Supporting Information

A New 2D Layered Aluminophosphate $|Hada|_6[Al_6(PO_4)_8](H_2O)_{11}$ Supported Highly Uniform Ag Nanoparticles for 4-Nitrophenol Reduction

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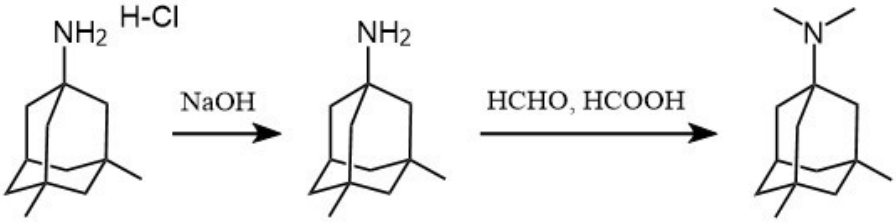
Experimental Section

Synthesis of 3,5,*N*,*N*-tetramethyladamantane-1-amine (ada). The synthesis route of *N*,*N*,-dimethylmemantin-1-amine is shown in Scheme S1. The details of synthesis of *N*,*N*,-dimethylmemantin-1-amine is reported in our previous work.[1]



Scheme S1. Synthesis of 3,5,*N*,*N*-tetramethyladamantane-1-amine.

Synthesis of ZHKU-1. The aluminophosphate of ZHKU-1 was obtained using ada as template molecule with the following gel composition: Al2O3:(1.3-1.4) P2O5:(0.5-0.6) ada:(20-30) H2O. In a typical synthesis, 0.65 g orthophosphoric acid (85 wt% H3PO4, Aladdin), 4.50 g deionized water, and 0.32 g boehmite (Catapal B, 70.3% Al2O3, Letai) were mixed to the Teflon liner container. After stirring for 2 hours, 1.25 g ada was added to the mixture, and the final gel was sealed in the autoclave. After hydrothermal crystallization at 150 °C for three days in static conditions, colorless block crystals were formed. Elemental analysis (%) calcd for ZHKU-1: C 42.57, N 3.54, H 7.57; found: C 42.36, N 3.45, H 7.40.

Synthesis of Ag@ZHKU-1. In a typical run, 0.3 g ZHKU-1 sample was added to 13.9 mL $AgNO_3$ (0.01 M) solution. Then, under the UV light (LED, *P* = 12 W, λ = 365 nm) irradiation, the mixture was stirring for 2 hours. The suspension was filtrated and washed by water several times, giving Ag NPs supported material named Ag@ZHKU-1.

Catalytic reduction of 4-NP. 5 mL 4-NP (3.0 mM) aqueous solution was mixed with 25 mL distilled water in the weighing bottle. Then 5 mL $NaBH_4$ aqueous solution (0.3 M) was added, and the solution immediately turned to the deep-yellow solution. After the catalyst of Ag@ZHKU-1 (10.0 mg) was added, a conversion of the 4-NP to 4-AP was rapidly triggered at room temperature. Time-dependent UV–vis spectroscopy was used to record the whole reaction progress.

Characterization. X-ray single-crystal diffraction data of ZHKU-1 were collected on a diffractometer (Bruker D8 QUEST) using Mo-K_α radiation(λ = 0.71073 Å) radiation at 120 K with a Bruker cooling system under a N_2 flow. The single crystal of ZHKU-1 was mounted in a loop. The crystal structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL 2014 and Olex 2 program. Hydrogen atoms on organic ligands were generated by the riding mode. The Cambridge Crystallographic Data Centre (CCDC) number is 2034965 for ZHKU-1. The data could be obtained free of charge from the via www.ccdc.cam.ac.uk/data_request/cif (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033).

XRD was collected using a Rigaku SmartLab diffractometer equipped with a rotating anode (Cu $K\alpha_1$ radiation, λ = 1.5406 Å). SEM images and high-resolution SEM were operated on an FEI Quanta 400 Thermal Field Emission Environmental SEM and GeminiSEM500 Field-Emission-SEM, respectively. HRTEM images, HAADF-STEM images, and corresponding EDX are acquired on a JEOL, JEM-ARM200P operating at 200 kV. The liquid ^{13}C-NMR spectrum was collected on a Bruker advance III 400MHz spectrometer and the solid-state ^{27}Al, ^{31}P, and ^{13}C MAS NMR spectra on a Bruker Advance 400 spectrometer with 79.49 MHz. The infrared (IR) spectrum was collected on Thermo Scientific Nicolet 6700 Fourier transform infrared spectroscopy. ICP-OES was obtained on an Optima 8300 spectrometer, Elemental analysis on a Vario EL Cube elemental analyzer., and the Raman spectra on inVia Qontor spectrometer. UV-vis spectroscopy was collected with a PerkinElmer UV750 spectrophotometer. N_2 adsorption was measured on a JWGB JW-BK200C instrument.

