Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information for

2-isopropyl-1,3-dimethylimidazolium as a versatile structure-directing agent in the synthesis of zeolites

Huajian Yu, Alex Rojas, Zihao Rei Gao, Luis Gómez-Hortigüela, Luis A. Villaescusa, Jian Li, Jean-Louis Paillaud and Miguel A. Camblor

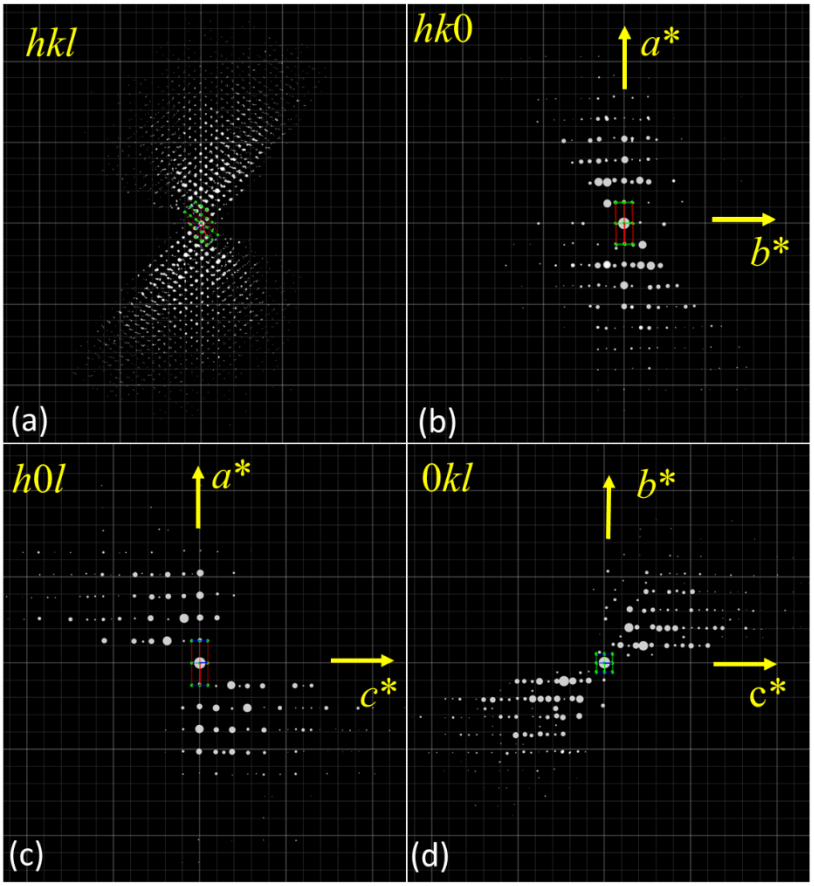

Figure S1 (a) Projection of 3D reciprocal space reconstructed from the typical cRED data of HPM-6 collected at 96K. The 2D slices of *hk*0 (b), *h*0*l* (c), and 0*kl* (d). The data indicate a *Pbcm* symmetry.

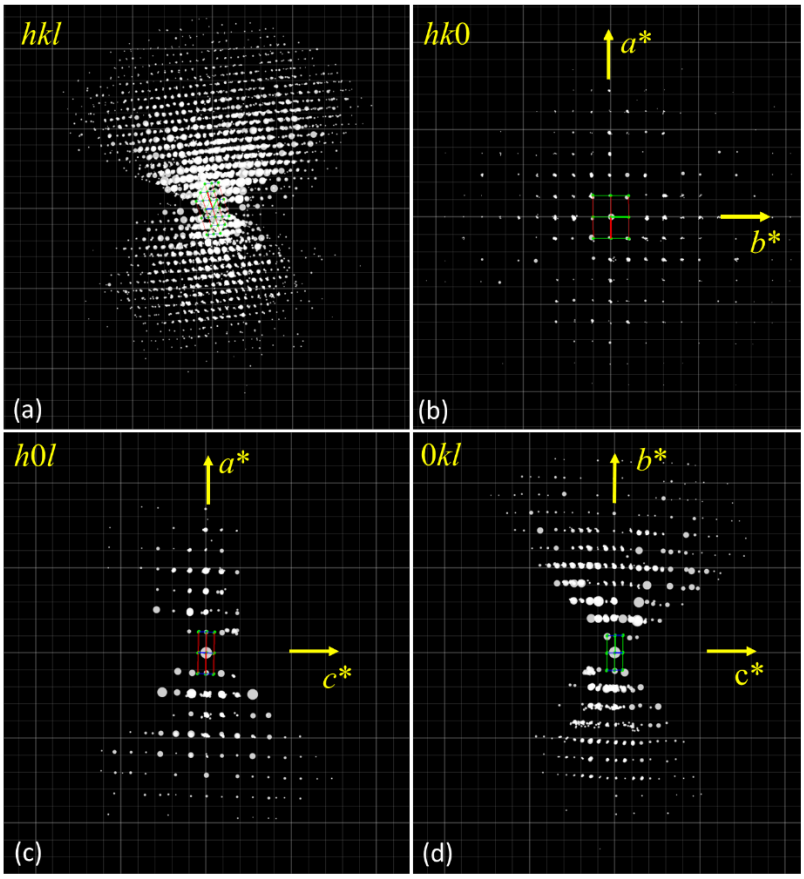

Figure S2 (a) Projection of 3D reciprocal space reconstructed from the typical cRED data of HPM-11 collected at 96K. The 2D slices of *hk*0 (b), *h*0*l* (c), and 0*kl* (d). The data indicate a *Pmcm* cell at this temperature (please note that the PXRD data collected at room temperature indicate a *Pbcm* symmetry with double *b).*

