Supplementary Material for:

Organotemplate-free Hydrothermal Synthesis of Aluminophosphate Molecular Sieve with AEN-zeotype Topology and Properties of Its Derivatives

Yanyan Wang, Yanjun Sun, Ying Mu, Chuanqi Zhang, Jiyang Li* and Jihong Yu*

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China. Fax: (+86) 431-85168608; E-mail: lijiyang@jlu.edu.cn; jihong@jlu.edu.cn

Experimental section

The reagents and solvents employed in the synthesis were commercially available and used as received without further purification.

Synthesis of JU93. Organotemplate-free synthesis of JU93 was carried out in the hydrothermal reaction system of Al_2O_3-P_2O_5-Na_2O-H_2O. Typically, aluminum triisopropoxide was dispersed in a solution of orthophosphoric acid (85 wt%) in water under vigorous stirring at room temperature. 5M NaOH solution was added to this mixture giving the pH value of about 5. After stirring for one hour, a homogeneous gel with an overall molar composition of $1.0Al_2O_3$: 4.5-5.2P_2O_5: 3.5-4.1Na_2O: 663-780H_2O was formed, which was heated under autogenous pressure in a 9 mL Teflon-lined stainless steel autoclave at 180 °C for 3 days. The obtained crystals were washed in distilled water and dried at room temperature overnight. The product was recovered with a yield of more than 95 % based on Al. ICP analysis of the product gave (in wt.%) Al: 18.4, P: 21.2, Na: 5.20 (calcd. Al: 18.3, P: 21.0, Na: 5.20), which was consistent with the elemental contents calculated from the molecular formula of $|Na(H_2O)_2|[(AlPO_4)_3OH]$.

Preparation of JU93(A), NH_4-JU93, JU93(B) and NH_4-JU93(r). JU93(A) with an identical framework topology of $AlPO_4$-53(C) was obtained by calcining the as-synthesized JU93 at 400 °C for 4 h. The NH_4^+ exchanged JU93 (denoted as NH_4-JU93) was obtained by immersing 1 g of JU93 sample in 30 mL of 1 M NH_4NO_3 (or NH_4HCO_3, CH_3COONH_4) solution at 85 °C for 5 h, and then washed by distilled water for several times. JU93(B) was produced by heating the NH_4-JU93 at 230 °C for 2 h to remove the NH_4^+ ions in the channels and OH^- ions on the framework. Rehydrated NH_4-JU93 (denoted as NH_4-JU93(r)) was prepared by immersing the JU93(B) samples in 1 M CH_3COONH_4 at 85 °C for 5 h, and then washing by distilled water for several times.

Characterization Methods. Powder X-ray diffraction (PXRD) data were collected on a Rigaku D/max-2550 diffractometer with Cu Kα radiation (λ = 1.5418 Å). The

crystal morphology was studied by field emission scanning electron microscopy (SEM) JEOL JSM-6510 using conventional sample preparation and imaging techniques. Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV spectrometer. Elemental analysis was conducted on a Vario MICRO elemental analyzer. Thermogravimetric analysis (TGA) was carried out on a TA Q500 analyzer in air with a heating rate of 10°C min^{-1} from RT to 800°C.

A tablet was prepared by pressing the JU93 samples on a tableting machine and calcined at 400 °C for 4 h for the electric conductivity. Electric conductivity measurement of the samples was carried out via impedance spectroscopy on a Solartron 1260 impedance analyzer over the frequency range from 0.1 Hz to 1 MHz and in the temperature range of 150–450 °C or 200–600 °C. Ionic conductivity values were calculated with $\sigma = d/(R \times S)$, where d denotes the sample thickness, S indicates the area of the electrodes and R is the sample resistance corresponding to the total resistance (R_t).

N_2 adsorption at 77K, and CO_2 and CH_4 adsorptions at 273K for the sample of JU93(B) were performed on an apparatus of Micromeritics ASAP 2020. Before the adsorption, the sample of JU93(B) was pretreated in vacuum at 80 ºC for 12 h to remove the physical adsorption of water in the holes. Specific surface area was calculated by using the Brunauer-Emmett-Teller (BET) equation.

