Electronic supplementary information (ESI)

An Open-Framework Beryllium Phosphite with Extra-Large 18-Ring Channels

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Experimental Section

Materials and methods.

All chemicals were reagent grade and used as purchased without further purification.

Elemental analyses (C, H, and N) were measured on a Perkin-Elmer 240C analyzer (Perkin-Elmer, USA). IR spectra were performed on a MAGNA-560 (Nicolet) FT-IR spectrometer with KBr pellets. Thermogravimetric analyses (TGA) were carried out on a Rigaku standard TG-DTA analyzer with a heating rate of 10 °C min^{-1} from ambient temperature to 800 °C. Gas adsorption measurements were performed on an ASAP 2020 M gas adsorption analyzer. Before CO_2 gas measurement, the sample was activated at 160°C under high vacuum. Before N_2 gas measurement, the sample was activated at 80°C, 150°C and 180°C under high vacuum, respectively. The temperature-dependent powder X-ray diffraction (PXRD) was recorded with a Bruker D8 diffractometer at 40 kV and 40 mA with a Cu-target tube and a graphite monochromator. Simulation of the PXRD curve was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge *via* the Internet at http://www.iucr.org.

X-ray Crystallography.

The crystallographic data for **1** (denoted as **1**) and primary crystals of **1** calcined at 180°C for 3 hours (denoted as **1′**) were collected on a Rigaku SCX-mini diffractometer at 293(2) K with Mo-Kα radiation (λ = 0.71073 Å) by ω scan mode. The program *CrystalClear* was used for the integration of the diffraction profiles.[1] The structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL (semi-empirical absorption corrections were applied using the SADABS program).[2] Detailed crystallographic data for **1** and **1′** are summarized in Table S1 and the selected bond lengths and angles are given in Table S2 and Table S3. Full crystallographic data for **1** has been deposited with the CCDC (1415272), which can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk).

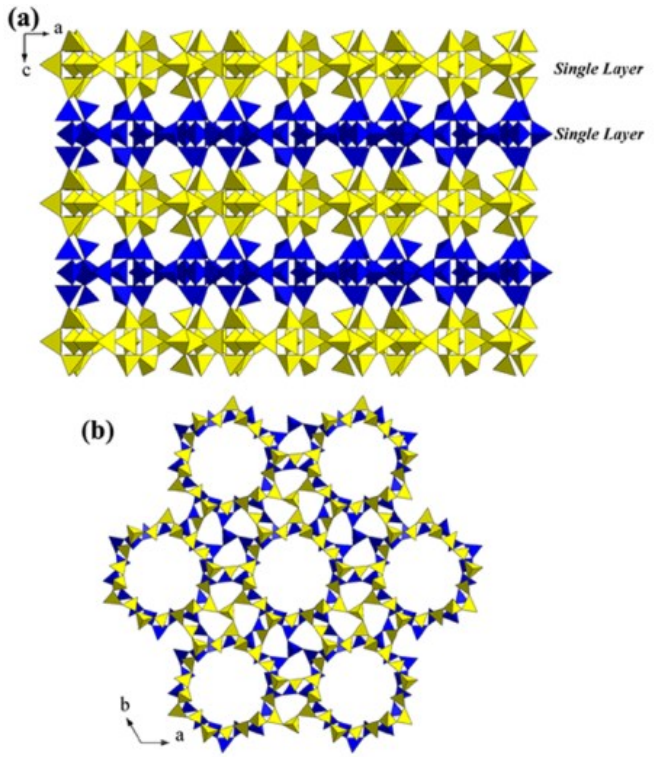

Fig. S1 The 3D structure of **1** along the *b* axis (a) and *c* axis (b).