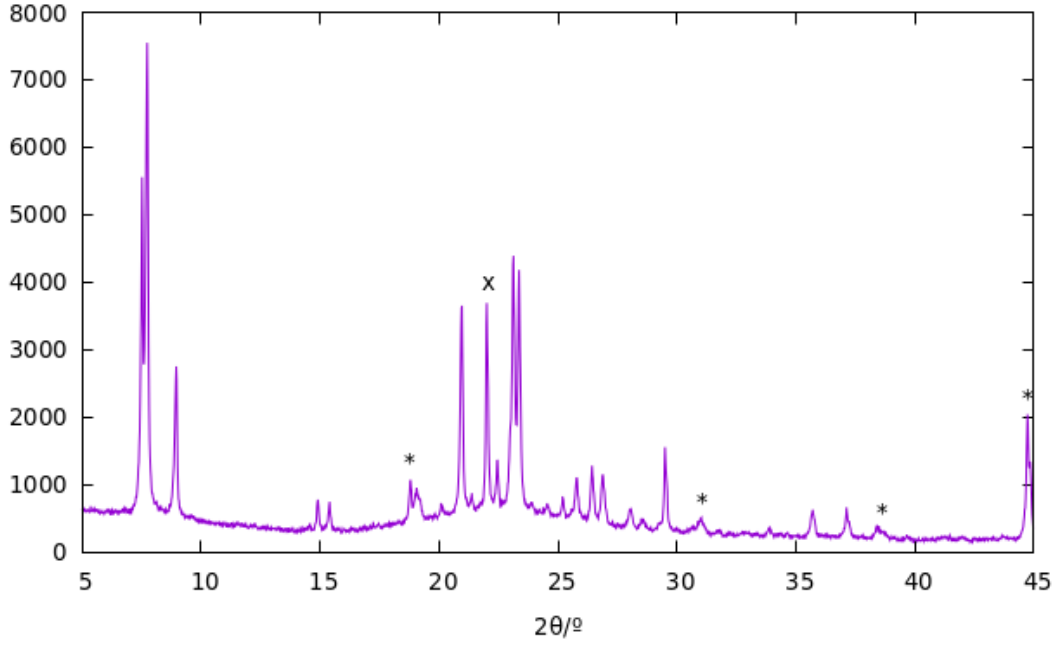

Figure S3.- PXRD pattern of the product obtained using 2iPr13DMI synthesized by method A at H_2O/SiO_2 = 6.5, consisting mainly on **MTW**, K_2SiF_6 (*) and cristobalite (x).

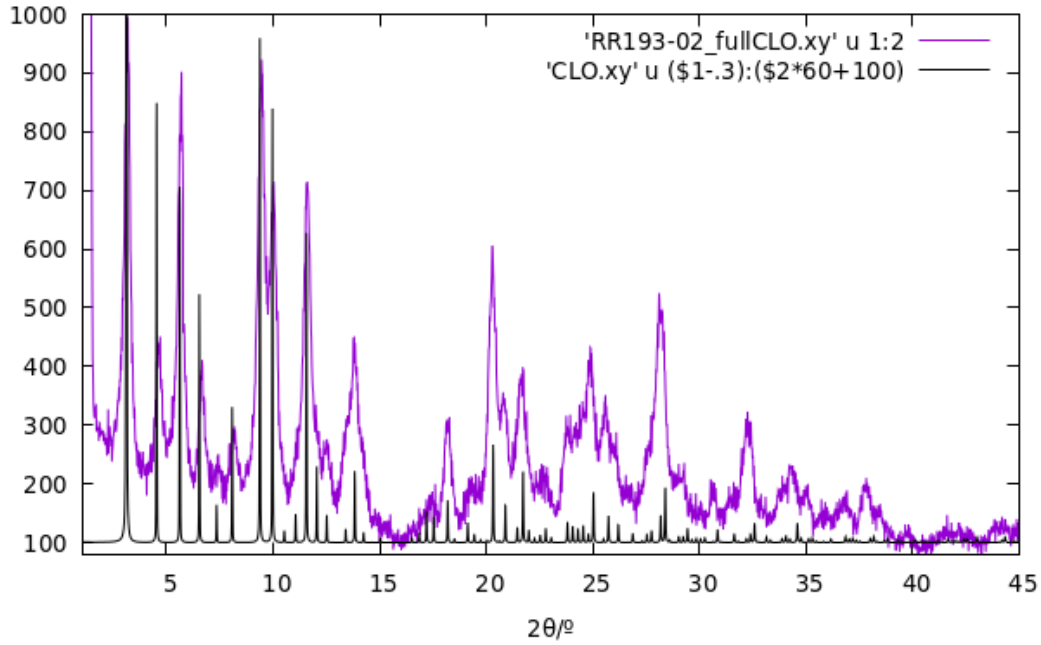

Figure S4. PXRD pattern of HPM-10 sample synthesized with 2iPr13DMI and comparison with a pattern simulated using VESTA and the **-CLO** cif file provided by the IZA-SC database.