Structural Determination. Suitable single crystal of JU93 with dimension of 0.41 × 0.35 × 0.12 mm^3 was selected for single-crystal X-ray diffraction analyses. The intensity data were collected on a Rigaku RAXIS-RAPID diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at temperature of 20±2 °C. Cell refinement and data reduction were accomplished with the SAINT processing program.[1] The structure of JU93 was solved in the space group $Pca2_1$ by direct methods and refined by full matrix least-squares technique with the SHELXTL crystallographic software package.[2] The heaviest atoms of Al, P, Na and O could be unambiguously located. The H atoms in the structure were not added. All non-hydrogen atoms were refined anisotropically. Crystal data and refinement parameters

for the structure determination are presented in Table S1. The selected bond distances and bond angles are listed in the Table S2.

Supplementary References

1 SAINT, Bruker AXS Inc., 5465 East Cheryl Parkway, Madison, WI, 53711–5373, USA, 2000.

2 SHELXTL, Bruker AXS Inc., 5465 East Cheryl Parkway, Madison, WI, 53711–5373, USA, 2000.

Table S1 Crystal data and structure refinement for JU93[a]

compound	JU93
empirical formula	$Na_2Al_6P_6O_{30}H_{10}$
formula weight	883.76
temperature	293(2) K
wavelength(Å)	0.71073
crystal system, space group	Orthorhombic, $Pca2_1$
unit cell dimensions	
a (Å)	17.495(4)
b (Å)	10.321(2)
c (Å)	13.577(3)
volume(Å^3)	2451.4(9)
Z, calculated density(mg/m^3)	4, 2.395
absorption coefficient(mm^{-1})	0.824
F(000)	1760
crystal size(mm^3)	0. 41 × 0.35 × 0.12
θ range(°) for data collection	3–27.48
limiting indices	$-22 \le h \le 22$, $-12 \le k \le 12$, $-17 \le l \le 17$
reflections collected/unique	21860/5516, [*R*(int) = 0.0345]
completeness to θ (%)	27.48, 98.8
absorption correction	Empirical
max and min transmission	0.9069 and 0.7278
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	5516/1/397
goodness-of-fit on F^2	1.037
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0295$, $wR_2 = 0.0798$
R indices (all data)	$R_1 = 0.0343$, $wR_2 = 0.0820$
Absolute structure parameter	0.21(11)
largest diff. peak and hole (eÅ^{-3})	0.668 and -0.441

a $R_1 = \sum(\Delta F/\sum(F_o))$, $wR_2 = (\sum[w(F_o2 - F_c2)])/\sum[w(F_o2)2]1/2$ and $w = 1/\sigma2(F_o2)$.

