Supplementary Information

for

Solid Solution of a Zeolite and a Framework-Bound OSDA-Containing Molecular Sieve

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Table S1 Data collection and crystallographic data for the as-made, hydrated ECR-40C-Model A, ECR-40C-Model B and PST-10C.

Material	As-made, hydrated ECR-40C-Model A	As-made, hydrated ECR-40C-Model B	As-made, hydrated PST-10C
Refined structure[a]	$\|HTMA^{+}_{6.0}(H_2O)_{5.5}\|$ $[Si^{T}_{30}O_{60}][Si^{O}_{4}O_{6}(OH_{3.9})]$	$\|(H_2O)_{5.6}\|$ $[Si^{T}_{30}O_{60}]$ $[Si^{O}_{4}O_{12}(HTMA^{+}_{6.0})]$	$\|(H_2O)_{6.6}\|$ $Ge^{T}_{6}P^{T}_{12}Al^{T}_{12}O_{60}]$ $[Al^{O}_{4}O_{12}(HTMA^{+}_{6.0})]$
Symmetry		hexagonal	
Space group		$P6_3$	
a (Å)	13.21548(17)	13.21570(12)	13.16753(15)
b (Å)	13.21548(17)	13.21570(12)	13.16753(15)
c (Å)	16.02366(22)	16.02404(23)	16.2454(3)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	120	120	120
Unit cell volume (Å^3)	2423.58(6)	2423.72(5)	2439.32 (7)
Diffractometer		9B, PAL	
Geometry		multiple analyzer system	
Wavelength (Å)		1.5475	
2θ scan range (°)	5.0-100.0	5.0-100.0	6.0-90
No. of contributing Reflections	875	875	696
No. of refined parameters	125	121	122
No. of geometric restraints	76	76	50
R_{wp} (%)	9.36	10.95	14.69
R_p (%)	6.66	7.98	11.38
R_F^2 (%)	12.14	12.80	7.05
X^2	9.33	13.24	9.69

[a] Superscripts T and O indicate tetrahedral and octahedral sites, respectively. The OSDA oxygen atoms bonded to the framework Al atoms have been included in the framework octahedral Al species.

Table S2 Atomic coordinates and thermal parameters for as-made, hydrated ECR-40C-Model A.

Atom	*x*	*y*	*z*	Occupancy	U_{iso} × 100 (Å^2)
T1	0.333333	0.666667	0.0784(5)	1	2.87(8)
T2	0.333333	0.666667	0.8722(5)	1	2.87(8)
T3	0.1163(5)	0.4514(5)	0.6577(4)	1	2.87(8)
T4	0.1152(5)	0.4510(4)	0.2932(4)	1	2.87(8)
T5	0.1493(4)	0.6748(4)	0.1959(4)	1	2.87(8)
T6	0.1471(4)	0.6738(4)	0.7552(4)	1	2.87(8)
T7	0.2123(4)	0.5282(4)	0.4759(7)	1	2.87(8)
O1	0.1309(7)	0.5772(4)	0.2662(4)	1	4.18(15)
O2	0.0204(4)	0.6522(5)	0.1699(5)	1	4.18(15)
O3	0.2266(7)	0.8041(3)	0.2337(4)	1	4.18(15)
O4	0.2129(2)	0.65791(16)	0.1147(4)	1	4.18(15)
O5	0.1980(4)	0.4208(5)	0.7147(4)	1	4.18(15)
O6	0.1300(7)	0.5760(5)	0.6858(4)	1	4.18(15)
O7	0.1489(7)	0.4555(7)	0.5593(4)	1	4.18(15)
O8	0.9805(4)	0.3460(4)	0.2820(5)	1	4.18(15)
O9	0.1509(7)	0.4579(7)	0.3913(4)	1	4.18(15)
O10	0.2143(2)	0.66123(16)	0.8359(4)	1	4.18(15)
O11	0.34815(16)	0.5594(3)	0.4765(8)	1	4.18(15)
N1	0.2681(8)	0.9419(9)	0.9475(8)	1	9.8(4)
C1	0.094(2)	0.8661(17)	1.0357(13)	1	9.8(4)
C2	0.1545(11)	0.8324(10)	0.9689(13)	1	9.8(4)
C3	0.3614(14)	0.942(3)	1.0010(13)	1	9.8(4)
C4	0.297(2)	0.946(3)	0.8554(9)	1	9.8(4)
C5	0.2548(16)	1.0487(11)	0.9651(16)	1	9.8(4)
O_R1	0.1693(16)	0.9915(18)	1.0562(9)	1	9.8(4)
O_H1	0.633(3)	0.2282(18)	0.477(4)	0.658(11)	8.4(7)
Ow1	0.058(3)	-0.080(3)	0.7520(15)	0.922(8)	8.4(7)

[a] O_R, O_H and O_W indicate oxygen atoms in the OSDA molecule, hydroxyl group and water, respectively.

Table S3 Selected bond lengths and angles for as-made, hydrated ECR-40C-Model A.