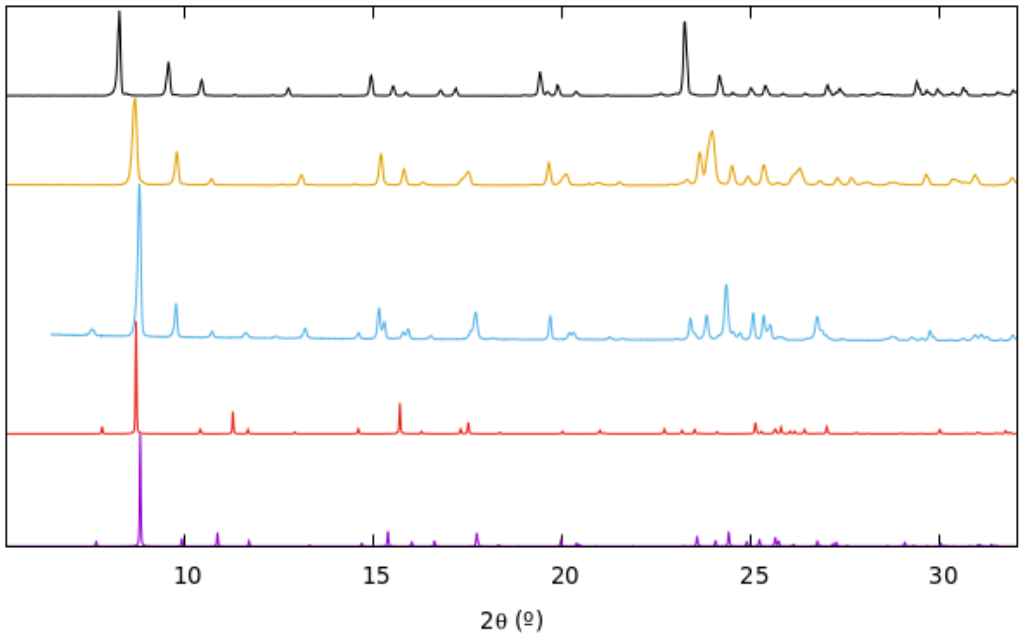

Figure S5. PXRD patterns of **UOS** and related materials (from bottom): IM-16 (**UOS** reference material) and ECNU-16 (**EOS**, UOS-related), both simulated with VESTA using the cif file from the IZA-SC database [ref. 21 in main text] and the reported structure [ref. 46 in main text], respectively, and experimental as-made IM-16 (Ge_f=0.43), HPM-11 (Ge_f= 0.66) and HPM-6 (Ge_f = 1) patterns.

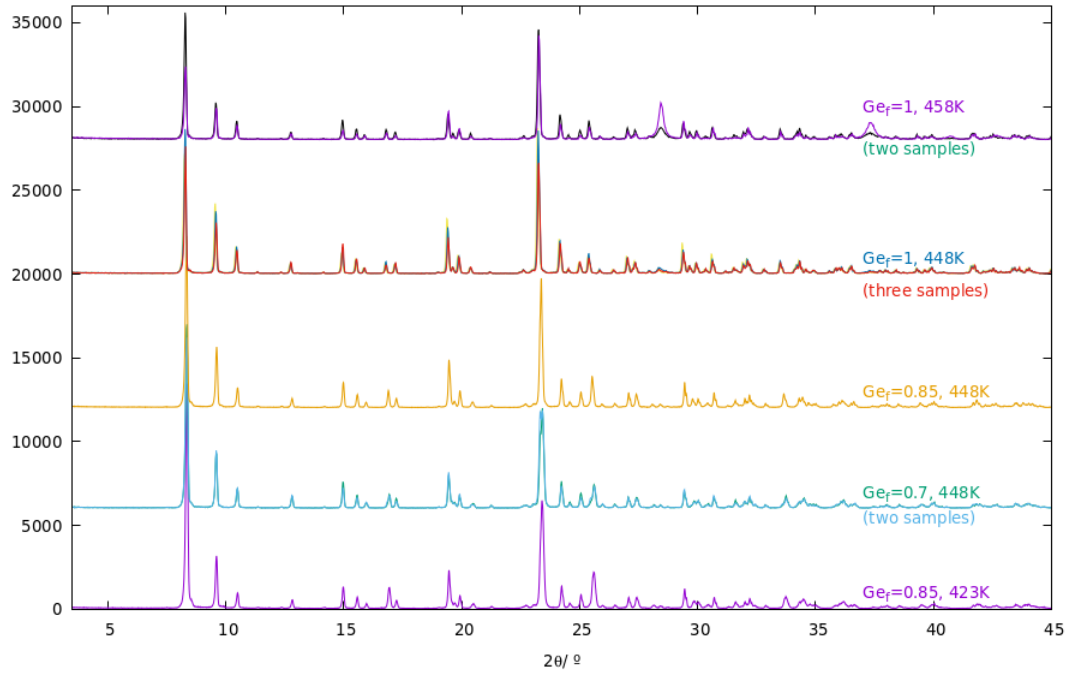

Figure S6. PXRD of **UOS** zeolite samples prepared at different Ge_f in the gel and at three different temperatures and identified as HPM-6.

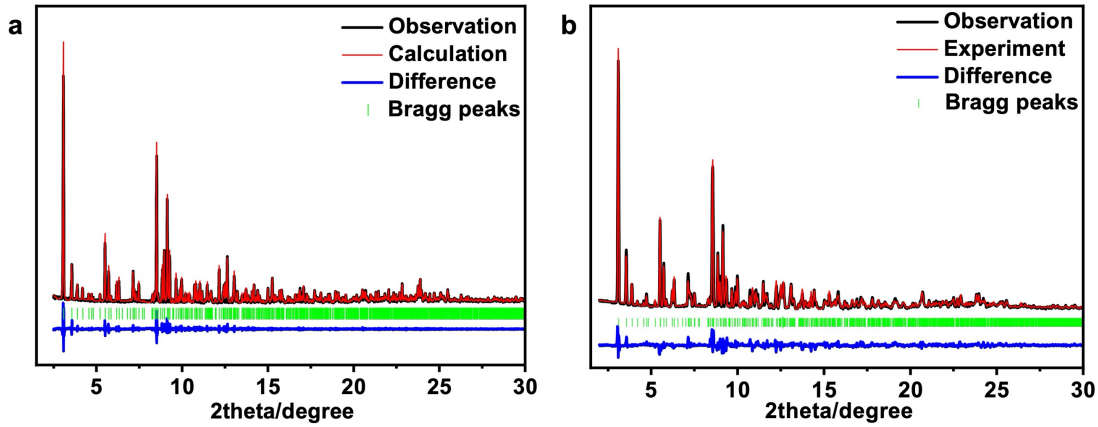

Figure S7. Rietveld refinement plots of HPM-6 (left: Ge_f=1, right: Ge_f=0.88) in space group *Pbcm*. Wavelength= 0.56383Å.

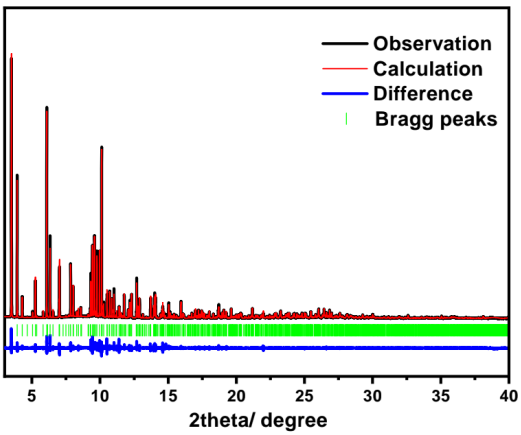

Figure S8. Rietveld refinement plots of HPM-11 (Ge_f=0.58) in space group *Pbcm*. Wavelength= 0.61928Å.