Table S2 Selected bond lengths [Å] and angles [°] for JU93

Selected bond lengths		Selected angles			
Al(1)-O(6)	1.780(2)	O(6)-Al(1)-O(10)	135.96(15)	O(16)-P(3)-O(18)	110.74(17)
Al(1)-O(10)	1.793(2)	O(6)-Al(1)-O(9)	114.52(13)	O(16)-P(3)-O(9)	108.56(16)
Al(1)-O(9)	1.801(3)	O(10)-Al(1)-O(9)	109.51(13)	O(18)-P(3)-O(9)	108.10(15)
Al(1)-O(7)	1.851(3)	O(6)-Al(1)-O(7)	90.47(11)	O(16)-P(3)-O(17)	109.22(15)
Al(1)-O(8)	1.904(3)	O(10)-Al(1)-O(7)	88.92(11)	O(18)-P(3)-O(17)	110.57(16)
Al(2)-O(11)	1.730(3)	O(9)-Al(1)-O(7)	90.14(13)	O(9)-P(3)-O(17)	109.61(16)
Al(2)-O(12)	1.726(2)	O(6)-Al(1)-O(8)	86.49(12)	O(12)#3-P(4)-O(1)	108.76(14)
Al(2)-O(26)	1.746(3)	O(10)-Al(1)-O(8)	89.61(12)	O(12)#3-P(4)-O(19)#4	109.90(17)
Al(2)-O(17)	1.758(2)	O(9)-Al(1)-O(8)	95.91(14)	O(1)-P(4)-O(19)#4	108.80(16)
Al(3)-O(19)	1.777(3)	O(7)-Al(1)-O(8)	173.91(14)	O(12)#3-P(4)-O(2)	109.77(16)
Al(3)-O(4)	1.824(3)	O(11)-Al(2)-O(12)	110.00(16)	O(1)-P(4)-O(2)	110.39(16)
Al(3)-O(20)	1.834(3)	O(11)-Al(2)-O(26)	105.24(15)	O(19)#4-P(4)-O(2)	109.20(15)
Al(3)-O(22)	1.859(2)	O(12)-Al(2)-O(26)	108.07(14)	O(6)-P(5)-O(4)	111.35(16)
Al(3)-O(21)	1.865(2)	O(11)-Al(2)-O(17)	109.51(15)	O(6)-P(5)-O(5)	111.74(14)
Al(4)-O(14)	1.797(3)	O(12)-Al(2)-O(17)	112.19(13)	O(4)-P(5)-O(5)	107.20(13)
Al(4)-O(16)#1	1.808(3)	O(26)-Al(2)-O(17)	111.59(14)	O(6)-P(5)-O(3)	110.94(15)
Al(4)-O(8)	1.833(3)	O(19)-Al(3)-O(4)	101.46(14)	O(4)-P(5)-O(3)	108.71(15)
Al(4)-O(15)	1.851(3)	O(19)-Al(3)-O(20)	109.61(14)	O(5)-P(5)-O(3)	106.70(16)
Al(4)-O(13)	1.886(3)	O(4)-Al(3)-O(20)	148.81(15)	O(21)-P(6)-O(10)#10	108.10(15)
Al(5)-O(24)	1.731(3)	O(19)-Al(3)-O(22)	98.01(14)	O(21)-P(6)-O(11)#3	108.99(17)
Al(5)-O(18)	1.724(2)	O(4)-Al(3)-O(22)	90.15(12)	O(10)#10-P(6)-O(11)#3	106.80(17)
Al(5)-O(3)#6	1.734(3)	O(20)-Al(3)-O(22)	88.23(12)	O(21)-P(6)-O(13)#10	110.71(13)
Al(5)-O(2)#6	1.755(2)	O(19)-Al(3)-O(21)	97.85(14)	O(10)#10-P(6)-O(13)#10	111.74(14)
Al(6)-O(20)	1.886(3)	O(4)-Al(3)-O(21)	84.21(11)	O(11)#3-P(6)-O(13)#10	110.36(17)
Al(6)-O(1)	1.799(3)	O(20)-Al(3)-O(21)	88.86(11)	O(3W)#4-Na(1)-O(4W)	111.98(14)
Al(6)-O(23)	1.797(2)	O(22)-Al(3)-O(21)	163.94(14)	O(3W)#4-Na(1)-O(4)#7	117.83(13)
Al(6)-O(25)#10	1.807(3)	O(14)-Al(4)-O(16)#4	102.36(14)	O(4W)-Na(1)-O(4)#7	115.16(12)
Al(6)-O(5)#7	1.882(3)	O(14)-Al(4)-O(8)	146.52(15)	O(3W)#4-Na(1)-O(23)	104.14(12)
P(1)-O(15)	1.516(3)	O(16)#4-Al(4)-O(8)	111.06(14)	O(4W)-Na(1)-O(23)	93.17(10)
P(1)-O(23)	1.528(3)	O(14)-Al(4)-O(15)	86.65(11)	O(4)#7-Na(1)-O(23)	111.14(10)
P(1)-O(24)	1.530(3)	O(16)#4-Al(4)-O(15)	96.53(13)	O(3W)#4-Na(1)-O(5)#7	101.82(14)
P(1)-O(22)	1.538(3)	O(8)-Al(4)-O(15)	87.62(11)	O(4W)-Na(1)-O(5)#7	141.86(12)
P(2)-O(25)	1.509(3)	O(14)-Al(4)-O(13)	91.03(12)	O(4)#7-Na(1)-O(5)#7	58.99(9)
P(2)-O(7)#6	1.512(2)	O(16)#4-Al(4)-O(13)	95.77(13)	O(23)-Na(1)-O(5)#7	60.87(8)
P(2)-O(14)	1.531(2)	O(8)-Al(4)-O(13)	87.68(12)	O(3W)#4-Na(1)-O(21)#7	96.81(11)
P(2)-O(26)	1.531(3)	O(15)-Al(4)-O(13)	167.69(14)	O(4W)-Na(1)-O(21)#7	77.47(9)
P(3)-O(16)	1.502(3)	O(18)-Al(5)-O(24)	109.80(16)	O(4)#7-Na(1)-O(21)#7	58.45(8)
P(3)-O(18)	1.522(2)	O(18)-Al(5)-O(3)#6	108.69(14)	O(23)-Na(1)-O(21)#7	159.00(12)
P(3)-O(9)	1.529(3)	O(24)-Al(5)-O(3)#6	104.31(16)	O(5)#7-Na(1)-O(21)#7	116.36(9)
P(3)-O(17)	1.548(2)	O(18)-Al(5)-O(2)#6	112.14(13)	O(4W)#4-Na(2)-O(2W)	95.05(14)
P(4)-O(12)#3	1.518(2)	O(24)-Al(5)-O(2)#6	109.34(15)	O(4W)#4-Na(2)-O(1W)#9	82.65(13)

