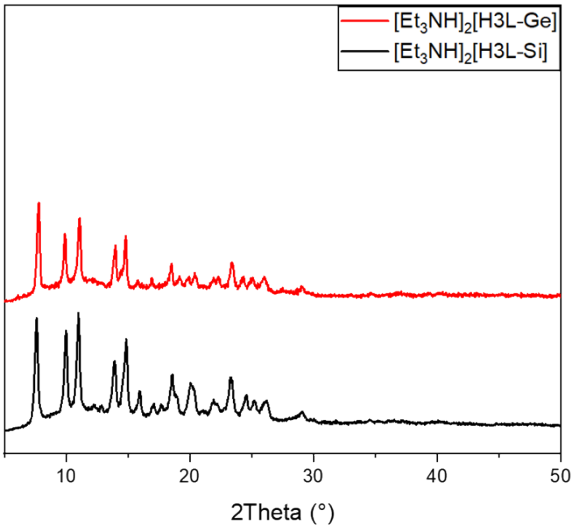

Figure S1 PXRD results of the measured Si and Ge linker.

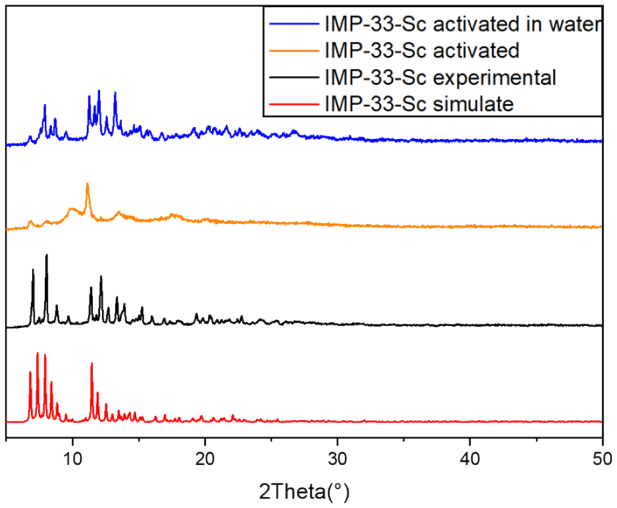

Figure S2 PXRD pattern of **IMP-33-Sc** (calculated, measured, activated, activated then soaked in water).

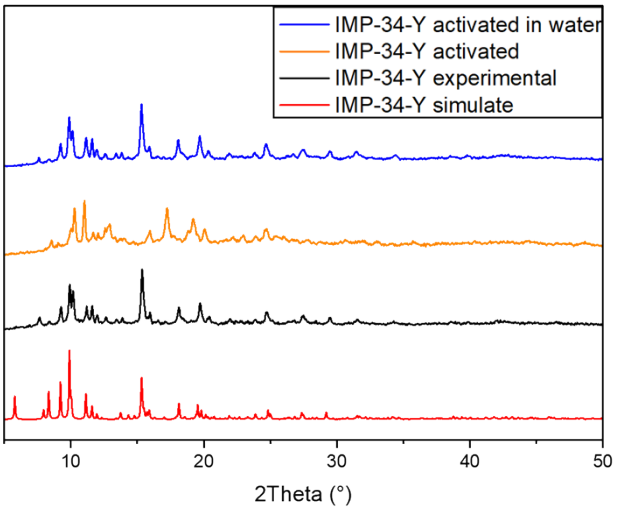

Figure S3 PXRD pattern of **IMP-34-Y** (calculated, measured, activated, activated then soaked in water).

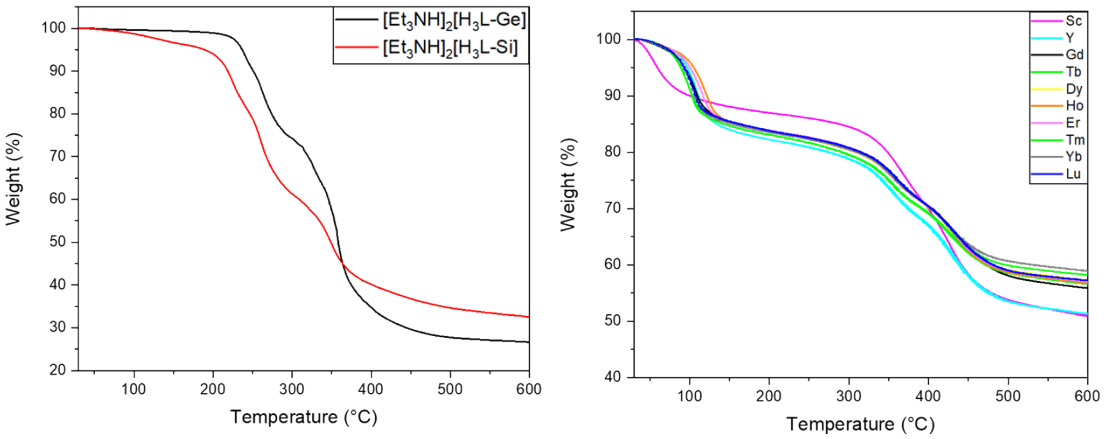

Figure S4 TGA results of the ligands and **IMP-RE** (all MOFs)

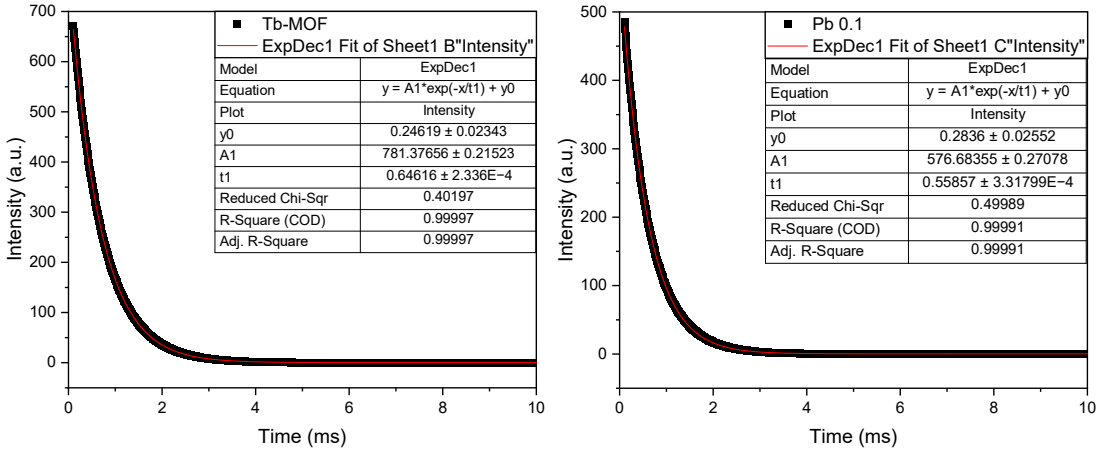

Figure S5 Lifetime of the peak at 545 nm of **IMP-34-Tb**, and Pb treated **IMP-34-Tb**

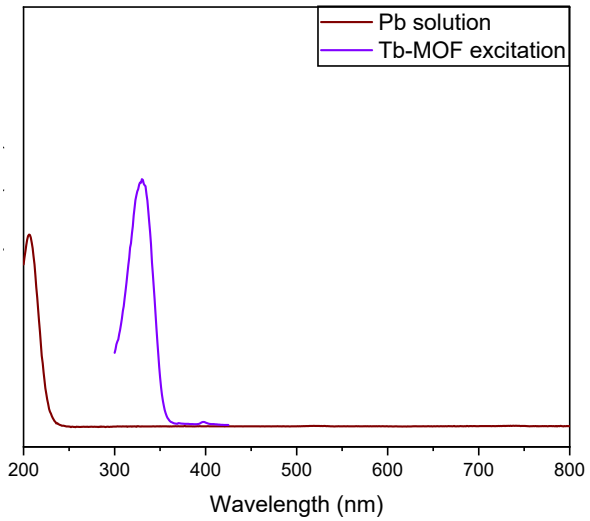

Figure S6 UV-vis absorption spectra of Pb^{2+} solution (brown) and excitation spectra of **IMP-34-Tb** (purple).