Bond length (Å)		Bond angle (°)	
T1-O4	1.643(3)	O4-T1-O4	108.20(22)
T1-O_H1	2.04(6)	O4-T1-O_H1	143.6(11)
T2-O10	1.645(3)	O4-T1-O_H1	101.7(7)
T2-O_H1	2.08(6)	O4-T1-O_H1	80.7(11)
T3-O2	1.644(4)	O_H1-T1-O_H1	62.9(20)
T3-O5	1.613(4)	O10-T2-O10	108.21(22)
T3-O6	1.627(4)	O10-T2-O_H1	143.5(11)
T3-O7	1.628(4)	O10-T2-O_H1	101.1(7)
T4-O1	1.632(4)	O10-T2-O_H1	81.8(11)
T4-O3	1.610(6)	O_H1-T2-O_H1	61.7(20)
T4-O8	1.630(4)	O2-T3-O5	108.6(3)
T4-O9	1.630(4)	O2-T3-O6	109.3(3)
T5-O1	1.637(4)	O2-T3-O7	107.9(3)
T5-O2	1.628(4)	O5-T3-O6	110.4(3)
T5-O3	1.607(4)	O5-T3-O7	110.9(3)
T5-O4	1.624(4)	O6-T3-O7	110.0(3)
T6-O5	1.612(5)	O1-T4-O3	108.8(5)
T6-O6	1.632(4)	O1-T4-O8	111.6(3)
T6-O8	1.629(4)	O1-T4-O9	108.3(3)
T6-O10	1.624(4)	O3-T4-O8	107.8(3)
T7-O7	1.614(4)	O3-T4-O9	112.1(5)
T7-O9	1.615(4)	O8-T4-O9	108.4(3)
T7-O11	1.629(3)	O1-T5-O2	107.6(3)
T7-O11	1.641(4)	O1-T5-O3	110.1(3)
T-O (Avg.)	1.663	O1-T5-O4	109.0(3)
		O2-T5-O3	110.1(3)
		O2-T5-O4	109.7(3)
		O3-T5-O4	110.6(3)
		O5-T6-O6	109.0(5)
		O5-T6-O8	108.9(4)
		O5-T6-O10	110.1(4)
		O6-T6-O8	109.3(3)
		O6-T6-O10	109.2(3)
		O8-T6-O10	110.4(3)
		O7-T7-O9	113.0(3)
		O7-T7-O11	108.9(3)
		O7-T7-O11	109.2(3)
		O9-T7-O11	108.9(3)
		O9-T7-O11	109.0(3)
		O11-T7-O11	107.8(3)
		O-T-O (Avg.)	106.93

[a] O_H indicates water oxygen atoms.

Table S4 Atomic coordinates and thermal parameters for as-made, hydrated ECR-40C-Model B.

Atom	*x*	*y*	*z*	Occupancy	U_{iso} × 100 (Å^2)
T1	0.333333	0.666667	0.0354(3)	1	2.21(5)
T2	0.333333	0.666667	0.8266(3)	1	2.21(5)
T3	0.1148(4)	0.4520(4)	0.61312(18)	1	2.21(5)
T4	0.1142(4)	0.4520(4)	0.24940(17)	1	2.21(5)
T5	0.1491(4)	0.6753(4)	0.1509(9)	1	2.21(5)
T6	0.1475(4)	0.6746(4)	0.71031(16)	1	2.21(5)
T7	0.2067(3)	0.5282(3)	0.43193(18)	1	2.21(5)
O1	0.1271(4)	0.57528(18)	0.22011(14)	1	3.15(10)
O2	0.02114(18)	0.6546(4)	0.1250(2)	1	3.15(10)
O3	0.2268(4)	0.8035(2)	0.19160(16)	1	3.15(10)
O4	0.2140(2)	0.66022(16)	0.07074(14)	1	3.15(10)
O5	0.1982(2)	0.4219(3)	0.66905(16)	1	3.15(10)
O6	0.1270(3)	0.57475(18)	0.64178(16)	1	3.15(10)
O7	0.1446(4)	0.4572(4)	0.51464(12)	1	3.15(10)
O8	0.9799(2)	0.3441(3)	0.23751(18)	1	3.15(10)
O9	0.1461(4)	0.4606(4)	0.34744(12)	1	3.15(10)
O10	0.21355(18)	0.65978(16)	0.79058(16)	1	3.15(10)
O11	0.34129(14)	0.5568(3)	0.4323(2)	1	3.15(10)
N1	0.22114(16)	0.9533(2)	0.95232(14)	1	5.0(3)
C1	0.3829(5)	0.9061(4)	0.9368(2)	1	5.0(3)
C2	0.3240(4)	0.9551(4)	0.99562(18)	1	5.0(3)
C3	0.1231(5)	0.8279(5)	0.9415(3)	1	5.0(3)
C4	0.1744(4)	1.0135(4)	1.00407(18)	1	5.0(3)
C5	0.2535(3)	1.0158(4)	0.8693(2)	1	5.0(3)
O_R1	0.3492(8)	0.7725(4)	0.9515(3)	1	5.0(3)
Ow1	0.1183(16)	0.088(3)	0.2296(3)	0.929(3)	7.6(10)

[a] O_R, O_H and O_W indicate oxygen atoms in the OSDA molecule, hydroxyl group and water, respectively.

