Electronic Supporting Information

for

Synthesis and structure of the medium-pore zeolite PST-35 with two interconnected cages of unusual orthorombic shape

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Organic structure-directing agent (OSDA) syntheses

Two general procedures for the preparation of alkyl-substituted imidazolium cations were used:

i) A mixture of 0.10 mol of the parent imidazole and 0.20 mol of iodoethane (98%, Kanto) in 100 ml of acetonitrile was stirred for 3 days at room temperature. The mixture was then evaporated under reduced pressure at 80 °C, and the resulting solid washed with acetone three times.

ii) A mixture of 0.10 mol of the parent imidazole and 0.12 mol of anhydrous potassium carbonate (99.5 %, Samchun) was mixed into 100 mL of acetonitrile and stirred for 0.5 h. To this mixture, 0.30 mol of iodomethane (98%, Kanto) or iodoethane (98%, Kanto) was added and stirred at 40 or 70 °C for 3 days, respectively. The mixture was then cooled and subsequently filtered. The filtrate was evaporated under reduced pressure at 80 °C, and the resulting solid washed with acetone three times.

1-Ethyl-3-methylimidazolium (1E3MI) iodide: procedure i; 1-methylimidazole (99%, Aldrich): ^{1}H NMR (300 MHz, D_2O): δ 8.68, 7.45, 7.38, 4.18, 3.85, 1.45. ^{13}C NMR (75 MHz, D_2O): δ 125.4, 123.8, 46.7, 37.7, 16.5.

1,3-Diethylimidazolium (13DEI) iodide: procedure i: 1-ethylimidazole (95%, Aldrich): ^{1}H NMR (300 MHz, D_2O): δ 8.76, 7.47, 4.20, 1.47. ^{13}C NMR (75 MHz, D_2O): δ 136.5, 123.9, 46.8, 16.6.

1-Ethyl-2,3-dimethylimidazolium (1E23DMI) iodide: procedure i: 1,2-dimethylimidazole (98%, Aldrich): ^{1}H NMR (300 MHz, D_2O): δ 7.30, 7.24, 4.08, 3.70, 2.53, 1.36. ^{13}C NMR (75 MHz, D_2O): δ 124.0, 121.9, 45.2, 36.5, 16.1, 10.8.

1,3-Diethyl-2-methylimidazolium (13DE2MI) iodide: procedure ii; 2-methylimidazole (99%, Aldrich). ^{1}H NMR (300 MHz, D_2O): δ 7.35, 4.09, 2.58, 1.38. ^{13}C NMR (75 MHz, D_2O): δ 122.2, 45.2, 16.1.

2-Ethyl-1,3,4-trimethylimidazolium (2E134TMI) iodide: procedure ii; 2-ethyl-4-methylimidazole (95%, Aldrich). ^{1}H NMR (300 MHz, D2O): δ 6.95, 3.66, 3.58, 2.91, 2.17, 1.15. ^{13}C NMR (75 MHz, D2O): δ 132.10, 120.64, 39.17, 36.05, 33.19, 18.74, 11.90, 10.53.

1,2,3-Triethylimidazolium (123TEI) iodide: procedure ii; 2-ethylimidazole (98%, Aldrich). ^{1}H NMR (300 MHz, D_2O): δ 7.32, 4.09, 2.96, 1.38, 1.20. ^{13}C NMR (75 MHz, D_2O): δ 148.8, 122.3, 44.8, 18.2, 16.5, 12.7.

1,2,3-Triethyl-4-methylimidazolium (123TE4MI) iodide: procedure ii; 2-ethyl-4-methylimidazole (95%, Aldrich). ^{1}H NMR (300 MHz, D2O): δ 7.06, 4.03, 2.93, 2.22, 1.34, 1.29, 1.19. ^{13}C NMR (75 MHz, D2O): δ 148.18, 131.66, 119.21, 44.42, 41.99, 19.71, 18.49, 16.45, 13.16, 10.32.

Table S1 SXRD Data collection conditions and crystallographic data for as-synthesised, hydrated PST-35(3.9)

Estimated chemical formula[a]	$\|(C_9H_{17}N_2)_{7.2}F_{7.2}(H_2O)_{3.8}\|[Si_{63.7}Ge_{16.3}O_{160}]$
Refined unit cell formula (X-ray)	$\|(C_9H_{17}N_2)_{4.3}F_{4.0}(H_2O)_{1.0}\|[Si_{67.5}Ge_{12.5}O_{160}]$
Crystal system	Monoclinic
Space group, No.	*C*2/*m* (no. 12)
a (Å)	21.573(4)
b (Å)	22.578(5)
c (Å)	12.562(3)
β2(°)	124.63(3)
V (Å^3)	5034.65
Z	2
Crystal shape	Prism
Crystal color	Colorless
X-ray source	Beamline 6D, PAL
Wavelength (Å)	0.95116
Detector	CCD area detector, MX225-HS
Crystal-to-detector distance (mm)	100.37
Temperature (°C)	-173(2)
No. of total reflections	3400
θ range for data refinement (°)	1.953 to 28.186
No. of unique reflections, *m*	1893
No. of unique reflections [$F_o > 4\sigma(F_o)$]	1509
No. of parameters, *s*	394
No. of restraints	576
Data/parameter ratio, *m/s*	4.80
Completeness (%)	70.4
Final R_1, wR_2 indices	0.0670, 0.2215
Goodness of fit	1.123
Largest diff. peak and hole (e·Å^{-3})	0.74, -0.54

[a] The cell composition was calculated using overall elemental and thermal analyses. F^- was introduced to compensate the charge imbalance of the imidazolium cation.

Table S2 Atomic coordinates and occupancy factors for as-synthesised, hydrated PST-35(3.9)

Atom	*x*	*y*	*z*	Multiplicity	Occupancy
T1[a]	0.4101	0.5673	1.0249	8	0.596(10)/0.404(10)[b]
T2	0.3103	0.5668	0.7240	8	0.549(10)/0.451(10)
T3	0.1684	0.5669	0.7250	8	0.638(9)/0.362(9)
T4	0.2664	0.5669	1.0244	8	0.662(9)/0.338(9)
Si5	0.3350(2)	0.6828(2)	0.6318(3)	8	1
Si6	0.5005(2)	0.6817(2)	1.1224(3)	8	1
Si7	0.0831(2)	0.6838(2)	0.6248(3)	8	1
Si8	0.3736(2)	0.7541(2)	1.1216(3)	8	1
Si9	0.2488(2)	0.6812(2)	0.1223(3)	8	1
Si10	0.2911(2)	0.7435(2)	0.3744(3)	8	1
O1	0.3704(4)	0.5927(4)	0.8753(7)	8	1
O2	0.2205(4)	0.5764(4)	0.6680(8)	8	1
O3	0.2065(4)	0.5912(4)	0.8736(7)	8	1
O4	0.3559(4)	0.5759(4)	1.0802(7)	8	1
O5	0.3224(4)	0.6122(4)	0.6301(7)	8	1
O6	0.4205(4)	0.6990(4)	0.7474(8)	8	1
O7	0.5000	0.7027(5)	1.0000	4	1
O8	0.4842(4)	0.6120(4)	1.1165(6)	8	1
O9	0.0940(4)	0.6132(4)	0.6337(7)	8	1
O10	0.0875(4)	0.7072(4)	0.7488(7)	8	1
O11	0.3319(4)	0.7954(4)	0.9954(7)	8	1
O12	0.2523(4)	0.6101(4)	1.1159(7)	8	1
O13	0.4364(4)	0.7176(4)	1.1218(7)	8	1
O14	0.1314(6)	0.5000	0.6972(10)	4	1
O15	0.3295(6)	0.5000	0.6990(10)	4	1
O16	0.2785(4)	0.7168(4)	0.6532(8)	8	1
O17	0.3227(4)	0.7029(4)	0.4982(8)	8	1
O18	0.2603(4)	0.6985(4)	0.2564(8)	8	1
O19	0.2489(6)	0.5000	1.0491(10)	4	1
O20	0.4441(6)	0.5000	1.0480(11)	4	1
O21	0.1439(4)	0.7173(4)	0.6114(8)	8	1
O22	0.3140(4)	0.7093(4)	1.1134(7)	8	1
O23	0.0000	0.6996(6)	0.5000	4	1
F1	0.2889(6)	0.5000	0.8681(11)	4	1
C1	0.1262(13)	0.6067(10)	0.332(2)	8	0.773(8)
C2	0.0680(11)	0.6386(11)	0.207(2)	8	0.773(8)
C3	0.136(2)	0.5000	0.297(4)	4	0.773(8)
C4	0.1863(17)	0.5000	0.253(4)	4	0.773(8)
C5	0.2708(19)	0.5000	0.364(3)	4	0.773(8)
C6	0.0535(11)	0.5323(2)	0.3606(17)	8	0.773(8)
C7	0.535(3)	0.3972(16)	0.572(5)	8	0.311(7)

