Electronic Supplementary Material (ESI) for Chemical Science.

A multi-dimensional quasi-zeolite with 12×10×7-ring channels demonstrates high thermal stability and good gas-adsorption selectivity

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1. Materials and Methods.

1.1 Characterisation

All reagents are of analytical grade and were used as obtained from commercial sources without further purification. The purity of the products was examined by powder X-ray diffraction (PXRD) on a Rigaku D/Max-2400 diffractometer with a CuK_α radiation (λ = 1.5418 Å). The morphology of PKU-15 was examined using a S4800 scanning electron microscope (SEM) with an accelerating voltage of 10.0kV. The elemental analysis for carbon, nitrogen and hydrogen was carried out with an Elementar Vario EL III microanalyzer. The elemental contents of silicon and germanium were measured by X-ray energy dispersive spectroscopy (EDS) on a JEOL JSM 820 scanning electron microscope. The ^{13}C NMR spectra of the SDA salt trimethylpropylammonium iodide were recorded at Bruker ARX-400 in a D_2O solution. The thermal analysis was done on TGA Q50 V20.6 with a heating rate of 10 °C min^{-1} from 50 to 1000 °C in air. *In-situ* PXRD data was collected from 50 to 800 °C with an increment of 50 °C per step on a Bruker D8 Advance diffractometer. The sample was equilibrated for two minutes prior to each PXRD data collection. Gas adsorption measurements were carried out with a QUANTACHROME AUTOSORB-iQ gas adsorption analyser. The N_2 sorption isotherms were collected in the pressure range from 0.01 to 0.99 P/P_0 at 77 K in a liquid nitrogen bath. The gas sorption experiments of CO_2, N_2, CH_4, C_2H_4, and C_2H_6 at 273 K were carried out in an ice-water bath. Prior to the adsorption measurement, the sample was first treated under ozone, and degassed at 200 °C for 6 hours prior to measurement. The tiling was calculated by using the software TOPOS.[1]

1.2. Synthesis of the structure-directing agent trimethylpropylammonium hydroxide ($M_3PN^+OH^-$)

A typical procedure for the synthesis of trimethylpropylammonium hydroxide ($M_3PrN^+OH^-$) was described as follows. Firstly, dimethylpropylammonium was obtained by Eschweiler-Clarke reaction from propylamine, formic acid and formaldehyde. Then the tertiary amine reacted with methyl iodide to obtain trimethylpropylammonium iodide. The solid product was filtered, washed with acetone, and characterised by ^{13}C NMR spectroscopy (see Fig.S7†). The hydroxide form of the SDA was obtained by the reaction of the iodide with Ag_2O in an aqueous solution. The concentration of the SDA solution was determined by titration with a 0.1 mol L^{-1} HCl solution.

1.3. Synthesis of PKU-15

A certain amount of amorphous SiO_2 and GeO_2 were mixed with $M_3PrN^+OH^-$ solution, and the mixture was stirred until a uniform suspension was formed. The water content was controlled by evaporation at 70 °C in an oven. The composition of the initial gel was 0.1 SiO_2: 0.9 GeO_2: 0.5 M_3PrNOH: *x* H_2O, *x*=3~7. The mixture was then transferred into a Teflon-lined stainless steel autoclave and heated at 175 °C for 14 days. The colourless single crystals were filtered and washed with ethanol, and then dried at 60 °C overnight. Elemental analysis (wt%) found for PKU-15: C 7.19%, N 1.70%, H 1.78%; calcd. C 7.20%, N 1.72%, H 1.76%. The samples were calcined at 200 °C in O_3 to remove organic species in the channels.

2. **Figures.**

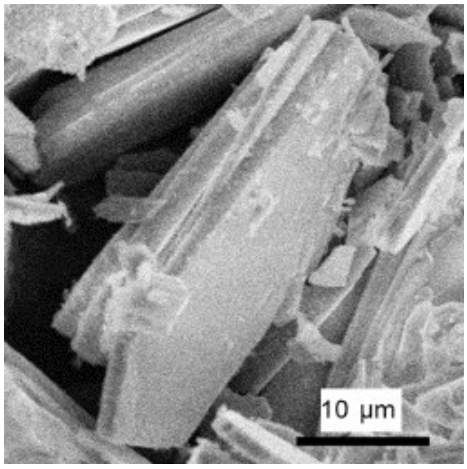

Fig. S1 SEM of PKU-15.