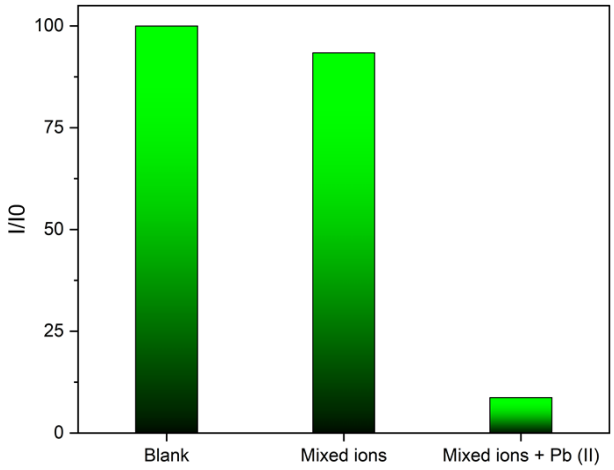

Figure S7 Comparison of the luminescence intensity of **IMP-34-Tb** in the presence of a solution of mixed ions: (10 mM Na^{+}, Mg^{2+}, K^{+}, Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Sr^{2+} and Cs^{+})

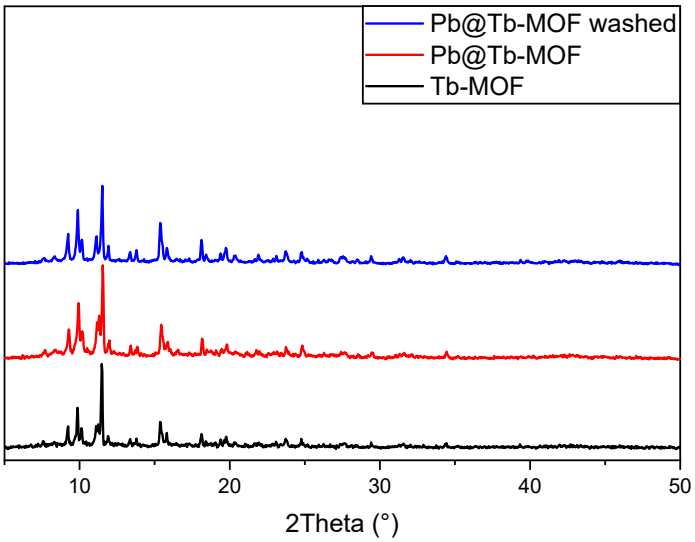

Figure S8 PXRD pattern of the **IMP-34-Tb** (Tb-MOF), Pb-treated Tb-MOF (Pb@Tb-MOF), and washed Pb-treated Tb-MOF.

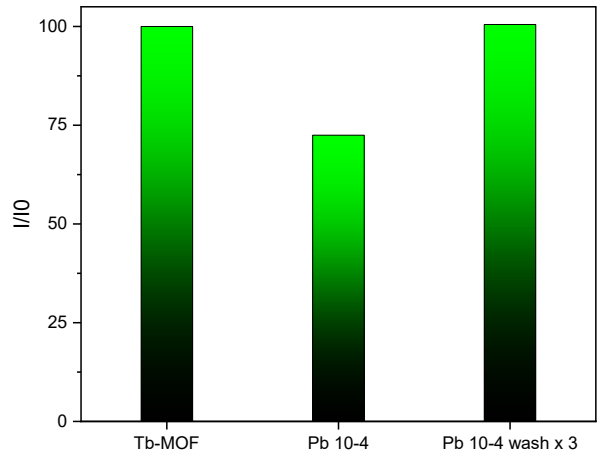

Figure S9 Relative luminescence intensity of the **IMP-34-Tb**, Pb-treated Tb-MOF and washed Pb-treated Tb-MOF.

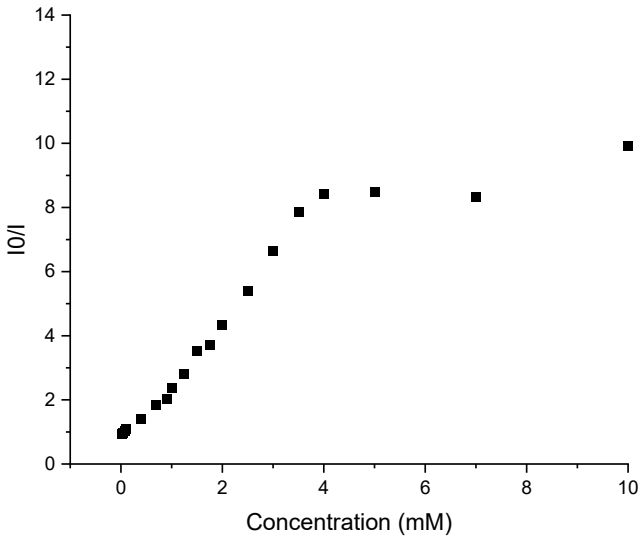

Figure S10 Stern-Volmer plot of relative intensity and Pb^{2+} in full concentration region.

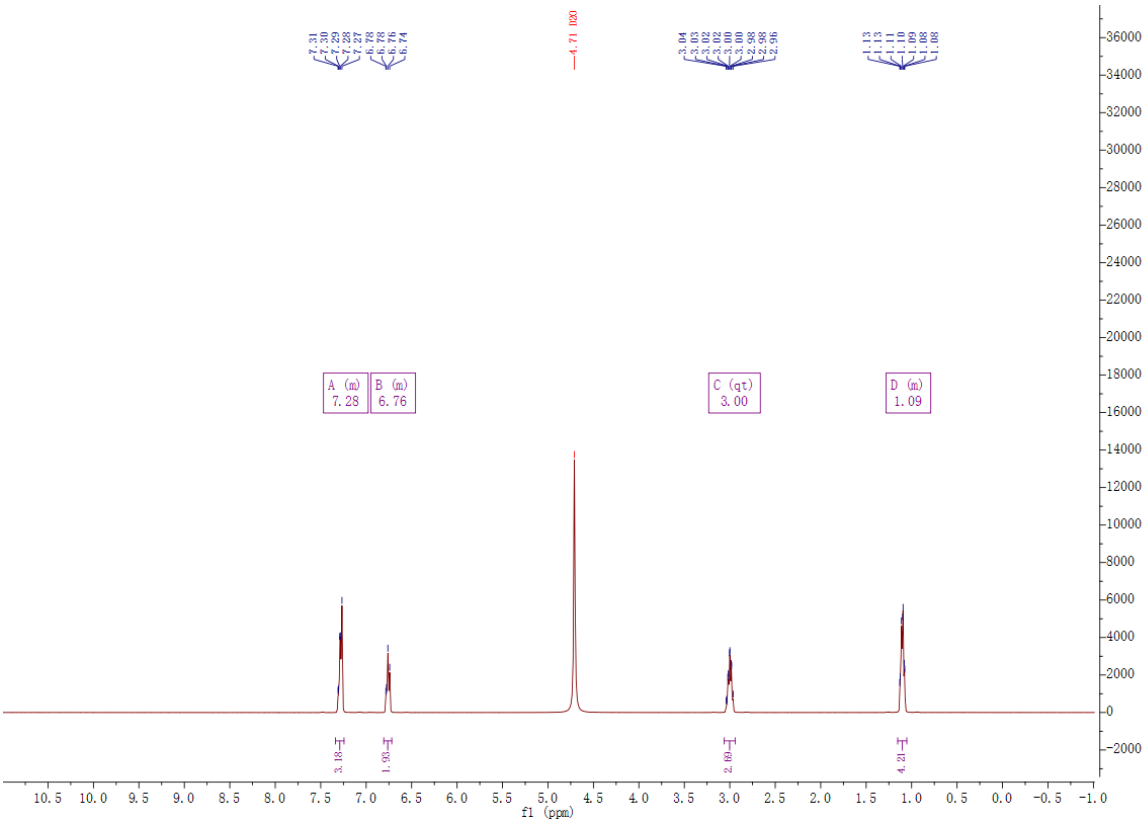

Figure S11 ^{1}H NMR of 3,4-dihydroxybenzoic acid and $[Et_3NH]_2[H_3\mathbf{L\text{-}Si}]$ in D_2O.