C8	0.473(2)	0.3643(18)	0.450(4)	8	0.311(7)
C9	0.461(3)	0.5000	0.471(4)	4	0.311(7)
C10	0.423(4)	0.5000	0.538(6)	4	0.311(7)
C11	0.340(4)	0.5000	0.421(7)	4	0.311(7)
C12	0.469(2)	0.4675(2)	0.618(3)	8	0.311(7)
N1	0.1037(10)	0.5459(9)	0.3263(19)	8	0.773(8)
N2	0.513(2)	0.4584(15)	0.568(3)	8	0.311(7)
O1W	0.058(7)	0.5000	-0.016(16)	4	0.27(7)

[a] T is either Si or Ge. [b] The occupancy of Si and Ge.

Table S3 Anisotropic displacement parameters for as-synthesised, hydrated PST-35(3.9)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
T1	0.0649(17)	0.114(2)	0.0815(18)	-0.0011(12)	0.0394(14)	-0.0007(11)
T2	0.0674(16)	0.119(2)	0.0812(17)	-0.0001(12)	0.0392(13)	-0.0003(11)
T3	0.0659(18)	0.113(2)	0.0820(18)	-0.0006(12)	0.0385(14)	0.0000(12)
T4	0.0648(18)	0.116(2)	0.0805(19)	0.0007(13)	0.0393(14)	-0.0002(12)
Si5	0.053(2)	0.113(3)	0.068(2)	0.0025(19)	0.0292(19)	0.0012(18)
Si6	0.050(2)	0.105(3)	0.067(2)	-0.0025(18)	0.0285(18)	0.0004(16)
Si7	0.055(2)	0.107(3)	0.073(2)	-0.0011(19)	0.031(2)	-0.0032(17)
Si8	0.059(2)	0.115(3)	0.078(2)	0.003(2)	0.0359(19)	0.0034(19)
Si9	0.059(2)	0.114(3)	0.068(2)	-0.001(2)	0.0289(19)	0.0007(18)
Si1	0.054(2)	0.102(3)	0.077(2)	0.0014(18)	0.035(2)	-0.0010(17)
O1	0.074(5)	0.127(6)	0.080(4)	0.001(4)	0.038(4)	-0.004(4)
O2	0.062(4)	0.132(7)	0.091(5)	0.004(5)	0.040(4)	-0.004(4)
O3	0.079(5)	0.126(6)	0.082(4)	-0.001(4)	0.036(4)	0.002(4)
O4	0.066(4)	0.130(6)	0.092(5)	0.000(5)	0.044(4)	0.003(4)
O5	0.073(5)	0.114(5)	0.088(5)	0.001(4)	0.042(4)	0.001(4)
O6	0.073(5)	0.126(7)	0.102(6)	0.007(5)	0.037(5)	-0.003(4)
O7	0.090(8)	0.109(9)	0.089(7)	0	0.051(6)	0
O8	0.065(4)	0.111(5)	0.080(5)	0.004(4)	0.035(4)	0.003(4)
O9	0.069(5)	0.112(5)	0.084(5)	-0.005(4)	0.040(4)	-0.004(4)
O10	0.094(6)	0.126(7)	0.082(5)	-0.011(5)	0.045(5)	0.003(5)
O11	0.072(5)	0.118(6)	0.082(5)	0.004(4)	0.037(5)	0.004(4)
O12	0.067(5)	0.107(6)	0.085(5)	-0.005(4)	0.037(4)	-0.001(4)
O13	0.072(5)	0.129(6)	0.099(5)	0.009(5)	0.049(4)	0.019(4)
O14	0.070(7)	0.112(6)	0.088(7)	0	0.043(6)	0
O15	0.077(7)	0.108(6)	0.094(7)	0	0.042(6)	0
O16	0.091(5)	0.122(7)	0.117(6)	0.000(5)	0.064(5)	0.012(5)
O17	0.098(6)	0.125(7)	0.093(5)	0.009(5)	0.053(5)	0.003(5)
O18	0.099(6)	0.129(7)	0.086(5)	-0.012(5)	0.052(5)	-0.003(5)
O19	0.073(7)	0.109(6)	0.090(7)	0	0.034(6)	0
O20	0.074(7)	0.103(6)	0.099(7)	0	0.044(6)	0
O21	0.087(5)	0.123(7)	0.116(6)	-0.002(5)	0.059(5)	-0.007(5)
O22	0.068(5)	0.128(7)	0.109(6)	0.007(5)	0.052(4)	-0.004(4)
O23	0.068(6)	0.134(9)	0.091(7)	0	0.019(6)	0
F1	0.144(12)	0.148(12)	0.178(13)	0	0.072(10)	0
C1	0.128(17)	0.233(18)	0.158(18)	-0.019(16)	0.047(13)	-0.036(15)
C2	0.109(16)	0.20(2)	0.22(2)	0.000(17)	0.064(14)	0.010(15)
C3	0.21(2)	0.24(2)	0.19(3)	0	0.120(17)	0
C4	0.16(2)	0.28(3)	0.23(3)	0	0.107(17)	0
C5	0.18(2)	0.36(5)	0.17(3)	0	0.08(2)	0
C6	0.153(17)	0.23(2)	0.083(12)	0.014(12)	0.046(11)	-0.004(13)
C7	0.14(3)	0.15(3)	0.09(2)	0.01(2)	0.039(18)	0.00(2)

C8	0.06(3)	0.09(3)	0.12(3)	0.045(17)	0.04(2)	-0.007(17)
C9	0.14(3)	0.14(3)	0.05(2)	0	0.037(18)	0
C10	0.18(3)	0.16(3)	0.07(3)	0	0.065(19)	0
C11	0.16(3)	0.28(6)	0.13(4)	0	0.07(2)	0
C12	0.17(3)	0.16(3)	0.04(2)	0.011(15)	0.032(17)	0.014(19)
N1	0.153(16)	0.221(16)	0.132(13)	-0.016(12)	0.065(10)	-0.023(11)
N2	0.17(3)	0.14(2)	0.068(18)	0.026(14)	0.046(15)	0.007(14)
O1W	0.29(13)	0.32(14)	0.6(2)	0	0.21(13)	0

Table S4 Selected bond lengths and angles for as-synthesised, hydrated PST-35(3.9)

