Electronic Supplementary Material (ESI) for Dalton Transactions.

An open-framework silicogermanate regularly constructed from natrolite zeolite chains and $Ge_9O_{18}(OH)_4$ clusters

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Structural analysis

Synchrotron single-crystal XRD data for as-made PST-18 were collected at -173 °C on the 2D beamline of the Pohang Acceleration Laboratory (PAL; Pohang, Korea) using an MX225-HS CCD area detector with monochromated X-ray (λ = 0.62000 Å) in a scan width of 1.00° around the omega axis by collecting 360 frames. The raw data were processed and scaled using the programs *HKL*-3000 and DENZO.[1] Corrections for the Lorentz and polarization effects, along with an empirical absorption correction, were applied. The space group was determined by the program XPREP, and the structure was solved by direct methods using SHELXS.[2] The structure refinement was carried out with full-matrix least-squares refinements on F^2 using the program SHELXL2018.[2] The data collection conditions and crystallographic parameters are summarized in Table S2. The space group of as-made PST-18 was determined as *Cccm* (No. 66) with unit cell parameters a = 12.895(3) Å, b = 20.421(4) Å, c = 20.281(4) Å, and V = 5340.6(19) Å^3.

Three crystallographically distinct tetrahedral sites (T-sites) and three Ge centers were found in the natrolite (NAT) chains and Ge_9 clusters, respectively. The terminal atoms bonded to Ge3 atoms were assigned to the OH O atom, the existence of which is evidenced by ^{1}H MAS NMR and IR analyses (Figs. 2 and 5). The locations of TMA cations were derived from Fourier difference maps, and their total content was restrained to make the as-made material electrically neutral. The Si/Ge occupancies of three different T-sites in the natrolite chain were constrained based on their average T-O bond distances: the average T1-O bond length was determined to be 1.60 Å, which is essentially the same as the average Si-O bond distance (1.61 Å) of typical zeolites,[3,4] but sites T2 and T3 have average T-O bond lengths of 1.68 and 1.70 Å, respectively. This suggests that site T1 in the natrolite chain may be almost exclusively occupied by Si atoms, whereas the Si and Ge atoms are distributed statistically over sites T2 and T3. Therefore, the Si/Ge occupancy of site T1 was fixed to 100% Si, and those of both sites T2 and T3 were constrained to 54.1% Si and 45.9% Ge (calculated from elemental analysis) during the refinements. All the framework and extraframework atoms were anisotropically refined. The final atomic positions, anisotropic displacement parameters, and selected bond distances and angles are listed in Tables S3-S5. The dimensions of the pore opening are calculated using an oxygen radius of 1.35 Å.