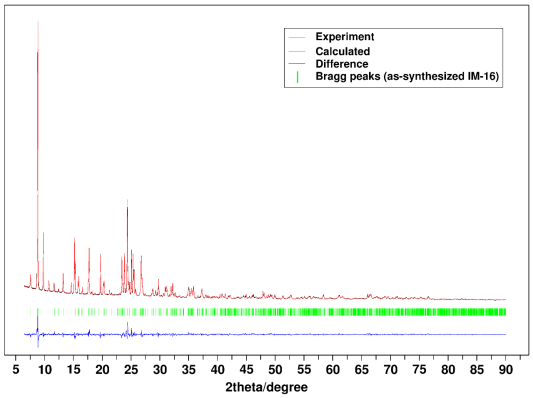

Figure S9. Rietveld refinement plots of as-made IM-16 (Ge_f=0.43) in space group $P2_1/m$. Wavelength=1.5406Å.

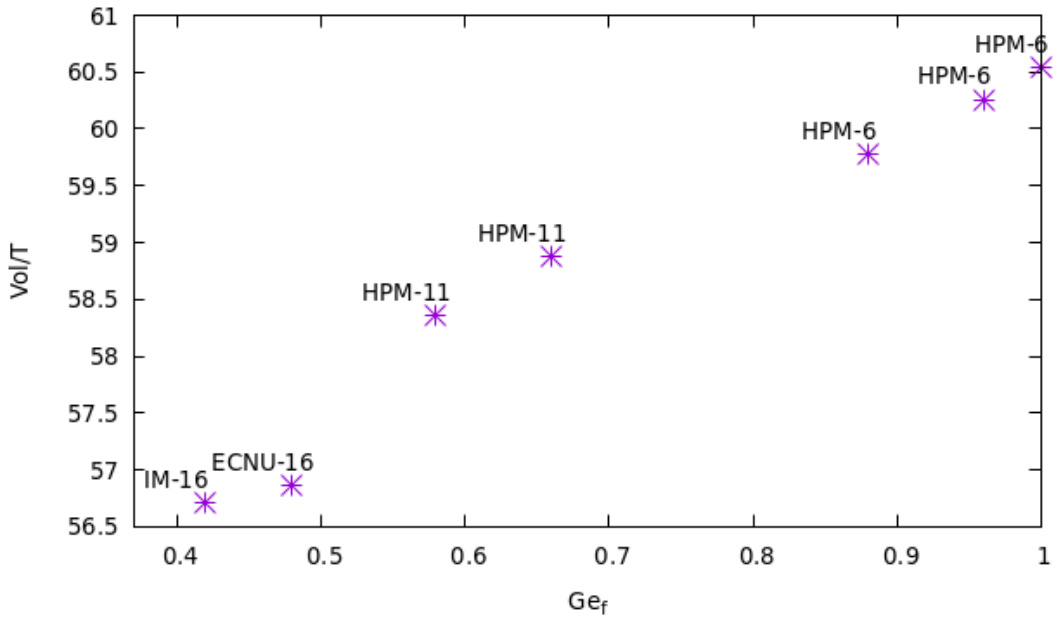

Figure S10. Variation of unit cell volume as a function of Ge_f for several **UOS** (and the related ECNU-16, **EOS**) zeolite phases. HPM-6 and HPM-11 are prepared with the same OSDA (2iPr13DMI) while IM-16 and ECNU-16 are each prepared with different ones.