Bond length (Å)		Bond angle (°)	
T1-O1	1.664(7)	T1-O1-T2	136.6(5)
T1-O4	1.677(7)	T2-O2-T3	135.8(5)
T1-O8	1.675(7)	T3-O3-T4	138.0(6)
T1-O20	1.639(4)	T4-O4-T1	137.2(5)
T1-O (Avg.)	1.664	Si5-O5-T2	132.8(5)
T2-O1	1.684(7)	Si7-O6-Si5	150.8(7)
T2-O2	1.656(7)	Si7-O7-Si7	145.6(8)
T2-O5	1.692(8)	Si7-O8-T1	136.2(5)
T2-O15	1.641(4)	Si8-O9-T3	134.6(5)
T2-O (Avg.)	1.668	Si8-O10-Si9	151.6(6)
T3-O2	1.656(7)	Si10-O11-Si9	144.0(5)
T3-O3	1.649(7)	Si10-O12-T4	130.7(5)
T3-O9	1.700(8)	Si9-O13-Si7	179.2(6)
T3-O14	1.650(4)	T3-O14-T3	132.5(6)
T3-O (Avg.)	1.664	T2-O15-T2	133.5(7)
T4-O3	1.666(7)	Si5-O16-Si11	161.1(6)
T4-O4	1.651(7)	Si11-O17-Si5	155.5(6)
T4-O12	1.661(8)	Si11-O18-Si10	149.6(6)
T4-O19	1.628(4)	T4-O19-T4	136.1(7)
T4-O (Avg.)	1.652	T1-O20-T1	135.9(6)
Si5-O5	1.614(9)	Si11-O21-Si8	168.1(6)
Si5-O6	1.613(8)	Si9-O22-Si10	162.6(6)
Si5-O16	1.588(8)	Si8-O23-Si8	154.4(10)
Si5-O17	1.608(9)	O1-T1-O4	113.3(4)
Si5-O (Avg.)	1.606	O1-T1-O8	104.2(4)
Si6-O6	1.601(8)	O8-T1-O4	105.2(4)
Si6-O7	1.604(5)	O20-T1-O1	114.3(5)
Si6-O8	1.604(8)	O20-T1-O4	112.4(4)
Si6-O13	1.598(7)	O20-T1-O8	106.4(4)
Si6-O (Avg.)	1.602	O1-T2-O5	104.5(4)
Si7-O9	1.606(9)	O2-T2-O1	113.5(4)
Si7-O10	1.597(8)	O2-T2-O5	103.4(4)
Si7-O21	1.604(9)	O15-T2-O1	114.8(5)
Si7-O23	1.614(5)	O15-T2-O2	113.6(5)
Si7-O (Avg.)	1.605	O15-T2-O5	105.5(4)
Si8-O10	1.601(8)	O2-T3-O9	104.0(4)
Si8-O11	1.603(8)	O3-T3-O2	115.0(4)
Si8-O13	1.584(8)	O3-T3-O9	103.4(4)
Si8-O22	1.592(8)	O3-T3-O14	114.5(5)
Si8-O (Avg.)	1.595	O14-T3-O2	113.1(5)
Si9-O11	1.603(8)	O14-T3-O9	105.2(4)
Si9-O12	1.612(9)	O4-T4-O3	114.0(4)

Si9-O22	1.605(8)	O4-T4-O12	105.3(4)
Si9-O18	1.605(8)	O12-T4-O3	105.3(4)
Si9-O (Avg.)	1.606	O19-T4-O3	114.1(5)
Si10-O16	1.609(8)	O19-T4-O4	112.0(4)
Si10-O21	1.580(9)	O19-T4-O12	105.1(5)
Si10-O17	1.588(9)	O6-Si5-O5	109.5(5)
Si10-O18	1.597(9)	O16-Si5-O5	109.9(5)
Si10-O	1.594	O16-Si5-O6	109.5(5)
		O16-Si5-O17	110.6(5)
		O17-Si5-O5	109.8(5)
		O17-Si5-O6	107.5(5)
		O6-Si6-O7	109.3(4)
		O6-Si6-O8	111.3(5)
		O7-Si6-O8	111.3(5)
		O13-Si6-O6	107.3(4)
		O13-Si6-O7	108.1(4)
		O13-Si6-O8	109.4(4)
		O9-Si7-O23	109.0(6)
		O10-Si7-O9	109.7(5)
		O10-Si7-O21	110.3(5)
		O10-Si7-O23	107.0(4)
		O21-Si7-O9	112.3(5)
		O21-Si7-O23	108.5(5)
		O10-Si8-O11	111.3(5)
		O13-Si8-O10	109.2(4)
		O13-Si8-O11	107.6(4)
		O13-Si8-O22	109.2(5)
		O22-Si8-O10	110.5(5)
		O22-Si8-O11	109.0(4)
		O11-Si9-O12	109.8(4)
		O11-Si9-O18	109.1(5)
		O11-Si9-O22	109.9(4)
		O18-Si9-O12	108.1(5)
		O18-Si9-O22	111.0(4)
		O22-Si9-O12	108.8(4)
		O17-Si10-O16	111.1(4)
		O17-Si10-O18	105.2(6)
		O18-Si10-O16	108.0(4)
		O21-Si10-O16	111.8(6)
		O21-Si10-O17	110.8(4)

Table S5 Fractional coordinates of the two hypothetical structures related to PST-35

PST-35h_1[a]				PST-35h_2[b]			
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Si1	0.00461	0.34391	0.37992	Si1	0.25194	0.00057	0.29187
Si2	0.08724	0.16340	0.11874	Si2	0.25245	0.00164	0.12562
Si3	0.12668	0.24552	0.38088	O1	0.32986	0.01656	0.08268
Si4	0.15304	0	0.21137	O2	0.33946	0	0.5
Si5	0.21036	0.26318	0.12514	O3	0.34451	0	0
Si6	0.24864	0.34166	0.38310	O4	0.44747	0.55253	0.36738
Si7	0.25521	0	0.52109	O5	0.53698	0.46302	0.20901
Si8	0.30122	0	0.20798	O6	0.54599	0.45401	0.04945
Si9	0.33030	0.15823	0.13875	O7	0.77385	0.22615	0.20408
Si10	0.40488	0	0.51891				
O1	0	0.18107	0				
O2	0	0.31688	0.5				
O3	0.04237	0.42687	0.40837				
O4	0.05209	0.28240	0.35960				
O5	0.10121	0.07338	0.13555				
O6	0.10348	0.19626	0.25391				
O7	0.14233	0.20359	0.08435				
O8	0.1664	0.19152	0.51000				
O9	0.18343	0	0.36614				
O10	0.18775	0.31065	0.41119				
O11	0.18863	0.31604	0.00221				
O12	0.22328	0.32162	0.23604				
O13	0.22484	0	0.20270				
O14	0.25047	0.43118	0.40034				
O15	0.28855	0.21536	0.18215				
O16	0.30018	0.07310	0.12883				
O17	0.33500	0	0.53427				
O18	0.37491	0	0.36348				
O19	0.42113	0.15783	0.24403				

[a] Space group *C*2/*m* with a = 21.1379 Å, b = 17.5721 Å , c = 12.2130 Å , β = 125.000°. [b] Space group *R*-3*m* with a = 12.4197 Å, c = 30.8526 Å.

Table S6 Structural information on the three members of the PST-35 family of zeolites

Structure[a]	Unit removed	Highest space group	Rings present	LID criteria	E_F[b]
PST-35		*C*2/*m* (no. 12)	4, 5, 6, 8, 10	Satisfied	17.4
PST-35h_1	*s4r* in *d4r*	*C*2/*m* (no. 12)	4, 5, 6, 8	Satisfied	15.0
PST-35h_2[c]	*d4r*	*R*-3*m* (no. 166)	4, 6	Satisfied	13.6

[a] PST-35h_1 and PST-35h_2 are the hypothetical structures created by removing a particular structure unit of the PST-35 structure. [b] Framework energy in kJ (mol Si)$^{-1}$) relative to α-quartz. [c] Isostructural to a 12-layer ABC-6 structure with the stacking sequence ABABCACABCBC.[1]

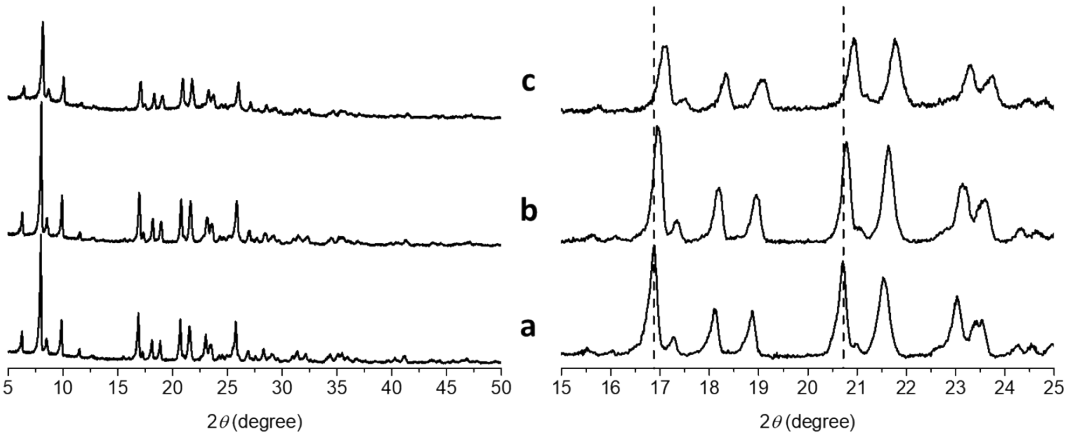

Fig. S1 PXRD patterns in the 2θ ranges 5-50º (left) and 15-25º (right) of as-synthesised, hydrated (a) PST-35(2.1), (b) PST-35(3.9) and (c) PST-35(6.6), where the values in parentheses are their Si/Ge ratios determined by elemental analysis. The right patterns show a clear shift of X-ray peaks to the higher 2θ region with a decrease in Ge content.