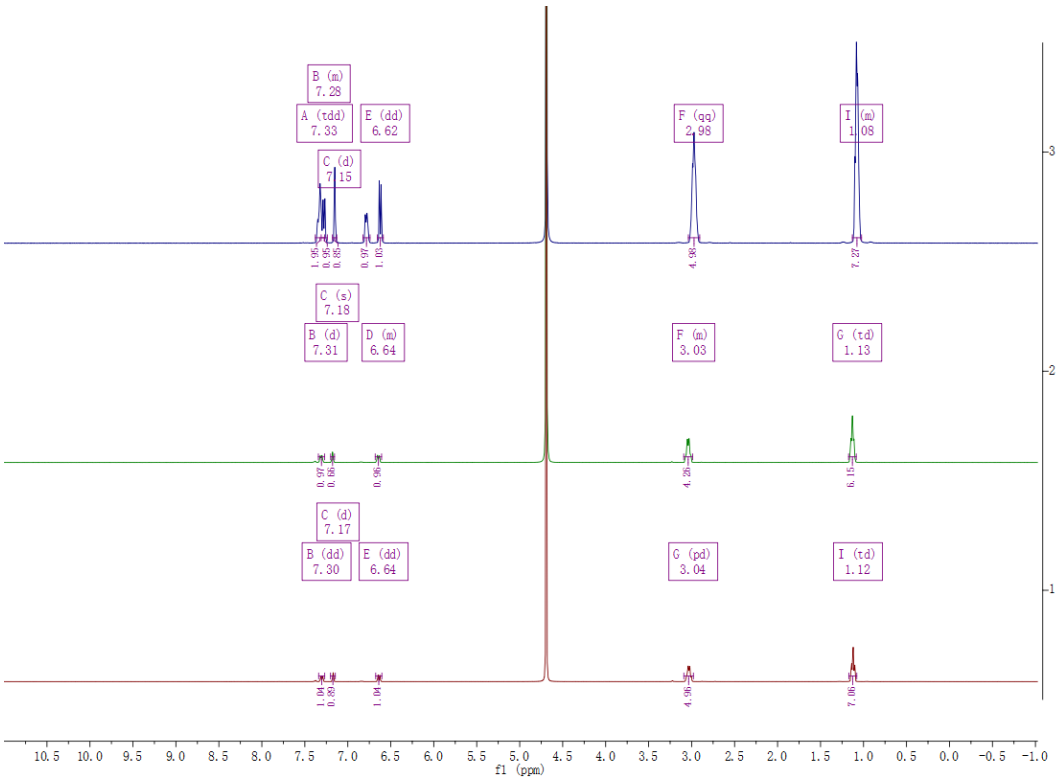

Figure S12 ^{1}H NMR (D_2O) of $[Et_3NH]_2[H_3$**L-Ge**$]$ (bottom), $[Et_3NH]_2[H_3$**L-Ge**$]$ heated at 80℃ for 3 days (middle), and the mixture of 3,4-dihydroxybenzoic acid and $[Et_3NH]_2[H_3$**L-Ge**$]$ (top).

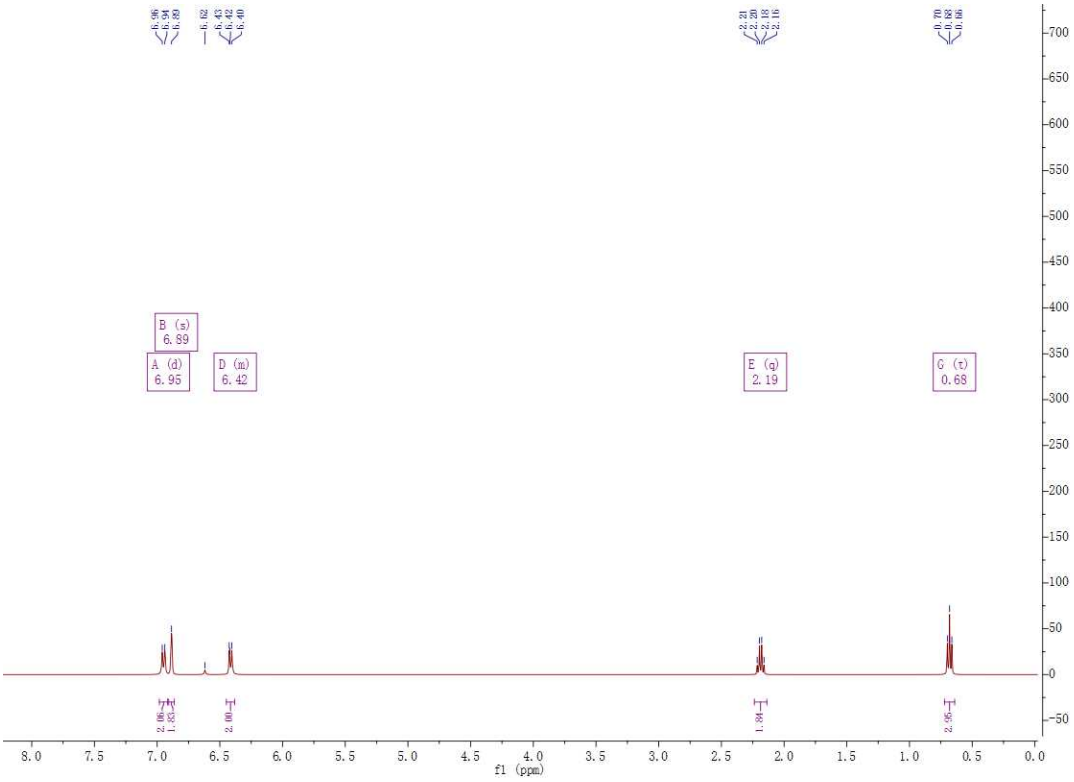

Figure S13 ^{1}H NMR of digested **IMP-33-Sc** (NaOD in D_2O)

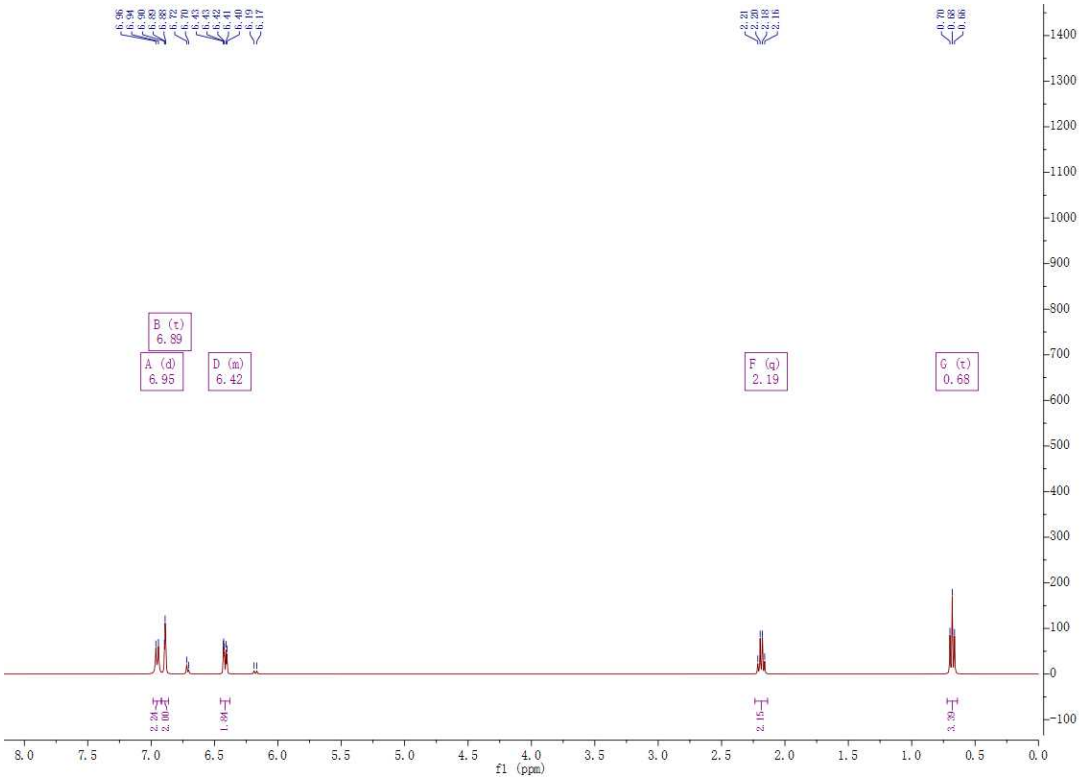

Figure S14 ^{1}H NMR of digested **IMP-34-Y** (NaOD in D_2O).