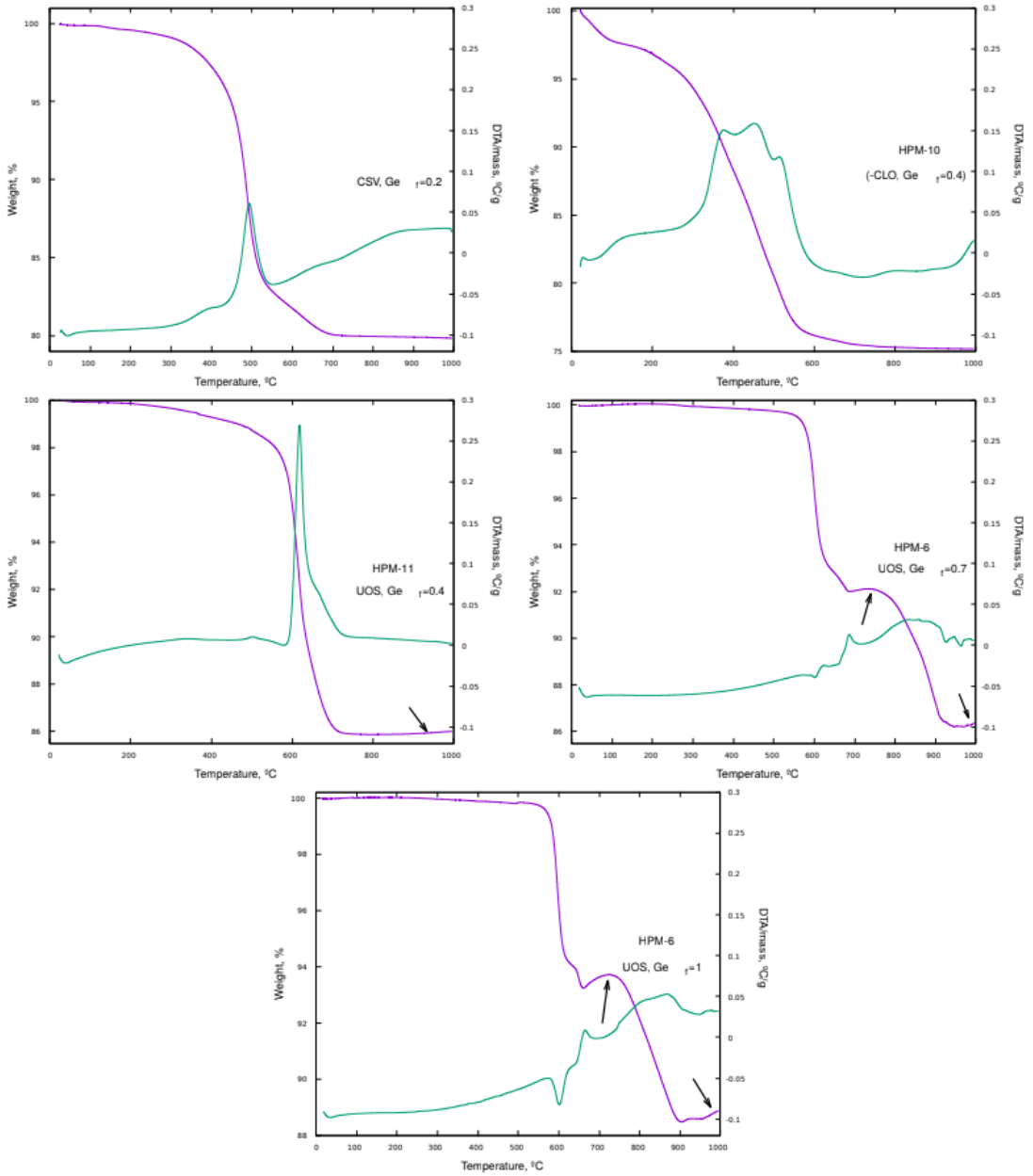

Figure S11. Thermogravimetric (purple traces) and mass normalized differential thermal analysis traces (green) of the pure germanosilicates synthesized in this work. Note the weight gaining events observed in some cases (arrows), which evidence reoxidation of previously organothermally reduced framework germanium oxide [ref. 47 in main text]. The DTA axis range is kept constant to ease comparison.

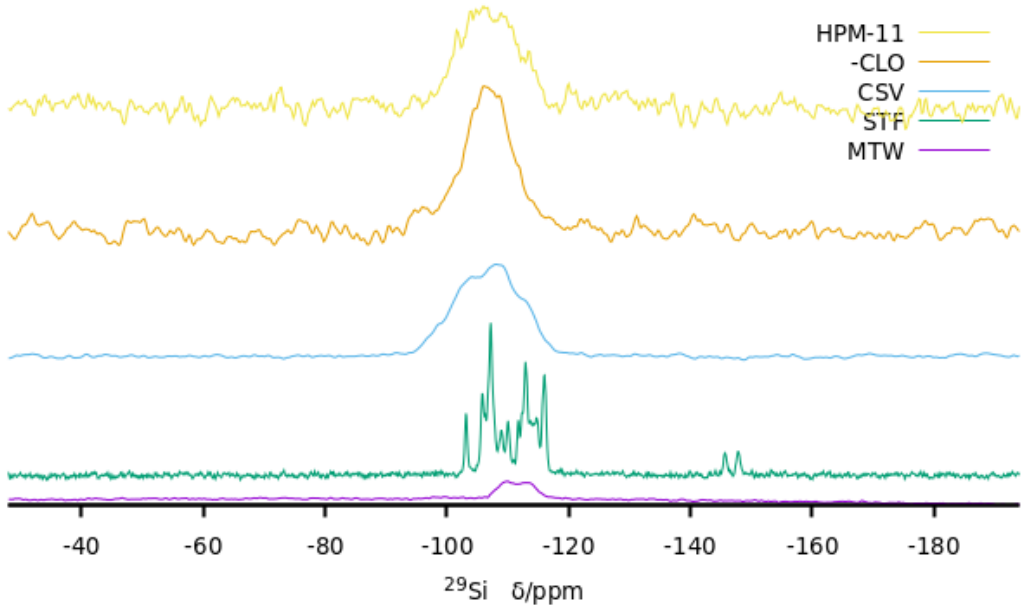

Figure S12. ^{29}Si MAS NMR of zeolites with increasing Ge_f: ZSM-12 (**MTW**), SSZ-35 (**STF**), CIT-7 (**CSV**), HPM-10 (**-CLO**) and HPM-11 (**UOS**) (from bottom).