Table S5 Selected bond lengths and angles for as-made, hydrated ECR-40C-Model B.

Bond length (Å)		Bond angle (°)	
T1-O4	1.638(3)	O4-T1-O4	108.70(14)
T1-O_R1	1.875(6)	O4-T1-O_R1	91.9(3)
T2-O10	1.645(3)	O4-T1-O_R1	79.72(19)
T2-O_R1	2.389(5)	O4-T1-O_R1	153.0(3)
T3-O2	1.648(4)	O_R1-T1-O_R1	74.3(3)
T3-O5	1.617(5)	O10-T2-O10	108.36(15)
T3-O6	1.615(5)	O10-T2-O_R1	97.3(3)
T3-O7	1.619(4)	O10-T2-O_R1	87.64(17)
T4-O1	1.620(5)	O10-T2-O_R1	142.9(3)
T4-O3	1.612(6)	O_R1-T2-O_R1	56.53(23)
T4-O8	1.640(4)	O2-T3-O5	108.2(3)
T4-O9	1.616(4)	O2-T3-O6	110.2(3)
T5-O1	1.636(11)	O2-T3-O7	106.67(22)
T5-O2	1.626(6)	O5-T3-O6	110.60(22)
T5-O3	1.616(7)	O5-T3-O7	111.7(3)
T5-O4	1.612(12)	O6-T3-O7	109.6(3)
T6-O5	1.608(4)	O1-T4-O3	109.0(3)
T6-O6	1.632(4)	O1-T4-O8	111.4(3)
T6-O8	1.634(5)	O1-T4-O9	108.6(3)
T6-O10	1.620(4)	O3-T4-O8	107.1(3)
T7-O7	1.594(4)	O3-T4-O9	113.2(4)
T7-O9	1.599(4)	O8-T4-O9	107.75(22)
T7-O11	1.624(4)	O1-T5-O2	106.7(4)
T7-O11	1.670(4)	O1-T5-O3	109.7(8)
T-O (Avg.)	1.667	O1-T5-O4	109.4(3)
		O2-T5-O3	110.0(4)
		O2-T5-O4	110.4(8)
		O3-T5-O4	110.6(4)
		O5-T6-O6	109.45(20)
		O5-T6-O8	109.1(3)
		O5-T6-O10	111.07(21)
		O6-T6-O8	108.34(22)
		O6-T6-O10	108.6(3)
		O8-T6-O10	110.28(21)
		O7-T7-O9	114.13(22)
		O7-T7-O11	108.2(3)
		O7-T7-O11	110.8(3)
		O9-T7-O11	108.6(3)
		O9-T7-O11	109.7(3)
		O11-T7-O11	105.0(3)
		O-T-O (Avg.)	107.09

[a] O_R indicates oxygen atoms in the OSDA molecule.

Table S6 Atomic coordinates and thermal parameters for as-made, hydrated PST-10C.

Atom	*x*	*y*	*z*	Occupancy	U_{iso} × 100 (Å^2)
Al1	0.666667	0.333333	0.3349(8)	1	1.93(21)
Al2	0.333333	0.666667	0.6266(8)	1	1.93(21)
Al3	0.4549(9)	0.1187(10)	0.5476(8)	1	1.93(21)
Al4	0.5432(11)	0.8878(10)	0.4323(7)	1	1.93(21)
P1	0.6761(13)	0.1596(11)	0.4520(7)	1	0.30(17)
P2	0.3238(13)	0.8455(11)	0.5149(5)	1	0.30(17)
Ge1	0.5128(3)	0.2039(3)	0.7445(7)	1	2.03(13)
O1	0.1938(13)	0.775(2)	0.4961(11)	1	0.28(16)
O2	0.8028(10)	0.229(3)	0.4792(10)	1	0.28(16)
O3	0.6453(16)	0.0362(11)	0.4283(13)	1	0.28(16)
O4	0.5577(4)	0.3602(4)	0.3727(7)	1	0.28(16)
O5	0.3569(16)	0.9716(11)	0.5304(14)	1	0.28(16)
O6	0.5978(11)	0.155(2)	0.5229(11)	1	0.28(16)
O7	0.4531(11)	0.171(2)	0.6434(7)	1	0.28(16)
O8	0.3945(10)	0.8411(18)	0.4423(11)	1	0.28(16)
O9	0.5726(10)	0.862(2)	0.3343(7)	1	0.28(16)
O10	0.4405(4)	0.6359(4)	0.5907(7)	1	0.28(16)
O11	0.6455(9)	0.1959(13)	0.7475(13)	1	0.28(16)
N1	0.7814(10)	0.7165(9)	0.2360(10)	1	0.5(4)
C1	0.6296(13)	0.5057(9)	0.2538(14)	1	0.5(4)
C2	0.6769(13)	0.6129(11)	0.1948(11)	1	0.5(4)
C3	0.823(3)	0.8260(11)	0.1822(13)	1	0.5(4)
C4	0.8807(13)	0.6877(18)	0.239(3)	1	0.5(4)
C5	0.754(3)	0.7386(18)	0.3240(11)	1	0.5(4)
O_R1	0.6731(14)	0.4317(13)	0.2289(18)	1	0.5(4)
Ow1	-0.004(3)	0.8584(17)	0.0371(15)	0.945(3)	1.3(8)
Ow2	0.0(4)	0.0(7)	0.282(5)	0.161(15)	1.3(8)

[a] O_R, O_H and O_W indicate oxygen atoms in the OSDA molecule, hydroxyl group and water, respectively.

