Supporting Information

Synthesis of an extra-large molecular sieve using proton sponges as organic structure directing agents

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Figure S1: Powder X-ray diffraction patterns of as-prepared and calcined ITQ-51

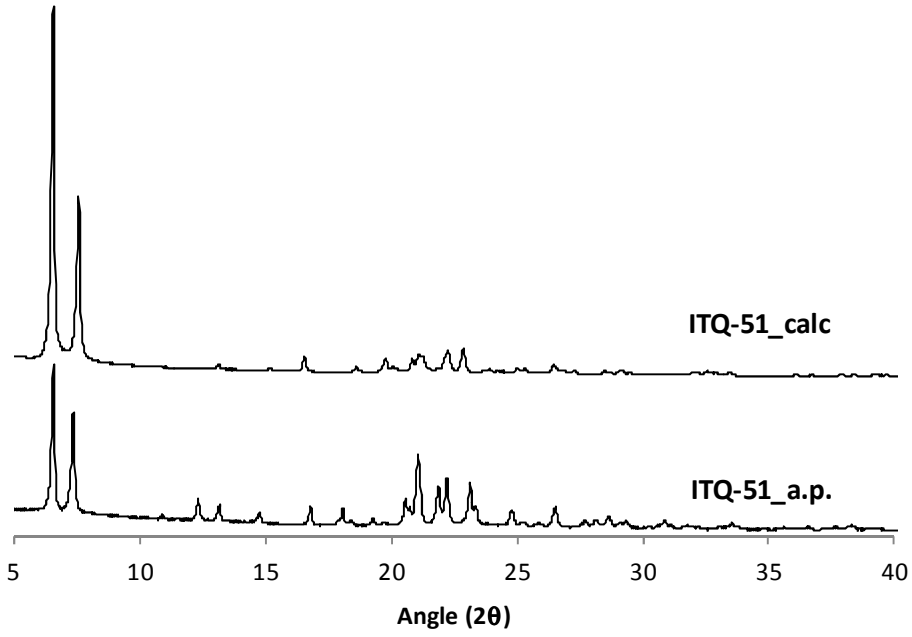


Figure S2: Powder X-ray diffraction patterns of ITQ-51 material treated "in-situ" at different temperatures