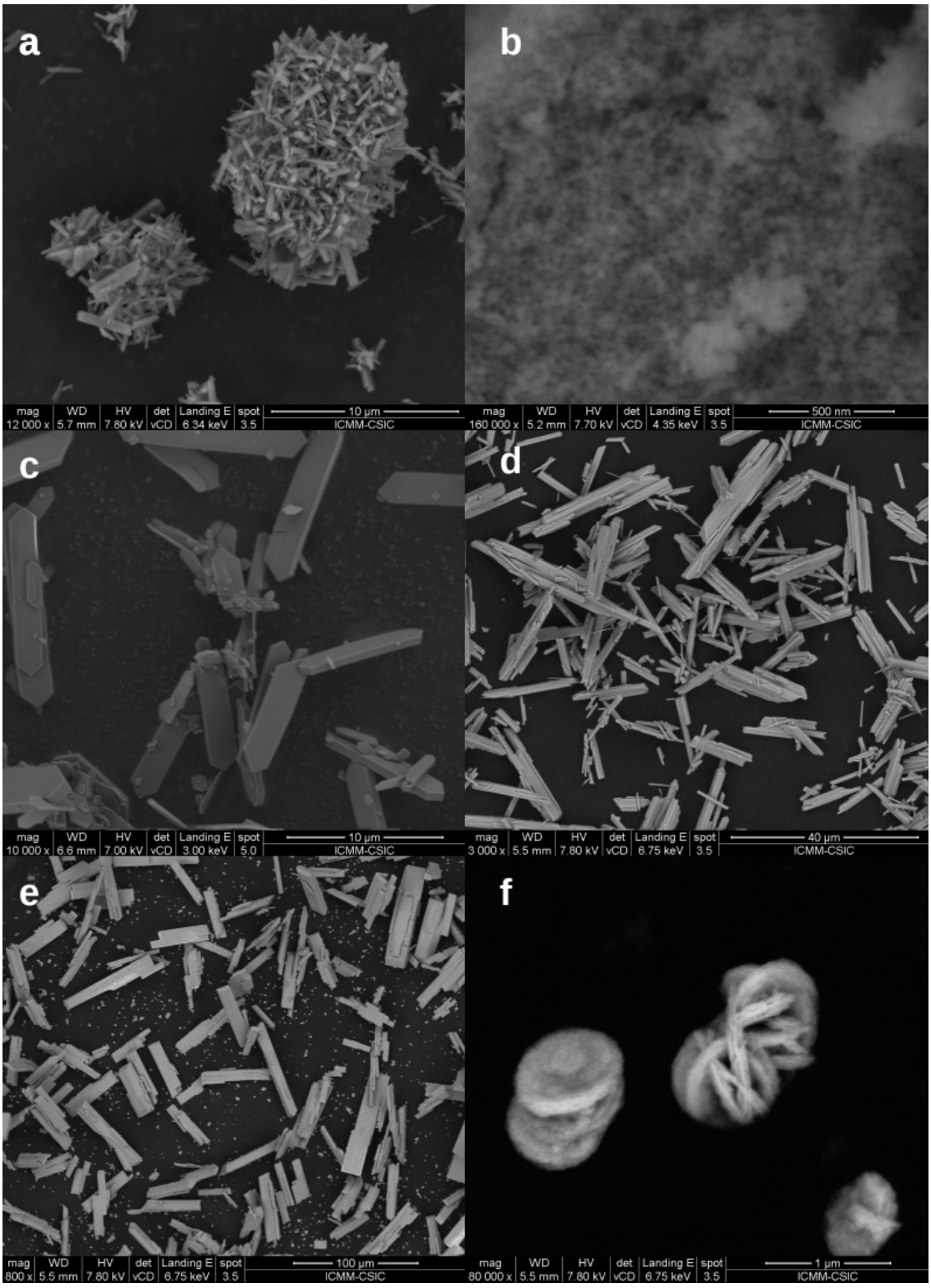

Figure S13. FESEM pictures of germanosilicates (Ge_f indicated in parenthesis, first in gel, then in solid) from top left to bottom right: CIT-7, **CSV** (0.09, 0.09); HPM-10, **-CLO** (0.4, 0.42), c) HPM-11 (**UOS**, 0.4, 0.58), d) HPM-6 (**UOS**, 0.7, 0.88), e) HPM-6 (**UOS**, 1.0, 1.0). The detail in f) corresponds to the small size impurity observed in e).

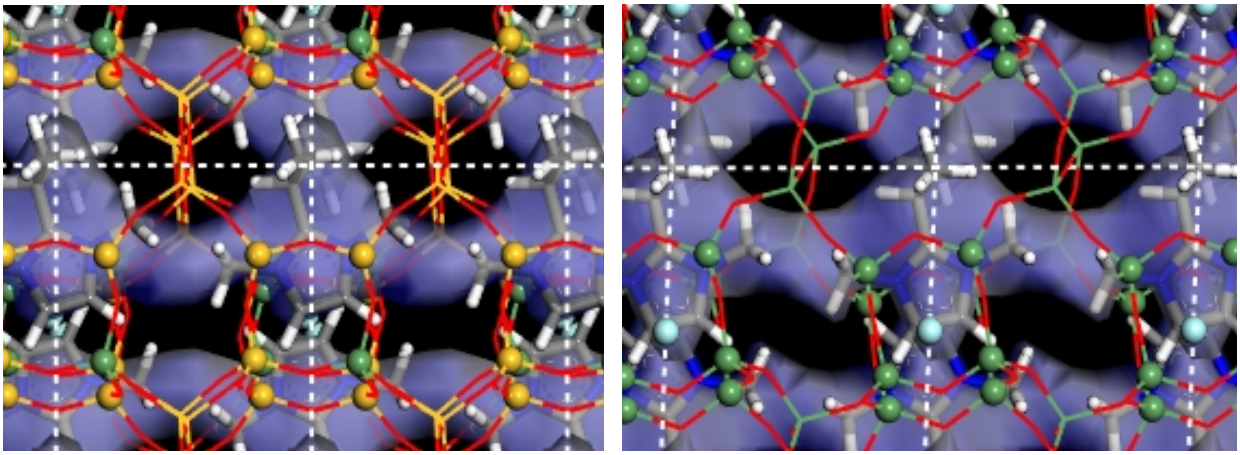

Figure S14. DFT-geometry optimized structure of 2iPr13DMI in the **UOS** frameworks for Ge_f of 0.33 (left) and 1 (right). Void volume is shown as transparent blue surface to facilitate pore visualization. Si and Ge atoms are displayed in yellow and green, respectively; atoms in the D4Rs are displayed as balls.

Table S1. CHN analysis of an OSDA synthesized by method A

%C	%H	%N	C/N	H/N	I/N[a]
35.70	5.53	10.58	3.94(4)	7.26(7.5)	0.50(0.5)

[a]Iodine content determined by difference

Table S2. Summary of zeolite synthesis results using the OSDA obtained by method A or B

Method	Ge_f	H_2O/SiO_2	Temp. (K)	Time (days)	Phase [a]
A	0	3.2	423	6	ZSM-12 (+ K_2SiF_6)
A	0	4.3	423	3	ZSM-12 + Am.
A	0	4.3	423	6	ZSM-12 (+ K_2SiF_6)
A	0	4.3	423[b]	6	ZSM-12 + Am.
A	0	6.5	423	13	ZSM-12 (+ C + K_2SiF_6)
B	0	2.9	423	3	Am.
B	0	2.9	423	5	Am.
B	0	2.9	423	12	Am. (+SSZ-35)
B	0	2.9	423	16	Am. (+SSZ-35)
B	0	2.9	423	22	SSZ-35
B	0	2.9	423	30	SSZ-35 (+ ZSM-12)
B	0	3	448	5	SSZ-35 (+T)
B	0	3	448	21	T (+SSZ-35)
B	0	3.2	448	3	SSZ-35
B	0	3.2	448	6	SSZ-35
B	0	6.7	448	6	ZSM-12 (+SSZ-35)
B	0	6.7	448	8	ZSM-12
B	0	6.7	448	9	ZSM-12
B	0.4	4	423	1	HPM-10
B	0.4	4	423	2	HPM-10
B	0.4	4	423	7	HPM-10
B	0.4	4	423	13	HPM-10
B	0.85	4	423	1	HPM-6 (+U)
B	0.85	4	423	2	HPM-6 (+U)