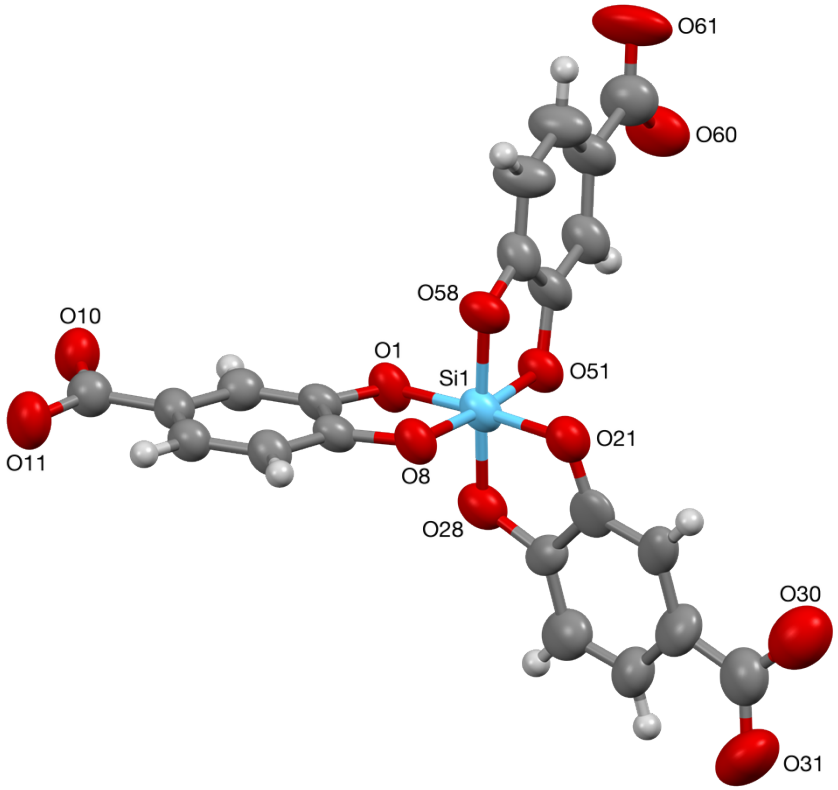

Figure S15 The structure of the di-anion present in the crystal of $[Et_3NH]_2[H_3$**L-Si**$]$ (50% probability ellipsoids).

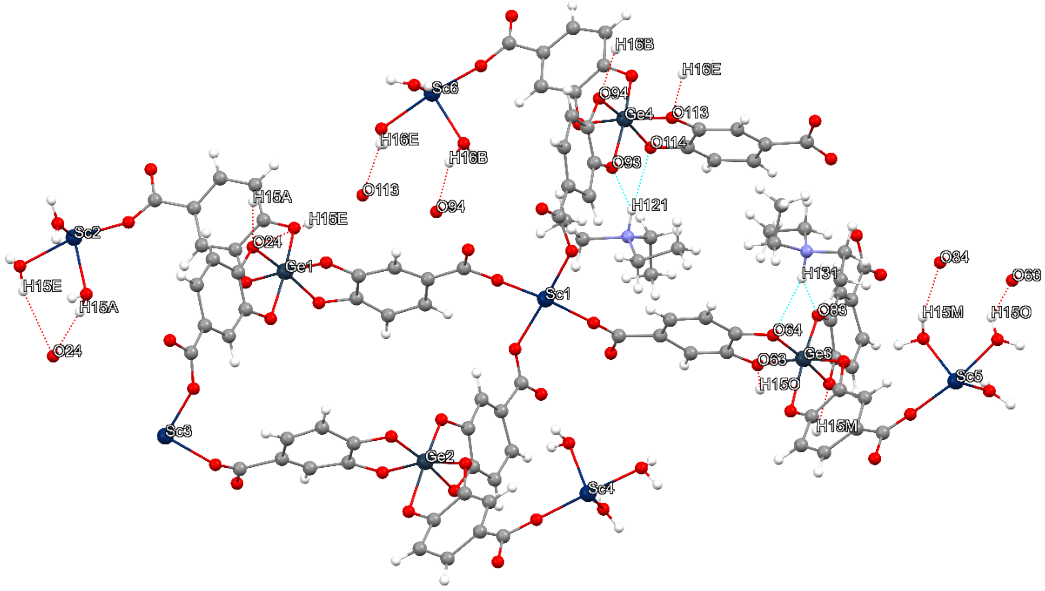

Figure S16 Crystal structure of **IMP-33-Sc** (asymmetric unit) with hydrogen bonds (red and blue dotted lines).

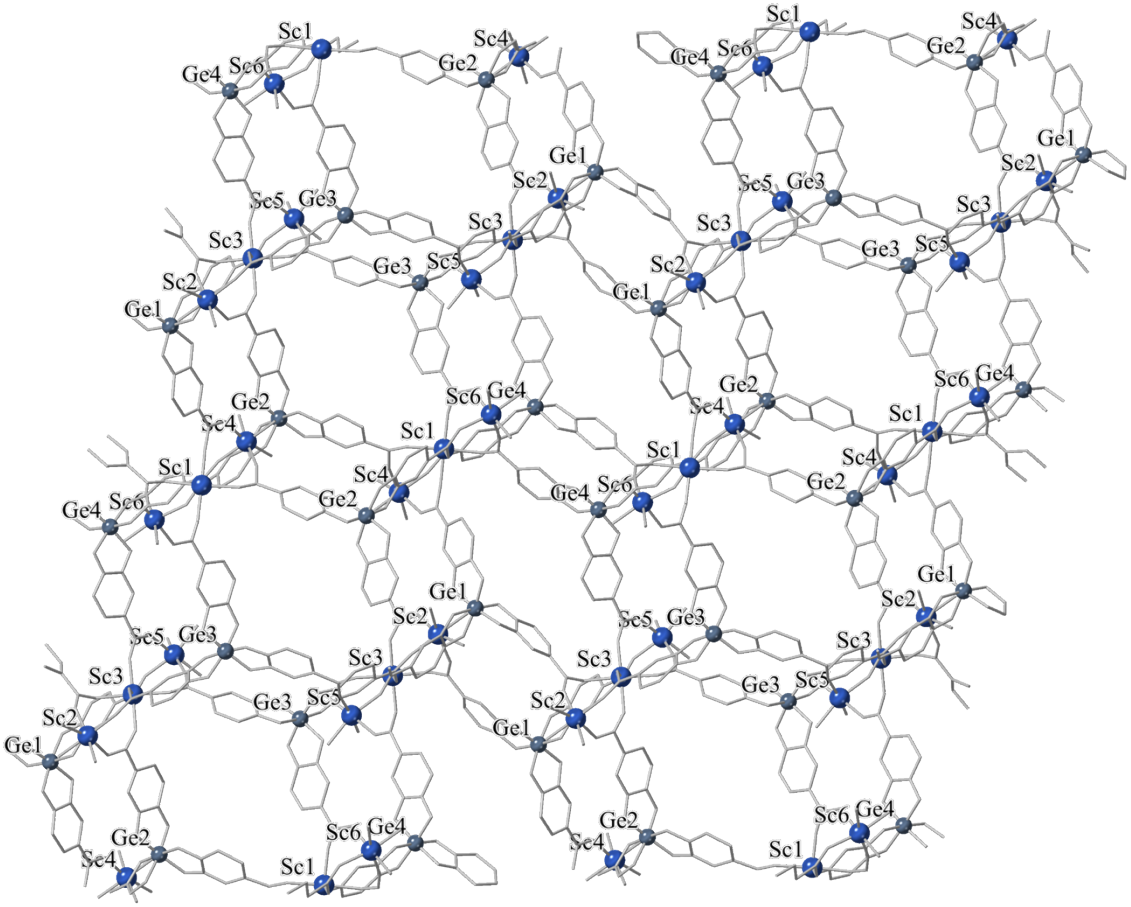

Figure S17 Packing structure of **IMP-33-Sc** showing two types of SBU (Sc1, Sc4, Sc6 and Sc2, Sc3, Sc5), ammonium cations and H atoms are not shown for clarity.

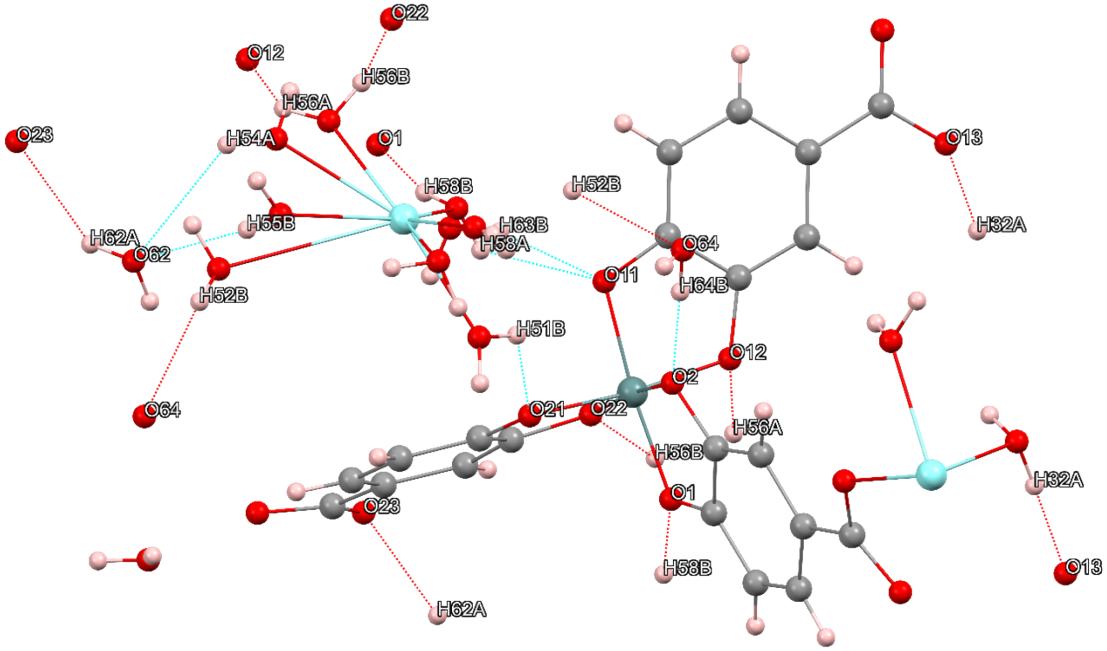

Figure S18 H-bonding interactions in **IMP-34-Y** (red and blue dotted lines).