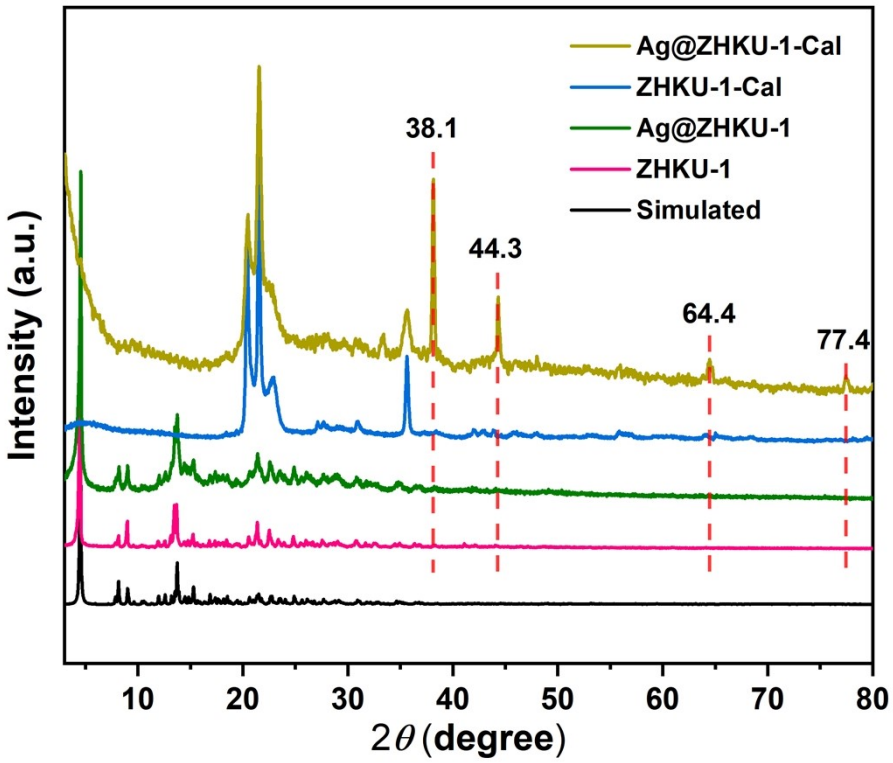


Figure S1. A comparison of the XRD patterns of ZHKU-1, Ag@ZHKU-1, ZHKU-1-Cal, Ag@ZHKU-1-Cal.

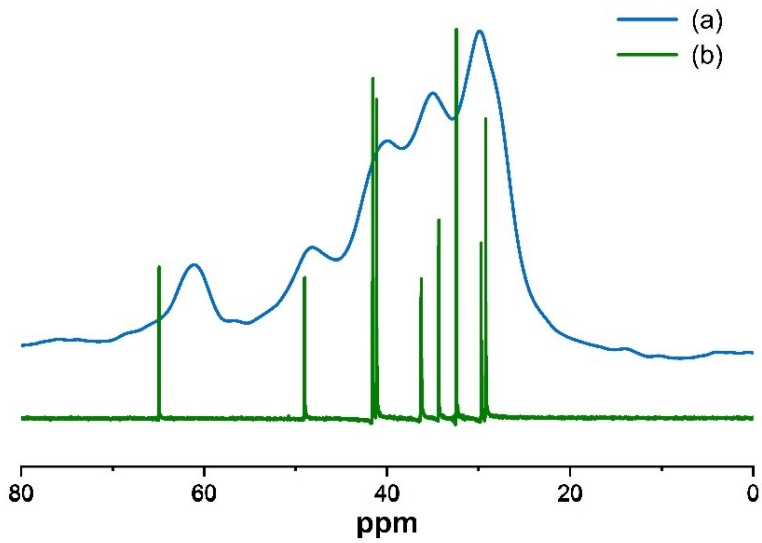


Figure S2. (a) The solid-state ^{13}C MAS NMR of ZHKU-1; (b) The ^{13}C liquid NMR of synthetic protonated 3,5,*N*,*N*-tetramethyladamantane-1-amine which was dissolved with concentrated HCl aqueous solution.