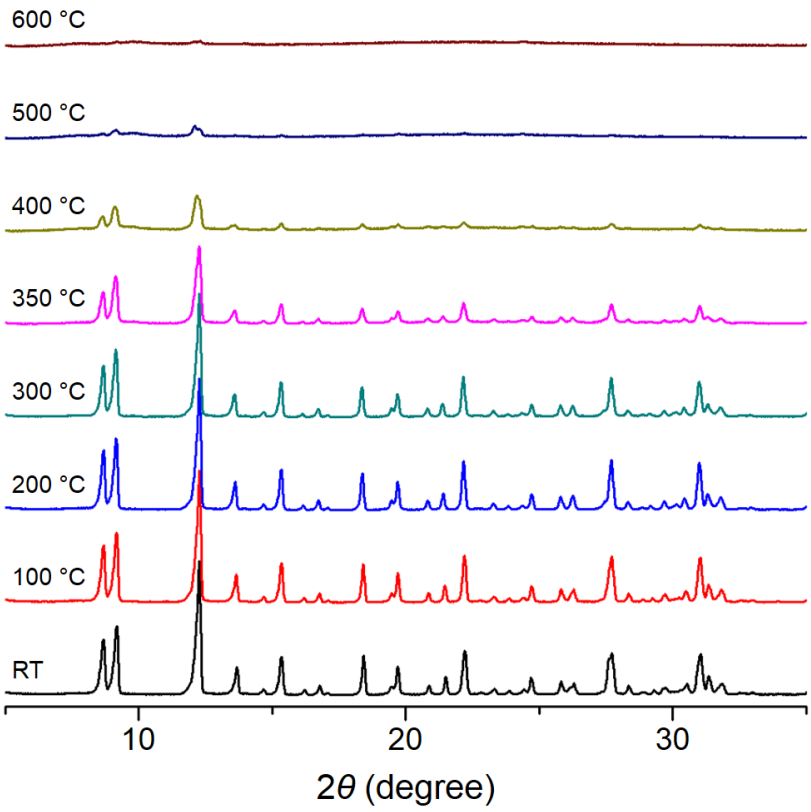

Fig. S1 Powder XRD patterns of as-made PST-18 recorded during *in situ* heating under vacuum to a residual pressure of 5×10^{-3} Torr.

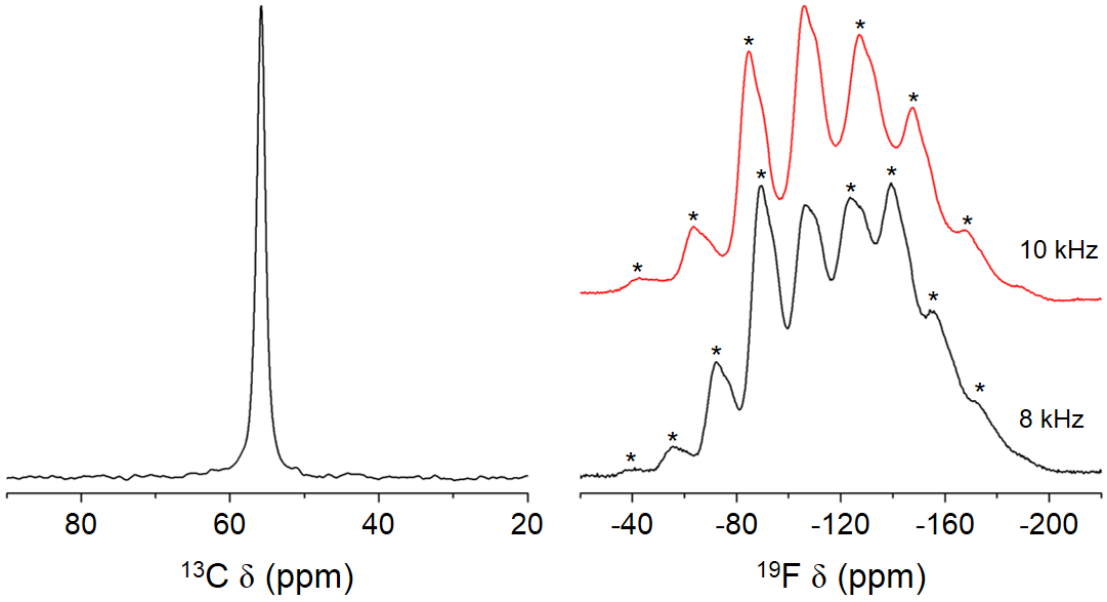

Fig. S2 ^{1}H-^{13}C CP (left) and ^{19}F (right) MAS NMR spectra of as-made PST-18. The ^{19}F MAS NMR spectra were measured at two different spinning rates (8 and 10 kHz) to identify spinning side bands, which are marked by asterisks.