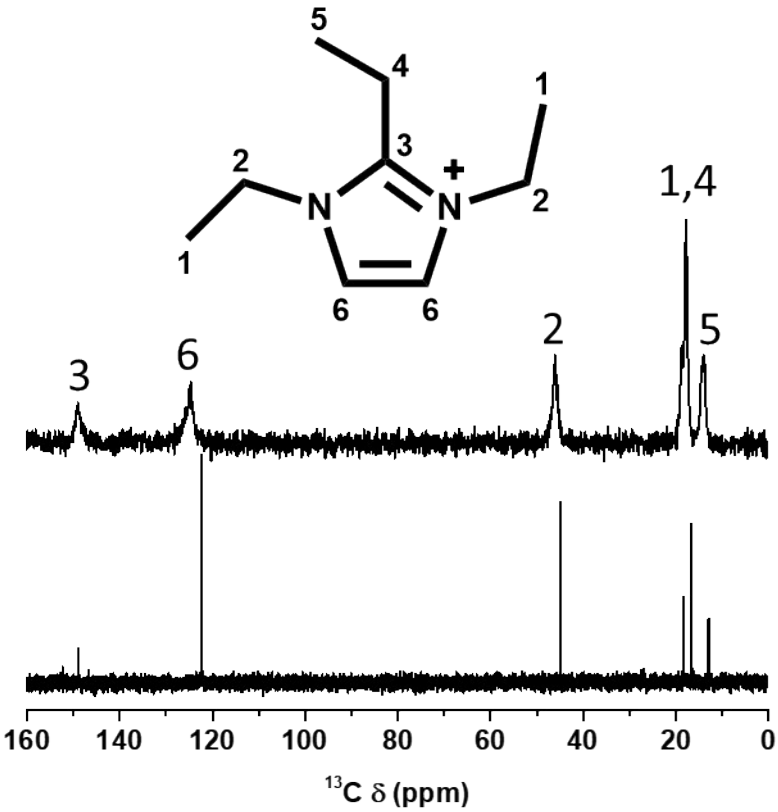

Fig. S2 ^{1}H-^{13}C CP MAS NMR spectrum (top) of as-synthesised PST-35(3.9). The solution ^{13}C NMR spectrum (bottom) of the iodide salt of 123TEI in D_2O is given for comparison.

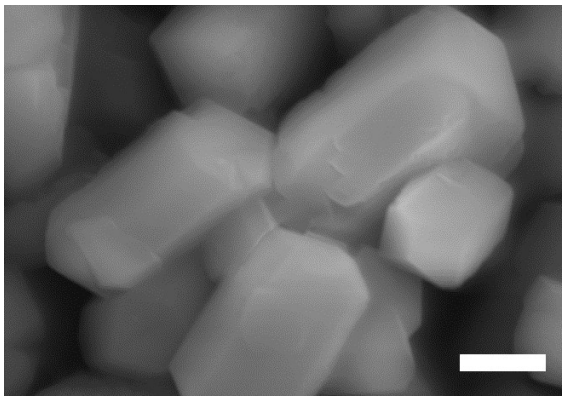

Fig. S3 SEM image of as-synthesised PST-35(3.9). Scale bar, 4 μm.

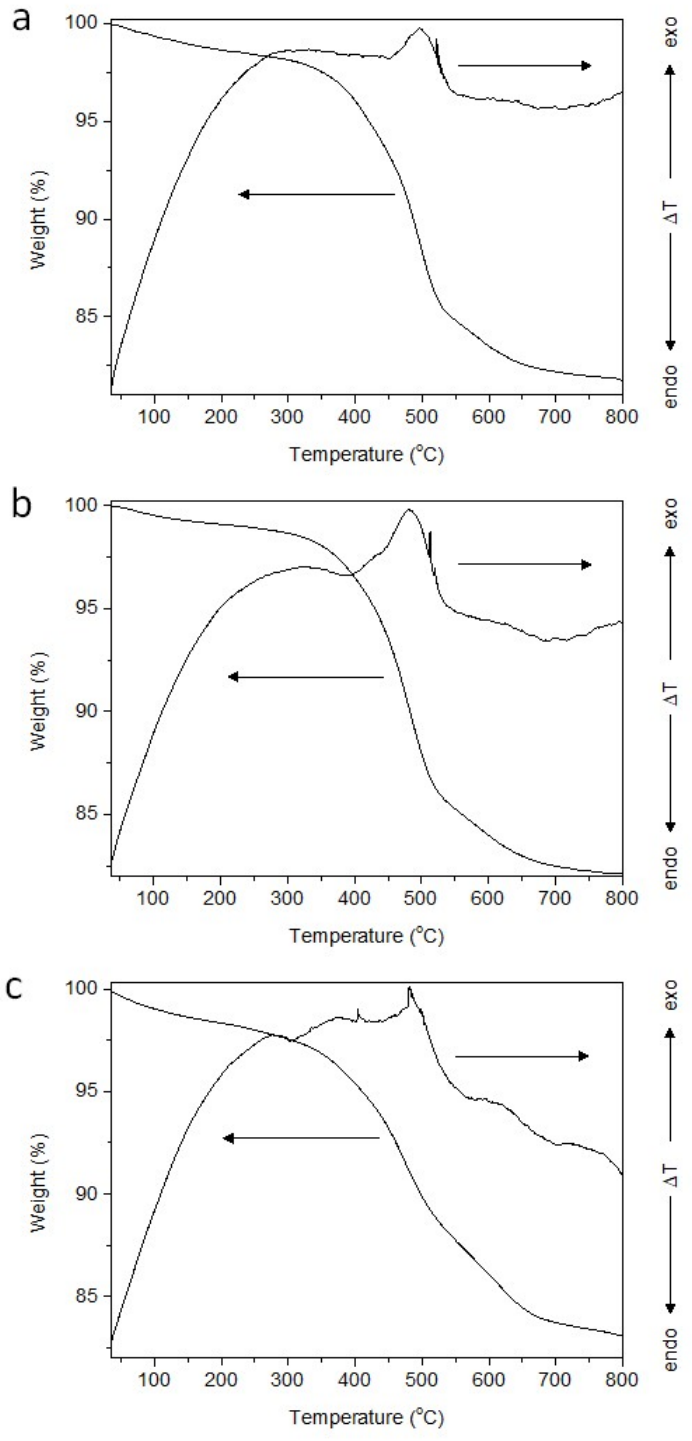

Fig. S4 TGA/DTA profiles for as-synthesised (a) PST-35(2.1), (b) PST-35(3.9) and (c) PST-35(6.6).

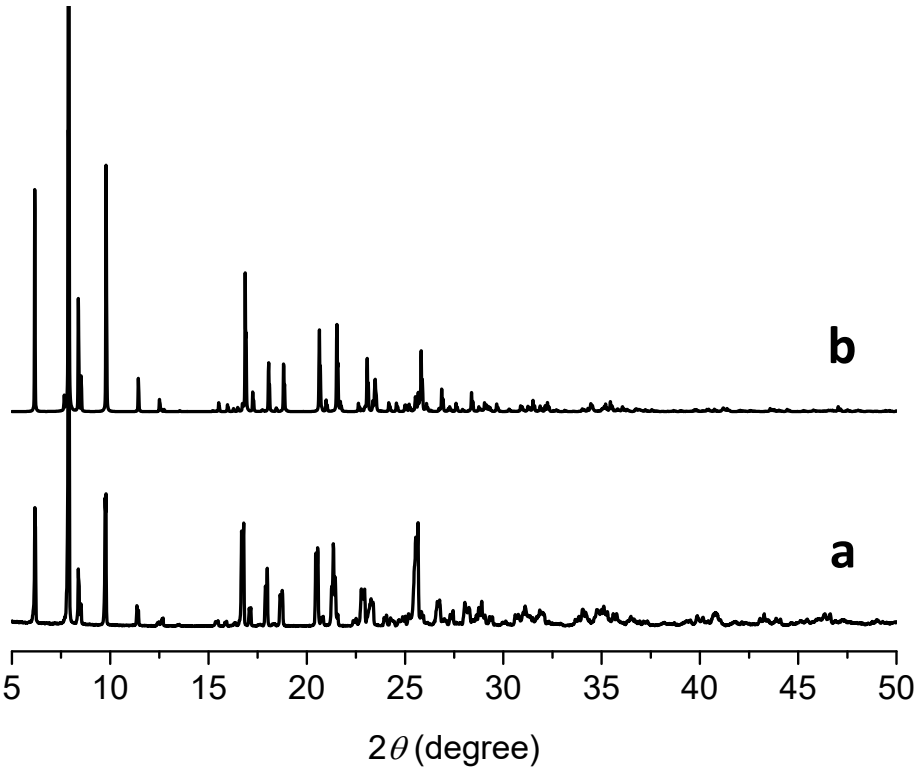

Fig. S5 Synchrotron (a) and simulated (b) PXRD patterns of as-synthesised, hydrated PST-35(3.9) (λ = 1.5223 Å).