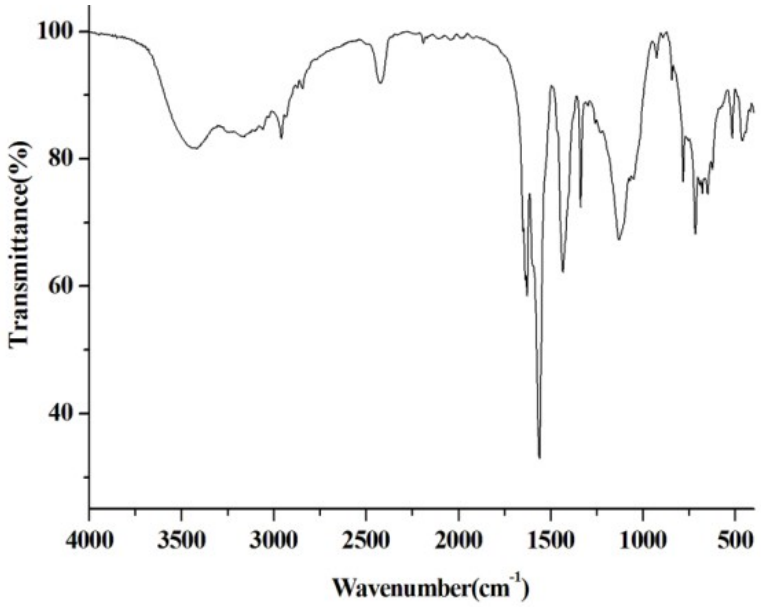

Fig. S2 IR pattern of **1**.

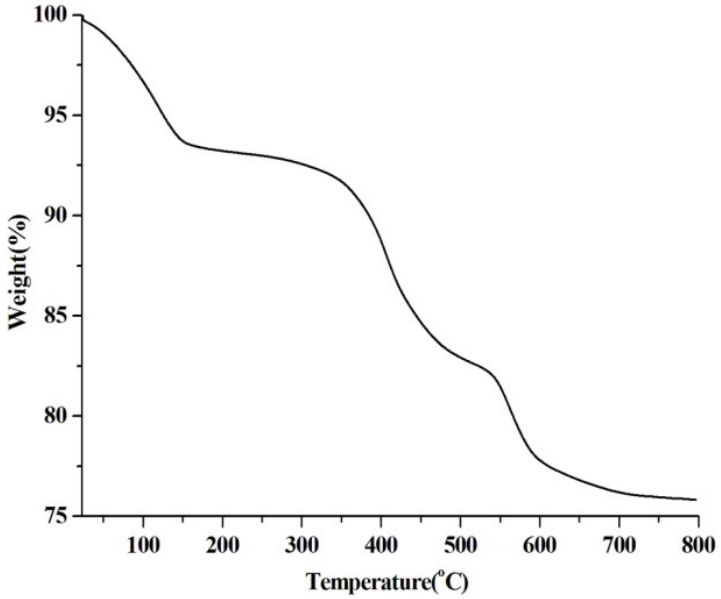

Fig. S3 TG plot of **1**.

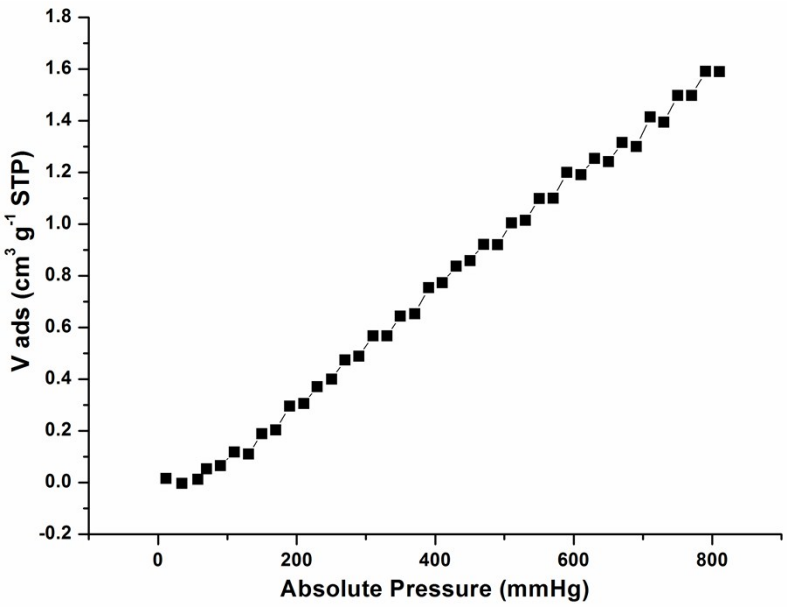

Fig. S4 The isothermal adsorption curve of CO_2 gas for **1** at 273 K.