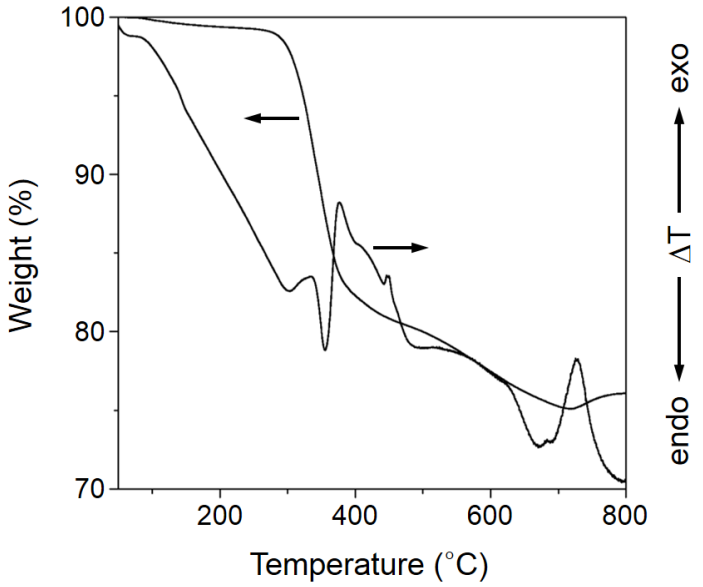

Fig. S3 TGA/DTA profiles for as-made PST-18.

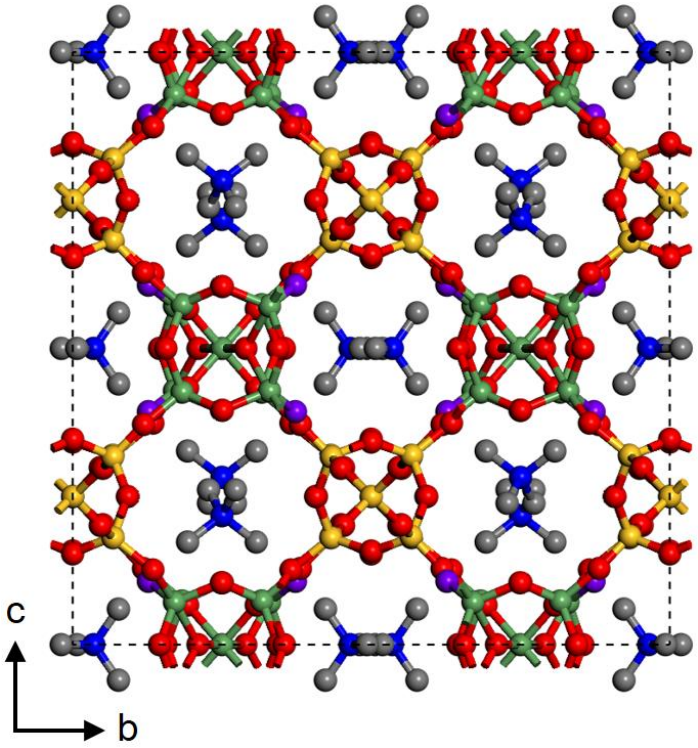

Fig. S4 Refined structure of as-made PST-18 with refined TMA locations viewed along the *a* axis. T-atoms in the chain, where T is Si or Ge, yellow; Ge atoms in the cluster, green; O atoms, red; OH O atoms, purple; C atoms, grey; N atoms, blue.

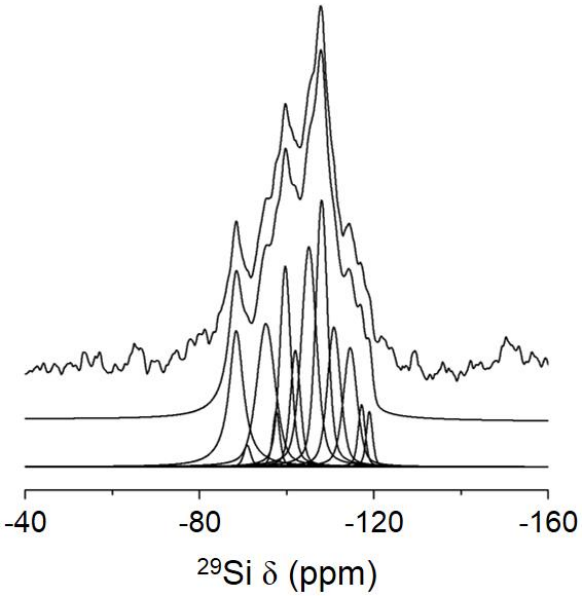

Fig. S5 ^{29}Si MAS NMR spectrum of as-made PST-18: (top to bottom) experimental, simulated, and deconvoluted components.