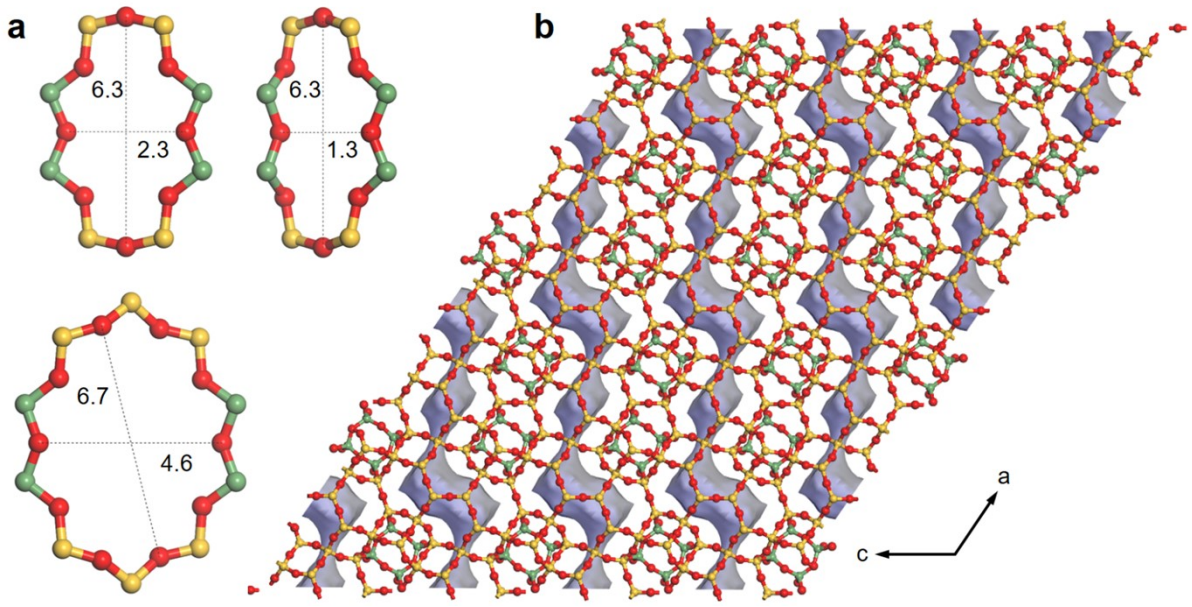

Fig. S6 (a) The 8-ring windows of *ptf-1* (top, left) and *ptf-2* (top, right) cages in PST-35(3.9) and the 10-ring window (bottom) shared by these two cages. The selective dimensions in Å of each pore opening are also given. (b) The PST-35 structure with accessible solvent surfaces calculated using the initial solvent radius of 1.4 Å marked in translucent blue. Color codes: Si atoms in *d4r*, green; rest Si atoms, yellow; O atoms, red.

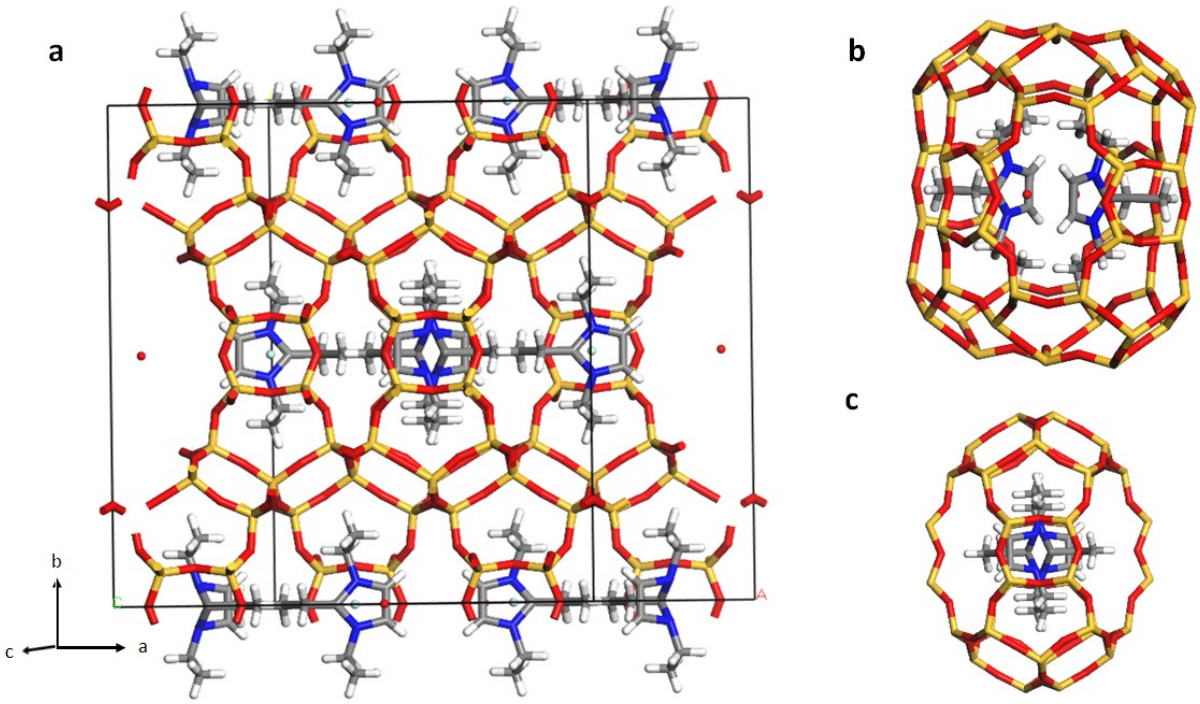

Fig. S7 (a) The SXRD refined structure of as-synthesised PST-35(3.9), showing the orientation of 123TEI molecules within the channel system. The locations of (b) two 123TEI molecules within the *ptf-1* cage and of (c) one 123TEI molecule within the *ptf-2* cage.