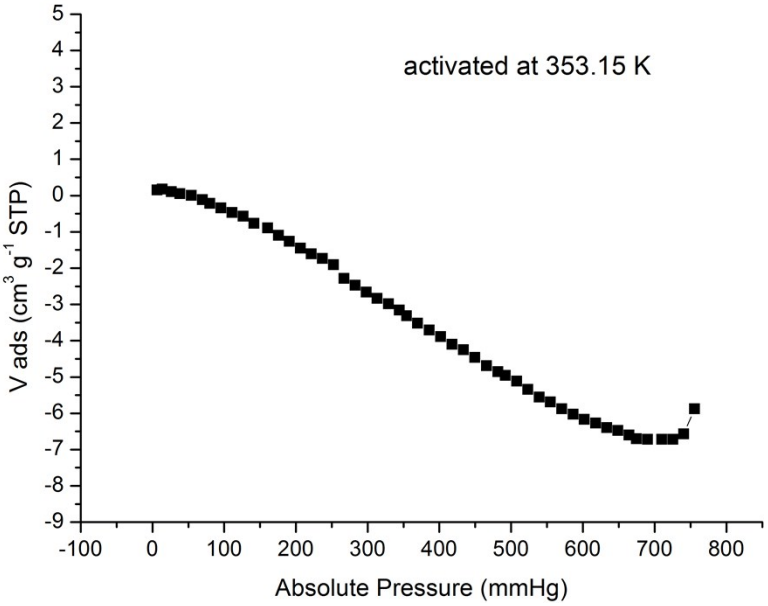

Fig. S5 The isothermal adsorption curve of N_2 gas for **1** at 77 K.

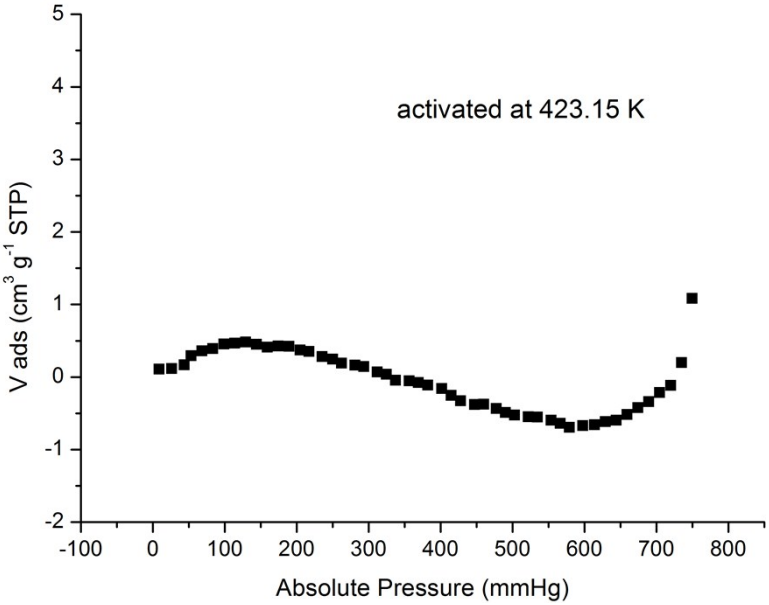

Fig. S6 The isothermal adsorption curve of N_2 gas for **1** at 77 K.