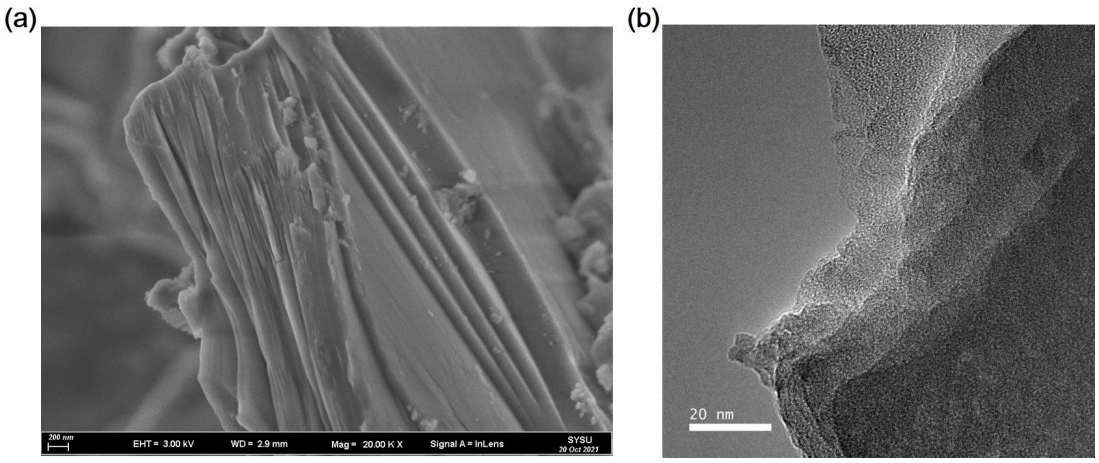


Figure S3. The high-resolution SEM (a) and TEM images (b).

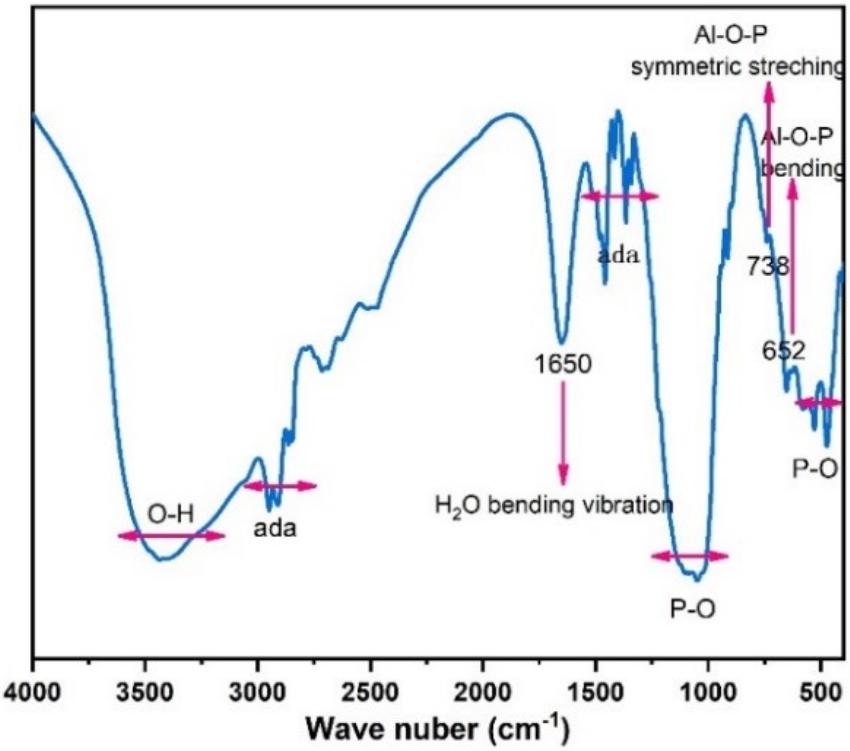


Figure S4. The IR spectrum of ZHKU-1 in the range of 400-4000 cm^{-1}.