B	0.85	4	423	6	HPM-6
B	1	4	423	6	Q
B	0.009	4	448	1	SSZ-35
B	0.009	4	448	2	SSZ-35
B	0.009	4	448	6	SSZ-35
B	0.009	4	448	13	SSZ-35
B	0.013	4	448	1	SSZ-35
B	0.013	4	448	2	SSZ-35
B	0.013	4	448	6	SSZ-35
B	0.013	4	448	12	SSZ-35
B	0.09	4	448	1	CIT-7
B	0.09	4	448	2	CIT-7 (+U)
B	0.09	4	448	6	CIT-7
B	0.09	4	448	7	CIT-7 (+U)
B	0.1	4	448	1	CIT-7
B	0.1	4	448	2	CIT-7 (+U)
B	0.1	4	448	6	CIT-7
B	0.1	4	448	15	CIT-7
B	0.2	4	448	1	HPM-10 + Am.
B	0.2	4	448	2	CIT-7 + HPM-10
B	0.2	4	448	6	CIT-7
B	0.2	4	448	9	CIT-7 (+ HPM-1)
B	0.4	4	448	2	HPM-10 + HPM-1
B	0.4	4	448	5	HPM-10 + HPM-1
B	0.4	4	448	7	HPM-10 + HPM-1
B	0.5	4	448	1	HPM-10
B	0.5	4	448	2	HPM-10
B	0.5	4	448	6	HPM-10 + HPM-1
B	0.6	4	448	1	HPM-10
B	0.6	4	448	2	HPM-10
B	0.6	4	448	6	HPM-10 + HPM-1

B	0.6	4	448	9	HPM-10 + HPM-1 + HPM-6
B	0.7	4	448	1	HPM-6 (+ HPM-1)
B	0.7	4	448	2	HPM-6 (+ HPM-1)
B	0.7	4	448	6	HPM-6
B	0.7	4	448	15	HPM-6
B	0.85	4	448	1	HPM-6 (+ HPM-1 + HPM-10)
B	0.85	4	448	2	HPM-6
B	0.85	4	448	6	HPM-6
B	1	4	448	2	HPM-6 + Q
B	1	4	448	3	HPM-6 + Q
B	1	4	448	5	HPM-6 (+ Q)
B	1	4	448	8	HPM-6
B	1	4	448	10	HPM-6
B	1	4	448	13	HPM-6
B	0.4	4	458	10	HPM-11+CIT-7
B	0.4	4	458	12	HPM-11+CIT-7
B	0.4	4	458	13	HPM-11+CIT-7
B	0.4	4	458	17	HPM-11+CIT-7
B	0.4	4	458	1	HPM-10
B	0.4	4	458	2	HPM-10 (+ HPM-11)
B	0.4	4	458	6	HPM-10 + HPM-11
B	0.4	4	458	13	HPM-11 (+CIT-7)
B	0.5	4	458	1	HPM-10
B	0.5	4	458	2	HPM-10 + HPM-1
B	0.5	4	458	6	HPM-10 + HPM-1
B	0.6	4	458	1	HPM-10
B	0.6	4	458	2	HPM-10 + HPM-1
B	0.6	4	458	6	HPM-10 + HPM-1
B	1	4	458	5	HPM-6 (+Arg)
B	1	4	458	8	HPM-6 + Arg
B	1	4	458	11	HPM-6 +Arg (+U)

B	0.4	4	468	5	HPM-11
B	0.4	4	468	7	HPM-11 (+ Arg)
B	0.4	4	468	9	HPM-11 (+ Arg)
B	0.4	4	468	10	HPM-11 (+ Arg)
B	0.5	4	468	3	HPM-11 + HPM-10
B	0.5	4	468	5	HPM-11 + HPM-10
B	0.6	4	468	3	HPM-11
B	0.6	4	468	5	HPM-11

[a]Major phases are listed first, very minor phases appear between parentheses. Am. = amorphous, T=Tridymite, C = Cristobalite, Q =quartz-like GeO_2 , Arg=argutite-like GeO_2 , U=unknown

[b]Synthesis in static conditions.

Table S3. Rietveld refinement for HPM-6.

Ge_f	1.0	0.88
Empirical formula	$Ge_{48}O_{96}(C_8N_2H_{15})_4F_4$	$Ge_{42.17}Si_{5.83}O_{96}(C_8N_2H_{15})_4F_4$
Wavelength	0.56383Å	0.56383Å
Radiation	Synchrotron Radiation	Synchrotron Radiation
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbcm*	*Pbcm*
Unit cell dimensions	a= 7.6816(6)Å b= 18.1027(2) Å c= 20.8952(9)Å	a = 7.6604(7)Å b= 18.0784(8)Å c = 20.7216(7)Å
Volume	2905.68(1) $Å^3$	2869.73(8)$Å^3$
Z	1	1
2θ range for data refinement	1.5° < 2θ < 30°	1.5° < 2θ < 30°
Number of parameters	96	84
Number of reflections	2600	2600
Number of data points	7305	7305
Number of restrains	24 for T-O and for 49 O-T-O and T-O-T (T=Si/Ge)	24 for T-O and for 49 O-T-O and T-O-T (T=Si/Ge)
Refinement method	Rietveld refinement	Rietveld refinement
$R_p/R_{wp}/R_{exp}$/Gof	0.0778/0.1096/0.0363/1.35	0.0483/0.0666/0.0145/1.56

Table S4. T-O bond distances (Å) for HPM-6 (T=Si and Ge).