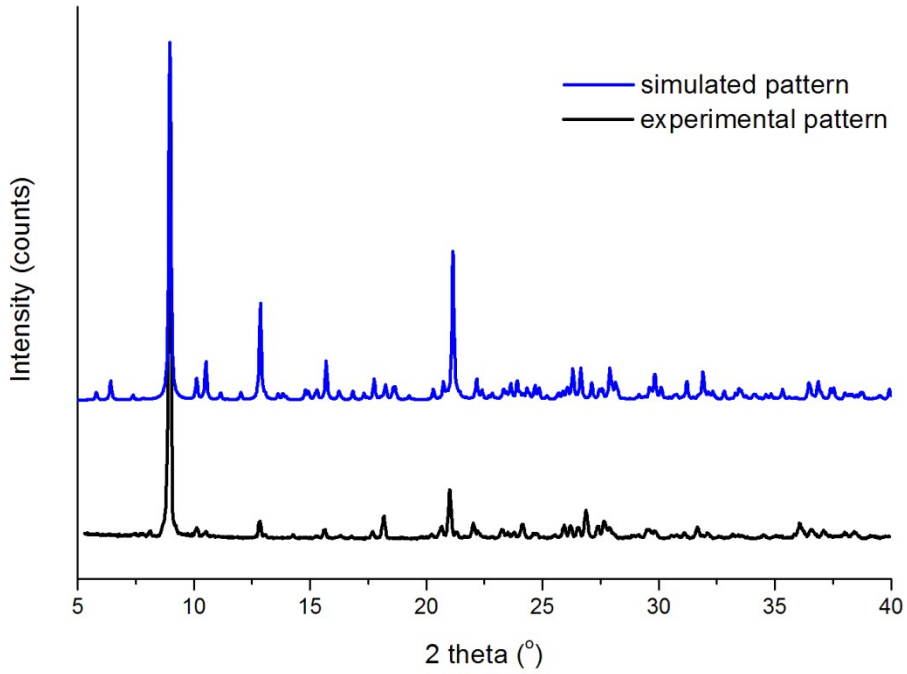

Fig. S2 Experimental and simulated PXRD patterns of as-made PKU-15. Cu Kα radiation, λ = 1.5418 Å