P(4)-O(1)	1.521(3)	O(3)#6-Al(5)-O(2)#6	112.27(14)	O(2W)-Na(2)-O(1W)#9	168.45(16)
P(4)-O(19)#4	1.530(3)	O(1)-Al(6)-O(23)	109.19(13)	O(4W)#4-Na(2)-O(5)	171.19(11)
P(4)-O(2)	1.538(3)	O(23)-Al(6)-O(25)#10	136.30(15)	O(2W)-Na(2)-O(5)	91.04(14)
P(5)-O(6)	1.514(3)	O(1)-Al(6)-O(25)#10	114.41(13)	O(1W)#9-Na(2)-O(5)	92.62(13)
P(5)-O(4)	1.521(2)	O(23)-Al(6)-O(5)#7	87.54(11)	O(4W)#4-Na(2)-O(1)#2	124.62(10)
P(5)-O(5)	1.526(3)	O(1)-Al(6)-O(5)#7	89.99(13)	O(2W)-Na(2)-O(1)#2	85.49(13)
P(5)-O(3)	1.553(3)	O(25)#10-Al(6)-O(5)#7	89.59(12)	O(1W)#9-Na(2)-O(1)#2	86.53(13)
P(6)-O(21)	1.513(2)	O(23)-Al(6)-O(20)	90.77(12)	O(5)-Na(2)-O(1)#2	62.16(9)
P(6)-O(11)#3	1.534(3)	O(1)-Al(6)-O(20)	96.79(14)	O(4W)#4-Na(2)-O(3)	114.94(10)
P(6)-O(13)#10	1.536(3)	O(25)#10-Al(6)-O(20)	87.09(13)	O(2W)-Na(2)-O(3)	98.70(13)
P(6)-O(10)#10	1.533(3)	O(5)#7-Al(6)-O(20)	173.19(15)	O(1W)#9-Na(2)-O(3)	92.51(14)
Na(1)-O(3W)#4	2.301(4)	O(15)-P(1)-O(23)	108.03(15)	O(5)-Na(2)-O(3)	57.64(9)
Na(1)-O(4W)	2.320(3)	O(15)-P(1)-O(24)	110.46(17)	O(1)#2-Na(2)-O(3)	119.69(11)
Na(1)-O(4)#7	2.347(3)	O(23)-P(1)-O(24)	107.02(17)		
Na(1)-O(23)	2.400(3)	O(15)-P(1)-O(22)	109.71(13)		
Na(1)-O(5)#7	2.612(3)	O(23)-P(1)-O(22)	111.56(15)		
Na(1)-O(21)#7	2.683(3)	O(24)-P(1)-O(22)	110.01(17)		
Na(2)-O(3)	2.616(3)	O(25)-P(2)-O(7)#1	111.54(14)		
Na(2)-O(1W)#9	2.373(4)	O(25)-P(2)-O(14)	109.52(16)		
Na(2)-O(2W)	2.312(4)	O(7)#1-P(2)-O(14)	110.13(13)		
Na(2)-O(4W)#4	2.309(3)	O(25)-P(2)-O(26)	109.57(15)		
Na(2)-O(5)	2.504(3)	O(7)#1-P(2)-O(26)	107.55(16)		
Na(2)-O(1)#2	2.538(3)	O(14)-P(2)-O(26)	108.46(15)		

