Supporting Information

Polyamine-Cladded 18-Ring-Channel Gallium Phosphites with High-Capacity Hydrogen Adsorption and Carbon Dioxide Capture

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Gas Sorption Experiments

Gas adsorption isotherms were measured by a volumetric method using a Micromeritics ASAP2020 system. Powder samples (~100 mg per batch) of the as-synthesized NTHU-15-TEPA and NTHU-15-PEHA were initially activated under ~$1x10^{-3}$ torr and 50 ºC for 12 h to remove lattice waters. For all isotherms, namely, N_2 (77 K and 298 K), CO_2 (273 K and 298 K), H_2 (77 K) and CH_4 (298 K), warm and cold free space correction measurements were performed using ultra-high purity He gas (99.999% purity).

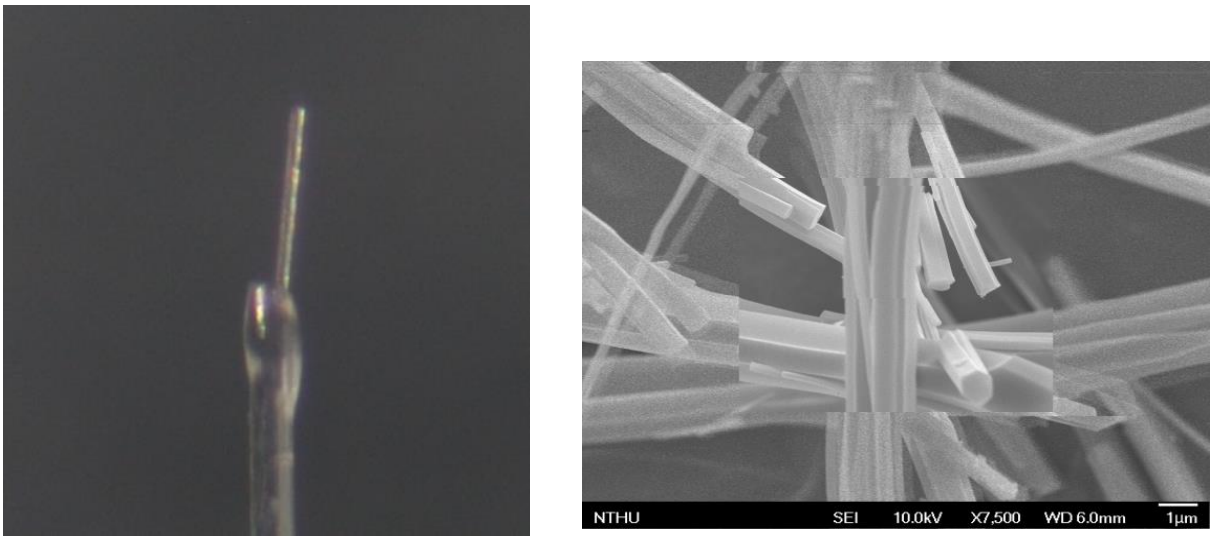


Figure S1. The crystal images of NTHU-15: (left) crystal photo; (right) SEM image.

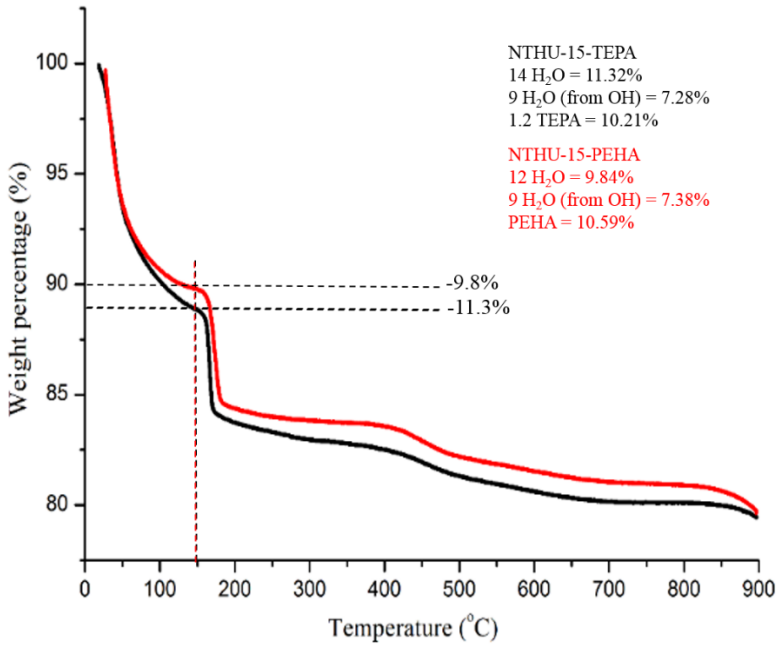


Figure S2. TGA curves for NTHU-15 in following N_2 gas: 15-TEPA in black and 15-PEHA in red. The weight loss before 150 ºC, ca. 10-11%, should correspond to the removal of lattice water. Beyond 150 ºC, the rapid mass loss beyond *ca*. ~7.3%, correspond to additional water molecules from inorganic hydroxyl groups and further gradual weight loss should correspond to decomposition of organic templates. The mass losses were estimated based on formula weights containing 14 and 12 lattice water molecules, respectively.