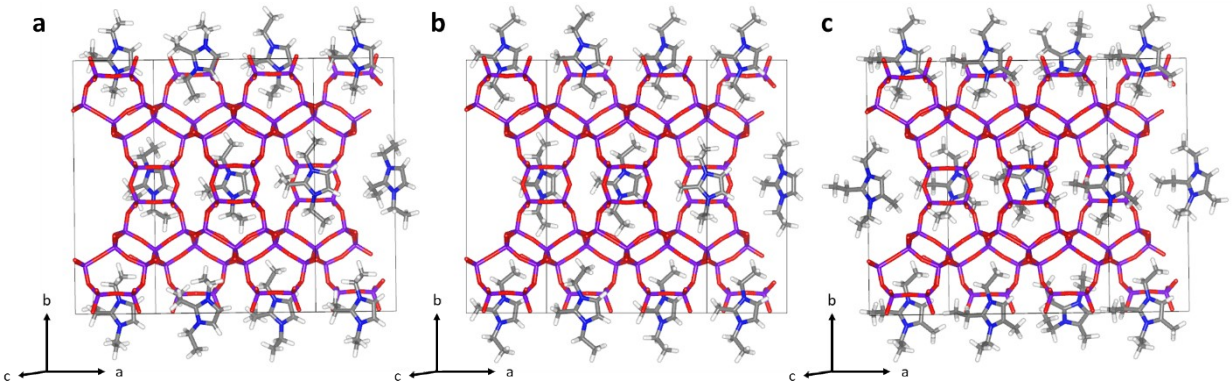

Fig. S8 Orientations of (a) 123TEI, (b) 13DE2MI and (c) 123TE4MI molecules within the PST-35 framework calculated using the method of Deem and co-workers.[2] The latter two OSDA molecules were manually located at the positions of 123TEI molecules in as-synthesised PST-35(3.9) determined using SXRD and direct methods. Color codes: Si, maroon; O, red; N, blue; C, gray; H, white. Figures generated using VESTA.[3]

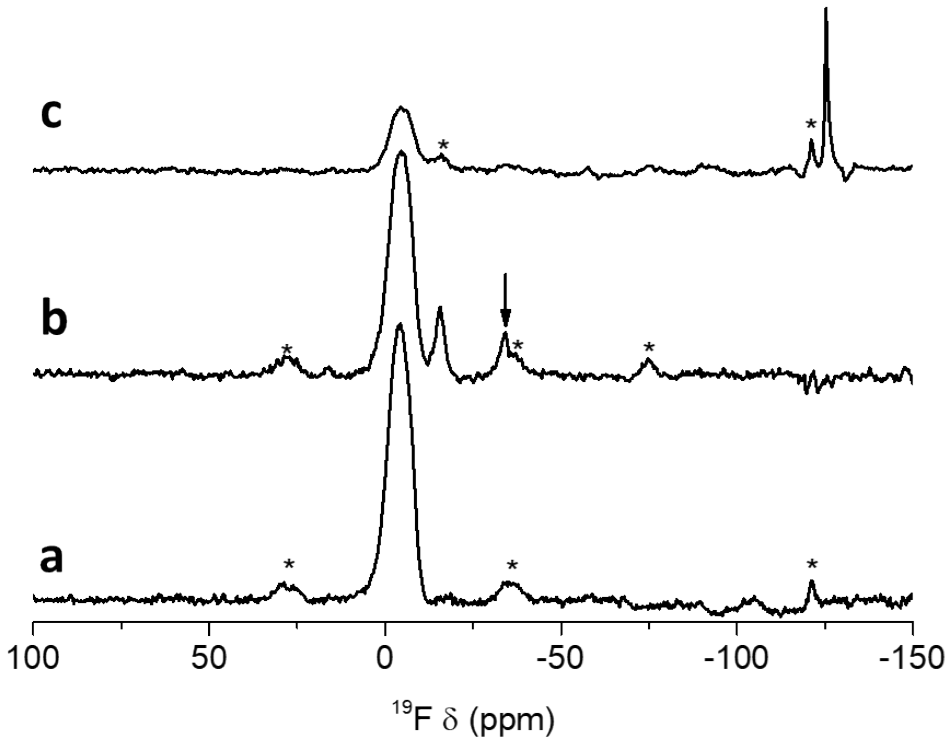

Fig. S9 ^{19}F MAS NMR spectra of as-synthesised (a) PST-35(2.1), (b) PST-35(3.9) and (c) PST-35(6.6). The F^- ions within the 8-Si *d4r*s in as- synthesised PST-35(3.9) are marked by an arrow, and spinning sidebands are indicated by asterisks.

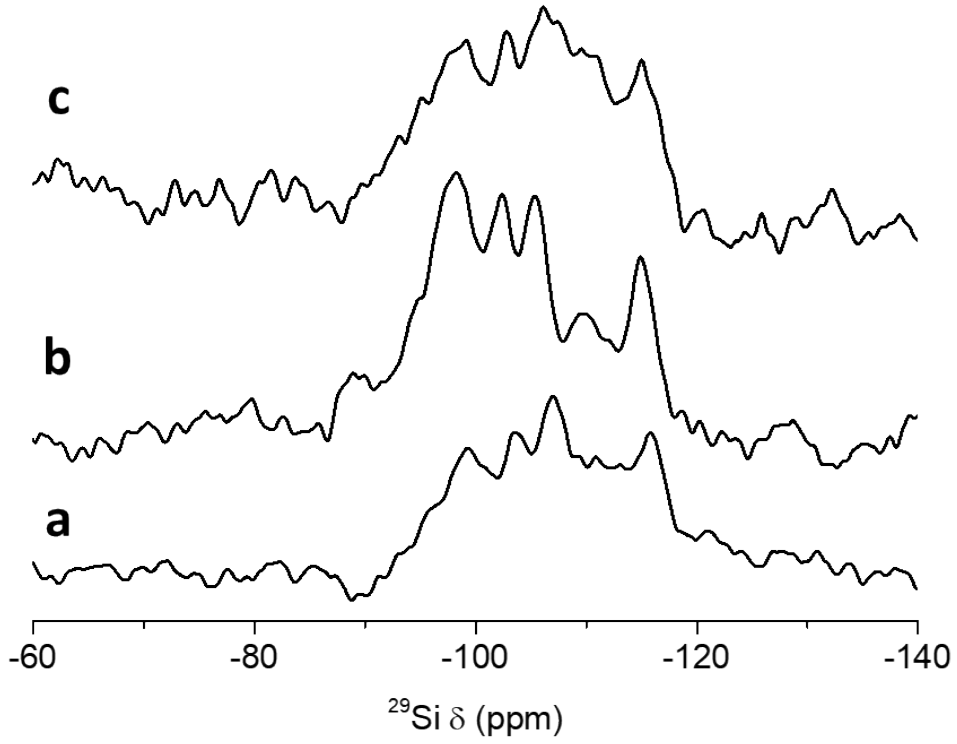

Fig. S10 ^{29}Si MAS NMR spectra of as-synthesised (a) PST-35(2.1), (b) PST-35(3.9) and (c) PST-35(6.6).

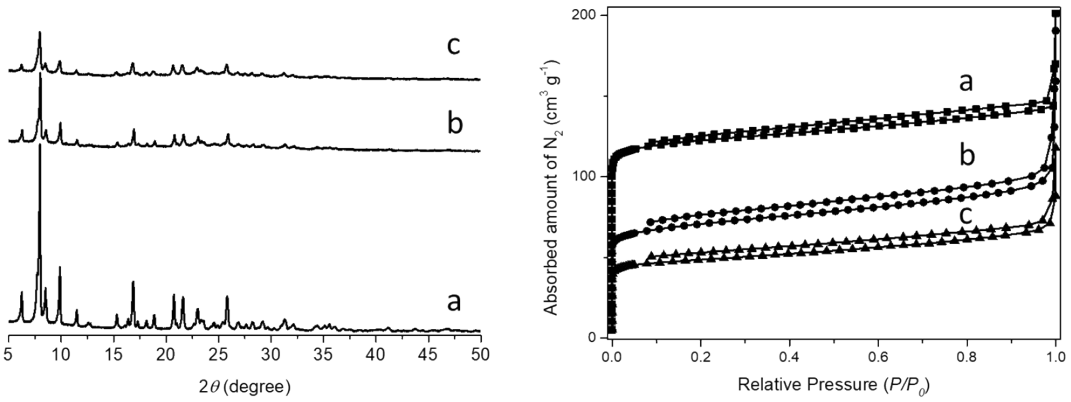

Fig. S11 PXRD patterns (left) and N_2 adsorption isotherms at -196 °C (right) of as-calcined PST-35(3.9) (a) before and after exposure to ambient moisture for (b) 7 and (c) 14 days. As previously reported, water cleavage of the Ge-O bonds in PST-35(3.9) seems evident with large decreases in PXRD peak intensity and N_2 adsorption capacity.[4] The BET surface areas in $m^2\ g^{-1}$ (micropore volumes in $cm^3\ g^{-1}$) of these three samples were calculated to be 490 (0.17), 220 (0.07) and 188 (0.06), respectively.