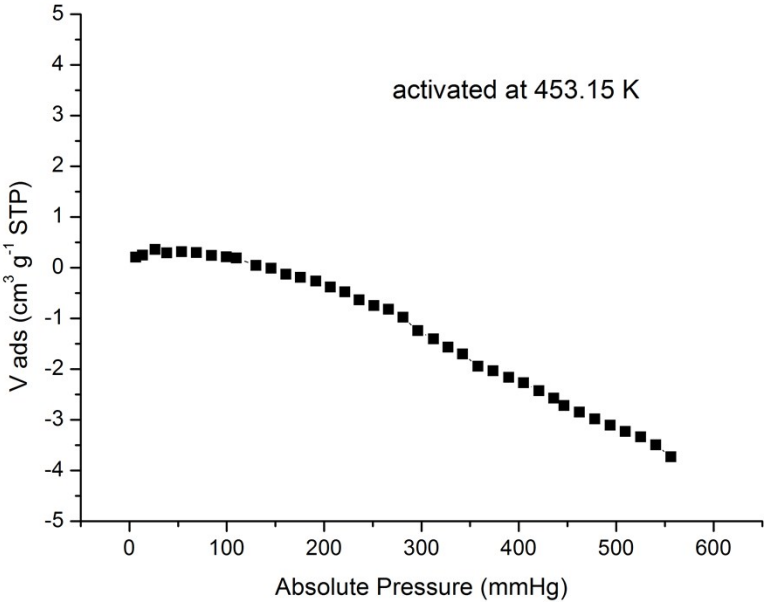

Fig. S7 The isothermal adsorption curve of N_2 gas for **1** at 77 K.

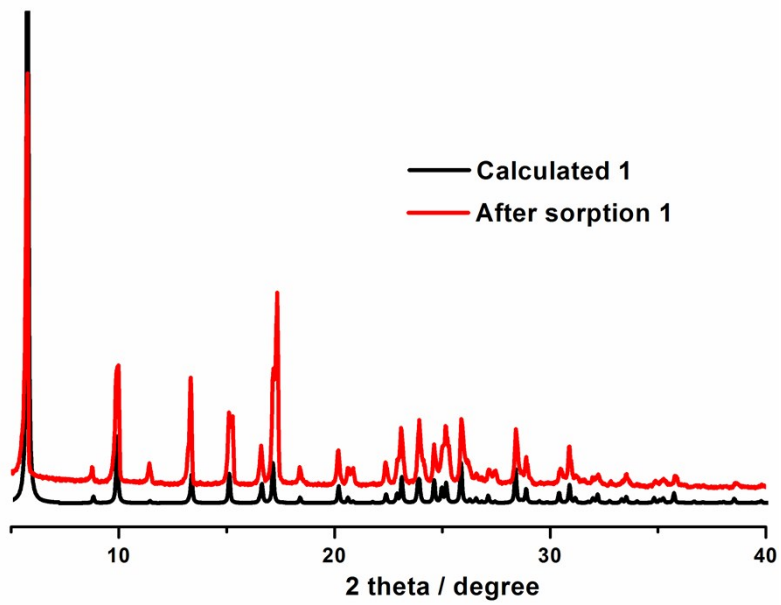

Fig. S8 The powder X-ray diffraction patterns after sorption measurements.

Table S1. Crystal data and structure refinement parameters for **1** and **1′**

	1		**1′**	
Formula	$C_6H_{36}N_4O_{27}P_8Be_6$		$C_6H_{30}N_4O_{24}P_8Be_6$	
*M*r (g mol^{-1})	898.21		844.16	
Space group	*P*6$_3$/*m*		*P*6$_3$/*m*	
Crystal system	Trigonal		Trigonal	
a (Å)	18.0026(5)		17.792(2)	
c (Å)	13.3316(2)		13.215(3)	
V (Å^3)	3741.82(16)		3622.8(10)	
Z	4		4	
F(000)	1840		1720	
Dc (gcm^{-3})	1.594		1.549	
μ (mm^{-1})	0.465		0.469	
R_{int}	0.0855		0.0459	
	-23≤ h ≤23		$-21 \le h \le 21$	
limiting indices	-23≤ k ≤23		$-21 \le k \le 21$	
	-17≤ l ≤17		$-15 \le l \le 15$	
Collected reflections	39483		31212	
Unique reflections	2980		2230	
GOF on F^2	1.228		1.274	
R_1, wR_2 [$I>2\sigma(I)$][a]	0.0783	0.1518	0.1865	0.4321
R_1, wR_2 [all data][b]	0.0929	0.1593	0.2024	0.4425

a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. *b* $wR_2 = \{\sum [w(F_o^2 - F_c^2)2] / \sum w(F_o^2)2\}1/2$.