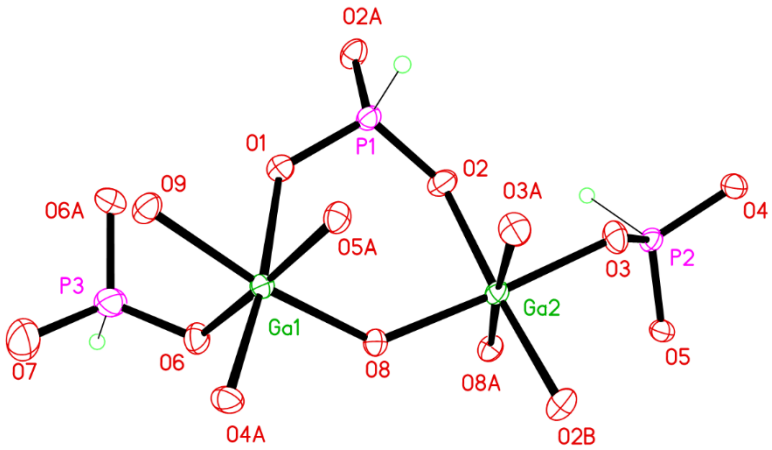


Figure S3. ORTEP drawing of NTHU-15, showing the atom-labelling scheme and coordination geometries.

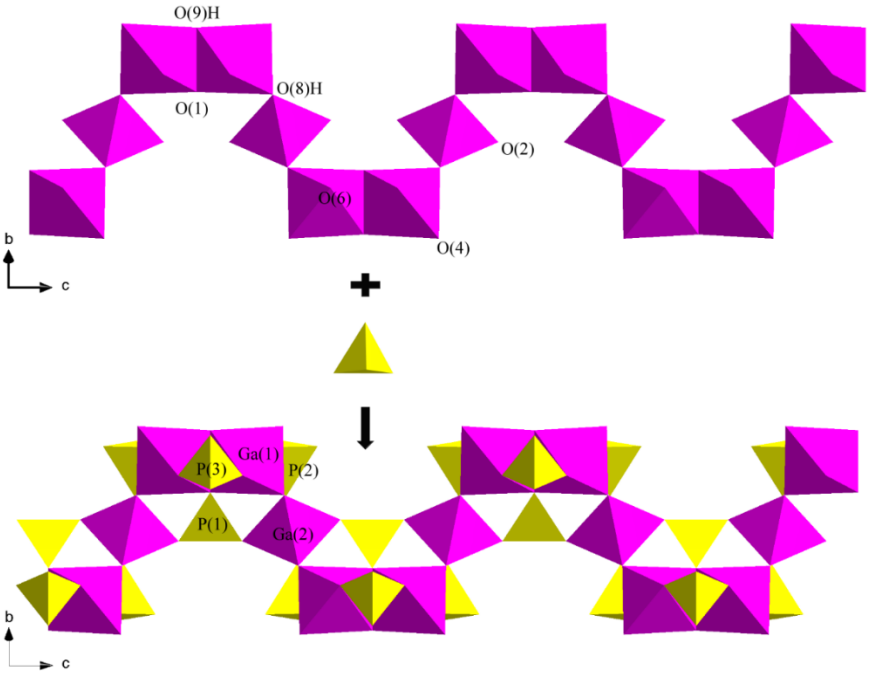


Figure S4. Infinite gallium chains in NTHU-15: (top) infinite Ga-OH-Ga chain of two $Ga(OH)_2O_4$ octahedra linked via corner- and edge- sharing by OH^- ions; (bottom) the infinite Ga-OH-Ga chain surrounded by HPO_3 group via corner-sharing.