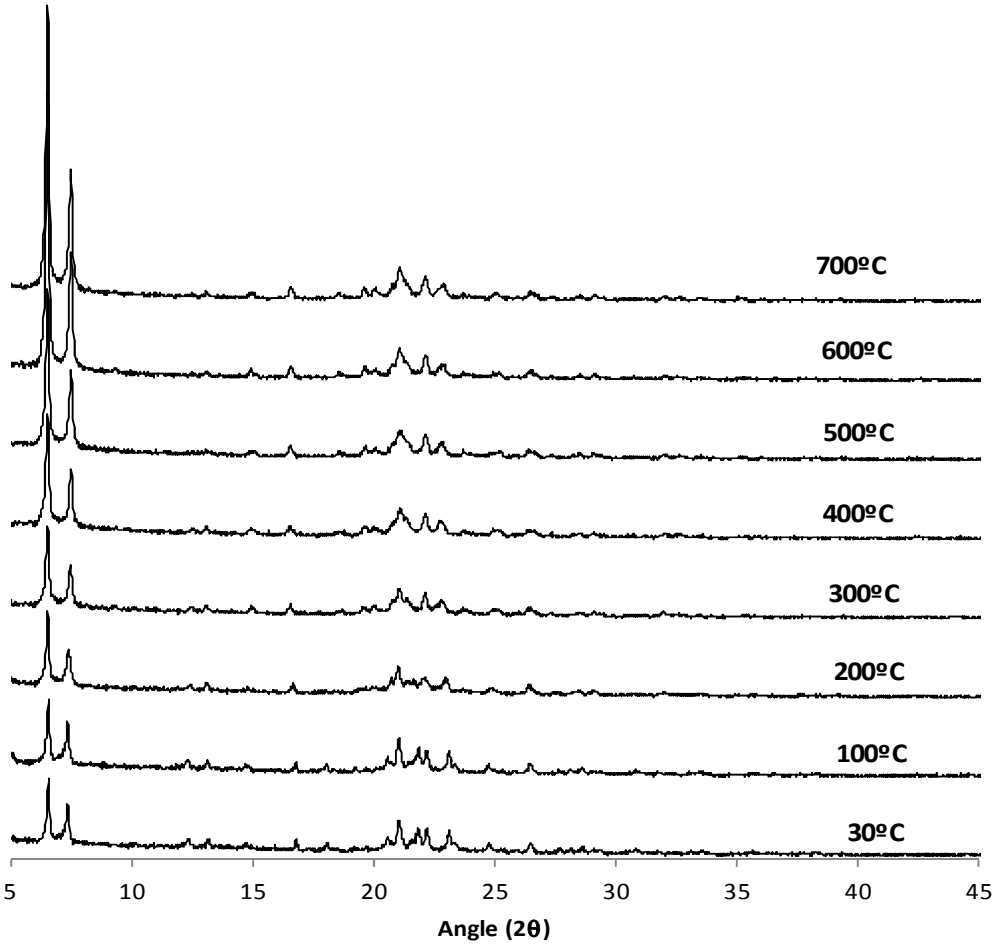


Figure S3: SEM image of ITQ-51

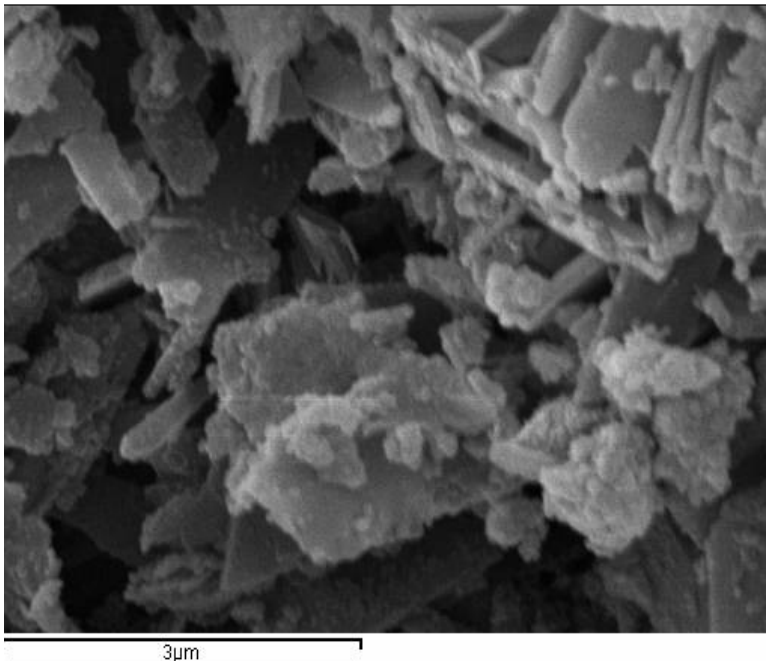


Figure S4: N_2 adsorption isotherm of