Table S7 Selected bond lengths and angles for as-made, hydrated PST-10C.

Bond length (Å)		Bond angle (°)	
Al1-O4	1.751(4)	O4-Al1-O4	108.40(23)
Al1-O_R1	2.13(3)	O4-Al1-O_R1	87.0(5)
Al2-O10	1.751(4)	O4-Al1-O_R1	94.1(5)
Al2-O_R1	2.13(3)	O4-Al1-O_R1	146.1(7)
Al3-O2	1.686(18)	O_R1-Al1-O_R1	61.3(11)
Al3-O5	1.731(4)	O10-Al2-O10	109.52(23)
Al3-O6	1.742(4)	O10-Al2-O_R1	84.7(5)
Al3-O7	1.708(4)	O10-Al2-O_R1	93.5(5)
Al4-O1	1.735(16)	O10-Al2-O_R1	145.8(6)
Al4-O3	1.733(4)	O_R1-Al2-O_R1	62.9(9)
Al4-O8	1.742(4)	O2-Al3-O5	108.0(11)
Al4-O9	1.714(4)	O2-Al3-O6	103.0(15)
Al-O (Avg.)	1.796	O2-Al3-O7	107.4(12)
P1-O2	1.513(5)	O5-Al3-O6	111.5(11)
P1-O3	1.515(4)	O5-Al3-O7	116.5(12)
P1-O4	1.541(5)	O6-Al3-O7	109.4(4)
P1-O6	1.525(4)	O1-Al4-O3	114.8(13)
P2-O1	1.516(4)	O1-Al4-O8	110.3(16)
P2-O5	1.512(4)	O1-Al4-O9	105.5(12)
P2-O8	1.522(4)	O3-Al4-O8	120.2(11)
P2-O10	1.542(6)	O3-Al4-O9	93.8(10)
P-O (Avg.)	1.523	O8-Al4-O9	110.0(4)
Ge1-O7	1.778(4)	O-Al-O (Avg.)	104.71
Ge1-O9	1.779(4)	O2-P1-O3	110.0(4)
Ge1-O11	1.803(4)	O2-P1-O4	118.5(14)
Ge1-O11	1.788(12)	O2-P1-O6	108.8(4)
Ge-O (Avg.)	1.787	O3-P1-O4	100.1(11)
T-O (Avg.)	1.704	O3-P1-O6	109.5(3)
		O4-P1-O6	109.4(11)
		O1-P2-O5	108.9(4)
		O1-P2-O8	110.2(4)
		O1-P2-O10	115.3(14)
		O5-P2-O8	109.1(3)
		O5-P2-O10	106.8(12)
		O8-P2-O10	106.4(11)
		O-P-O (Avg.)	109.41
		O7-Ge1-O9	122.9(4)
		O7-Ge1-O11	109.6(4)
		O7-Ge1-O11	97.9(10)
		O9-Ge1-O11	110.2(7)
		O9-Ge1-O11	105.9(11)
		O11-Ge1-O11	109.0(8)
		O-Ge-O (Avg.)	109.25
		O-T-O (Avg.)	106.81

[a] O_R indicates oxygen atoms in the OSDA molecule.

Figure Captions

Fig. S1 Powder XRD patterns of as-made (a) ECR-40A, (b) ECR-40B, (c) ECR-40C, (d) ECR-40D, (e) ECR-40E, (f) PST-10A, (g) PST-10B and (h) PST-10C.

Fig. S2 Rietveld plots for as-made, hydrated (a) ECR-40C-Model A and (b) ECR-40C-Model B: observed data (crosses), calculated fit (solid line) and difference plot (lower trace). The tick marks represent the positions of allowed reflections (synchrotron, λ = 1.5475 Å, R_{wp} = 9.36 and 10.95% for ECR-40C-Model A and ECR-40C-Model B, respectively). Overall counts over 40 degree were multiplied by 3.

Fig. S3 (a) Rietveld plot for as-made, hydrated PST-10C: observed data (crosses), calculated fit (solid line) and difference plot (lower trace). The tick marks represent the positions of allowed reflections (synchrotron, λ = 1.5475 Å, R_{wp} = 14.69%). (b) Crystal structures of as-made, hydrated PST-10C. Top view (left) of the 12-ring channel and top (middle) and side (right) views of its structural building unit. Color code: blue, Al; orange, P; cyan, Ge; red, O; gray, C; black, N. Hydrogen atoms are omitted for clarity. The $HTMA^+$ ions covalently bonded to the framework Al atoms are indicated with a ball-and-stick model, and the water oxygen atoms are represented with dots. Overall counts over 40 degree were multiplied by 3.