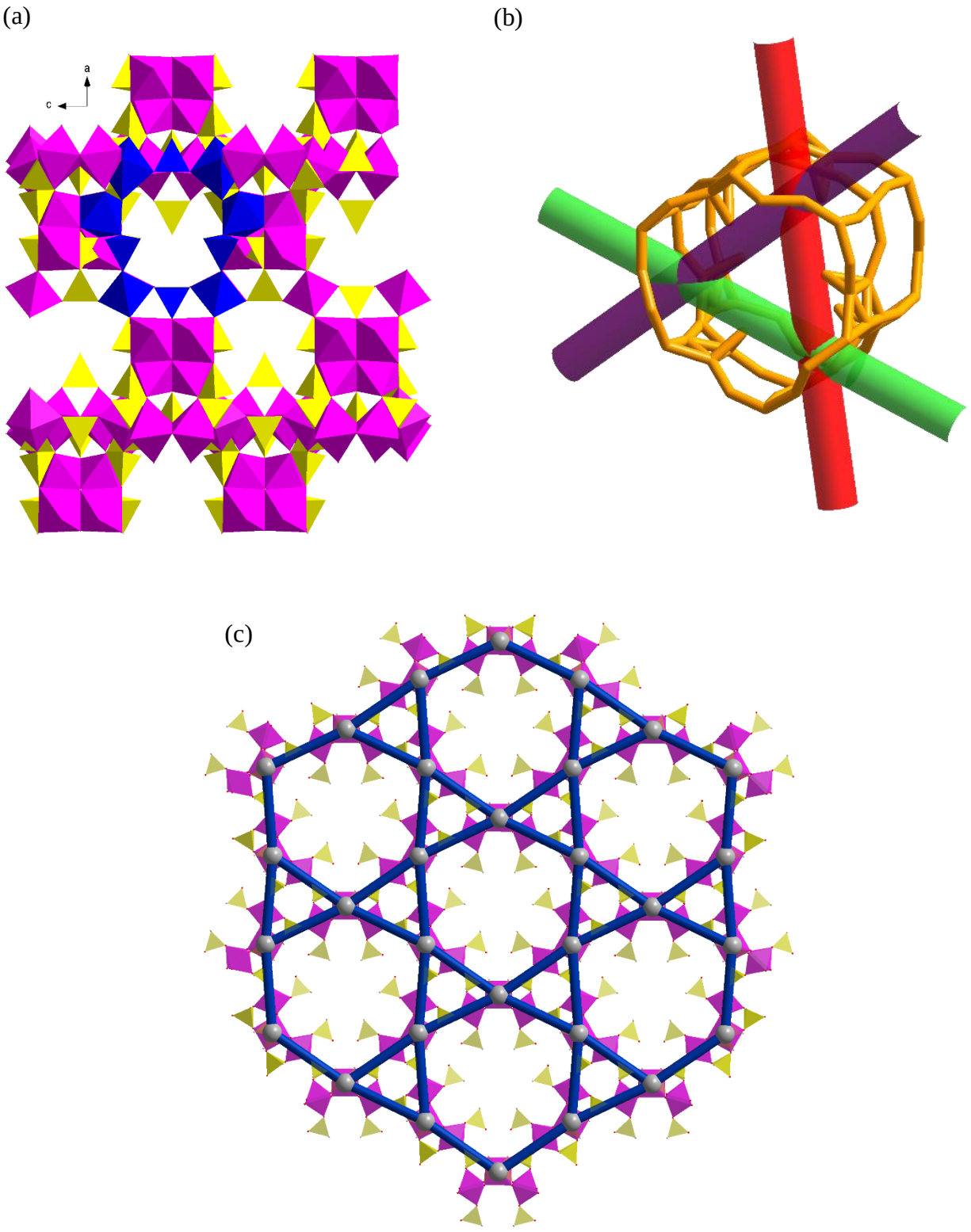


Figure S5. Channels topology of NTHU-15: (a) polyhedral plot showing the projection of 10-ring channels along [010], and (b) wire drawing showing 10-ring channels along [100], [010], and [110], the directions are respectively highlighted by red, green, and purple rods. (c) The topology of NTHU-15 showing hexagonal bronze structure, also observed in MIL-50 and MIL-68.

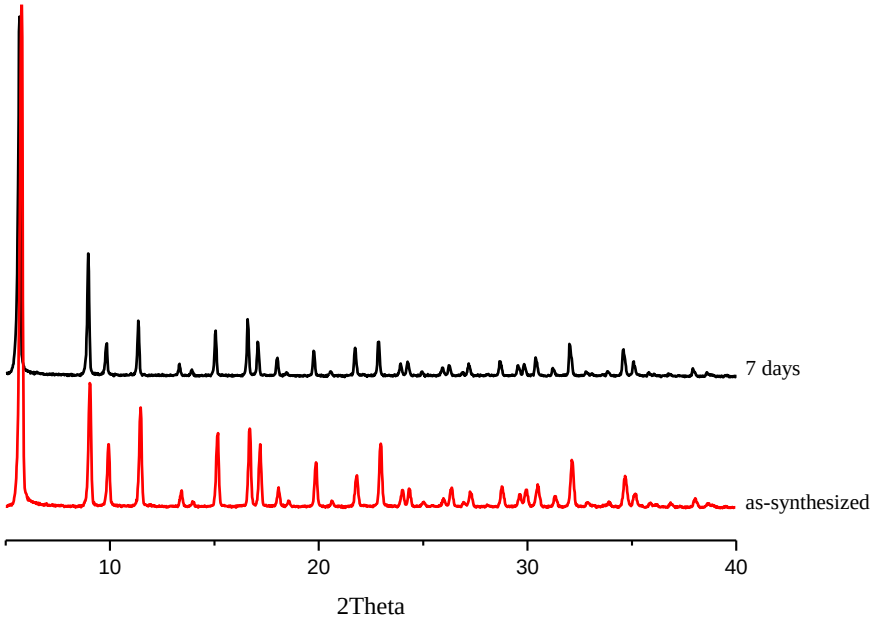


Figure S6. PXRD patterns of NTHU-15, showing the sample of 15-TEPA before and after heating at 100°C in water for 7 days.

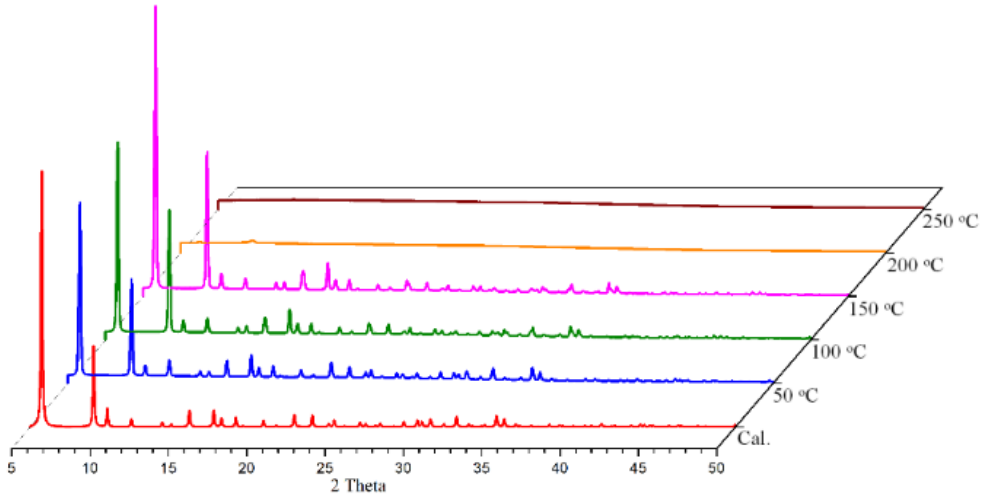


Figure S7. Temperature-dependent PXRD patterns of NTHU-15.