calcined ITQ-51 zeolite

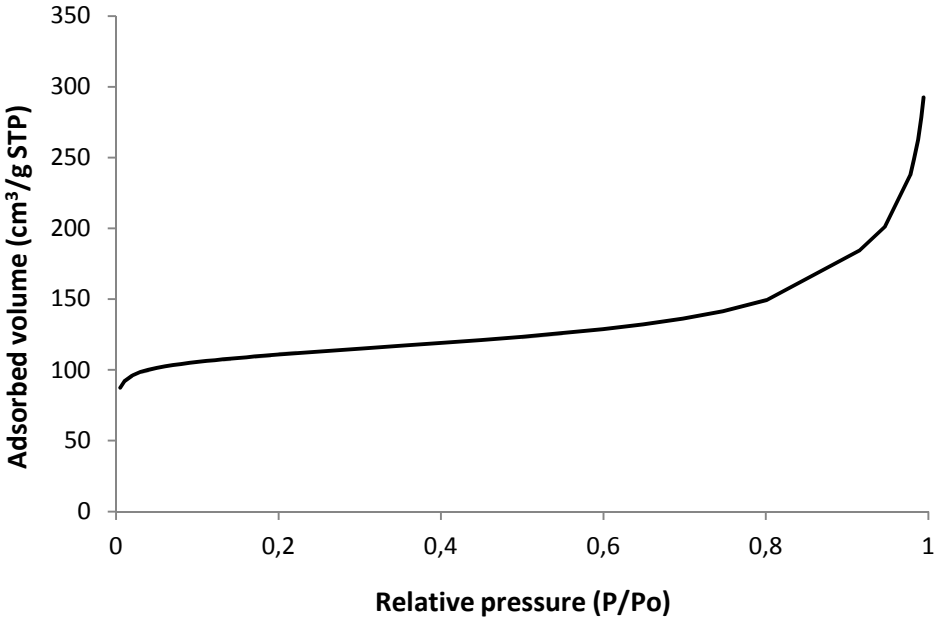


Figure S5: Experimental pore distribution of calcined ITQ-51 deduced from Ar adsorption