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y-1,z; #2 x+1/2,-y,z; #3 -x-1/2,y+1,z-1/2; #4 -x-1/2,y,z-1/2; #5 x,y-1,z; #6 -x-1/2,y,z+1/2; #7 x-1/2,-y,z; #8 -x-1/2,y-1,z+1/2; #9 x+1/2,-y-1,z; #10 x,y+1,z

Table S3 Compositional analyses of JU93 samples ion-exchanged by different ammonium salts

Sample	Ammonium salts used for ion-exchange	Na^+content (wt%)	Ncontent (wt%)	Degree of Na^+ ion-exchanged (%)[a]
JU93	--	5.20	--	--
NH_4-JU93	CH_3COONH_4	0.288	3.20	94
	NH_4NO_3	0.556	3.08	89
	NH_4HCO_3	1.03	2.89	80

[a] the degree of Na^+ ion-exchange is calculated based on the Na^+ content.

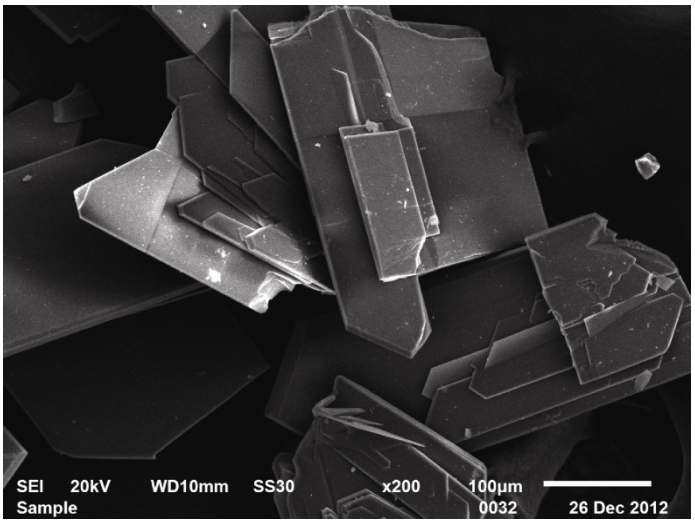


Figure S1. SEM image of JU93.

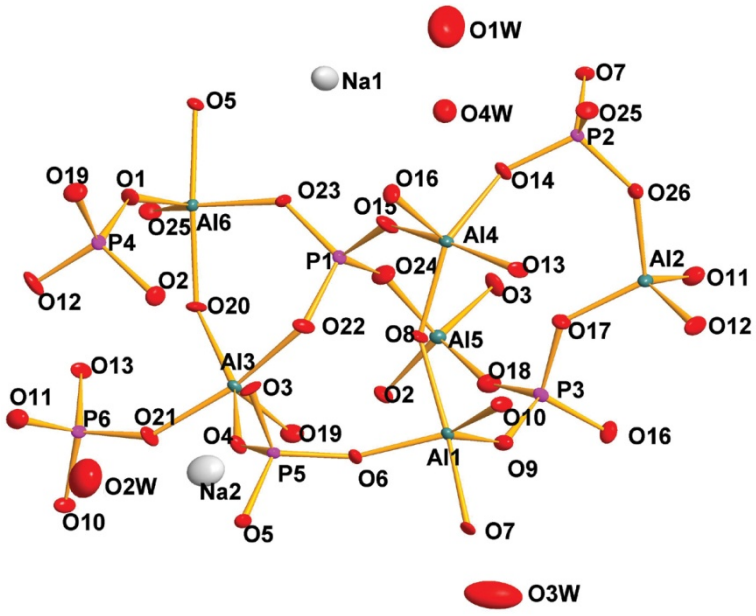


Figure S2. Thermal ellipsoids given at 50% probability, showing the atomic labeling scheme of JU93.