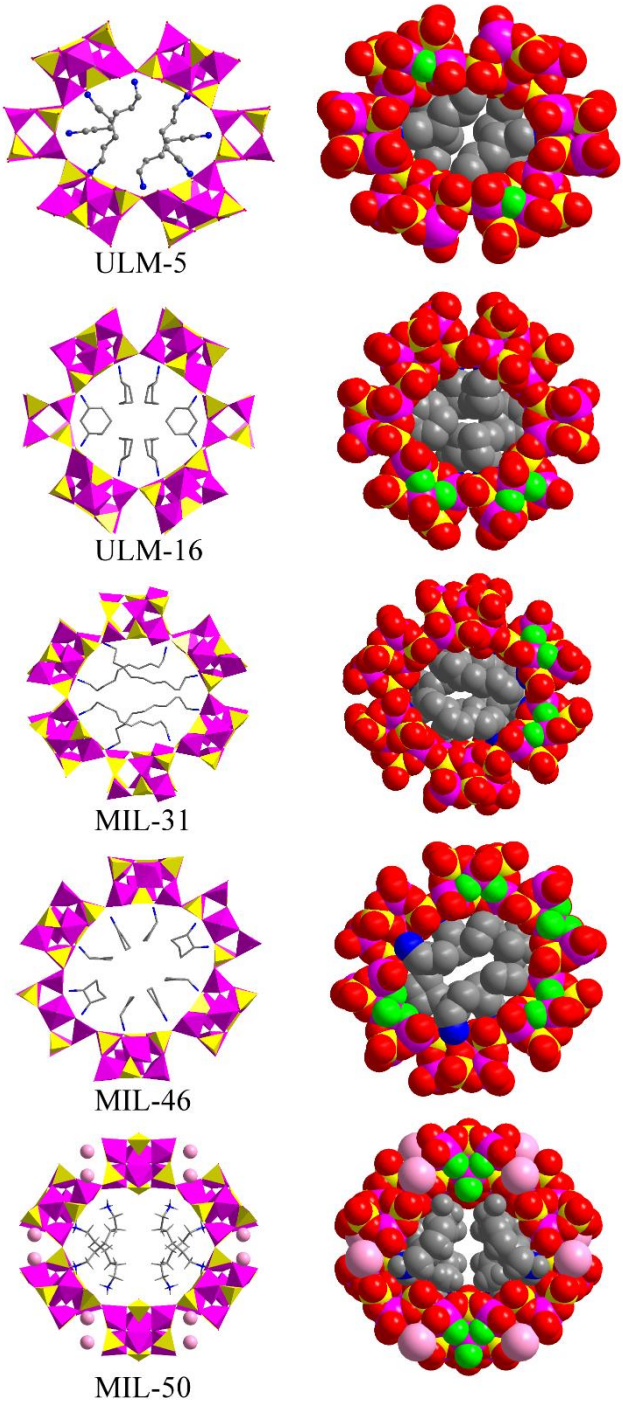
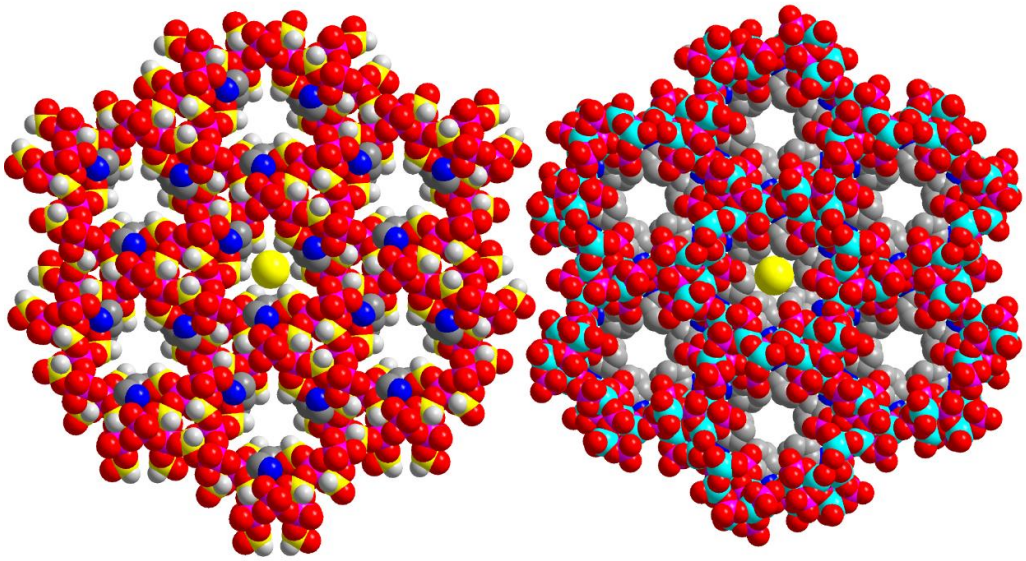


Figure S8. Examples of extra-large channels occupied by template moieties: (Left) polyhedral plots of the inorganic frameworks with templates (in ball-and-stick drawing); (Right) space filling plots showing the interior space are nearly fully occupied by templates.