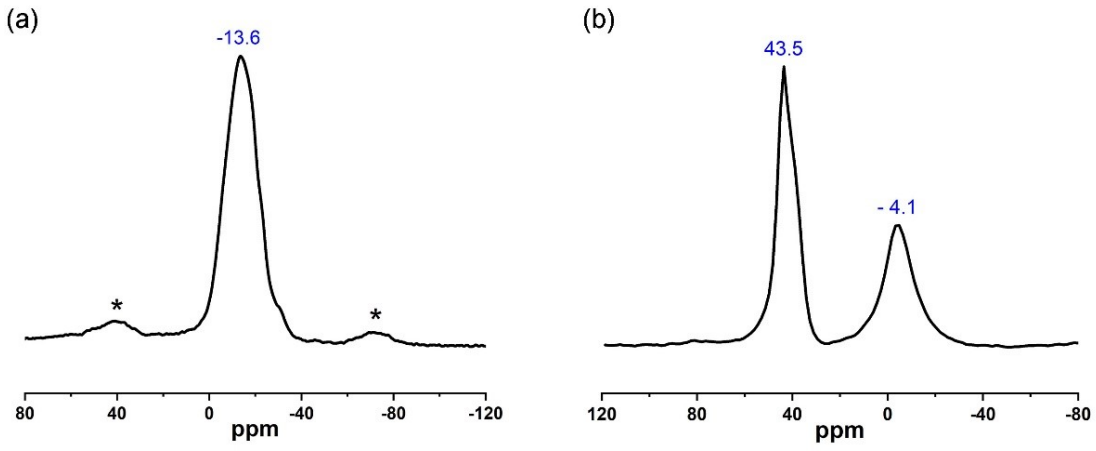


Figure S5. (a) ^{31}P magic angle spinning (MAS) NMR spectra of ZHKU-1. Asterisks (*****) denote the spinning sidebands. (b) ^{27}Al MAS NMR spectra of ZHKU-1.

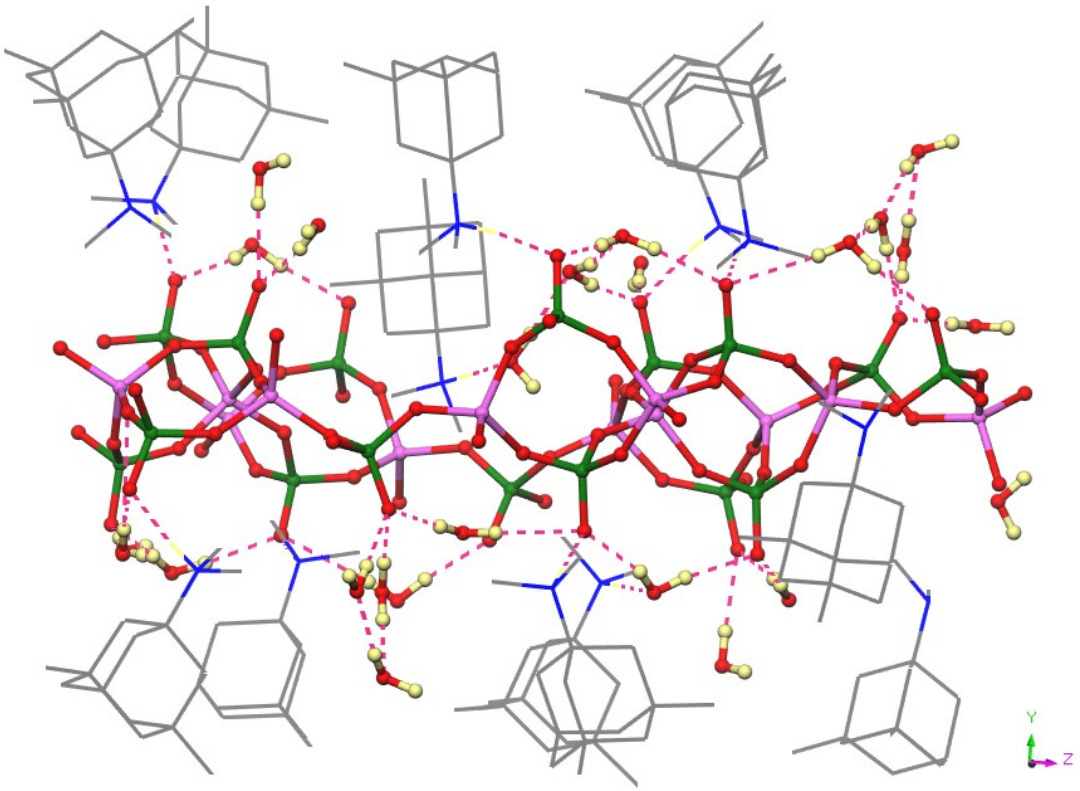


Figure S6. An enlarged view of figure 3b.