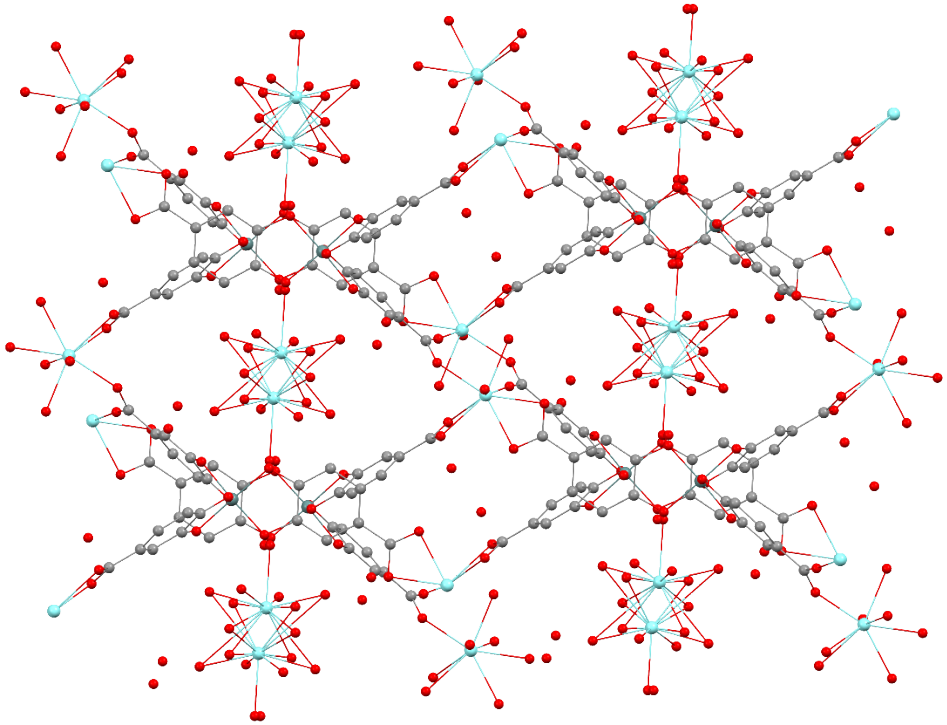

Figure S19 Packing diagram of **IMP-34-Y** (0 1 0), with molecules occupying void space. H atoms are omitted for clarity.

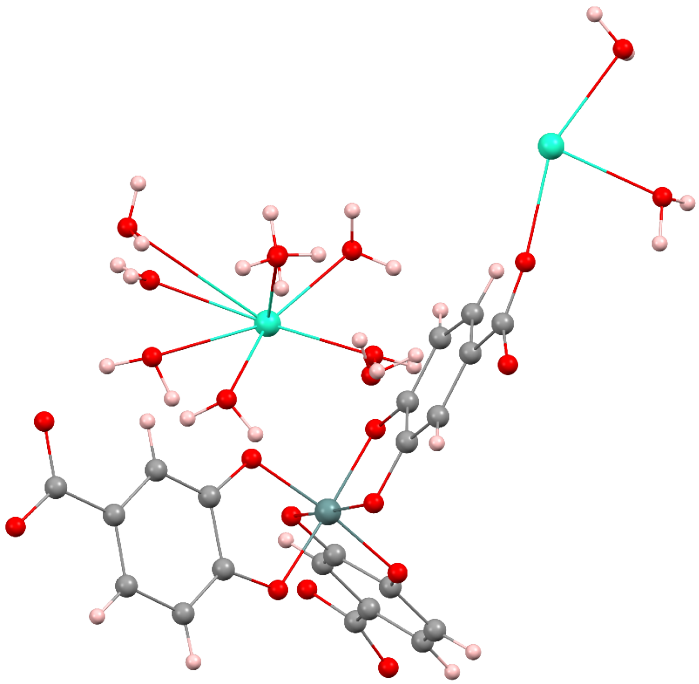

Figure S20 Crystal structure of **IMP-34-Dy** (asymmetric unit).

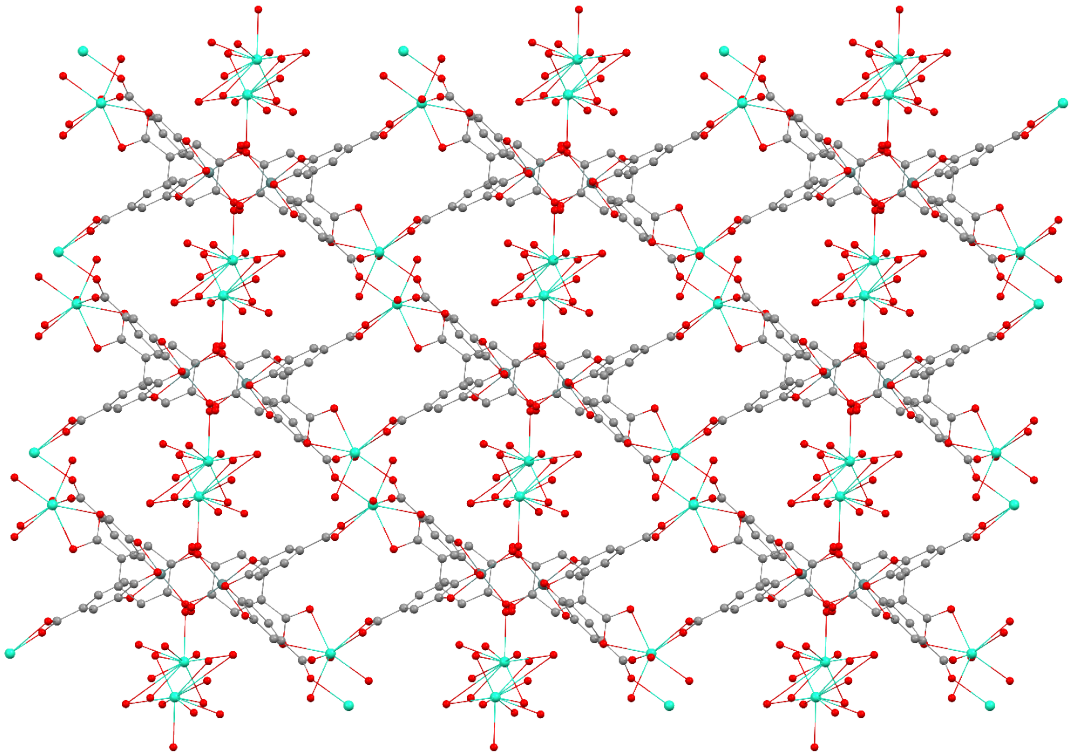

Figure S21 Packing diagram of **IMP-34-Dy**.

Notes on the X-ray crystal structure of $[Et_3NH]_2[H_3L\text{-}Si]$

Crystal data for **$[Et_3NH]_2[H_3L\text{-}Si]$**: $[C_{21}H_{12}O_{12}Si](C_6H_{16}N)_2\cdot 3(C_3H_7NO)$, M = 908.08, triclinic, P-1 (no. 2), a = 9.8788(4), b = 14.7468(7), c = 16.5789(8) Å, α = 95.373(4), β = 90.577(4), γ = 97.219(4)°, V = 2384.97(19) Å^3, Z = 2, D_c = 1.265 g cm^{-3}, μ(Mo-Kα) = 0.119 mm^{-1}, T = 173 K, colourless tablets, Agilent Xcalibur 3 E diffractometer; 9373 independent measured reflections (R_{int} = 0.0308), F^2 refinement,[2-4] R_1(obs) = 0.01042, wR_2(all) = 0.3578, 4837 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, completeness to $\theta_{full}(25.2°)$ = 98.5%], 505 parameters.