(a)



(b)

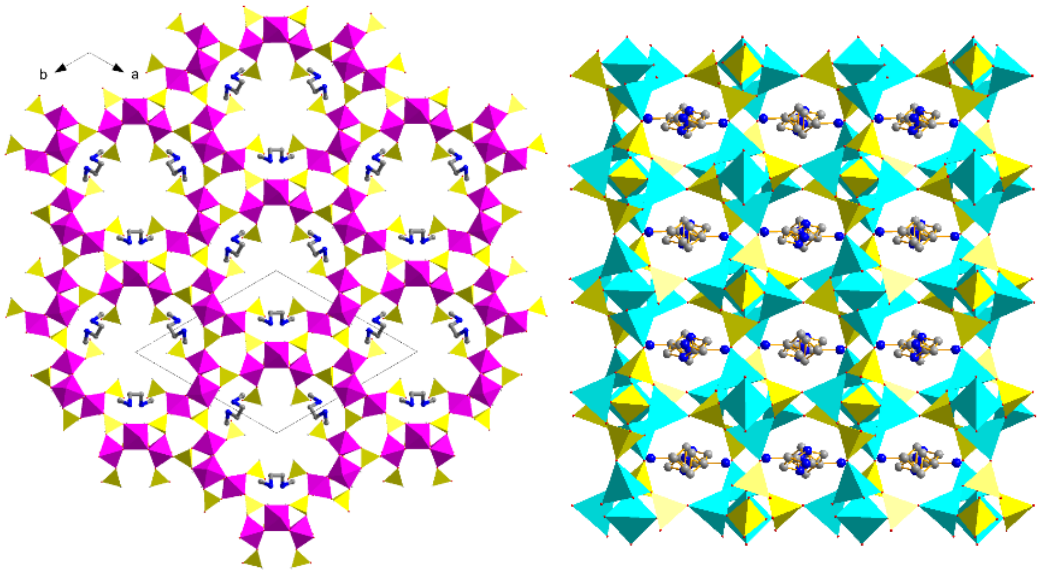


Figure S9. Space-filling models of NTHU-15, ND-1 and two template modes of TEPA: (a) The free pore diameters with templates in presence, estimated by the diameter of inserted balls (in yellow), are almost equal (~ 5 Å) in the two structures; (b) TEPA templates are often located in the central part of channels as reported in $[C_8N_5H_{28}][Zn_5(PO_4)_5] \cdot H_2O$[1] shown in the right, rarely observed to anchor on the inorganic channel walls like in NTHU-15 (left).

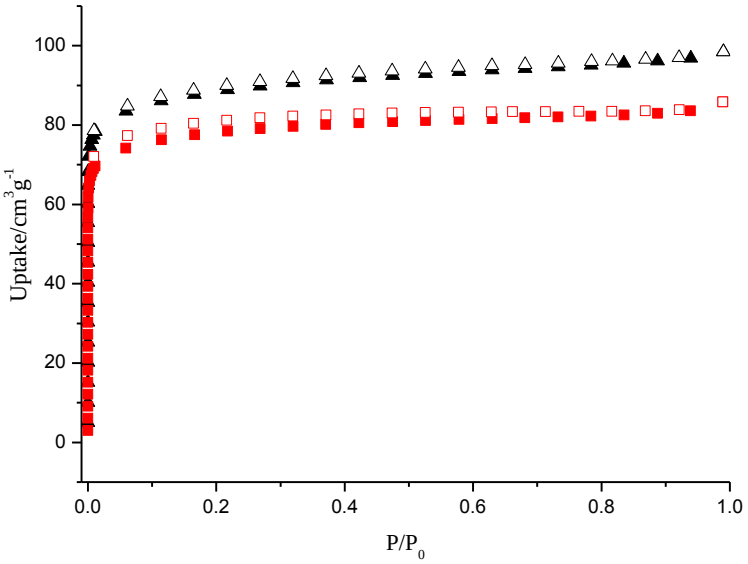


Figure S10. N_2 sorption isotherms of NTHU-15 at 77 K, 15-TEPA in black triangle and 15-PEHA in red square; solid symbols, adsorption; open symbols, desorption.