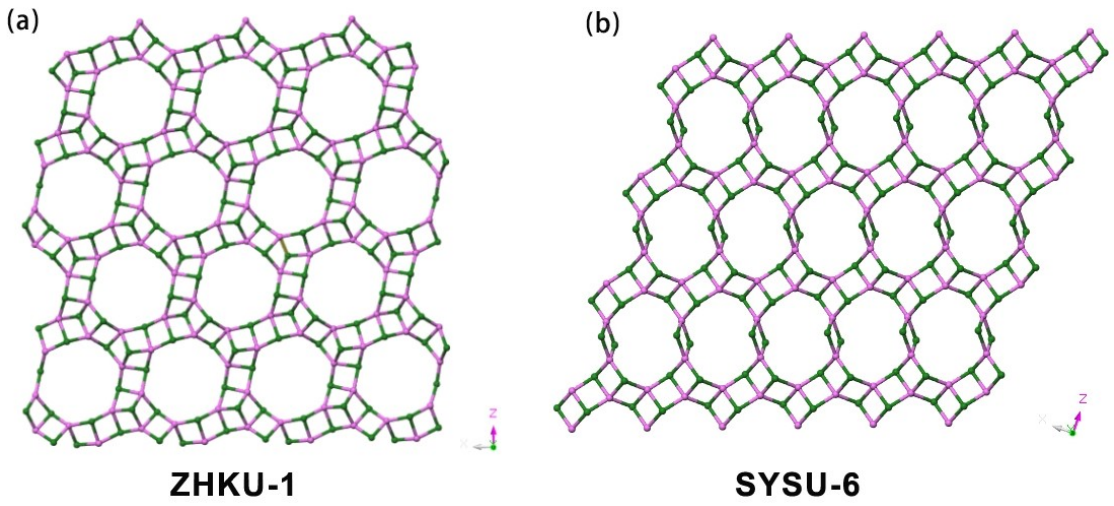


Figure S7. The different layers between ZHKU-1 (a) and SYSU-6 (b).

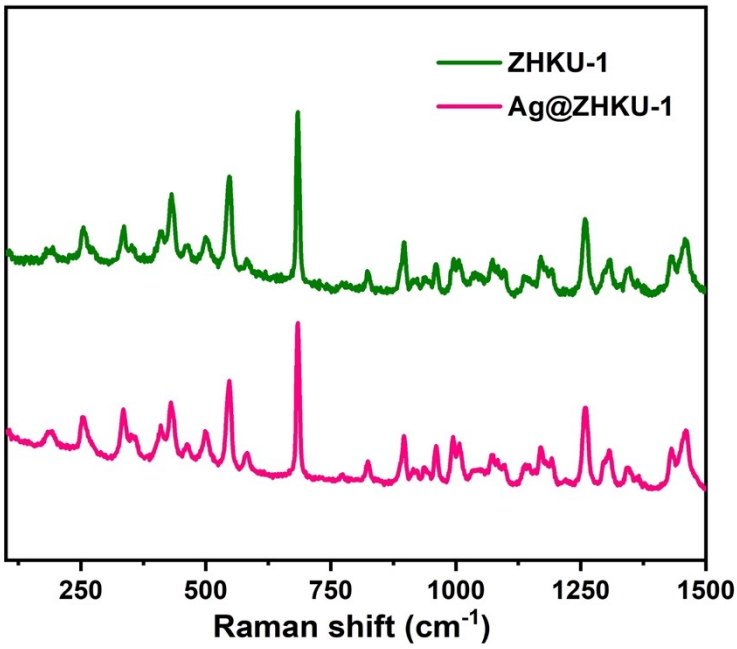


Figure S8. Raman spectra excited with 785 nm of ZHKU-1 and Ag@ZHKU-1 in the range of 100–1500 cm^{-1}.