The $-C_6H_3CO_2H$ portion of the O21-based dihydroxybenzoate moiety, and the whole of both the N70- and N80-based triethylammonium cations were all found to be disordered, and in each case two orientations were identified of *ca*. 64:36, 69:31 and 66:34% occupancy respectively. The geometries of each pair of orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientations were refined anisotropically (those of the minor occupancy orientations were refined isotropically). The presumed O–H hydrogen atoms of the C9-, C29- and C59-based carboxylate groups, and the presumed N–H hydrogen atoms of the two disordered triethylammonium cations, could not be located. Whilst the latter were placed in idealised positions with an N–H distance of 0.90 Å, the former were omitted, making the atom list for the asymmetric unit low by 3H. The included solvent was found to be highly disordered, and the best approach to handling this diffuse electron density was found to be the SQUEEZE routine of PLATON.[5] This suggested a total of 229 electrons per unit cell, equivalent to 114.5 electrons per asymmetric unit. Before the use of SQUEEZE the solvent clearly resembled dimethylformamide (C_3H_7NO, 40 electrons) distributed over three sites, and three dimethylformamide molecules corresponds to 120 electrons, so this was used as the solvent present. As a result, the atom list for the asymmetric unit is low by $3(C_3H_7NO) + 3H = C_9H_{24}N_3O_3$ (and that for the unit cell low by $C_{18}H_{48}N_6O_6$) compared to what is actually presumed to be present. All this disorder (which amounts to *ca*. 62% of the total electrons in the structure) has a marked impact on the intensity distribution of the data set, with the drop off at higher angles being significantly steeper than would otherwise be expected to be the case, as can be seen from the mean $F^2/\sigma(F^2)$ column of Table S1 below.

Table S1. Statistics vs resolution (taking redundancy into account) - point group symmetry: P-1.

resolution	# kept	# theory	# unique	% complete	average redundancy	mean F2	mean F2/sig(F2)	Rint	RsigmaB
inf-1.74	2617	945	939	99.4	2.8	42668.13	52.87	0.026	0.011
1.74-1.38	1933	943	939	99.6	2.1	9257.88	17.31	0.028	0.037
1.38-1.21	1631	943	939	99.6	1.7	4559.36	9.34	0.050	0.063
1.21-1.10	1428	940	939	99.9	1.5	3941.75	7.50	0.067	0.077
1.10-1.02	1218	940	939	99.9	1.3	1910.68	3.84	0.107	0.150
1.02-0.96	1127	942	939	99.7	1.2	1090.37	2.27	0.213	0.269
0.96-0.91	1060	947	939	99.2	1.1	726.51	1.55	0.268	0.373
0.91-0.87	1003	956	939	98.2	1.1	560.57	1.20	0.306	0.392
0.87-0.84	975	997	939	94.2	1.0	456.22	0.93	0.262	0.333
0.84-0.75	979	3250	947	29.1	1.0	355.01	0.73	0.365	0.465
inf-0.75	13971	11803	9398	79.6	1.5	10615.12	14.99	0.030	0.024
inf-0.84	12886	8435	8348	99.0	1.5	11479.50	16.19	0.030	0.024

Notes on the X-ray crystal structure of IMP-33-Sc

The structure was solved as an inversion twin (Flack parameter: 0.499(8)). Attempts at solving in higher symmetry space groups failed and nothing was suggested using ADDSYM in PLATON.[5] Various restraints (DFIX, SADI, RIGU and SIMU) were employed based on the assumption that like molecules within the sub-structure would be expected to have near identical geometries. There were also some highly disordered solvent cavities for which a solvent mask was calculated and 908 electrons were found in a volume of 3887Å^3 in 1 void per unit cell. This is consistent with the presence of 6[C_2H_3N], 9[H_2O] per asymmetric unit which account for 888 electrons per unit cell.

Notes on the X-ray crystal structure of IMP-34-Y

The crystal used was a non-merohedral twin (180° rotation about the reciprocal axis 0 0 1) with ratio 52:48. The overall structure as currently presented does not charge balance, at -0.5 for the asymmetric unit, with the required +0.5 charge assumed to come from a disordered Et_3NH cation mixed in with the solvent water. It was just not possible to locate this disordered cation in the cavities, along with highly disordered solvent, that was assumed to be water (8 per asymmetric unit). For this the SQUEEZE program within PLATON was used,[5] which suggested a solvent accessible volume of 3107Å^3, accounting for 934 electrons per unit cell (117 electrons per asymmetric unit, with 8 water and ½ Et_3NH = 110). Finally, the disordered hydrated Y cation lies just slightly off-set over a symmetry site, requiring the use of various restraints (SADI, BUMP, RIGU, SIMU) but was finally held as a rigid body.

Notes on the X-ray crystal structure of IMP-34-Dy

The crystal used was a non-merohedral twin (180° rotation about the reciprocal axis 0 0 1) with ratio 54:46. The overall structure as currently presented does not charge balance, at -0.5 for the asymmetric unit, with the required +0.5 charge assumed to come from a disordered Et_3NH cation mixed in with the solvent water. It was just not possible to locate this disordered cation in the cavities, along with highly disordered solvent, that was assumed to be water (9 per asymmetric unit). For this the SQUEEZE program within PLATON was used,[5] which suggested a solvent accessible volume of 3448Å^3, accounting for 980 electrons per unit cell (123 electrons per asymmetric unit, with 9 water and ½ Et_3NH = 120). Finally, the disordered hydrated Dy cation lies just slightly off-set over a symmetry site, requiring the use of various restraints (DELU, SIMU) but was finally held as a rigid body.

Table S2 Crystallography data

Compound	$[Et_3NH]_2[H_3L\text{-}Si]$	IMP-33-Sc	IMP-34-Y	IMP-34-Dy
CCDC	2331262	2348717	2348718	2348719
Formula	$[C_{21}H_{12}O_{12}Si](C_6H_{16}N)_2$ $3(C_3H_7NO)$	$C_{42}H_{30}Ge_2O_{30}Sc_3$, $C_6H_{16}N$, $6(C_2H_3N)$, $9(H_2O)$	$C_{42}H_{26}Ge_2O_{28}Y_2$, $5(H_2O)$, $H_{16}O_8Y$	$C_{42}H_{26}Ge_2O_{28}Dy_2$, $H_{16}O_8Dy$, H_2O
Formula weight	908.08	1805.38	1624.74	1773.45
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P-1	$P2_1$	C2/c	C2/c
a / Å	9.8788(4)	25.1090(8)	19.9205(2)	19.5343(3)
b / Å	14.7468(7)	13.1102(2)	14.33510(10)	14.22670(10)
c / Å	16.5789(8)	27.1137(6)	30.7566(2)	30.9853(3)
α / deg	95.373(4)	90	90	90
β / deg	90.577(4)	107.410(3)	97.0890(10)	96.9100(10)
γ / deg	97.219(4)	90	90	90
V / Å^3	2384.97(19)	8516.5(4)	8715.79(12)	8548.53(17)
Z	2	4	4	4
$D_{calc.}$ mg/mm^3	1.265	1.408	1.238	1.378
Radiation used	Mo K_α	Mo K_a	Cu K_a	Cu K_a
Temperature / K	173(2)	100(2)	100(2)	100(2)
Absorption coefficient /mm^{-1}	0.119	1.014	4.018	15.185
θ range / deg	2.353 to 28.269	2.076 to 28.701	2.896 to 68.273	2.873 to 70.051
No. of unique reflections	13899	43773	27185	13640
R_1(obs), $_wR_2$(all)	0.1042, 0.3578	0.0683, 0.1823	0.0658, 0.1842	0.0558, 0.1511