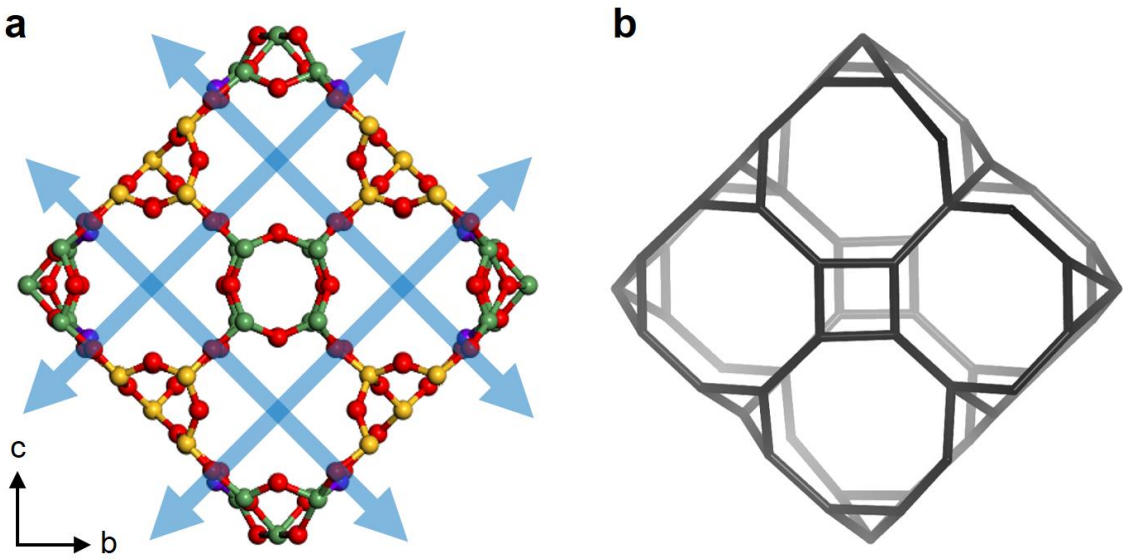

Fig. S6 The cuboid-shaped cavity in PST-18 containing eight 7-ring and eight 8-ring windows. (a) T-atoms in the chain, where T is Si or Ge, yellow; Ge atoms in the cluster, green; O atoms, red; OH O atoms, purple. The blue arrows present the interrupted 7-ring channels by one OH group perpendicular to the *a* axis. (b) The black lines indicate the connections between Si and Ge atoms while all O atoms have been omitted.

Table S1 Effects of the type of TMA and F sources on PST-18 synthesis

Run[a]	F source	TMA source	x	Product[c]
1	TMAF	TMAF	0.0	PST-18
2	HF	-	0.0	GeO_2 + dense phase
3	HF	TMACl	1.0	GeO_2 + dense phase
4	NH_4F	-	0.0	Pharmacosiderite + (amorphous)
5	NH_4F	TMACl	1.0	Pharmacosiderite + (amorphous)
6[b]	NH_4F	TMAOH	1.0	AST + unknown

[a] The composition of the final synthesis mixture was $1.0AF{\cdot}xR{\cdot}0.4GeO_2{\cdot}0.6SiO_2{\cdot}4.0H_2O$, where A is TMA, H, or NH_4, x is 0.0 or 1.0, and R is TMACl or TMAOH, unless otherwise stated. All syntheses were performed under static condition at 175 °C for 28 days. [b] Run performed at $H_2O/(Si+Ge) = 5.0$. [c] The product appearing first is the major phase, and the product obtained in a trace amount is given in parentheses.