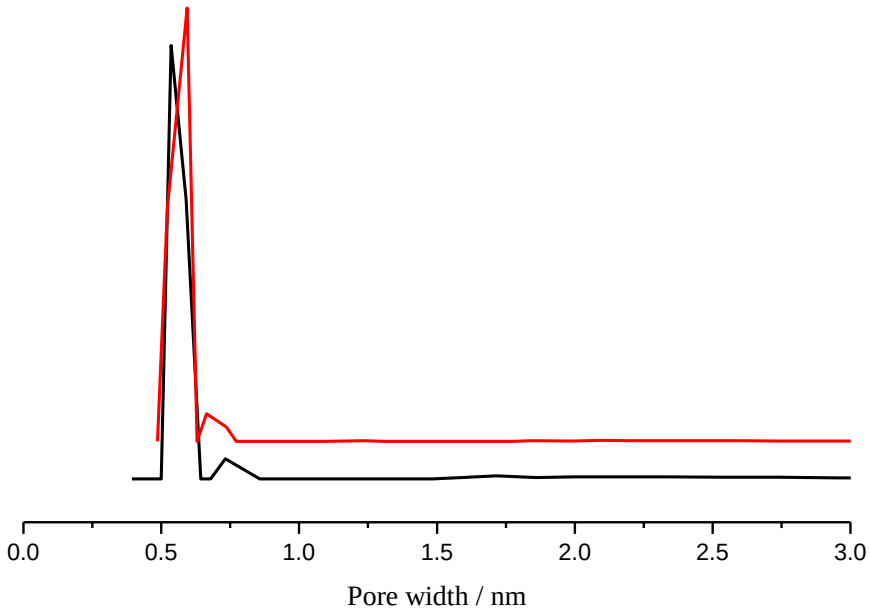


Figure S11. Pore-size distribution of NTHU-15: the curves (15-TEPA in black and 15-PEHA in red) were derived from the nitrogen adsorption isotherms by using NLDFT model.

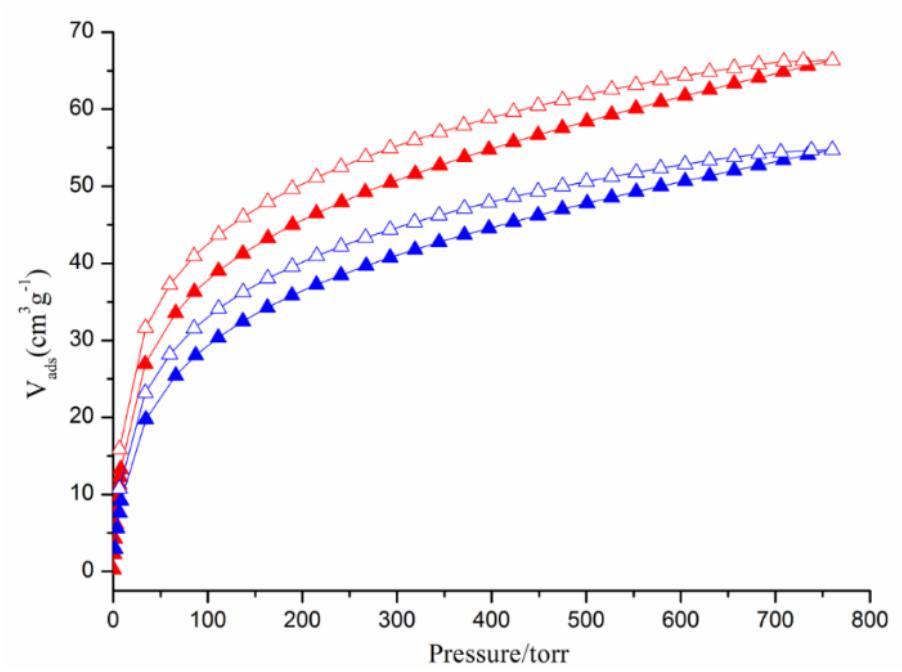


Figure S12. CO_2 sorption isotherms for NTHU-15 measured at 273 K: blue for 15-TEPA and red for 15-PEHA; solid symbols for adsorption and open symbols for desorption.

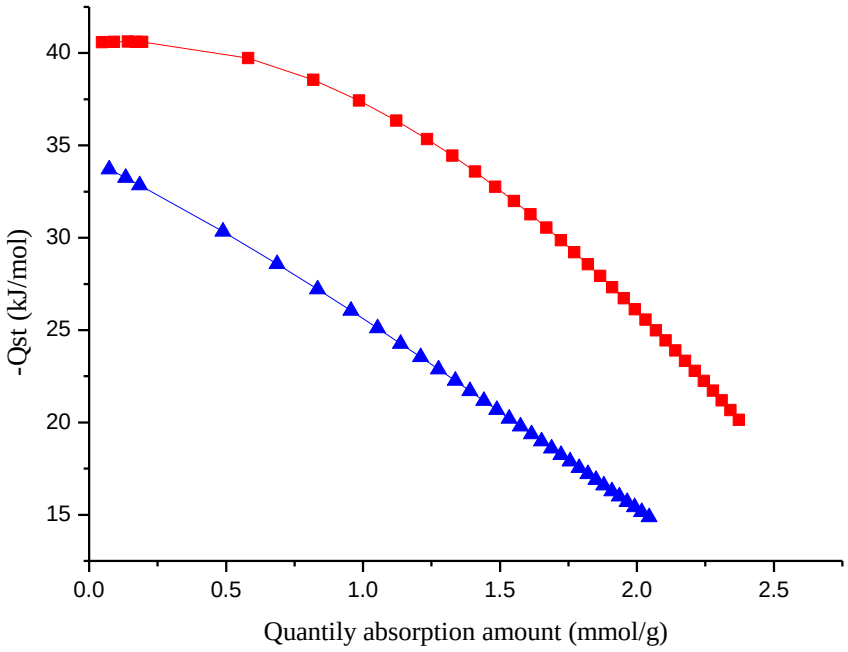


Figure S13. The isosteric heats of adsorption for NTHU-15: the observed values are presented in blue triangles for 15-TEPA and red squares for 15-PEHA. The data were fitted by Virial type equation.