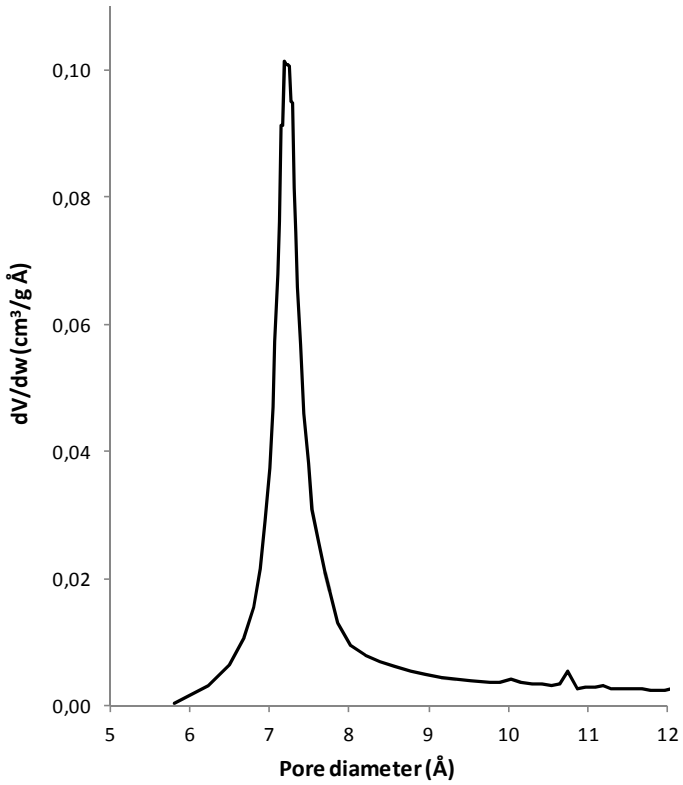


Figure S6: Solid-state ^{31}P MAS NMR spectrum of calcined ITQ-51

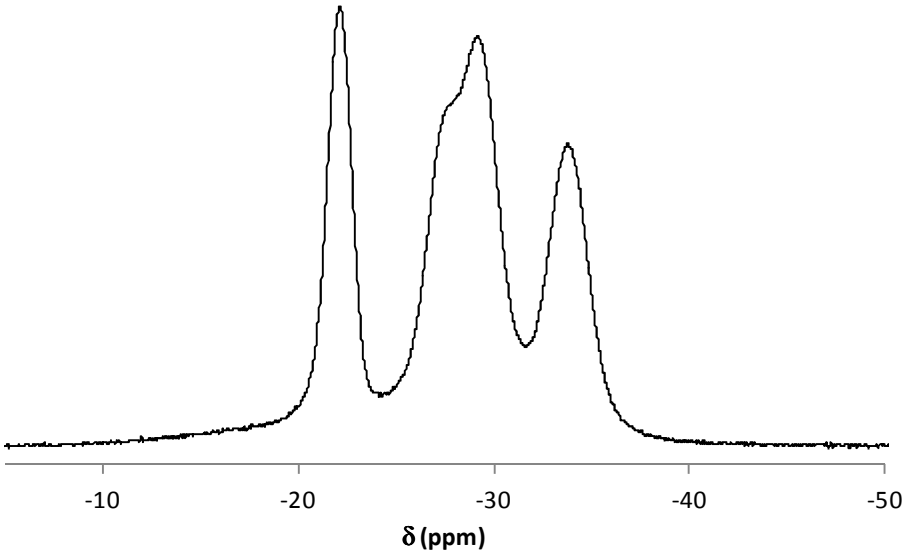


Figure S7: Solid-state ^{27}Al MAS NMR spectrum of calcined ITQ-51

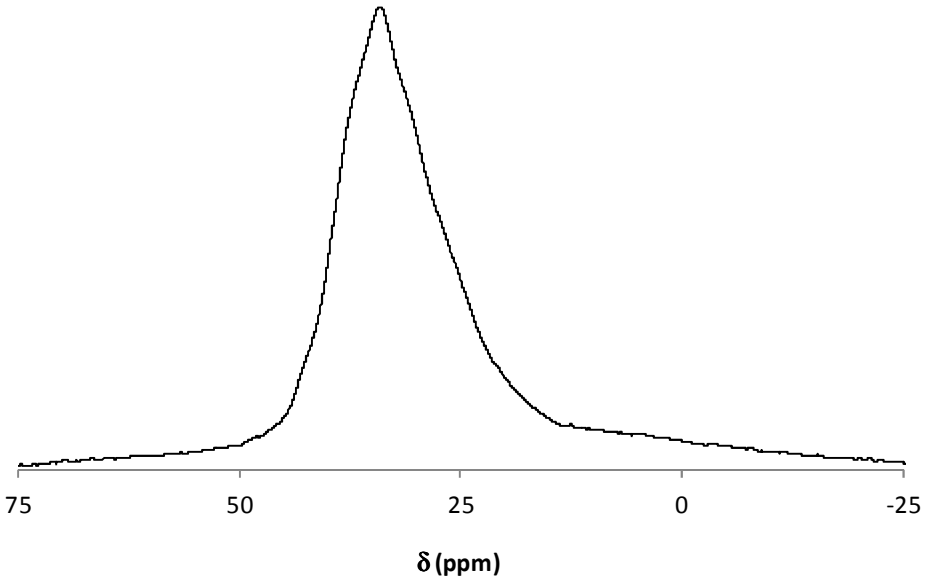


Figure S8: Two-dimensional ^{27}Al MQMAS NMR spectra of calcined-dehydrated ITQ-51