Table S2 Single-crystal XRD data collection conditions and crystallographic data for as-made PST-18

Refined unit cell composition	$\|TMA_{16.0}\|[Si_{29}Ge_{11}O_{80}][Ge_9O_{18}(OH)_4]_4$
Crystal system	Orthorhombic
Space group	*Cccm* (No. 66)
a (Å)	12.895(3)
b (Å)	20.421(4)
c (Å)	20.281(4)
Unit cell volume ($Å^3$)	5340.6(19)
Z	8
Crystal shape	Prismatic
Crystal color	Colorless
Crystal size (mm)	0.007 × 0.002 × 0.001
X-ray source	2D, PAL
Wavelength (Å)	0.62000
Detector	CCD area detector, MX225-HS
Crystal-to-detector distance (mm)	66
Temperature (°C)	-173(2)
No. of total reflections collected	4224
θ range for data collection (^{o})	1.629-21.129
No. of unique reflections, *m*	2272
No. of unique reflections [$F_o > 4\sigma(F_o)$]	1058
No. of parameters, *s*	199
No. of restraints	315
Data/parameter ratio, *m/s*	11.42
Completeness (%)	100
Final R_1, wR_2 indices	0.1031, 0.3558
Goodness of fit	1.089
Largest diff. peak and hole ($e \cdot Å^{-3}$)	1.71, -3.31

Table S3 Atomic coordinates and occupancy factors for as-made PST-18

Atom	*x*	*y*	*z*	Wyckoff position	Occupancy
T1	0.0563(6)	0.0668(3)	0.1829(3)	16*m*	1/0[a]
T2	0.24840	0	1/4	8*g*	0.541/0.459(1)[a]
T3	0.44150	0.06760	0.31960	16*m*	0.541/0.459(1)[a]
Ge1	0.0692(2)	0.18328(13)	0.07370(14)	16*m*	1
Ge2	1/4	1/4	0	4*e*	1
Ge3	0.0293(2)	0.32951(13)	0.07164(13)	16*m*	1
O1	0.1323(14)	0.3731(8)	0.1069(8)	16*m*	1
O2	-0.0674(14)	0.3657(8)	0.1262(9)	16*m*	1
O3	-0.039(2)	0.3543(12)	0	8*l*	1
O4	0.0045(14)	0.2508(8)	0.1044(8)	16*m*	1
O5	0.1192(19)	0.2900(11)	0	8*l*	1
O6	0.2016(13)	0.1924(7)	0.0668(8)	16*m*	1
O7	0.317(3)	0.0463(17)	0.2987(16)	16*m*	1
O8	1/2	0.093(2)	1/4	8*h*	1
O9	1/2	0	0.342(2)	8*j*	1
O10	0.172(2)	0.0505(14)	0.2024(15)	16*m*	1
O11	0	0.0916(13)	1/4	8*h*	1
O12	0	0	0.1531(14)	8*i*	1
O13	0.0415(17)	0.1187(8)	0.1283(9)	16*m*	1
O14	0.014(2)	0.1561(11)	0	8*l*	1
C1	-0.285(3)	0.3075(14)	0.1732(18)	16*m*	1.000(1)
C2	-0.158(2)	0.2723(18)	0.2613(17)	16*m*	1.000(1)
C3	-0.355(4)	0.518(3)	0	8*l*	1.000(1)
C4	-0.291(3)	0.4228(18)	-0.0601(13)	16*m*	1.000(1)
C5	-0.170(4)	0.493(2)	0	8*l*	1.000(1)
N1	-1/4	1/4	0.2176(15)	8*k*	1.000(1)
N2	-0.276(2)	0.4642(15)	0	8*l*	1.000(1)

[a] Si/Ge occupancy.