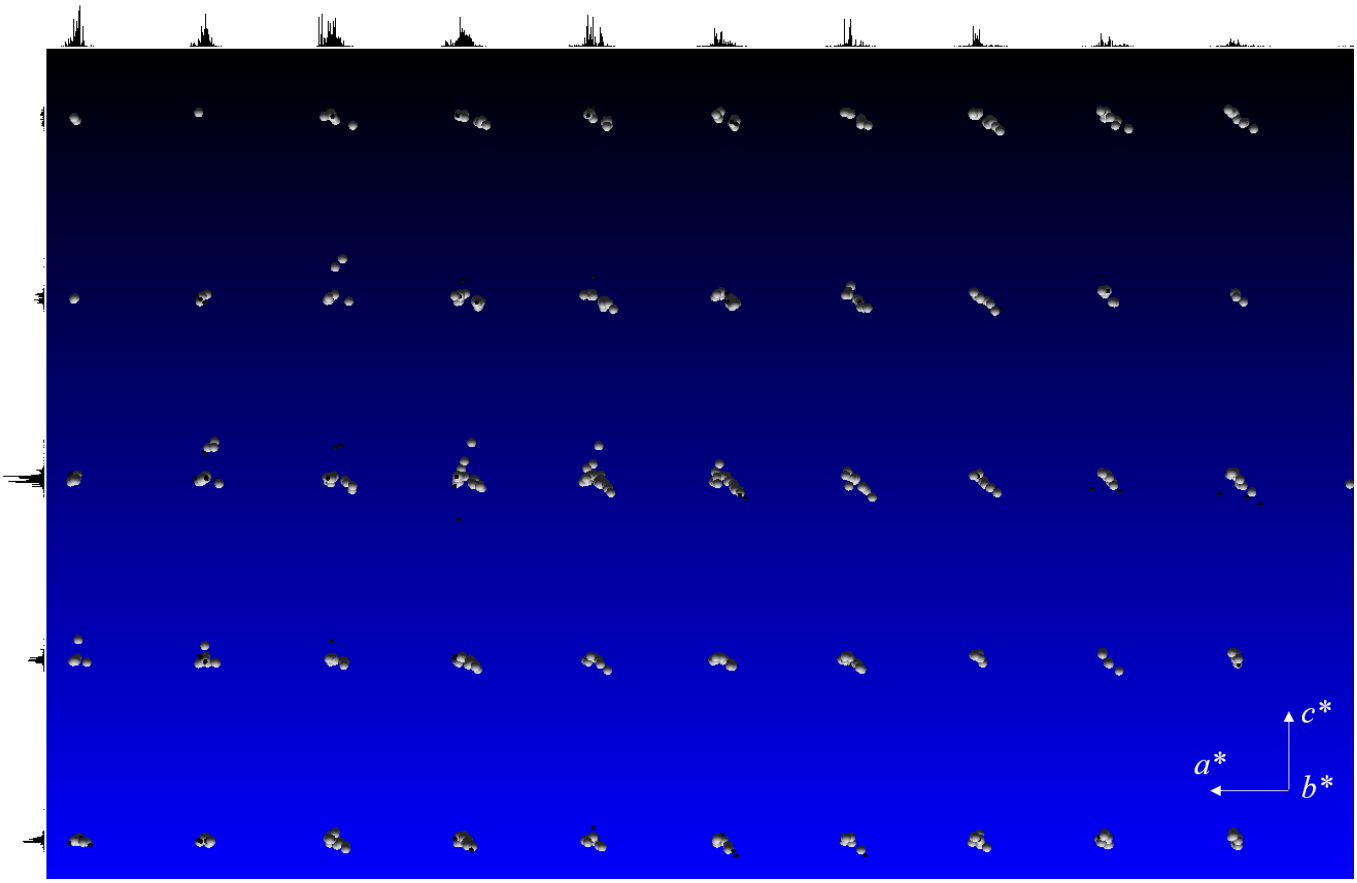


Figure S14. The reciprocal lattice for 15-TEPA crystal with observed satellite diffraction spots along both *a** and *c** directions revealing large superlattice of a modulated structure.

Table S1. Crystal Data and refinement results for NTHU-15

Compound name	15-TEPA	15-PEHA[b]
Chemical formula[a]	$(H_5TEPA)_{1.2}[(GaOH)_9(HPO_3)_{12}] \cdot xH_2O$	$(H_6PEHA)[(GaOH)_9(HPO_3)_{12}] \cdot xH_2O$
Formula weight	1973.51	1978.72
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	1.54178 Å
Crystal system	Hexagonal	
Space group	*P*-62*c*	
Unit cell dimensions	*a* = 17.727(1) Å	*a* = 17.8213(4) Å
	c = 12.651(1) Å	*c* = 12.6592(3) Å
Volume	3443.0(6) $Å^3$	3481.9(2) $Å^3$
Z	2	2
Density (calculated)	1.904 Mg/m^3	1.887 Mg/m^3
Absorption coefficient	3.836 mm^{-1}	7.290 mm^{-1}
F(000)	1946	1952
Crystal size	0.03 x 0.03 x0.2 mm^3	0.015 x 0.02x 0.18 mm^3
Theta range of data collection	1.326 to 28.340°	4.517 to 66.577°
Index ranges	$-23 \leqq h \leqq 23$, $-23 \leqq k \leqq 23$, $-16 \leqq l \leqq 16$	$-21 \leqq h \leqq 21$, $-21 \leqq k \leqq 21$, $-11 \leqq l \leqq 14$
Reflections collected	40366	30680
Independent reflections	2987 [R(int) = 0.0776]	2151 [R(int) = 0.1527]
Completeness	99.8%	97.1%
Max. and min. transmission	0.9485 and 0.8507	0.9492 and 0.6588
Data / restraints / parameters	2987 / 0 / 142	2151 / 0 / 145
Goodness-of-fit on F^2	1.079	1.072
Final R indices [I>2sigma(I)]	*R*1 = 0.0343, *wR*2 = 0. 0967	*R*1 = 0.0545, *wR*2 = 0.1372
R indices (all data)	*R*1 = 0.0372, *wR*2 = 0.0982	*R*1 = 0.0667, *wR*2 = 0.1447
Largest diff. peak and hole	1.364 and -0.591 e.$Å^{-3}$	0.837 and -0.717 e.$Å^{-3}$

[a]The lattice waters were not included in the calculation of formula weight, density and absorption coefficient.