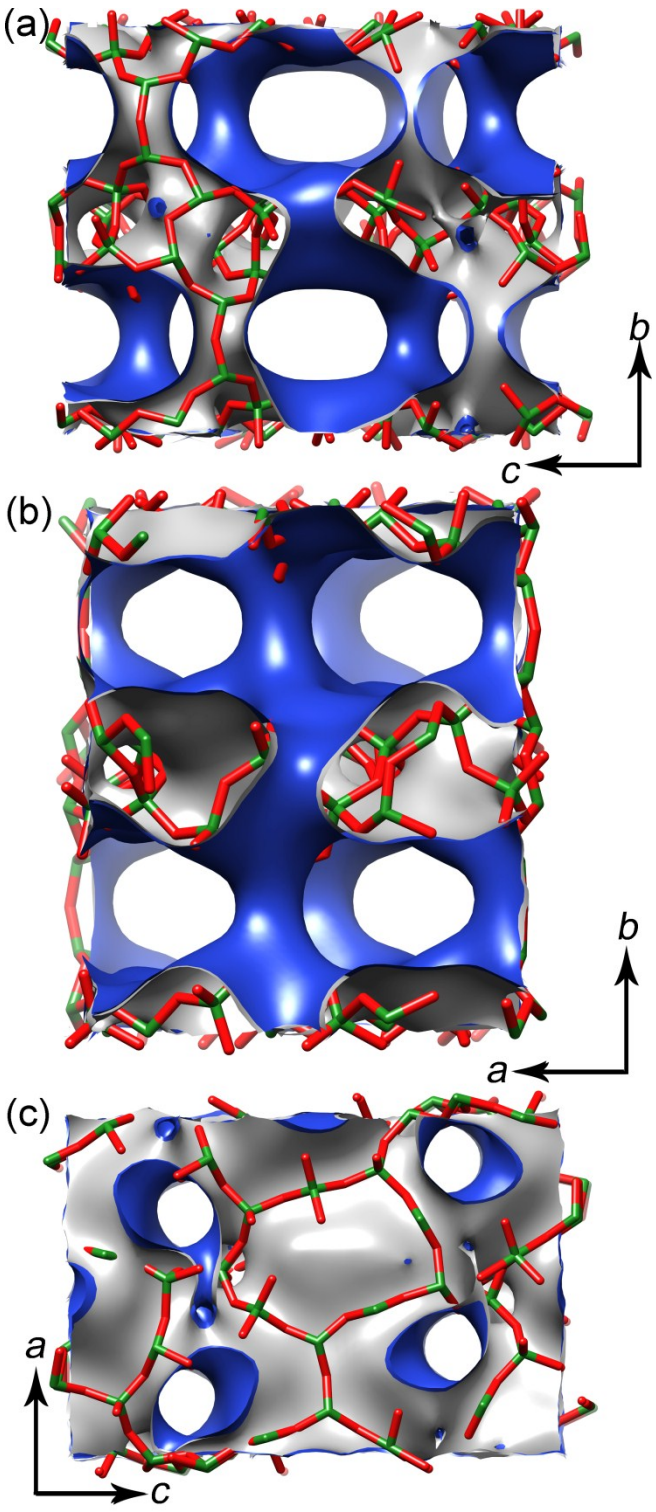

Fig. S3 Interconnected 12×10×7-ring channel system in PKU-15. (a) The sinusoidal 12-ring channel viewed along the *a*-axis. (b) The elliptical 10-ring channel viewed along the *c*-axis. (c) The straight 7-ring channel viewed along the *b*-axis. The channel system is superimposed by the 3D structure model. The blue surfaces are toward the channels while the grey surfaces are toward the framework. The T (T = Si, Ge) atoms are shown in green and the O atoms in red. The SDA molecules are omitted for clarity.

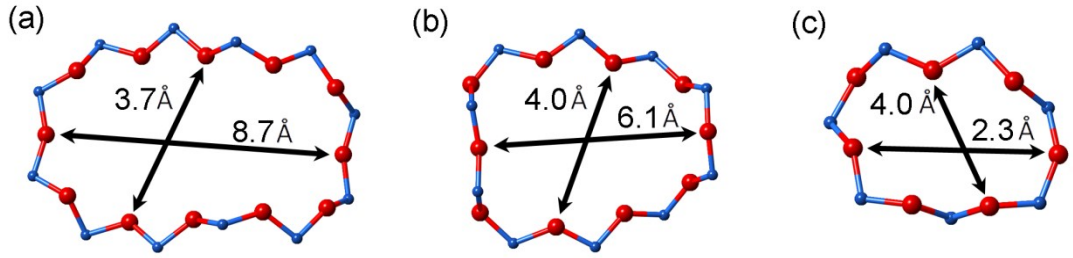

Fig. S4 Effective openness of the (a) 12-ring, (b) 10-ring, and (c) 7-ring channels in PKU-15.

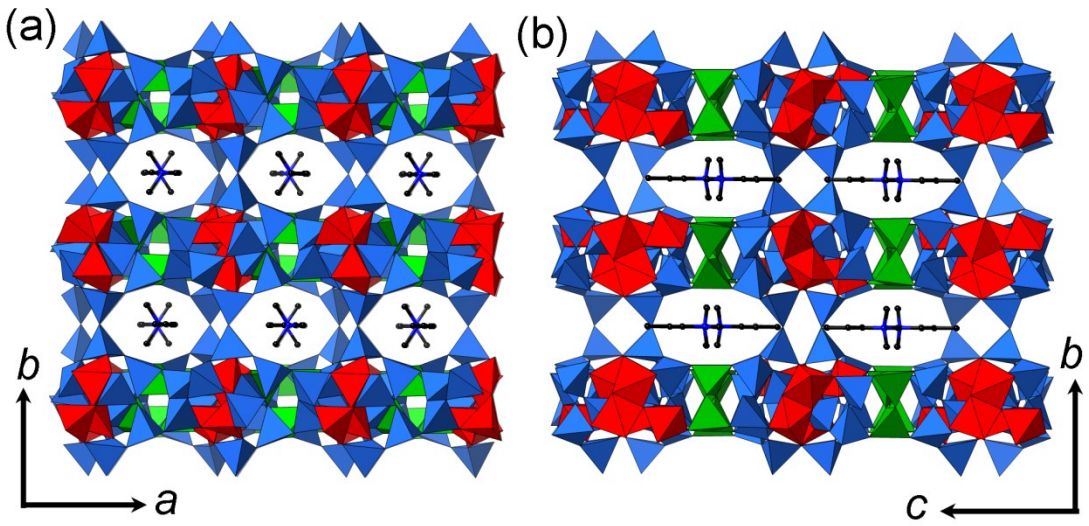

Fig. S5 Locations of the SDA cations in PKU-15. (a) Two M_3PN^+ cations are located in the 10-ring channels. (b) The other two M_3PN^+ cations lie in the 12-ring channels alternatively. The C and N atoms in the SDA are shown in black and blue, respectively. H atoms are omitted for clarity.