Fig. S4 Changes in the content of $HTMA^+$ (▲), $BHDMA^+$ (●) and $THMA^+$ (■) ions as a function of the number of each organic cation exchange in calcined UZM-22. OSDA exchange was performed at 80 °C for 4 h using with 1.0 M solutions of the iodide salt of the corresponding OSDA cations. The organic content in each solid product was determined by TGA/DTA.

Fig. S5 (a) ^{29}Si and (b) ^{31}P NMR spectra of the mother liquors separated after ECR-40C crystallization at 140 °C for 0 and 0.5 days and (c) ^{29}Si and (d) ^{31}P MAS NMR

spectra of the solid products recovered after ECR-40C crystallization at 140 °C for different times.

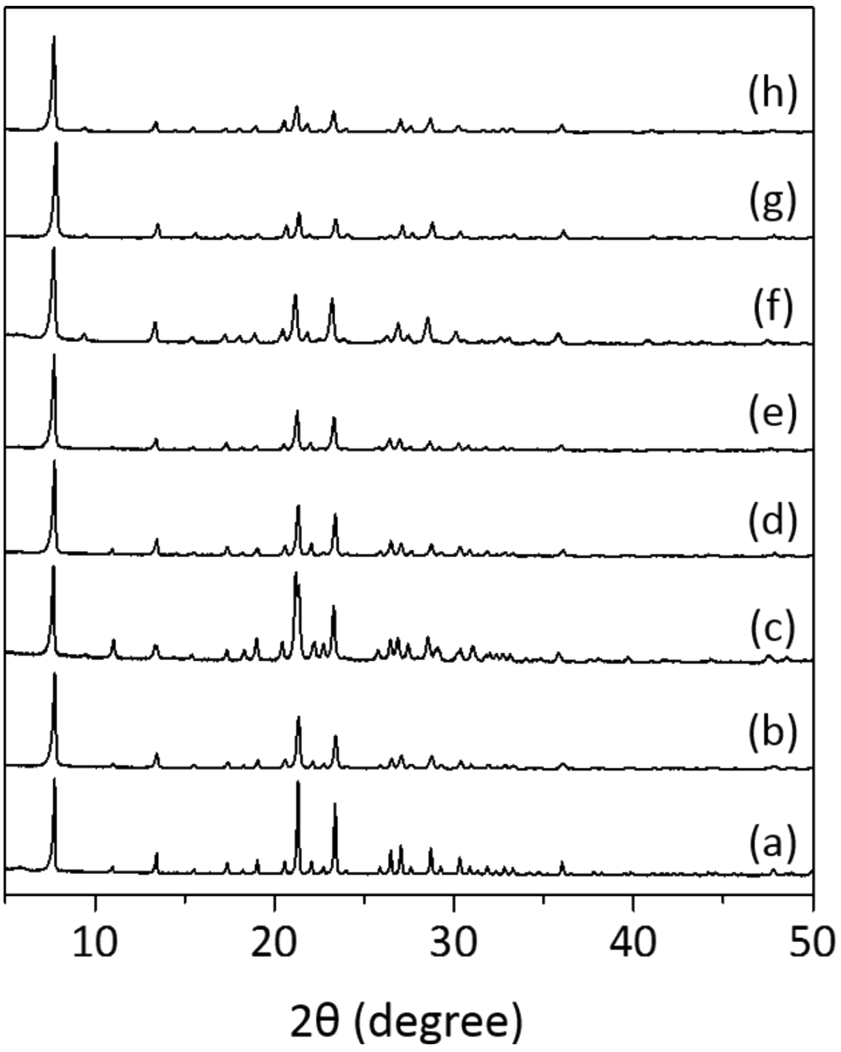
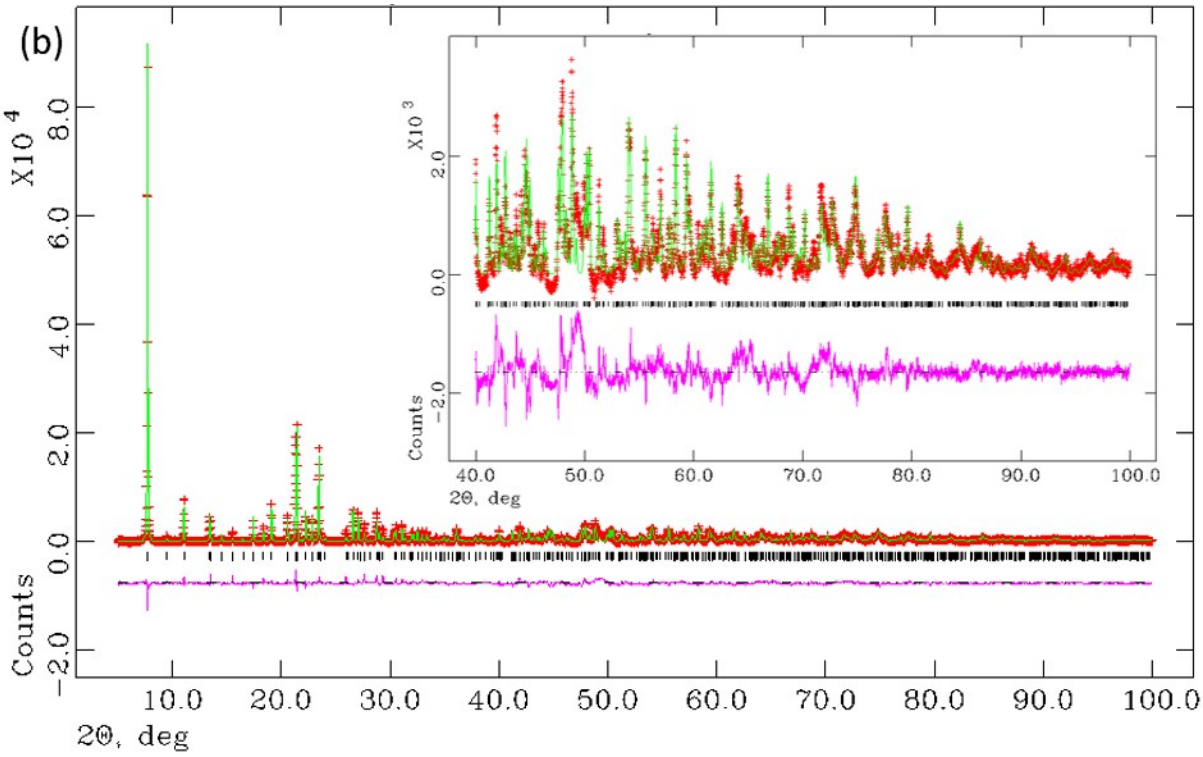