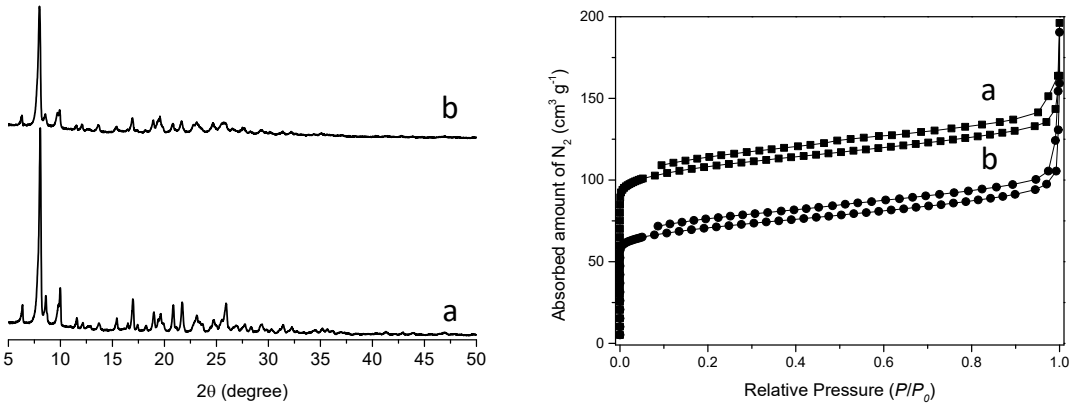

Fig. S12 PXRD patterns (left) and N_2 adsorption isotherms at -196 °C (right) of as-calcined PST-35(6.6) (a) before and (b) after exposure to ambient moisture for 7 days. As for PST-35(3.9), water cleavage of the Ge-O bonds in PST-35(6.6) seems evident with a notable decreases in PXRD peak intensity and N_2 adsorption capacity. The BET surface area in $m^2\ g^{-1}$ (micropore volume in $cm^3\ g^{-1}$) was calculated to decrease from 419 (0.14) to 270 (0.08).

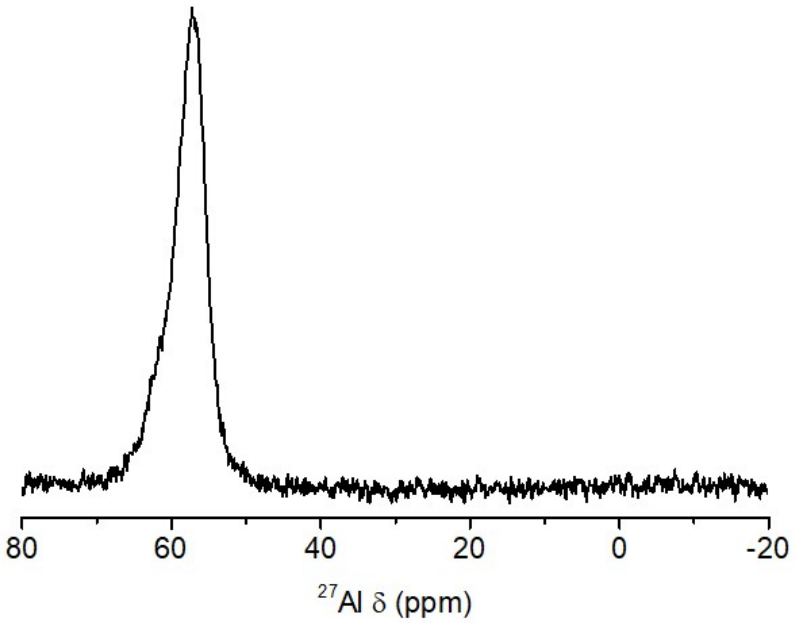

Fig. S13 ^{27}Al MAS NMR spectrum of as-synthesised Al-PST-35 obtained from a synthesis mixture with Si/Ge = 4.0 and (Si+Ge)/Al = 30.0 in the presence of 123TEI as an OSDA. Elemental analysis indicates that its (Si+Ge)/Al ratio is about 80.

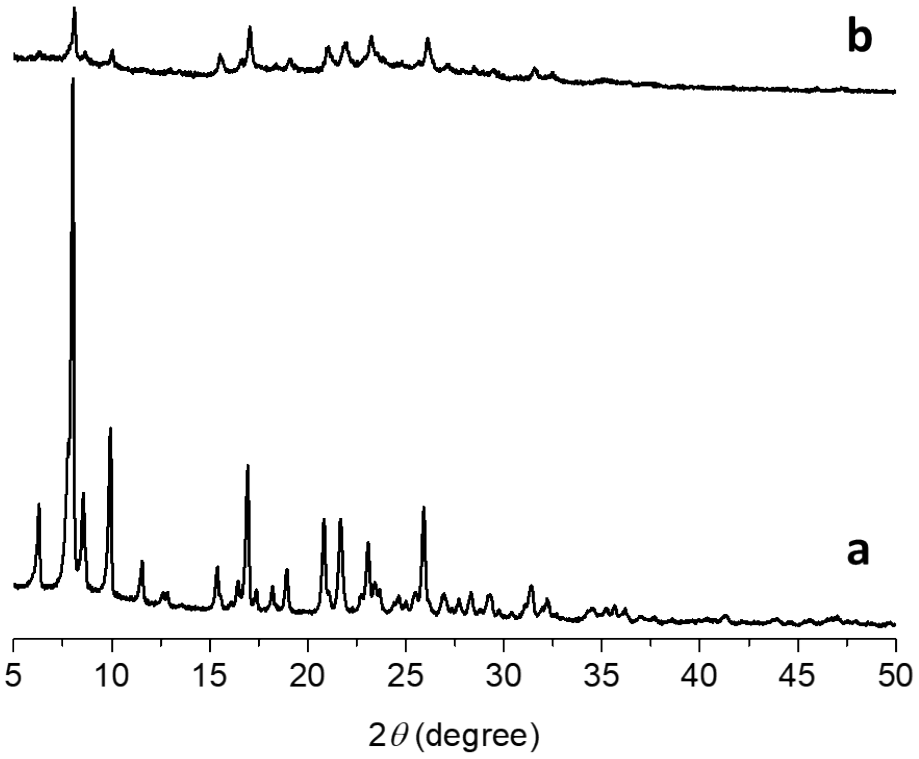

Fig. S14 PXRD patterns of Al-PST-35 obtained from a synthesis mixture with Si/Ge = 4.0 and (Si+Ge)/Al = 30 in the presence of 123TEI as an OSDA: (a) as-calcined and (b) after 7 days under ambient moisture. Elemental analysis indicates that its (Si+Ge)/Al ratio is about 80.