Table S2. Selected bond lengths (Å) and angles (°) for **1**

Be(1)-O(4)#1	1.607(8)	P(1)-O(2)	1.502(3)
Be(1)-O(10)#2	1.614(5)	P(1)-O(2)#5	1.502(3)
Be(1)-O(10)#3	1.614(5)	P(1)-O(1)	1.504(4)
Be(1)-O(1)	1.617(7)	P(2)-O(4)	1.507(4)
Be(2)-O(3)	1.607(6)	P(2)-O(3)#5	1.513(3)
Be(2)-O(2)	1.612(6)	P(2)-O(3)	1.513(3)
Be(2)-O(9)#4	1.617(6)	P(3)-O(6)	1.499(4)
Be(2)-O(5)	1.637(6)	P(3)-O(5)#5	1.517(3)
Be(3)-O(8)	1.599(5)	P(3)-O(5)	1.517(3)
Be(3)-O(8)#5	1.599(5)	P(4)-O(7)	1.434(4)
Be(3)-O(7)	1.600(8)	P(4)-O(7)#6	1.434(4)
Be(3)-O(6)	1.630(8)	P(4)-O(7)#7	1.434(4)
O(4)-Be(1)#8	1.607(8)	P(5)-O(10)	1.501(3)
O(9)-Be(2)#9	1.617(6)	P(5)-O(9)	1.509(3)
O(10)-Be(1)#10	1.614(5)	P(5)-O(8)	1.517(3)
O(4)#1-Be(1)-O(10)#2	113.0(3)	O(7)-Be(3)-O(6)	108.2(5)
O(4)#1-Be(1)-O(10)#3	113.0(3)	O(2)-P(1)-O(2)#5	113.3(3)
O(10)#2-Be(1)-O(10)#3	108.5(5)	O(2)-P(1)-O(1)	111.05(15)
O(4)#1-Be(1)-O(1)	109.6(5)	O(2)#5-P(1)-O(1)	111.05(15)
O(10)#2-Be(1)-O(1)	106.1(3)	O(4)-P(2)-O(3)#5	111.16(15)
O(10)#3-Be(1)-O(1)	106.1(3)	O(4)-P(2)-O(3)	111.16(15)
O(3)-Be(2)-O(2)	113.8(4)	O(3)#5-P(2)-O(3)	112.6(3)
O(3)-Be(2)-O(9)#4	104.9(3)	O(6)-P(3)-O(5)#5	109.92(15)
O(2)-Be(2)-O(9)#4	109.3(3)	O(6)-P(3)-O(5)	109.92(15)
O(3)-Be(2)-O(5)	108.7(3)	O(5)#5-P(3)-O(5)	113.7(2)
O(2)-Be(2)-O(5)	110.8(4)	O(7)-P(4)-O(7)#6	120.000(1)
O(9)#4-Be(2)-O(5)	109.2(3)	O(7)-P(4)-O(7)#7	120.000(3)
O(8)-Be(3)-O(8)#5	112.9(5)	O(7)#6-P(4)-O(7)#7	120.000(2)
O(8)-Be(3)-O(7)	106.3(3)	O(10)-P(5)-O(9)	112.6(2)
O(8)#5-Be(3)-O(7)	106.3(3)	O(10)-P(5)-O(8)	113.4(2)
O(8)-Be(3)-O(6)	111.3(3)	O(9)-P(5)-O(8)	108.64(19)
O(8)#5-Be(3)-O(6)	111.3(3)		

[a]Symmetry codes: #1: -x+y, -x+2, z; #2: -y+1, x-y+2, -z+3/2; #3: -y+1, x-y+2, z; #4: x-y+1, x+1, -z+1; #5: x, y, -z+3/2; #6: -x+y,-x+1,z; #7: -y+1, x-y+1, z; #8: -y+2, x-y+2, z; #9: y-1, -x+y, -z+1; #10: -x+y-1, -x+1, z.