Fig. S1


(b)
X10 4
8.0
6.0
4.0
2.0
0.0
−2.0
Counts
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
2θ, deg
X10 3
2.0
0.0
−2.0
Counts
40.0
50.0
60.0
70.0
80.0
90.0
100.0
2θ, deg

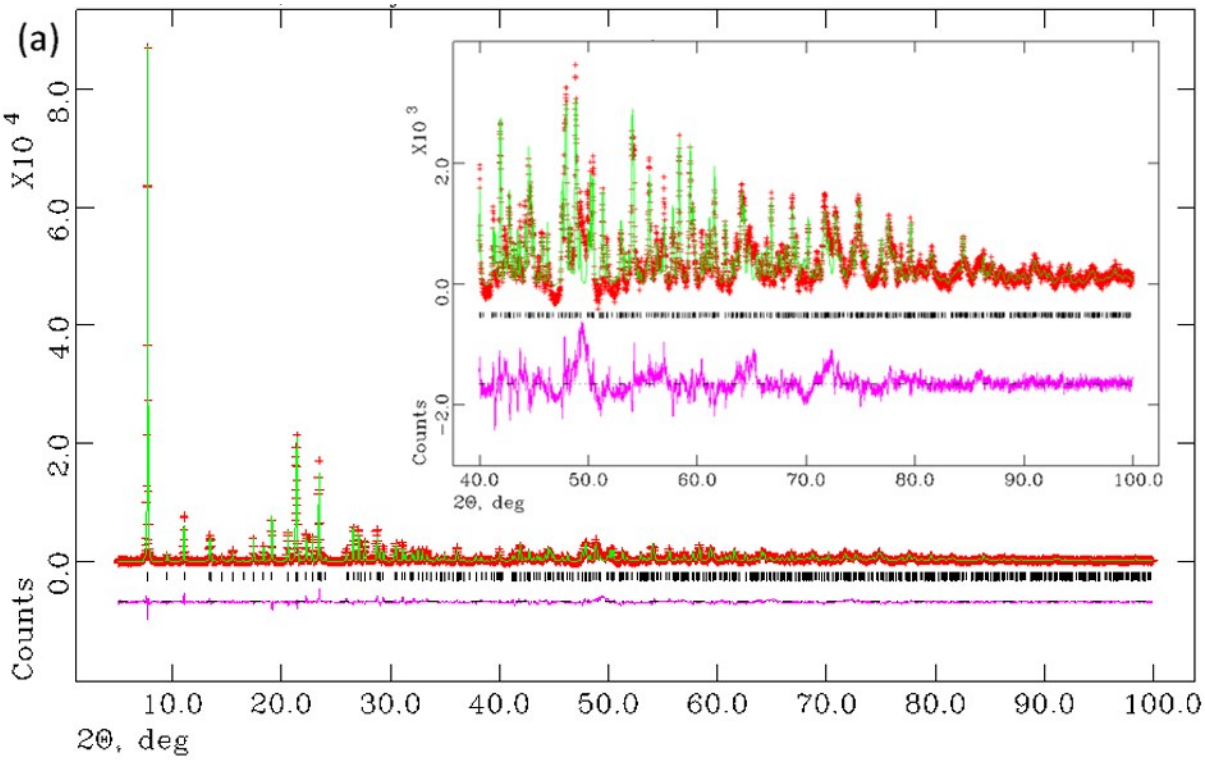

(a)
X10 4
8.0
6.0
4.0
2.0
0.0
Counts
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
2θ, deg
X10 3
2.0
0.0
−2.0
Counts
40.0
50.0
60.0
70.0
80.0
90.0
100.0
2θ, deg