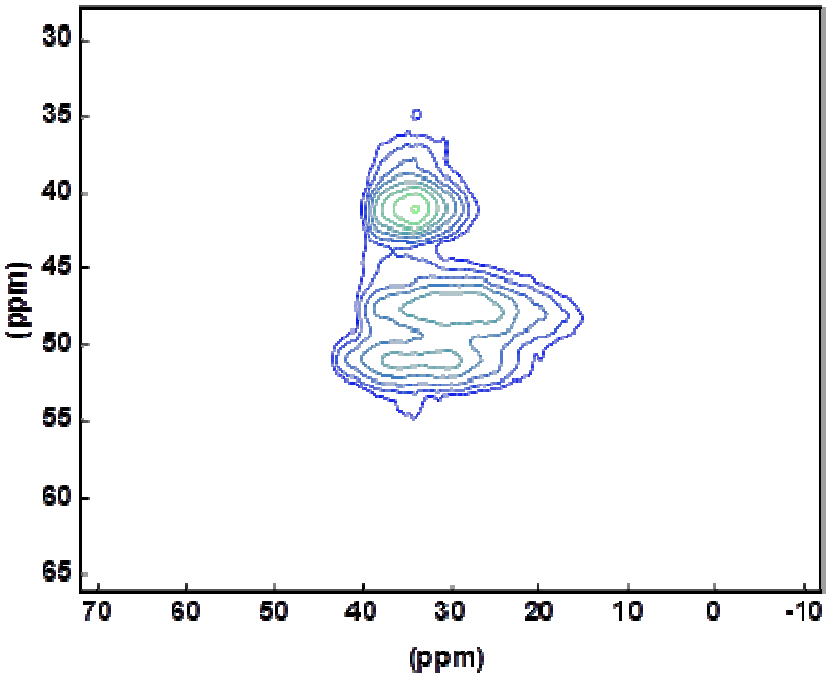


Figure S9: Solid-state ^{29}Si MAS NMR spectrum of calcined ITQ-51

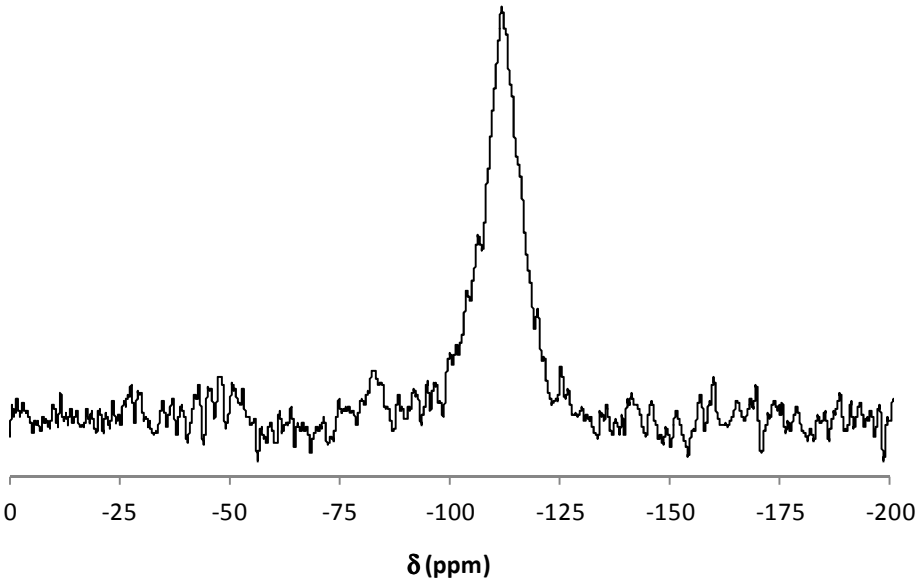
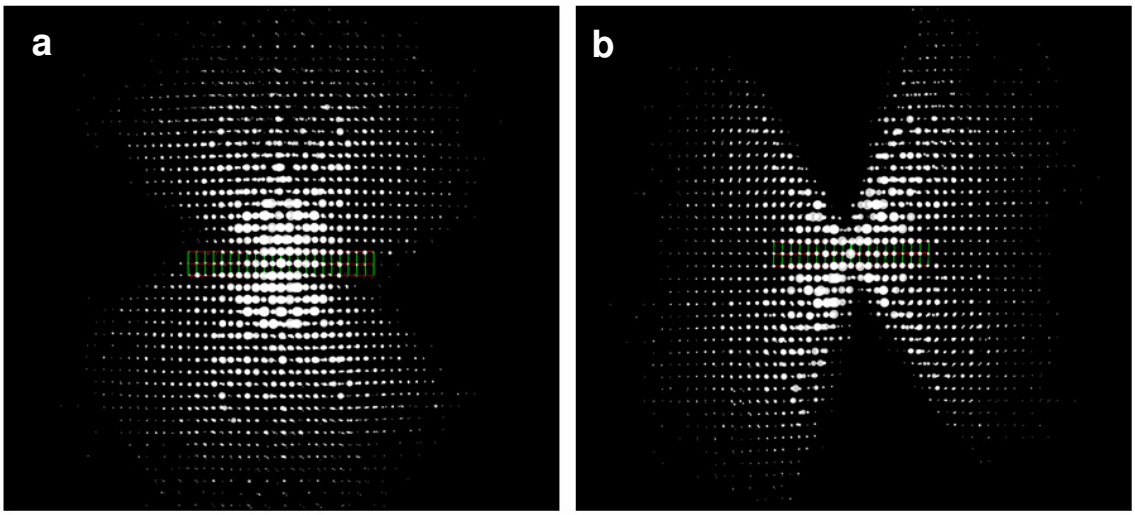


Figure S10: Reconstructed reciprocal lattices of the calcined-hydrated ITQ-51 from 3D-RED data. (a) Dataset 1 from crystal 1 and (b) Dataset 2 from crystal 2. The two datasets are complementary which together cover most reciprocal space. Although the crystals diffract to 0.6 Å, the data at high resolution are with low completeness. Only reflections with $d \geq 0.90$ Å were used for the final refinement.



Dataset 1 Dataset 2

Figure S11: 2D slices of the reconstructed reciprocal lattice obtained from the 3D-RED (Rotation Electron Diffraction) data. (a-c) 2D-slices from dataset 1. The crystal is shown as an insert in **(c). (d)** 2D (*h*0*l*) slice from dataset 2, showing that the two datasets cover different part of the reciprocal lattice. The systematic absences can be deduced as *h*0*l*: $h+l = 2n+1$ (more obvious in (**d**)) and 0*k*0: $k = 2n+1$.The possible space group is $P2_1/n$.