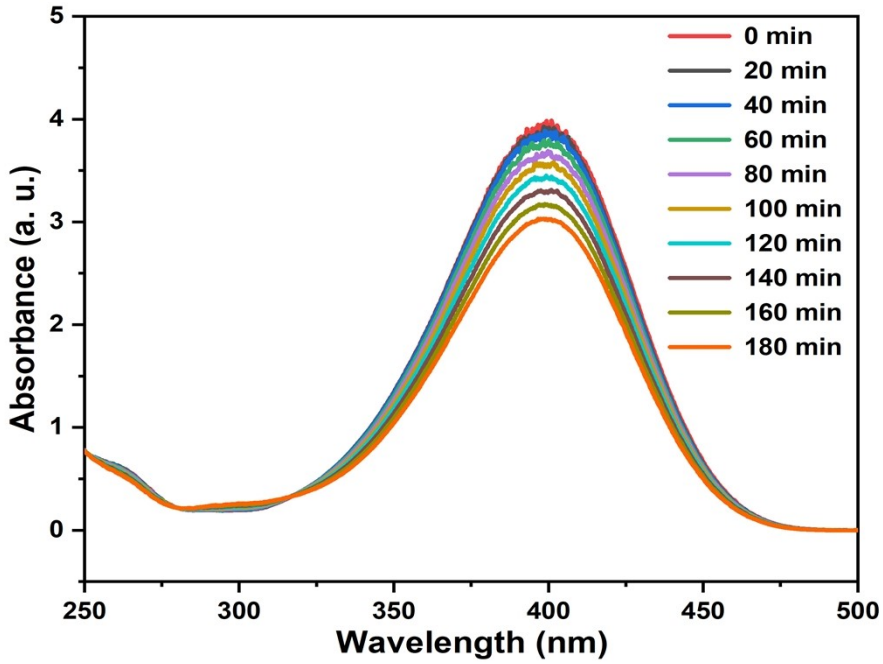


Figure S9. Time-dependent UV-vis absorption of 4-NP with $NaBH_4$ alone in the absence of Ag@ZHKU-1 catalyst.

Table S1. Comparison of ZHKU-1 with SYSU-1.

Name	Formula	Coordination Sequence	Stacking Sequence	Ring Size
SYSU-6	$\|Hada\|_2[Al_2(HPO_4)(PO_4)_2]$	2 5 6 12 12 20 12 24 20 32 3 7 6 12 10 19 16 26 18 31 4 4 8 9 18 12 20 17 30 22 4 5 10 7 14 14 24 17 28 19	AB	4,12
ZHKU-1 **(this work)**	$\|Hada\|_6[Al_6(PO_4)_8](H_2O)_{11}$	3 6 6 12 12 21 18 24 21 33 3 7 7 12 12 20 17 25 21 32 4 5 9 9 16 15 23 19 28 24	AAAA	4,6,12

Table S2. Summary of 4,6,12-net layered aluminophosphates for the same coordination sequence with Al:P = 3:4.

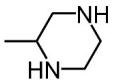
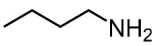
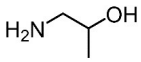
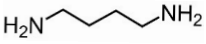
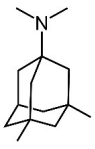
Name	Formula and OSDA	Coordination Sequence	stacking sequence
2.3.4.143.001 APMeP150	$\|(C_5N_2H_{14})_3(H_2O)_{10}\|[Al_6P_8O_{32}(H_2O)_2]$ 	3 7 7 12 12 20 17 25 21 32 3 6 6 12 12 21 18 24 21 33 4 5 9 9 16 15 23 19 28 24	AAAA
2.3.4.147.001	$[BuNH_3]_3[Al_3P_4O_{16}]$ 	3 7 7 12 12 20 17 25 21 32 3 6 6 12 12 21 18 24 21 33 4 5 9 9 16 15 23 19 28 24	AAAA
2.3.4.148.001	$[NH_3CH_2CH(OH)CH_3]_3[Al_3P_4O_{16}]$ 	3 7 7 12 12 20 17 25 21 32 3 6 6 12 12 21 18 24 21 33 4 5 9 9 16 15 23 19 28 24	ABCABC
2.3.4.165.001	$[Al_3P_4O_{16}][1.5NH_3(CH_2)_4NH_3]$ 	3 7 7 12 12 20 17 25 21 32 3 6 6 12 12 21 18 24 21 33 4 5 9 9 16 15 23 19 28 24	ABCABC
ZHKU-1	$\|Hada\|_6[Al_6(PO_4)_8](H_2O)_{11}$ 	3 7 7 12 12 20 17 25 21 32 3 6 6 12 12 21 18 24 21 33 4 5 9 9 16 15 23 19 28 24	AAAA

Table S3. Al, P, N, O, and C Atoms Fractional Atomic Coordinates (×10^4) for ZHKU-1.