Fig. S2

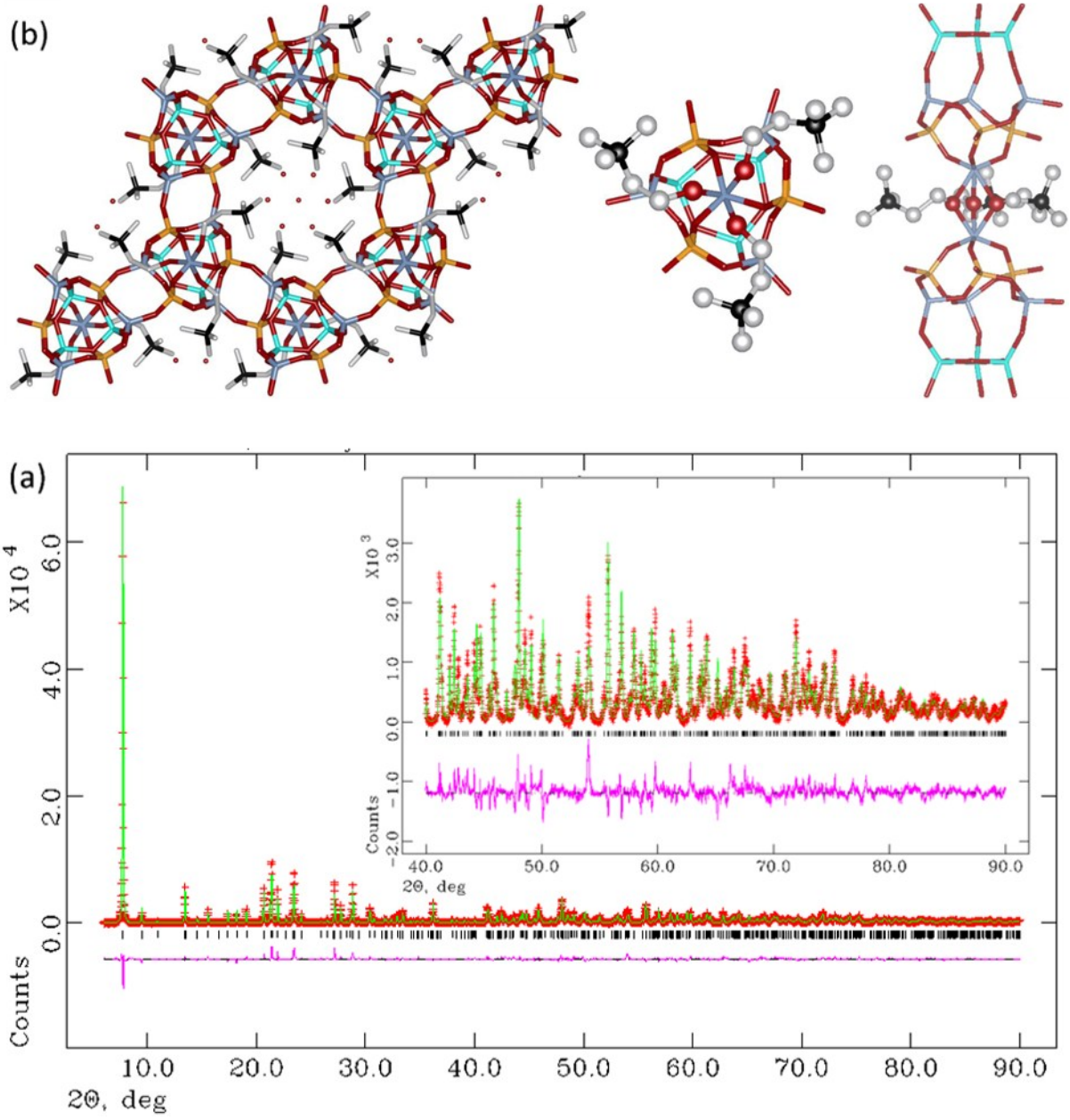

(b)
(a)
X10 4
6.0
4.0
2.0
0.0
Counts
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
2Θ, deg
X10 3
3.0
2.0
1.0
0.0
−1.0
−2.0
Counts
40.0
50.0
60.0
70.0
80.0
90.0
2Θ, deg