[b]The crystal quality of 15-PEHA was generally poor.

Table S2. Results of EA analysis

		N (%)	C (%)	H (%)
15-TEPA	Obsd.	3.72	5.38	3.74
	Calcd.[a]	3.84	5.27	3.62
	Calcd.[b]	3.81	5.22	3.68
	Calcd.[c]	3.78	5.18	3.74
15-PEHA	Obsd.	3.87	5.55	3.94
	Calcd.[a]	3.83	5.47	3.63
	Calcd.[b]	3.80	5.43	3.69
	Calcd.[c]	3.77	5.38	3.75

[a]Based on formula weight containing 12 lattice water molecules; [b]13 lattice water molecules; [c]14 lattice water molecules

Table S3. Pore related data on extra-large-channel GaPO structures

Structure	Ring size	Template	FD	*SAV*[a]	Free space[b]	ref.
ULM-5	16	1,6-diaminohexane	13.8	44.8%	14.3%	2
ULM-16	16	cyclopentylamine cyclohexylamine	13.2	48.2%	10.2%	3
MIL-31	18	1,9-diaminonane, 1,10-diaminodecane	12.6	48.7%	7.5%	4
MIL-46	18	cyclopentylamine	12.0	51.1%	12.3%	5
MIL-50	18	1,6-diaminohexane	12.7	42.0%	15.2%	6
ICL-1	20	1,4-diaminobutane	10.7	*N/A*	*N/A*	7
Cloverite	20	quinuclidine	11.1	58.5%	*N/A*	8
NTHU-1	24	N/A	10.1	23.0%	23.0%	9
NTHU-15	18	TEPA or PEHA	~12	~45%	~24%	this work
1[c]	18	tris(2-aminoethyl)amine	15.0	47.3%	24.0%	10
ND-1[c]	24	1,2-DACH	12.1	49.8%	17.1%	11

a. The results from PLATON, no counter species were included in calculation.

b. Estimated using PLATON, with organic templates in presence.

c. Extra-large-channel non-GaPO structures.

Table S4. Hydrogen bonding in NTHU-15

15-TEPA	15-PEHA
O(3)···N(1) = 3.13 Å	O(3)···N(1) = 3.15 Å
O(3)···N(1) = 2.80 Å	O(3)···N(1) = 2.81 Å
O(7)···N(1) = 2.61 Å	O(7)···N(1) = 2.59 Å

Table S5. Various gas uptake (in cm^3g^{-1}) for NTHU-15.

Gas (T, P)	15 -TEPA	15-PEHA
N_2 (77 K, 1 bar)	98.5	85.8
H_2 (77 K, 1 bar)	85.2	83.9
CO_2 (273 K, 1 bar)	54.7	66.4
CO_2 (298 K, 1 bar)	45.8	53.2
CH_4 (298 K, 1 bar)	5.1	3.5
N_2 (298 K, 1 bar)	0.3	0.9
N_2 (298 K, 0.75 bar)	0.18	0.67
CO_2 (298 K, 0.15 bar)	21.5	25.5

References:

1. Neeraj, S.; Natarajan, S., *J. Phys. Chem. Solids*, **2001**, *62*, 1499
2. Loiseau, T.; Férey, G., *J. Solid State Chem.* **1994,** *111*, 403.
3. Loiseau, T.; Férey, G., *J. Mater. Chem.* **1996,** *6*, 1073.
4. Sassoye, C.; Loiseau, T.; Férey, G.; Taulelle, F., *Chem. Commun.* **2000**, 943.
5. Sassoye, C.; Marrot, J.; Loiseau, T.; Férey, G., *Chem. Mater.* **2002,** *14*, 1340.
6. Beitone, L.; Marrot, J.; Loiseau, T.; Férey, G.; Henry, M.; Huguenard, C.; Gansmuller, A.; Taulelle, F., *J. Am. Chem. Soc.* **2003,** *125*, 1912.
7. Walton, R. I.; Millange, F.; Loiseau, T.; O'Hare, D.; Férey, G., *Angew. Chem. Int. Ed.* **2000,** *39*, 4552.
8. Estermann, M.; Mccusker, L. B.; Baerlocher, C.; Merrouche, A.; Kessler, H., *Nature* **1991,** *352*, 320.
9. Lin, C.-H.; Wang, S.-L.; Lii, K.-H., *J. Am. Chem. Soc.* **2001,** *123*, 4649.
10. Wang, G.-M.; Li, J.-H.; Wei, L.; Han, S.-D.; Zhao, X.-M.; Bao, Z.-Z., *CrystEngComm* **2015,** *17*, 8414.
11. Yang, G. Y.; Sevov, S. C., *J. Am. Chem. Soc.* **1999,** *121*, 8389.