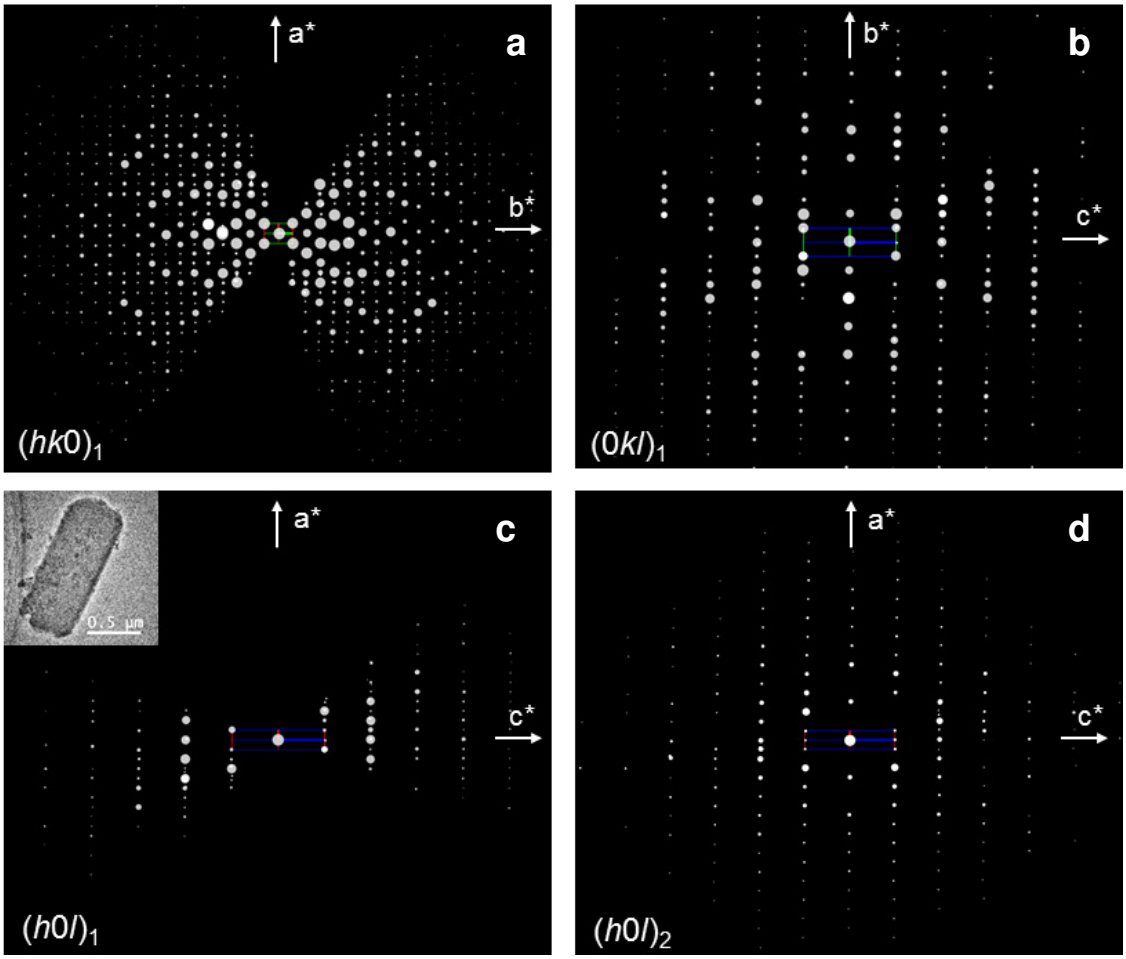


Figure S12: The building chains found (a-b) in ITQ-51 and (c-d) in the hypothetical 16-ring T16MR; (a) lau chain; (b) a new helical 4-ring chain; (c) double crankshaft chain and (d) double narsarsukite chain. The chains have similar periodicity so that they can be combined to form different frameworks.