Fig. S3

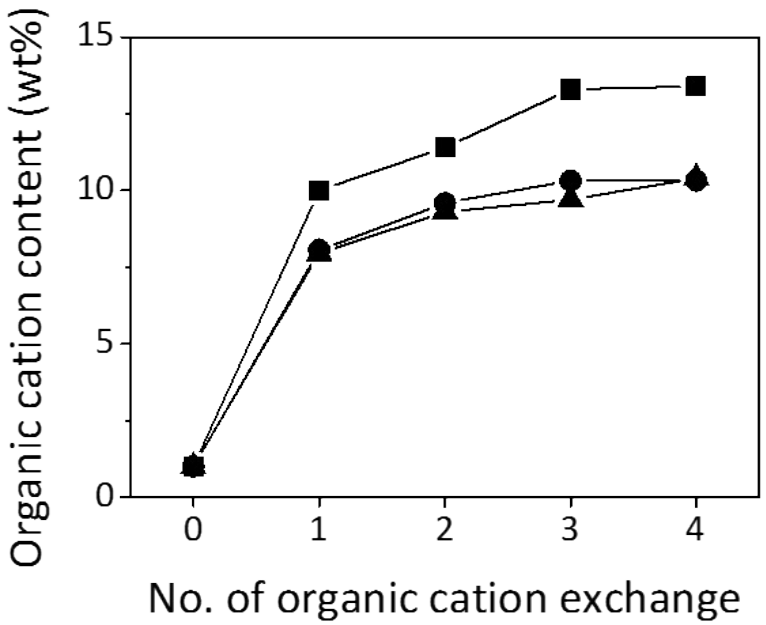

Organic cation content (wt%)
15
10
5
0
0
1
2
3
4
No. of organic cation exchange

Fig. S4

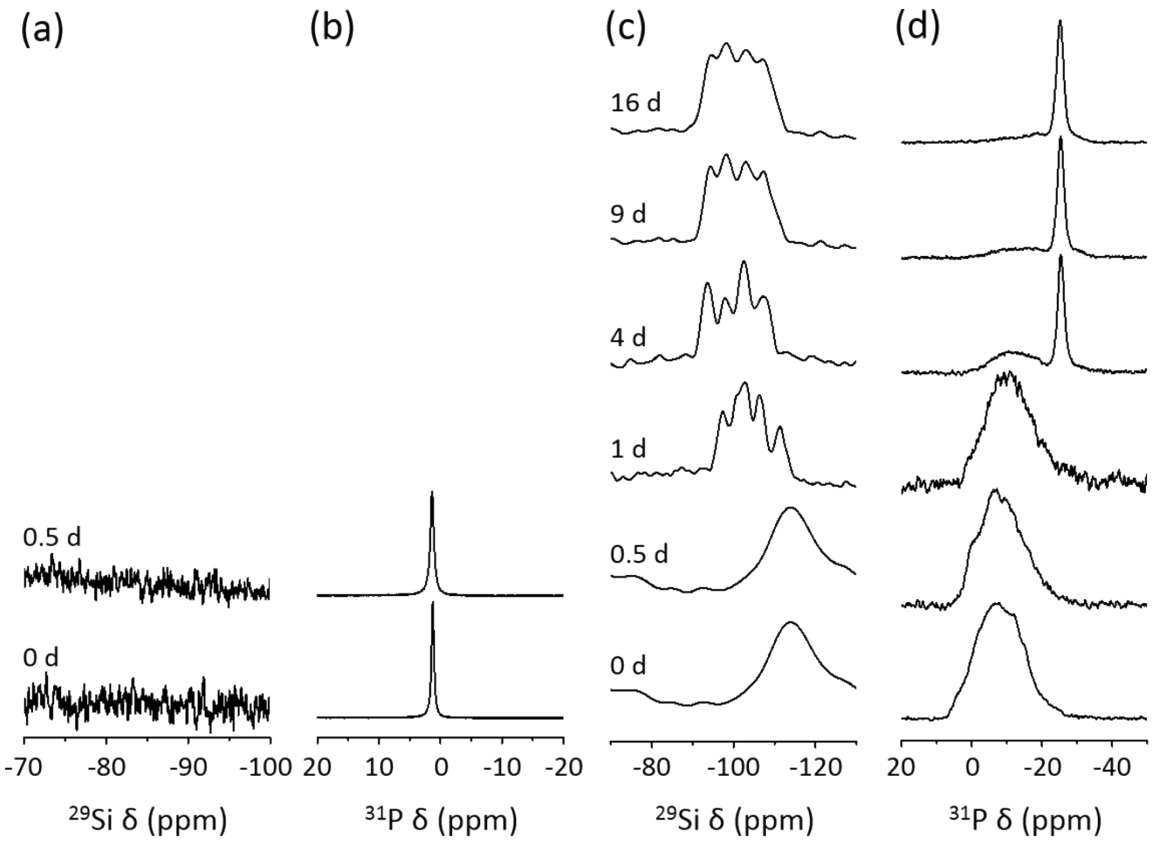

(a)
(b)
(c)
(d)
16 d
9 d
4 d
1 d
0.5 d
0 d
0.5 d
0 d
-70 -80 -90 -100
20 10 0 -10 -20
-80 -100 -120
20 0 -20 -40
29Si δ (ppm)
31P δ (ppm)
29Si δ (ppm)
31P δ (ppm)

Fig. S5