Table S3. Selected bond lengths and angles for **IMP-33-Sc**

Atom	Atom	Length/Å
Ge1	O3	1.829(5)
Ge1	O4	1.915(5)
Ge1	O13	1.900(5)
Ge1	O14	1.817(5)
Ge1	O23	1.960(5)
Ge1	O24	1.850(5)
Ge2	O33	1.762(5)
Ge2	O34	1.951(6)
Ge2	O43	1.913(5)
Ge2	O44	1.807(7)
Ge2	O53	1.847(6)
Ge2	O54	1.981(6)
Ge3	O63	1.931(5)
Ge3	O64	1.787(5)
Ge3	O73	1.812(5)
Ge3	O74	2.032(5)
Ge3	O83	1.812(5)
Ge3	O84	1.952(5)
Ge4	O93	1.912(5)
Ge4	O94	1.857(5)
Ge4	O103	1.926(5)
Ge4	O104	1.736(5)
Ge4	O113	1.874(5)
Ge4	O114	1.974(5)
Sc1	O1	1.947(6)
Sc1	O32	2.130(5)
Sc1	O51[1]	2.128(7)
Sc1	O61	2.066(6)
Sc1	O92	2.006(5)
Sc1	O101[2]	2.108(5)
Sc2	O12	2.035(5)
Sc2	O42[3]	2.030(5)
Sc2	O81[2]	2.067(6)
Sc2	O151	2.199(5)
Sc2	O152	2.132(6)
Sc2	O153	2.169(6)
Sc3	O11[4]	2.097(5)
Sc3	O22	1.991(5)
Sc3	O41	2.075(6)
Sc3	O71[5]	2.057(5)
Sc3	O82[6]	2.127(5)
Sc3	O111[6]	2.054(5)
Sc4	O2[5]	2.081(5)
Sc4	O52	2.077(6)
Sc4	O91[5]	2.058(5)
Sc4	O154	2.050(6)
Sc4	O155	2.117(6)
Sc4	O156	2.091(5)
Sc5	O21[1]	2.058(5)
Sc5	O72	2.082(5)
Sc5	O112[7]	2.077(5)
Sc5	O157	2.078(5)
Sc5	O158	2.116(5)
Sc5	O159	2.127(6)
Sc6	O31[8]	2.090(6)
Sc6	O62[8]	2.044(6)
Sc6	O102	1.999(5)
Sc6	O160	2.118(5)
Sc6	O161	2.083(6)
Sc6	O162	2.172(5)

[1]1-x,1/2+y,-z; [2]1-x,-1/2+y,1-z; [3]2-x,1/2+y,1-z; [4]2-x,-1/2+y,1-z; [5]1-x,-1/2+y,-z; [6]1+x,-1+y,+z; [7]-x,-1/2+y,-z; [8]1-x,1/2+y,1-z

Atom	Atom	Atom	Angle/°
O3	Ge1	O4	86.3(2)
O3	Ge1	O13	174.9(2)
O3	Ge1	O23	93.6(2)
O3	Ge1	O24	90.7(2)
O4	Ge1	O23	85.9(2)
O13	Ge1	O4	88.8(2)
O13	Ge1	O23	87.3(2)
O14	Ge1	O3	91.9(2)
O14	Ge1	O4	95.2(2)
O14	Ge1	O13	87.3(2)
O14	Ge1	O23	174.4(2)
O14	Ge1	O24	93.3(2)
O24	Ge1	O4	171.1(2)
O24	Ge1	O13	94.4(2)
O24	Ge1	O23	86.0(2)
O33	Ge2	O34	87.8(3)
O33	Ge2	O43	98.7(3)
O33	Ge2	O44	93.9(3)
O33	Ge2	O53	94.2(3)
O33	Ge2	O54	174.4(3)
O34	Ge2	O54	86.8(3)
O43	Ge2	O34	84.5(2)
O43	Ge2	O54	79.5(2)
O44	Ge2	O34	170.6(2)
O44	Ge2	O43	86.1(3)
O44	Ge2	O53	98.0(3)
O44	Ge2	O54	91.3(3)
O53	Ge2	O34	91.1(3)
O53	Ge2	O43	166.1(3)
O53	Ge2	O54	87.1(3)
O63	Ge3	O74	85.1(2)
O63	Ge3	O84	85.0(2)
O64	Ge3	O63	85.8(2)
O64	Ge3	O73	93.9(2)
O64	Ge3	O74	92.5(2)
O64	Ge3	O83	95.5(2)
O64	Ge3	O84	170.7(2)
O73	Ge3	O63	168.9(2)

Atom	Atom	Atom	Angle/°
O73	Ge3	O74	83.9(2)
O73	Ge3	O84	95.4(2)
O83	Ge3	O63	93.6(2)
O83	Ge3	O73	97.4(2)
O83	Ge3	O74	171.8(2)
O83	Ge3	O84	83.8(2)
O84	Ge3	O74	88.1(2)
O93	Ge4	O103	87.3(2)
O93	Ge4	O114	86.9(2)
O94	Ge4	O93	85.4(2)
O94	Ge4	O103	94.2(2)
O94	Ge4	O113	92.8(2)
O94	Ge4	O114	172.3(2)
O103	Ge4	O114	86.2(2)
O104	Ge4	O93	173.3(2)
O104	Ge4	O94	96.1(2)
O104	Ge4	O103	86.0(2)
O104	Ge4	O113	94.3(2)
O104	Ge4	O114	91.6(2)
O113	Ge4	O93	92.2(2)
O113	Ge4	O103	172.9(2)
O113	Ge4	O114	86.7(2)
O1	Sc1	O32	87.0(2)
O1	Sc1	O51[1]	89.7(3)
O1	Sc1	O61	175.0(2)
O1	Sc1	O92	89.6(2)
O1	Sc1	O101[2]	87.6(2)
O51[1]	Sc1	O32	87.0(2)
O61	Sc1	O32	88.0(2)
O61	Sc1	O51[1]	90.6(3)
O61	Sc1	O101[2]	92.1(2)
O92	Sc1	O32	176.3(2)
O92	Sc1	O51[1]	91.4(2)
O92	Sc1	O61	95.4(2)
O92	Sc1	O101[2]	89.1(2)
O101[2]	Sc1	O32	92.3(2)
O101[2]	Sc1	O51[1]	177.2(3)
O12	Sc2	O81[2]	91.3(2)
O12	Sc2	O151	87.7(2)
O12	Sc2	O152	88.1(2)
O12	Sc2	O153	167.2(2)
O42[3]	Sc2	O12	103.4(2)
O42[3]	Sc2	O81[2]	96.9(2)
O42[3]	Sc2	O151	164.1(2)
O42[3]	Sc2	O152	84.9(2)
O42[3]	Sc2	O153	89.4(2)
O81[2]	Sc2	O151	94.2(2)
O81[2]	Sc2	O152	178.2(3)
O81[2]	Sc2	O153	88.5(2)
O152	Sc2	O151	84.1(2)
O152	Sc2	O153	91.7(2)
O153	Sc2	O151	79.5(2)
O11[4]	Sc3	O82[5]	90.33(19)
O22	Sc3	O11[4]	88.9(2)
O22	Sc3	O41	92.7(2)
O22	Sc3	O71[6]	92.8(2)
O22	Sc3	O82[5]	176.0(2)
O22	Sc3	O111[5]	92.1(2)
O41	Sc3	O11[4]	90.1(2)
O41	Sc3	O82[5]	83.4(2)
O71[6]	Sc3	O11[4]	176.6(2)
O71[6]	Sc3	O41	86.9(2)
O71[6]	Sc3	O82[5]	87.7(2)
O111[5]	Sc3	O11[4]	89.3(2)
O111[5]	Sc3	O41	175.2(2)
O111[5]	Sc3	O71[6]	93.6(2)
O111[5]	Sc3	O82[5]	91.8(2)
O2[6]	Sc4	O155	85.5(3)
O2[6]	Sc4	O156	84.7(2)
O52	Sc4	O2[6]	95.2(2)
O52	Sc4	O155	83.4(2)
O52	Sc4	O156	174.9(2)
O91[6]	Sc4	O2[6]	92.6(2)
O91[6]	Sc4	O52	95.4(2)
O91[6]	Sc4	O155	177.7(2)
O91[6]	Sc4	O156	89.7(2)
O154	Sc4	O2[6]	169.7(3)
O154	Sc4	O52	90.0(2)
O154	Sc4	O91[6]	95.7(3)
O154	Sc4	O155	86.3(3)
O154	Sc4	O156	89.2(2)
O156	Sc4	O155	91.5(2)
O21[1]	Sc5	O72	98.7(2)
O21[1]	Sc5	O112[7]	86.8(2)
O21[1]	Sc5	O157	97.9(2)
O21[1]	Sc5	O158	83.7(2)
O21[1]	Sc5	O159	164.8(2)
O72	Sc5	O158	170.0(2)
O72	Sc5	O159	93.1(2)
O112[7]	Sc5	O72	90.1(2)
O112[7]	Sc5	O157	170.1(2)
O112[7]	Sc5	O158	99.8(2)
O112[7]	Sc5	O159	83.7(2)
O157	Sc5	O72	80.6(2)
O157	Sc5	O158	89.4(2)
O157	Sc5	O159	93.4(2)
O158	Sc5	O159	86.3(2)
O31[8]	Sc6	O160	88.9(2)
O31[8]	Sc6	O162	84.6(2)
O62[8]	Sc6	O31[8]	91.2(3)
O62[8]	Sc6	O160	175.9(2)
O62[8]	Sc6	O161	84.2(2)
O62[8]	Sc6	O162	88.1(2)
O102	Sc6	O31[8]	101.4(3)
O102	Sc6	O62[8]	99.1(2)
O102	Sc6	O160	84.8(2)
O102	Sc6	O161	89.6(2)
O102	Sc6	O162	170.4(2)
O160	Sc6	O162	87.9(2)
O161	Sc6	O31[8]	168.6(3)
O161	Sc6	O160	94.9(2)
O161	Sc6	O162	84.8(2)