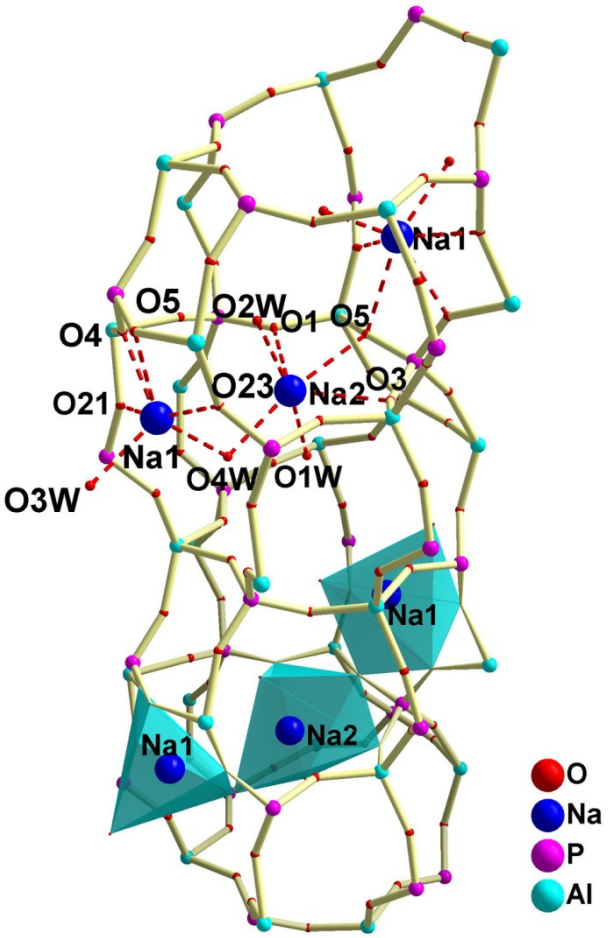


Figure S3. Coordination geometry of Na^+ ions in JU93.