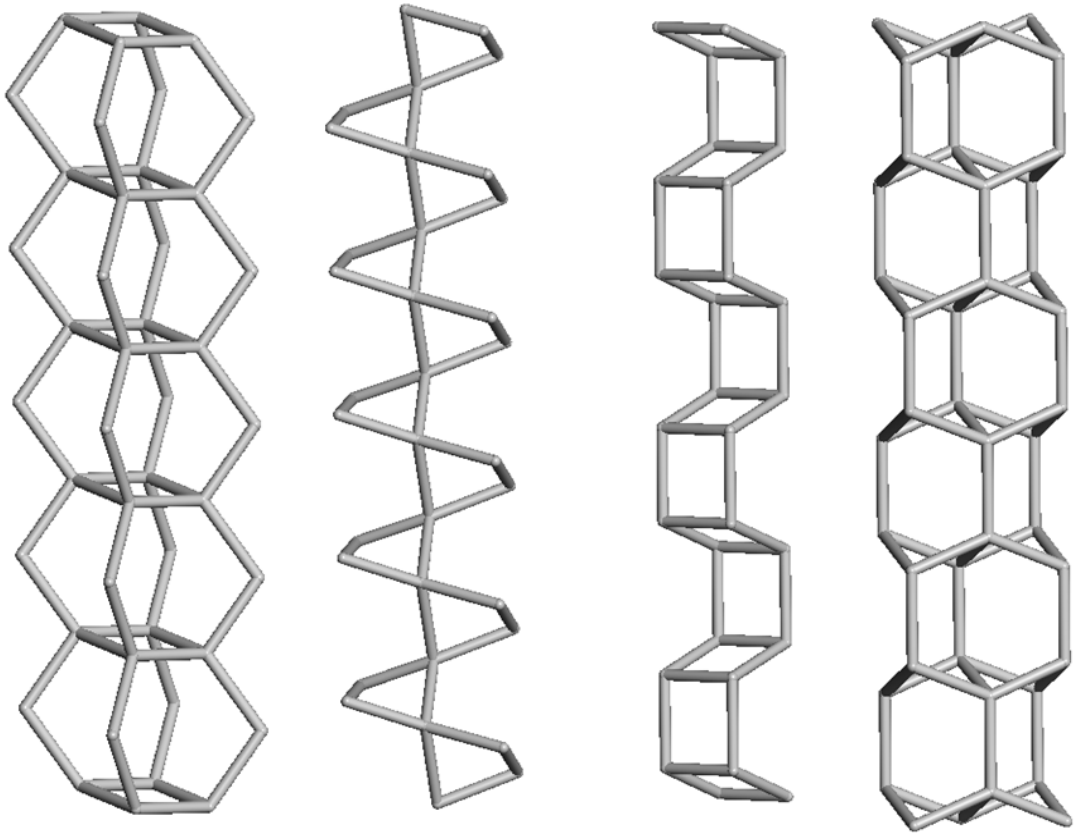


Table S1: 3D-RED data collection, crystal data and structure refinement details of ITQ-51 (resolution cut to 0.90 Å)

	Dataset 1	Dataset 2
Crystal	1	2
Tilt angle	- 60.92° to +70.88°	-62.79° to + 73.70°
Tilt step	0.1°	0.1°
No. of RED frames	1377	1553
Exposure time/frame	1.0 s	1.0 s
a / Å	23.418	23.418
b / Å	16.324	16.450
c / Å	4.964	4.924
α / °	90.93	89.97
β / °	90.01	91.28
γ / °	90.48	92.20
Completeness	0.678	0.615
Rint	0.1992	0.2525
No. of measured reflections	6441	4583
No. of independent reflections	1910	1750
h	-23 ≤ h ≤23	-24 ≤ h ≤ 24
k	-18 ≤ k ≤ 18	-17 ≤ k ≤17
l	-5 ≤ l ≤ 5	-5 ≤ l ≤ 5
R1	0.35	0.42
No. of parameters	97	97

After merging the two datasets, the number of independent reflections is 2310, the completeness is 0.818 and the R1 is 0.37.

Table S2: Crystallographic data for Rietveld refinement of calcined dehydrated ITQ-51

Chemical formula	$Al_4P_4O_{16}$
Formula weight	1922.89
a	23.345(2) Å
b	16.513(2) Å
c	4.9814(5) Å
β	90.620(5)°
V	1920.2(3) $Å^3$
Z	4
Space group	$P2_1/n$ (no.14)
CuKα	1.5418 Å
No. of reflections	994
No. of parameters	106
No. of restraints	32 T-O distances
R_p	0.060
R_{wp}	0.082
R_{exp}	0.019
GOF	4.39
R_F	0.012

Table S3: Crystal data for the six structures related to ITQ-51 given in Figure 6

Structures	**ATO (AlPO-31)**	**ITQ-51**	**T18MR**	**T12MR (umk)**	**T16MR**	**VFI (VPI-5)**
Space group	*R-3m*	$P2_1/n$	$P6_1$	$P6_3/mcm$	*Cmcm*	$P6_3/mcm$
Unit cell	a = 20.914 Å	a = 23.345 Å	a = 16.348 Å	a = 13.784 Å	a = 27.395 Å	a = 18.284 Å
parameters	c = 5.061 Å	b = 16.510 Å	c = 4.957 Å	c = 9.133 Å	b = 18.284 Å	c = 8.589 Å
		c = 4.9814 Å			c = 8.589 Å	
		β = 90.620°				

Table S4: Coordination sequences and vertex symbols of ITQ-51 and three hypothetical zeolites