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[1]1-x,1/2+y,-z; [2]1-x,-1/2+y,1-z; [3]2-x,1/2+y,1-z; [4]2-x,-1/2+y,1-z; [5]1+x,-1+y,+z; [6]1-x,-1/2+y,-z; [7]-x,-1/2+y,-z; [8]1-x,1/2+y,1-z; [9]-1+x,1+y,+z; [10]-x,1/2+y,-z

Table S4. Selected bond lengths and angles for **IMP-34-Y**

Atom	Atom	Length/Å
Y1	O3	2.313(4)
Y1	O4[1]	2.258(4)
Y1	O13[2]	2.375(4)
Y1	O14[2]	2.446(4)
Y1	O23[3]	2.415(4)
Y1	O24[3]	2.378(4)
Y1	O31	2.352(4)
Y1	O32	2.359(4)
Ge1	O1	1.891(4)
Ge1	O2	1.888(4)
Ge1	O11	1.905(4)
Ge1	O12	1.875(5)

Atom	Atom	Length/Å
Ge1	O21	1.884(4)
Ge1	O22	1.880(4)
Y5	O56	2.3296
Y5	O51	2.3376
Y5	O52	2.3621
Y5	O53	2.3866
Y5	O57	2.3874
Y5	O55	2.4018
Y5	O54	2.4152
Y5	O58	2.4447

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[1]1-x,1-y,1-z; [2]1/2+x,1/2+y,+z; [3]1/2+x,1/2-y,1/2+z

Atom	Atom	Atom	Angle/˚
O3	Y1	O13[1]	81.66(15)
O3	Y1	O14[1]	73.96(15)
O3	Y1	O23[2]	143.09(16)
O3	Y1	O24[2]	146.92(16)
O3	Y1	O31	75.52(16)
O3	Y1	O32	78.20(16)
O4[3]	Y1	O3	115.03(15)
O4[3]	Y1	O13[1]	75.06(14)
O4[3]	Y1	O14[1]	127.08(15)
O4[3]	Y1	O23[2]	83.45(15)
O4[3]	Y1	O24[2]	91.57(16)
O4[3]	Y1	O31	152.70(17)
O4[3]	Y1	O32	77.28(16)
O13[1]	Y1	O14[1]	53.96(13)
O13[1]	Y1	O23[2]	135.16(14)
O13[1]	Y1	O24[2]	87.09(15)
O23[2]	Y1	O14[1]	121.64(15)
O24[2]	Y1	O14[1]	74.27(14)
O24[2]	Y1	O23[2]	54.24(15)
O31	Y1	O13[1]	132.24(16)
O31	Y1	O14[1]	79.40(16)
O31	Y1	O23[2]	75.33(16)
O31	Y1	O24[2]	89.83(18)
O31	Y1	O32	80.78(17)
O32	Y1	O13[1]	134.46(15)
O32	Y1	O14[1]	149.04(15)
O32	Y1	O23[2]	75.21(16)
O32	Y1	O24[2]	129.24(16)
O1	Ge1	O11	174.04(16)
O2	Ge1	O1	86.18(16)
O2	Ge1	O11	89.66(17)
O12	Ge1	O1	89.94(19)
O12	Ge1	O2	93.0(2)
O12	Ge1	O11	86.01(17)
O12	Ge1	O21	173.65(19)
O12	Ge1	O22	90.54(19)
O21	Ge1	O1	96.0(2)

Atom	Atom	Atom	Angle/˚
O21	Ge1	O2	89.70(19)
O21	Ge1	O11	88.24(18)
O22	Ge1	O1	87.85(18)
O22	Ge1	O2	173.1(2)
O22	Ge1	O11	96.54(18)
O22	Ge1	O21	87.44(19)
O56	Y5	O51	148.1
O56	Y5	O52	108.1
O56	Y5	O53	140.3
O56	Y5	O57	76.1
O56	Y5	O55	76.5
O56	Y5	O54	69.5
O56	Y5	O58	72.8
O51	Y5	O52	77.4
O51	Y5	O53	71.3
O51	Y5	O57	83.8
O51	Y5	O55	121.1
O51	Y5	O54	136.8
O51	Y5	O58	79.1
O52	Y5	O53	77.6
O52	Y5	O57	148.9
O52	Y5	O55	137.8
O52	Y5	O54	66.6
O52	Y5	O58	73.9
O53	Y5	O57	119.4
O53	Y5	O55	74.5
O53	Y5	O54	78.1
O53	Y5	O58	142.6
O57	Y5	O55	73.3
O57	Y5	O54	138.7
O57	Y5	O58	78.4
O55	Y5	O54	77
O55	Y5	O58	142.2
O54	Y5	O58	111.2

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[1]1/2+x,1/2+y,+z; [2]1/2+x,1/2-y,1/2+z

Table S5. Selected bond lengths and angles for **IMP-34-Dy**

Atom	Atom	Length/Å
Dy1	O3[1]	2.322(5)
Dy1	O4	2.277(4)
Dy1	O13[2]	2.383(5)
Dy1	O14[2]	2.474(5)
Dy1	O23[3]	2.436(5)
Dy1	O24[3]	2.372(5)
Dy1	O31	2.378(6)
Dy1	O32	2.369(6)
Ge1	O1	1.891(4)
Ge1	O2	1.888(5)
Ge1	O11	1.896(4)
Ge1	O12	1.877(5)
Ge1	O21	1.876(5)
Ge1	O22	1.882(4)
Dy5	O53	2.3628
Dy5	O51	2.3164
Dy5	O52	2.413
Dy5	O54	2.4919
Dy5	O55	2.4291
Dy5	O56	2.4705
Dy5	O57	2.3778

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[1]1-x,1-y,1-z; [2]1/2-x,1/2-y,1-z; [3]1/2-x,1/2+y,1/2-z

Atom	Atom	Atom	Angle/˚
O3[1]	Dy1	O13[2]	82.29(19)
O3[1]	Dy1	O14[2]	73.5(2)
O3[1]	Dy1	O23[3]	143.14(19)
O3[1]	Dy1	O24[3]	145.9(2)
O3[1]	Dy1	O31	74.8(2)
O3[1]	Dy1	O32	77.5(2)
O4	Dy1	O3[1]	115.96(19)
O4	Dy1	O13[2]	75.21(17)
O4	Dy1	O14[2]	126.70(18)
O4	Dy1	O23[3]	83.20(18)
O4	Dy1	O24[3]	92.3(2)
O4	Dy1	O31	152.8(2)
O4	Dy1	O32	78.19(18)
O13[2]	Dy1	O14[2]	53.30(16)
O13[2]	Dy1	O23[3]	134.39(17)
O23[3]	Dy1	O14[2]	121.74(18)
O24[3]	Dy1	O13[2]	87.32(19)
O24[3]	Dy1	O14[2]	74.26(18)
O24[3]	Dy1	O23[3]	53.54(18)
O24[3]	Dy1	O31	88.8(2)
O31	Dy1	O13[2]	132.01(19)
O31	Dy1	O14[2]	79.7(2)
O31	Dy1	O23[3]	75.62(19)
O32	Dy1	O13[2]	134.91(18)
O32	Dy1	O14[2]	148.12(19)
O32	Dy1	O23[3]	76.21(19)
O32	Dy1	O24[3]	129.70(18)
O32	Dy1	O31	80.3(2)
O1	Ge1	O11	173.75(19)
O2	Ge1	O1	85.66(19)
O2	Ge1	O11	89.9(2)
O12	Ge1	O1	90.1(2)
O12	Ge1	O2	92.4(2)
O12	Ge1	O11	85.7(2)
O12	Ge1	O22	91.3(2)
O21	Ge1	O1	95.7(2)
O21	Ge1	O2	90.0(2)
O21	Ge1	O11	88.6(2)
O21	Ge1	O12	173.9(2)
O21	Ge1	O22	86.9(2)
O22	Ge1	O1	89.0(2)
O22	Ge1	O2	173.5(2)
O22	Ge1	O11	95.7(2)

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[1]1-x,1-y,1-z; [2]1/2-x,1/2-y,1-z; [3]1/2-x,1/2+y,1/2-z;

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