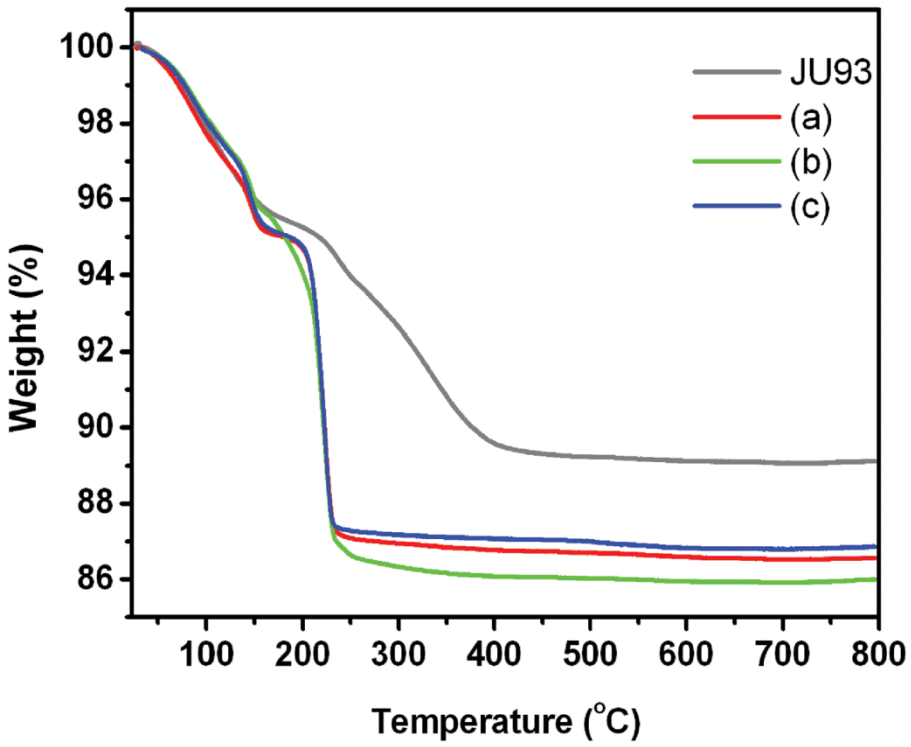
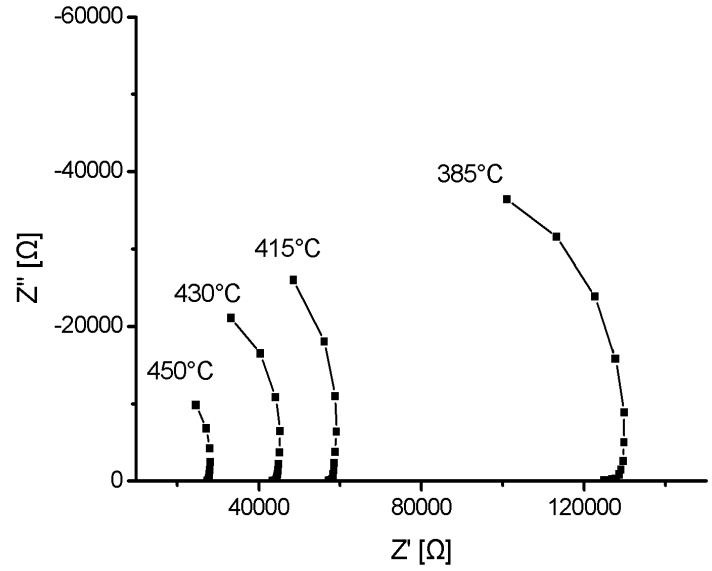
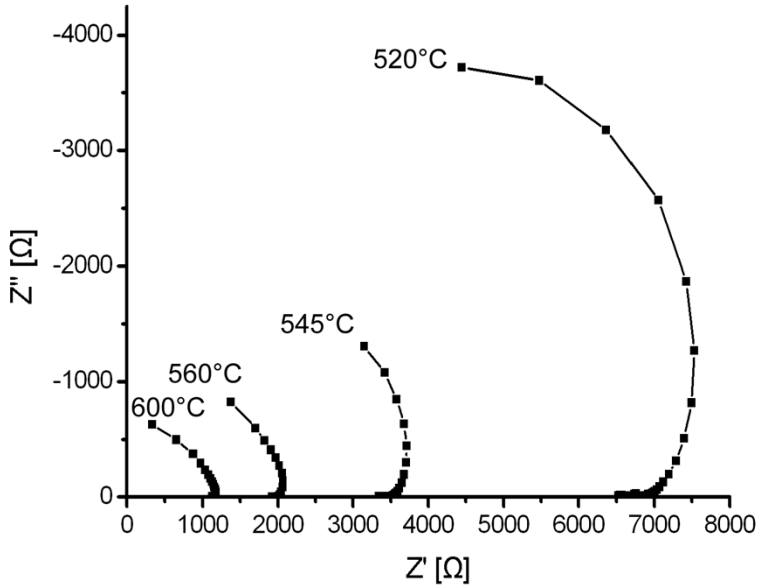


Figure S4. TGA curves of as-synthesized JU93 and NH_4-JU93 exchanged by (a) NH_4NO_3, (b)NH_4HCO_3 and (c) CH_3COONH_4, respectively.



(a)



(b)

Figure S5. Impedance spectra of (a) JU93(A) and (b) JU93-550 under different temperatures.