Table S3. Selected bond lengths (Å) and angles (°) for **1′**

Be(1)-O(4)#3	1.568(14)	P(1)-O(1)#1	1.431(15)
Be(2)-O(5)#3	1.60(2)	P(1)-O(1)#2	1.431(15)
Be(3)-O(2)#2	1.62(2)	P(1)-O(1)	1.431(14)
Be(3)-O(8)#7	1.62(2)	P(2)-O(3)	1.488(12)
Be(3)-O(6)#8	1.627(17)	P(2)-O(2)#3	1.498(9)
O(9)-Be(2)	1.53(4)	P(2)-O(2)	1.498(9)
O(10)-Be(3)	1.61(3)	P(3)-O(5)	1.457(11)
O(2)-Be(3)#4	1.62(2)	P(3)-O(6)	1.459(8)
O(3)-Be(1)	1.63(2)	P(3)-O(4)	1.494(8)
O(1)-Be(1)	1.56(2)	P(4)-O(10)	1.464(11)
O(4)-Be(1)	1.568(14)	P(4)-O(10)#3	1.464(11)
O(5)-Be(2)	1.60(2)	P(4)-O(9)	1.497(15)
O(6)-Be(3)#5	1.627(17)	P(5)-O(7)	1.319(13)
O(7)-Be(2)	1.65(3)	P(5)-O(8)#3	1.447(10)
O(8)-Be(3)#6	1.62(2)	P(5)-O(8)	1.447(10)
O(1)#1-P(1)-O(1)#2	120.000(1)	O(4)-Be(1)-O(4)#3	114.3(15)
O(1)#1-P(1)-O(1)	120.000(6)	O(1)-Be(1)-O(3)	108.2(14)
O(1)#2-P(1)-O(1)	120.000(5)	O(4)-Be(1)-O(3)	110.2(9)
O(3)-P(2)-O(2)#3	109.8(5)	O(4)#3-Be(1)-O(3)	110.2(9)
O(3)-P(2)-O(2)	109.8(5)	O(9)-Be(2)-O(5)	114.5(14)
O(2)#3-P(2)-O(2)	113.6(8)	O(9)-Be(2)-O(5)#3	114.5(14)
O(5)-P(3)-O(6)	112.4(8)	O(5)-Be(2)-O(5)#3	109(2)
O(5)-P(3)-O(4)	114.4(6)	O(9)-Be(2)-O(7)	108(2)
O(6)-P(3)-O(4)	110.4(7)	O(5)-Be(2)-O(7)	105.1(14)
O(10)-P(4)-O(10)#3	111.2(11)	O(5)#3-Be(2)-O(7)	105.1(14)
O(10)-P(4)-O(9)	111.0(6)	O(10)-Be(3)-O(2)#2	109.0(13)
O(10)#3-P(4)-O(9)	111.0(6)	O(10)-Be(3)-O(8)#7	113.1(13)
O(7)-P(5)-O(8)#3	116.5(6)	O(2)#2-Be(3)-O(8)#7	112.2(14)
O(7)-P(5)-O(8)	116.5(6)	O(10)-Be(3)-O(6)#8	105.6(14)
O(8)#3-P(5)-O(8)	118.1(8)	O(2)#2-Be(3)-O(6)#8	108.8(13)
O(1)-Be(1)-O(4)	106.9(9)	O(8)#7-Be(3)-O(6)#8	107.8(12)
O(1)-Be(1)-O(4)#3	106.9(9)		

[a]Symmetry codes: #1: -x+y, -x+1, -z+1/2; #2: -y+1, x-y+1, z; #3: x, y, -z+1/2; #4: -x+y, -x+1, z; #5: -x+1, -y+1, z-1/2; #6: -y+1, x-y, z; #7: -x+y+1, -x+1, z; #8: -x+1, -y+1, z+1/2.

References

[1] Rigaku, Process-Auto; Rigaku Americas Corporation: The Woodlands, Texas, **1998**.

[2] G. M. Sheldrick, *SHELXS97 Program for Solution of Crystal Structures*, University of Göttingen, Göttingen, Germany, **1997**.