Atom	x	y	z
P1	-2376.8(8)	7928.6(3)	4298.1(4)
P2	1365.5(8)	7852.3(3)	5529.8(4)
P3	-244.7(8)	7055.2(3)	4518.6(4)
P4	1224.1(8)	7790.8(3)	3221.4(4)
P5	3901.1(8)	7108.3(3)	3889.6(4)
P6	5028.0(8)	7917.0(3)	2598.1(4)
P7	3742.0(8)	7076.4(3)	1543.5(4)
P8	7359.6(8)	7093.7(3)	2817.0(4)
Al1	-912.0(9)	7660.5(3)	5314.9(5)
Al2	-973.0(9)	7514.7(3)	3447.9(5)
Al3	1845.1(9)	7452.5(3)	4422.1(5)
Al4	3135.3(9)	7406.4(3)	2684.4(5)
Al5	5922.7(9)	7497.9(3)	3667.7(5)
Al6	5902.8(9)	7350.9(3)	1796.5(5)
O1	-2721(2)	8291.4(7)	4254.5(12)
O2	-3285(2)	7673.5(7)	4224.3(11)
O3	-1893(2)	7859.5(7)	4912.5(11)
O4	-1568(2)	7844.7(7)	3828.9(12)
O5	1792(3)	8187.7(8)	5690.6(13)
O6	263(2)	7877.4(7)	5239.4(11)
O7	1278(2)	7606.3(7)	6064.8(12)
O8	2062(2)	7666.9(8)	5079.5(11)
O9	-740(2)	7249.1(7)	5033.3(12)
O10	-711(2)	7183.8(7)	3931.3(12)
O11	-419(2)	6678.8(7)	4583.7(11)
O12	922(2)	7132.4(8)	4515.4(13)
O13	1383(2)	8146.6(7)	3031.0(13)
O14	107(2)	7667.4(8)	3097.6(12)
O15	1431(2)	7743.7(8)	3893.6(11)
O16	1915(2)	7532.4(8)	2896.0(12)

O17	2998(2)	7258.9(8)	4230.8(12)
O18	4849(2)	7334.9(7)	4026.2(11)
O19	3661(2)	7132.7(7)	3218.3(11)
O20	4098(2)	6745.2(7)	4066.3(12)
O21	4963(2)	8294.0(7)	2539.9(11)
O22	3936(2)	7755.1(7)	2607.2(12)
O23	5634(2)	7750.2(7)	2088.3(12)
O24	5583(2)	7818.3(7)	3185.4(12)
O25	6891(2)	7152.2(8)	2198.9(12)
O26	6539(2)	7171.3(7)	3289.1(12)
O27	7735(2)	6735.1(7)	2877.4(12)
O28	8244(2)	7355.2(7)	2884.7(12)
O29	3737(2)	7356.8(7)	1054.8(11)
O30	2965(2)	7186.0(7)	2020.7(11)
O31	4825(2)	7083.9(7)	1846.5(11)
O32	3495(2)	6732.8(8)	1296.3(13)
O1W	6503(3)	7237.6(9)	5244.0(14)
O2W	5997(3)	6645.9(9)	4711.1(13)
O3W	-2332(3)	6466.2(9)	4035.8(14)
O4W	1837(3)	6420.9(11)	4263(2)
O5W	5715(2)	8594.6(8)	3570.6(13)
O6W	2810(3)	8490.8(9)	2327.7(16)
O7W	1355(3)	8872.9(9)	3112.9(17)
O8W	1909(3)	8602.1(9)	6634.3(15)
O9W	4809(4)	6167.3(11)	1475.6(19)
O10W	3442(6)	5688.9(18)	1224(4)
O11W	2039(5)	6265.7(19)	1414(3)
O12W	1450(5)	6683.2(15)	628(3)
N1	71(3)	7654.6(9)	1076.1(16)
N2	4169(3)	8499.5(9)	713.7(15)
N3	-371(3)	6516.3(10)	2519(2)
N4	4052(3)	8494.1(9)	4278.8(16)