Ge_f=1				Ge_f=0.88			
T01-O08	1.6962	T04-O04	1.7037	T01-O08	1.6750	T04-O04	1.6905
T01-O03	1.7076	T04-O02	1.7004	T01-O03	1.6778	T04-O02	1.6904
T01-O06	1.7146	T04-O09	1.6923	T01-O06	1.6981	T04-O09	1.6947
T01-O09	1.6943	T04-O13	1.7150	T01-O09	1.6918	T04-O13	1.7038
T02-O01	1.7236	T05-O04	1.6907	T02-O01	1.7044	T05-O04	1.6866
T02-O05	1.7204	T05-O05	1.7118	T02-O05	1.7100	T05-O05	1.7053
T02-O07	1.7127	T05-O12	1.7446	T02-O07	1.7118	T05-O12	1.7115
T02-O06	1.7147	T05-O11	1.6939	T02-O06	1.6937	T05-O11	1.6848
T03-O01	1.7291	T06-O02	1.7043	T03-O01	1.7004	T06-O02	1.6895
T03-O10	1.6999	T06-O07	1.7161	T03-O10	1.6947	T06-O07	1.7161
T03-O11	1.6947	T06-O10	1.6959	T03-O11	1.6846	T06-O10	1.7017
T03-O08	1.6839	T06-O12	1.7403	T03-O08	1.6728	T06-O12	1.7124

Table S5. Bond angles for HPM-6 (T=Si and Ge).

Ge_f=1	Ge_f=0.88

Bond Angles (°)	Min	Max	Bond Angles (°)	Min	Max
T-O-T	131.7	151.9	T-O-T	130.6	152.8
O-T-O	107.5	111.6	O-T-O	107.5	111.6

Table S6. Rietveld refinement for HPM-11.

Empirical formula	$Ge_{24.44}Si_{23.56}O_{48}(C_8N_2H_{15})_4F_4$
Wavelength	0.61928Å
Radiation	Synchrotron Radiation
Crystal system	Orthorhombic
Space group	*Pbcm*
Unit cell dimensions	a= 7.6212(9)Å b= 18.1181 (2) Å c= 20.2859 (7)Å
Volume	2801.14(7) $Å^3$
Z	1
2θ range for data refinement	$3° < 2\theta < 40°$
Number of parameters	96
Number of reflections	2044
Number of data points	12333
Number of restrains	24 for T-O and for 49 O-T-O and T-O-T (T=Si/Ge)
Refinement method	Rietveld refinement
$R_p/R_{wp}/R_{exp}$/Gof	0.0975/0.1542/0.0316/1.87

Tab. S7. T-O bond distances (Å) for HPM-11 (T=Si or Ge).

T1-O1	1.6648	T3-O7	1.6542	T5-O9	1.6285
T1-O3	1.6721	T3-O4	1.6648	T5-O12	1.6059
T1-O11	1.6864	T3-O11	1.6667	T5-O5	1.6484
T1-O8	1.6819	T3-O5	1.6867	T5-O1	1.6142
T2-O8	1.6697	T4-O10	1.6867	T6-O13	1.6166
T2-O7	1.6593	T4-O3	1.6671	T6-O2	1.6455
T2-O10	1.6751	T4-O4	1.6638	T6-O9	1.6241
T2-O2	1.6908	T4-O6	1.6717	T6-O6	1.6208

Tab. S8. Bond angles for HPM-11 (T=Si-Ge).

Bond Angles (°)	Min	Max
T-O-T	138.2	180.0
O-T-O	106.1	111.1

Table S9. Rietveld refinement parameters for as-synthesized IM-16.

Refined chemical formula	$Ge_{10.369}Si_{13.631}O_{48}(C_{12}N_4H_{22})_2F_2$
Wavelength (CuKα_1)	1.5406 Å
Crystal system	Monoclinic
Space group	$P2_1/m$
Unit cell dimensions	a = 11.8269(2) Å b = 19.9543(2) Å c = 11.7185(3) Å β= 99.710(1) °
Volume	V = 2725.91(4) Å^3
Z	2
2θ range for data refinement	1.5° < 2θ < 90°
Number of parameters	202
Number of reflections	2295
Number of data points	9994
Number of restrains	224 (86 bonds,138 angles)
Refinement method	Rietveld refinement (GSAS2)
$R_p/R_{wp}/R_{exp}/R_F/R_F^2/Gof$	0.052/ 0.069/ 0.032/0.039/0.067/2.339

Table S10.T-O bond distances (Å) for IM-16 (T=Si or Ge).

T1-O1	1.706 (12)	T5-O8	1.622 (12)	T9-O3	1.596 (13)
T1-O2	1.660 (12)	T5-O13	1.644 (12)	T9-O14	1.636 (12)
T1-O10	1.664 (12)	T5-O16	1.647 (13)	T9-O17	1.705 (12)
T1-O15	1.676 (12)	T5-O23	1.657 (12)	T9-O25	1.658 (12)
T2-O1	1.714 (12)	T6-O10	1.668 (12)	T10-O6	1.689 (13)
T2-O6	1.696 (12)	T6-O11	1.676 (12)	T10-O18	1.612 (12)
T2-O8	1.649 (12)	T6-O17	1.713 (12)	T10-O19	1.605 (12)
T2-O9	1.641 (13)	T6-O23	1.639 (12)	T10-O24	1.613 (12)
T3-O2	1.589 (12)	T7-O7	1.630 (12)	T11-O9	1.565 (13)
T3-O3	1.560 (12)	T7-O11	1.656 (12)	T11-O20	1.611 (12)
T3-O4	1.758 (8)	T7-O12	1.647 (12)	T11-O21	1.644 (12)
T3-O5	1.644 (12)	T7-O20	1.616 (12)	T11-O22	1.743 (6)
T4-O5	1.647 (12)	T8-O12	1.652 (12)	T12-O13	1.638 (12)
T4-O7	1.639 (12)	T8-O14	1.642 (12)	T12-O21	1.638 (12)
T4-O16	1.629 (12)	T8-O15	1.701 (12)	T12-O24	1.635 (12)
T4-O19	1.618 (12)	T8-O18	1.594 (12)	T12-O25	1.678 (12)

Tab. S11. Bond angles for IM-16 (T=Si-Ge).

Bond Angles (°)	Min	Max
T-O-T	129.2	155.0
O-T-O	101.1	118.5