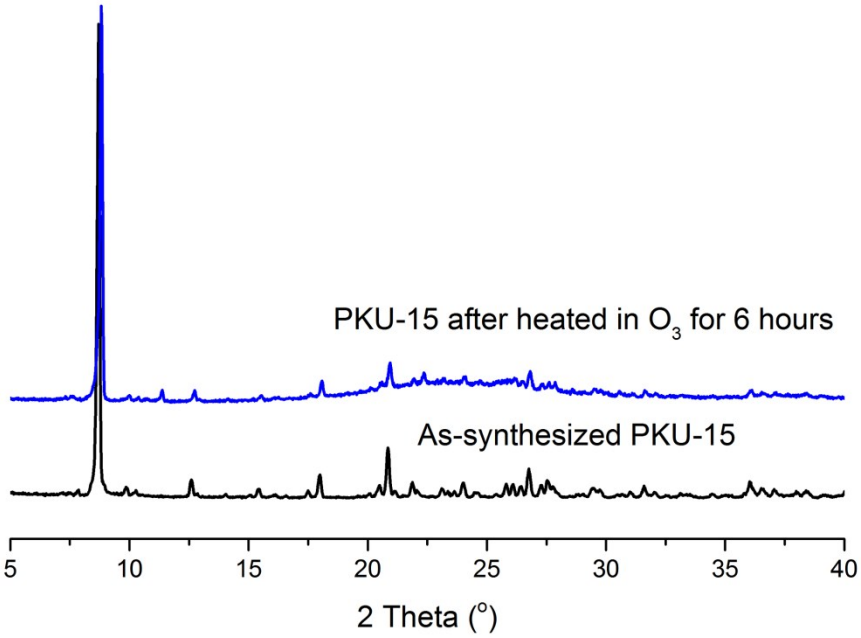

Fig. S6 PXRD patterns of PKU-15 before and after ozone treatment. The calcined PKU-15 sample was treated in O_3 at 200 °C for 6 hours.

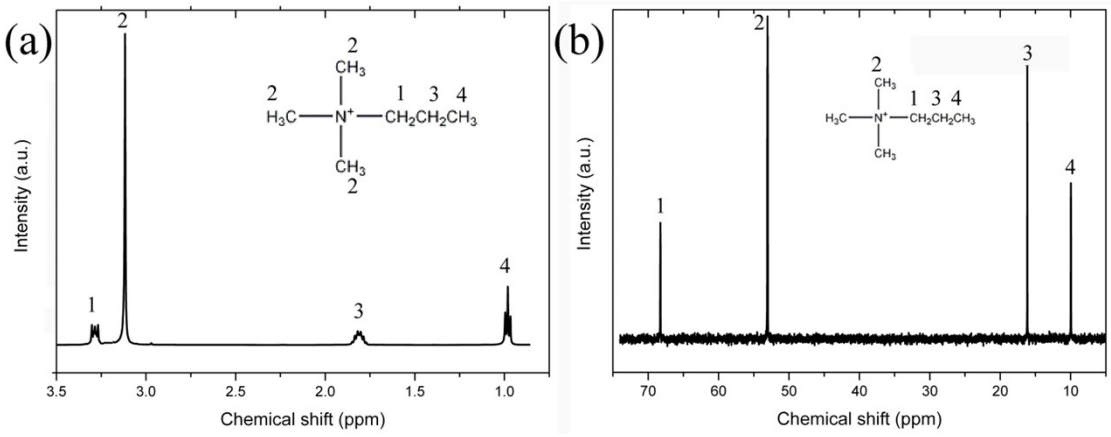

Fig. S7 NMR spectra of $M_3PrN^+I^-$. The (a) ^1H and (b) ^{13}C NMR spectra of trimethylpropylammonium iodide ($M_3PrN^+I^-$).

3. Tables.

Table S1 Crystallographic data and structure refinement results for as-made PKU-15

Sample	PKU-15
Estimated chemical formula	$Ge_{14.3}Si_{0.7}O_{31}C_{12}H_{32}N_2$
Formula weight	1758.16
Temperature (K)	100
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pnma* (no. 62)
a (Å)	16.8108(5)
b (Å)	19.7138(7)
c (Å)	23.9394(9)
V (Å^3)	7933.6(5)
Z	8
ρ_{calcd} (g/cm^3)	2.938
μ (mm^{-1})	10.775
2θ range/^{o}	2.94–25.00
Number of reflections measured	20441
Number of independent reflections	7130
R_{int}	0.0413
Number of observed reflections	5500
Final *R* indices[$I \geq 2\sigma(I)$]	0.0492, 0.1363
R indices (all data)	0.0686, 0.1502
GOF	1.018

4. Reference:

1. V. A. Blatov, O. Delgado-Friedrichs, M. O'Keeffe, D. M. Proserpio, *Acta Crystallogr. Sect. A* **2007**, 63, 418.