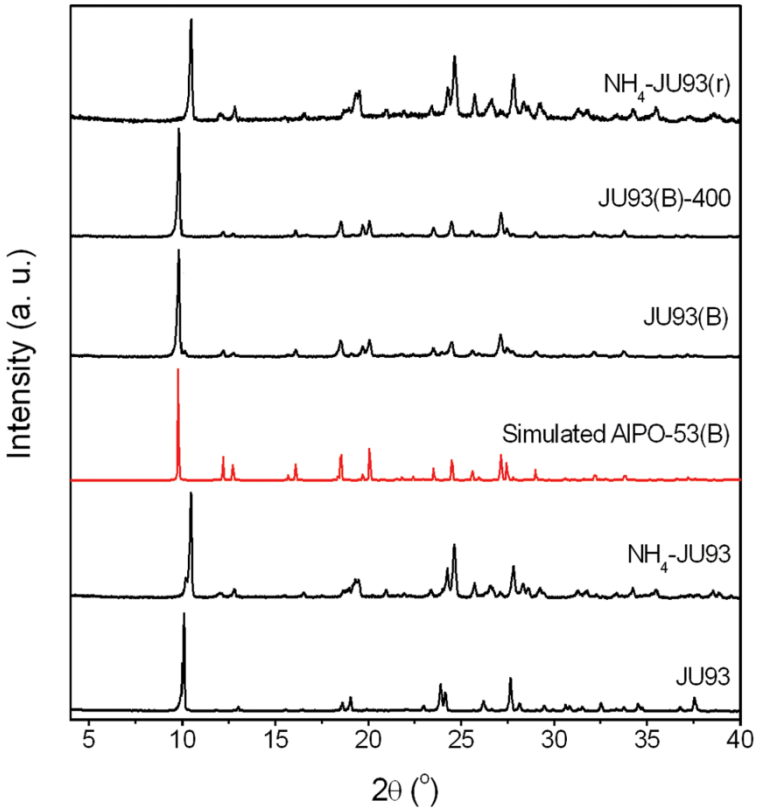


Figure S6. Experimental PXRD patterns of NH_4-JU93, JU93(B), the calcined JU93(B) at 400 °C (JU93(B)-400) and NH_4-JU93(r), compared with the as-synthesized JU93 and the simulated AlPO-53(B).

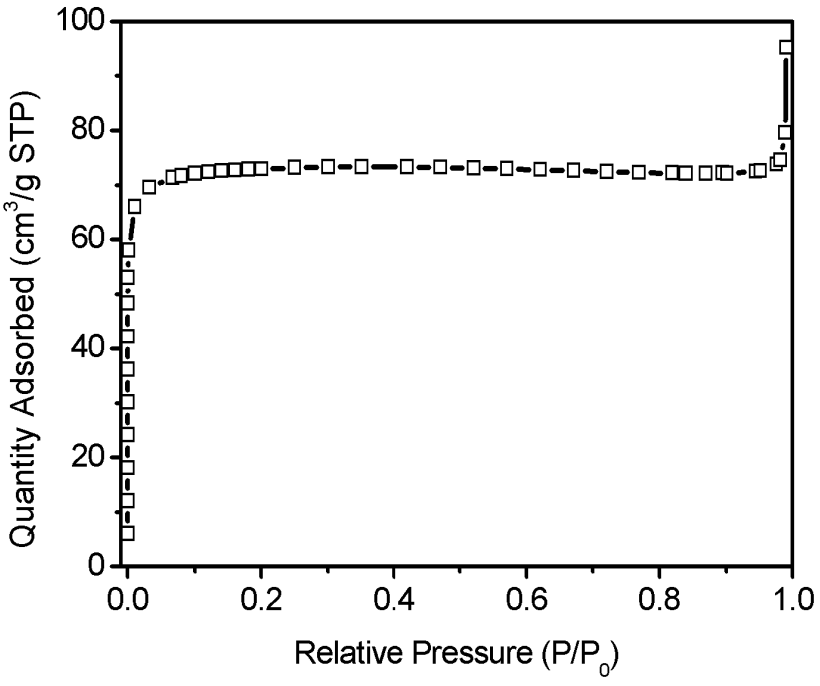


Figure S7. Nitrogen adsorption isotherm of JU93(B).