ITQ-51

T-atom name	N1 to N10	Vertex Symbol
Al1	4 10 20 32 47 70 97 126 160 196	$4\bullet4\bullet6_2\bullet8_8\bullet6_3\bullet6_3$
Al2	4 11 22 33 47 69 95 125 165 203	$4\bullet6_3\bullet6\bullet6_2\bullet6\bullet6_3$
Al3	4 11 20 33 49 66 96 132 159 188	$4\bullet6_2\bullet6\bullet6_2\bullet6_2\bullet6_4$
Al4	4 11 20 31 49 72 98 127 161 193	$4\bullet6_3\bullet6\bullet6_2\bullet6_2\bullet6_4$
P1	4 10 20 32 47 70 97 126 160 196	$4\bullet4\bullet6_2\bullet8_8\bullet6_3\bullet6_3$
P2	4 11 22 33 47 69 95 125 165 203	$4\bullet6_3\bullet6\bullet6_2\bullet6\bullet6_3$
P3	4 11 20 33 49 66 96 132 159 188	$4\bullet6_2\bullet6\bullet6_2\bullet6_2\bullet6_4$
P4	4 11 20 31 49 72 98 127 161 193	$4\bullet6_3\bullet6\bullet6_2\bullet6_2\bullet6_4$

T12MR, topology type: umk

T-atom name	N1 to N10	Vertex Symbol
Si1	4 10 20 33 50 72 98 128 160 196	$4\bullet6\bullet4\bullet6_2\bullet6_2\bullet8_6$

T16MR

T-atom name	N1 to N10	Vertex Symbol
Si1	4 10 20 33 47 64 87 115 148 186	$4\bullet6_2\bullet4\bullet6_2\bullet6_2\bullet8_7$
Si2	4 11 20 31 46 64 87 117 150 182	$4\bullet6\bullet6\bullet6_3\bullet6_2\bullet6_3$
Si3	4 11 20 31 45 64 89 117 149 182	$4\bullet6_2\bullet6\bullet6_3\bullet6_2\bullet6_3$
Si4	4 10 18 30 45 63 86 113 145 180	$4\bullet6_3\bullet4\bullet6_3\bullet6_2\bullet6_4$

T18MR

T-atom name	N1 to N10	Vertex Symbol
Si1	4 11 20 30 45 64 86 116 154 191	$4\bullet6_3\bullet6\bullet6_2\bullet6_2\bullet6_4$
Si2	4 11 20 30 45 64 86 116 154 191	$4\bullet6_3\bullet6\bullet6_2\bullet6_2\bullet6_4$
Si3	4 10 20 32 44 62 90 118 148 192	$4\bullet4\bullet6_2\bullet8_8\bullet6_3\bullet6_3$

Table S5: List of mono-directional medium, large and extra-large pore AlPOs or SAPOs

Zeotype	Pore T-atoms	Pore openings (Å)	Reference
AlPO-11 (AEL)	10	6.5 x 4.0	[1]
AlPO-5 (AFI)	12	7.3 x 7.3	[2]
AlPO-31 (ATO)	12	5.4 x 5.4	[3]
AlPO-8 (AET)	14	8.7 x 7.9	[4]
ITQ-51	16	9.9 x 7.7	This work
VPI-5 (VFI)	18	12.7 x 12.7	[5]

References:

[1] Bennett, J. M., Richardson, J. W., Pluth, J. J. & Smith, J. V. Aluminophosphate molecular sieve AlPO4-11: partial refinement from powder data using a pulsed neutron source. *Zeolites*, **7**, 160-162 (1987).

[2] Bennett, J. M., Cohen, J. P., Flanigen, E. M., Pluth, J. J. & Smith, J. V. Crystal structure of tetrapropylammonium hydroxide-aluminum phosphate number 5. *ACS Sym. Ser*. **218**, 109-118 (1983).

[3] Bennett, J. M. & Kirchner, R. M. The structure of calcined AlPO4-31 - A new framework topology containing one-dimensional 12-ring pores, *Zeolites*, **12**, 338-342 (1992).

[4] Dessau, R. M., Schlenker, J. L. & Higgins, J. B. Framework topology of AlPO4-8: the first 14-ring molecular sieve. *Zeolites*. **10**, 522-524 (1990).

[5] Davis, M. E., Saldarriaga, C., Montes, C., Garces, J. & Crowder, C. A molecular sieve with eighteen-membered rings. *Nature*. **331**, 698-699 (1988).