N5	-1013(3)	8716.1(9)	4423.6(15)
N6	4394(3)	6255.5(9)	3244.9(16)
C1	5361(4)	6372.7(13)	2939(2)
C2	3494(4)	6297.9(13)	2830(2)
C3	4473(4)	5901.9(11)	3536(2)
C4	3527(5)	5860.0(13)	3935(3)
C5	5440(5)	5885.8(14)	3923(3)
C6	4501(4)	5617.3(12)	3072(2)
C7	3613(5)	5229.5(13)	3779(2)
C8	3576(6)	5507.8(14)	4241(3)
C9	4505(6)	5495.8(15)	4624(3)
C10	5473(5)	5538.6(14)	4257(3)
C11	5524(5)	5256.5(14)	3777(3)
C12	4553(4)	5269.5(12)	3383(2)
C13	6405(7)	5531(2)	4662(4)
C14	4580(6)	4989.2(14)	2918(3)
C15	3079(3)	8382.0(12)	806(2)
C16	4886(4)	8276.5(12)	1066.5(19)
C17	4332(3)	8881.7(11)	820.5(19)
C18	3743(5)	9074.6(14)	340(3)
C19	3978(5)	8981.6(14)	1427(3)
C20	5480(4)	8965.4(13)	760(2)
C21	3936(6)	9460.9(16)	421(4)
C22	3526(6)	9554.1(19)	1015(5)
C23	4126(8)	9370(2)	1514(4)
C24	5291(5)	9447.4(14)	1457(3)
C25	5670(4)	9350.6(14)	848(2)
C26	5072(5)	9543.4(16)	383(3)
C27	3734(7)	9470(2)	2113(4)
C28	6826(6)	9431(2)	826(5)
C29	-465(5)	6596.9(15)	1873(3)
C30	482(4)	6730.0(14)	2786(3)

C31	-310(4)	6136.1(13)	2672(3)
C32	-1331(4)	5971.2(12)	2469(2)
C33	-191(5)	6092.4(14)	3343(3)
C34	593(4)	5963.3(14)	2367(3)
C35	-1337(4)	5591.3(13)	2617(3)
C36	-1209(6)	5550.3(15)	3285(3)
C37	-192(6)	5712.7(15)	3500(3)
C38	688(6)	5538.9(18)	3217(3)
C39	631(5)	5580.5(15)	2544(4)
C40	-412(4)	5421.7(14)	2316(3)
C41	1515(6)	5412.3(18)	2260(4)
C42	-2354(5)	5433.5(15)	2395(3)
C43	4317(4)	8223.5(12)	4724(2)
C44	3234(4)	8355.6(12)	3866(2)
C45	3798(3)	8841.9(11)	4547.6(19)
C46	2793(4)	8832.7(13)	4902(2)
C47	4695(4)	8949.7(13)	4952(2)
C48	3687(4)	9099.8(11)	4040.5(18)
C49	2586(4)	9189.3(14)	5154(2)
C50	3490(4)	9294.8(15)	5554(2)
C51	4490(4)	9305.3(14)	5206(2)
C52	4360(4)	9560.9(13)	4700(2)
C53	3477(4)	9459.8(12)	4284(2)
C54	2480(4)	9442.1(12)	4645(2)
C55	1760(11)	9195(4)	5587(7)
C56	5328(7)	9378(2)	5675(3)
C57	3364(5)	9709.6(14)	3782(3)
C58	-749(5)	8705.6(15)	5077(2)
C59	-169(4)	8546.7(12)	4090(2)
C60	-1328(3)	9068.3(11)	4193.4(18)
C61	-2168(4)	9212.3(14)	4609(2)
C62	-402(3)	9311.5(11)	4170(2)

C63	-1792(4)	9026.2(12)	3569.0(19)
C64	-1247(4)	9612.0(12)	3320(2)
C65	-2178(4)	9370.5(12)	3328(2)
C66	-2992(4)	9513.6(14)	3747(2)
C67	-2530(4)	9556.8(14)	4364(2)
C68	-1606(4)	9803.3(13)	4342(2)
C69	-768(4)	9661.5(11)	3937(2)
C70	152(4)	9908.5(13)	3903(3)
C71	-2650(4)	9324.9(14)	2707(2)
C72	-645(4)	7379.1(14)	890(2)
C73	788(4)	7529.6(13)	1558(2)
C74	-467(4)	7993.1(11)	1214.0(19)
C75	-1251(4)	8070.6(13)	717.7(19)
C76	348(3)	8274.6(12)	1237(2)
C77	-1025(3)	7976.9(11)	1806.8(18)
C79	-940(4)	8696.3(13)	866(2)
C80	-144(4)	8622.9(12)	1359(2)
C81	-714(4)	8595.9(12)	1952(2)
C82	-1540(3)	8319.8(12)	1938.5(18)
C83	-2326(4)	8399.5(14)	1438(2)
C84	-1768(4)	8418.9(13)	841(2)
C85	681(4)	8899.1(13)	1382(3)
C86	-2099(4)	8298.1(13)	2534(2)

References

(1) J.-Z. Qiu, L.-F. Wang and J. Jiang, SYSU-6, A New 2-D Aluminophosphate Zeolite Layer Precursor. *Molecules*, 2019, **24**, 2972.