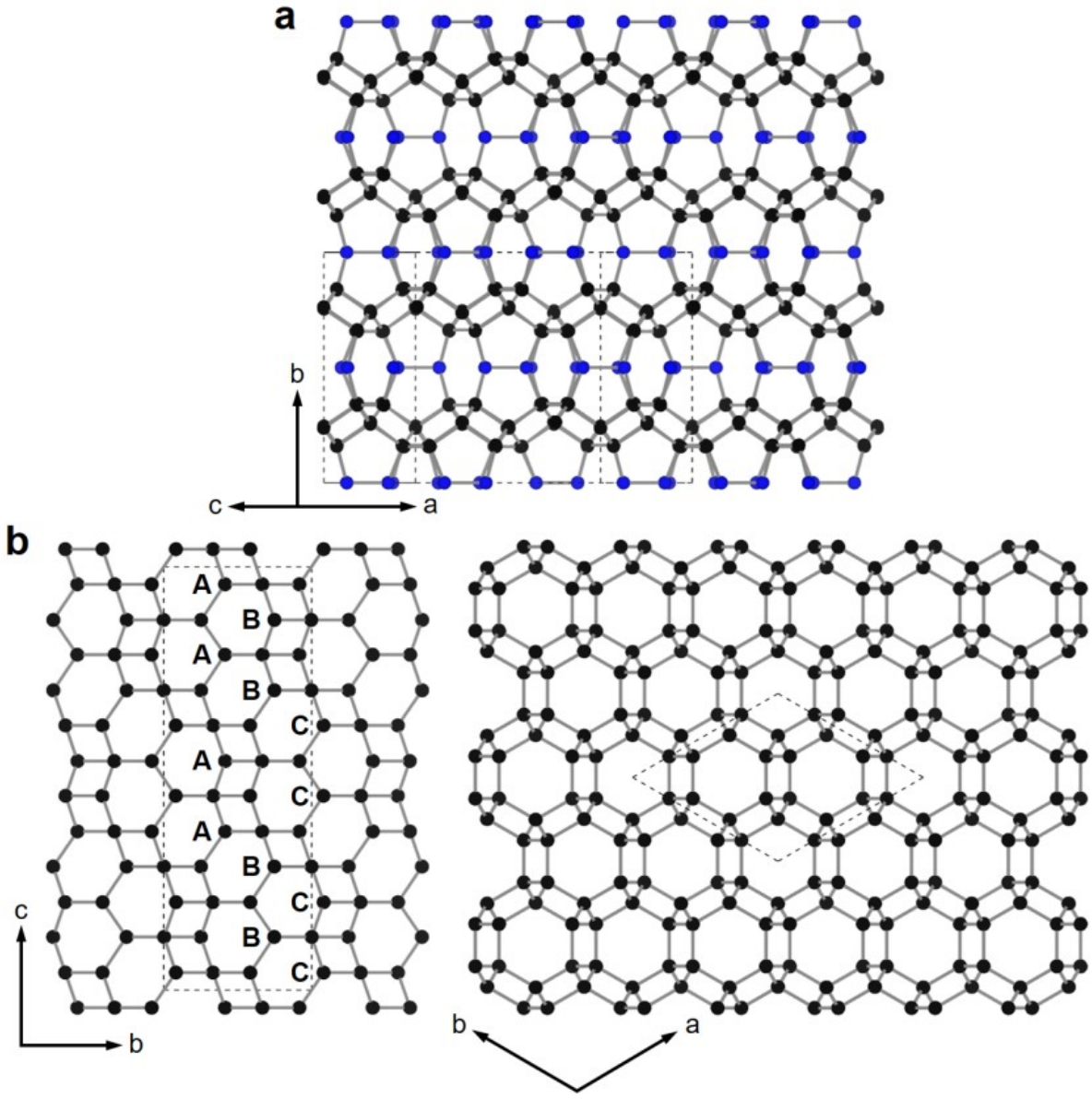

Fig. S15 Hypothetical structures (a) PST-31h_1 and (b) PST-35h_2 related to the PST-35 structure. While PST-31h_1 was created by removing the single 4-ring (*s4r*) in *d4r*s, PST-35h_2 was generated by removing the entire *d4r*s in the PST-35 structure. Bridging O atoms have been omitted for clarity. The remained *s4r*s in PST-31h_1 during removal of *s4r* in *d4r*s are marked in blue. It should be noted that PST-35h_2 is a 12-layer ABC-6 structure with the stacking sequence ABABCACABCBC.

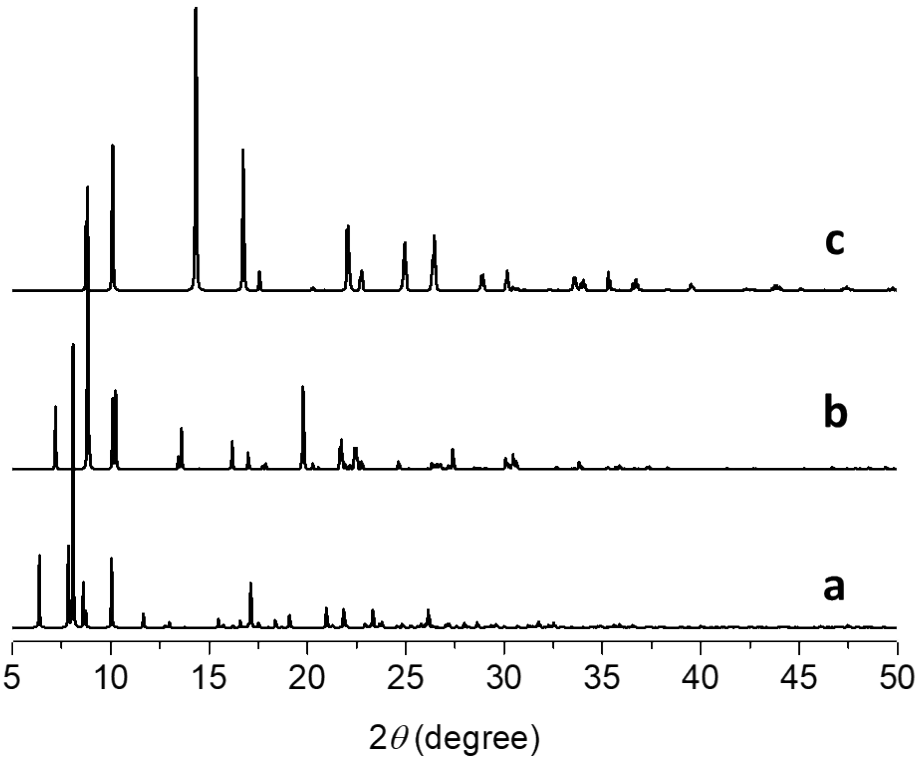

Fig. S16 Simulated PXRD patterns of (a) PST-35, (b) PST-35h_1 and (c) PST-35h_2 with pure-silica composition optimised using the SLC potential with their own highest symmetries (Table S5; λ = 1.5406 Å).

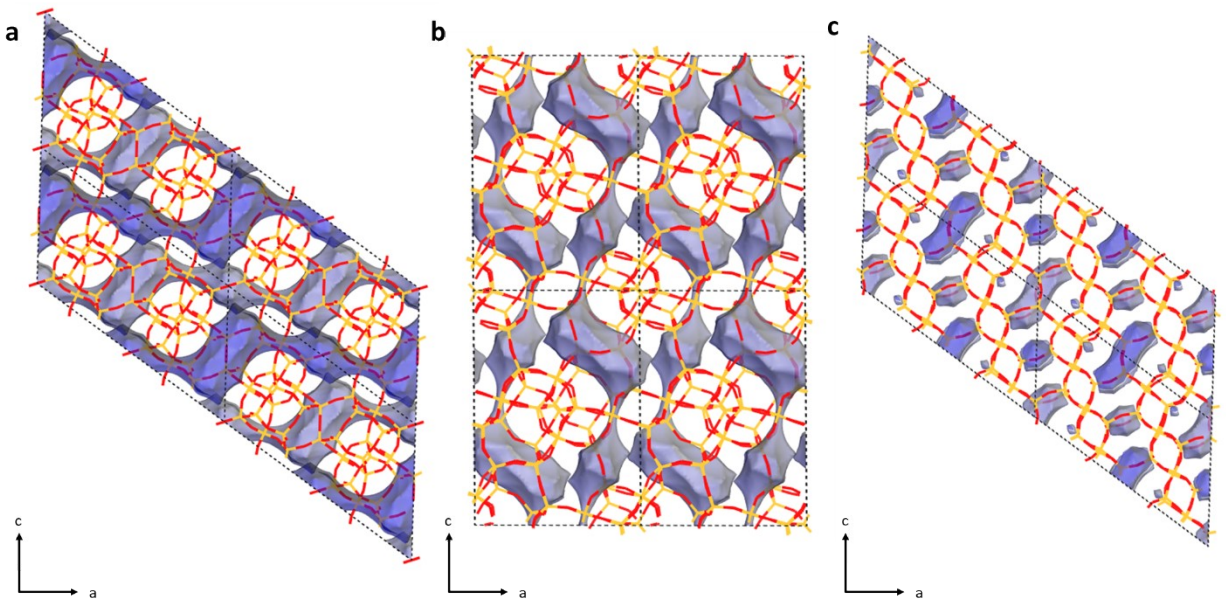

Fig. S17 Solvent surfaces, marked in translucent blue, of the (a) PST-35, (b) PST-35h_1 and (c) PST-35h_2 structures with pure-silica composition optimised using the SLC potential. (a) and (b) show the zig-zag channel systems, while (c) shows the zig-zag arrangement of a small and large cage in the PST-35h_2 clathrasil. The minor remaining solvent surface in PST-35h_2 is occupied by the 11-hedral ([$4^6 6^5$]) *can* cages. The initial solvent radius was 1.4 Å. Color codes: Si, yellow; O, red.

References

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3 K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2011, **44**, 1272.
4 D. L. Dorset, K. G. Strohmaier, C. E. Kliewer, A. Corma, M. J. Diaz-Cabanas, F. Rey and C. J Gilmore, *Chem. Mater.*, 2008, **20,** 5325.