Table S4 Anisotropic displacement parameters for as-made PST-18

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
T1	0.037(5)	0.009(3)	0.011(3)	-0.010(3)	0.011(3)	-0.004(2)
T2	0.046(6)	0.104(8)	0.085(7)	0	0	0.003(5)
T3	0.057(5)	0.074(4)	0.062(4)	0.003(3)	0.001(3)	0.002(4)
Ge1	0.0169(17)	0.0239(14)	0.0226(15)	-0.0054(12)	0.0029(13)	0.0035(13)
Ge2	0.001(3)	0.013(3)	0.012(2)	-0.0024(19)	0	0
Ge3	0.0112(16)	0.0237(14)	0.0187(14)	-0.0026(12)	-0.0003(12)	-0.0008(13)
O1	0.020(7)	0.017(8)	0.030(9)	-0.003(6)	0.002(6)	-0.010(7)
O2	0.022(8)	0.034(7)	0.022(7)	0.004(8)	0.011(7)	0.002(8)
O3	0.019(10)	0.035(12)	0.019(6)	0.017(9)	0	0
O4	0.007(6)	0.024(4)	0.021(6)	-0.007(4)	0.000(5)	0.000(4)
O5	0.011(9)	0.016(10)	0.017(7)	0.004(7)	0	0
O6	0.012(5)	0.021(8)	0.014(7)	0.001(5)	-0.001(5)	0.005(5)
O7	0.067(8)	0.130(16)	0.089(13)	-0.01(1)	-0.012(9)	-0.008(12)
O8	0.099(17)	0.098(18)	0.068(14)	0	0.021(14)	0
O9	0.092(16)	0.072(13)	0.092(18)	0.015(13)	0	0
O10	0.041(8)	0.089(14)	0.092(14)	0.004(9)	-0.004(8)	-0.006(11)
O11	0.093(18)	0.028(13)	0.029(10)	0	0.038(13)	0
O12	0.092(17)	0.024(9)	0.035(13)	-0.035(12)	0	0
O13	0.063(10)	0.024(6)	0.026(7)	-0.020(7)	0.014(8)	0.006(6)
O14	0.015(11)	0.014(10)	0.028(6)	-0.005(10)	0	0
C1	0.05(3)	0.10(3)	0.16(4)	0.01(3)	0.00(3)	0.04(3)
C2	0.18(5)	0.16(4)	0.09(3)	-0.11(3)	-0.08(3)	0.03(3)
C3	0.14(4)	0.15(5)	0.07(4)	0.11(4)	0	0
C4	0.11(4)	0.12(4)	0.10(3)	0.01(3)	0.01(3)	-0.05(2)
C5	0.10(3)	0.05(3)	0.09(4)	0.02(2)	0	0
N1	0.04(3)	0.07(2)	0.05(2)	-0.028(19)	0	0
N2	0.08(3)	0.07(3)	0.06(2)	0.04(2)	0	0

Table S5 Selected bond lengths and angles for as-made PST-18

Bond length (Å)		Bond angle (°)	
T1-O10	1.57(3)	T1-O10-T2	144.0(19)
T1-O11	1.623(11)	T1-O11-T1	143.6(19)
T1-O12	1.659(12)	T1-O12-T1	137.3(19)
T1-O13	1.545(19)	T1-O13-Ge1	160.2(15)
T1-O (Avg.)	1.60	T2-O7-T3	144(2)
T2-O7 (×2)	1.63(3)	T3-O2-Ge3	130.5(11)
T2-O10 (×2)	1.73(3)	T3-O8-T3	144(3)
T2-O (Avg.)	1.68	T3-O9-T3	148(3)
T3-O2	1.756(18)	Ge1-O4-Ge3	120.2(10)
T3-O7	1.71(3)	Ge1-O6-Ge2	116.8(8)
T3-O8	1.684(13)	Ge1-O14-Ge1	117.9(13)
T3-O9	1.637(12)	Ge2-O5-Ge3	133.5(5)
T3-O (Avg.)	1.70	Ge3-O3-Ge3	110.2(13)
Ge1-O4	1.728(17)		
Ge1-O6	1.724(17)		
Ge1-O13	1.758(17)		
Ge1-O14	1.745(12)		
Ge1-O (Avg.)	1.74		
Ge2-O5 (×2)	1.87(2)		
Ge2-O6 (×4)	1.900(15)		
Ge2-O (Avg.)	1.89		
Ge3-O1	1.751(17)		
Ge3-O2	1.823(17)		
Ge3-O3	1.772(14)		
Ge3-O4	1.768(16)		
Ge3-O5	2.026(16)		
Ge3-O (Avg.)	1.83		

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