Supporting Information

Open Hollow Polyoxovanadate Cage based on {Nb(V_5)} Pentagons with Size-Selective Encapsulation Properties

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1. Experimental Procedures

1.1 Materials and methods.

All reagents were purchased from commercial sources and used without further purification. IR spectra were recorded in the range 4000-400 cm^{-1} as the pressed KBr pellets on a Bruker Fourier transform infrared spectrophotometer. Elemental analyses were analyzed on a Thermo ICP atomic emission spectrometer. Thermogravimetric analyses (TG) were performed on a TG-DTA 6200 device from room temperature to 900 °C in flowing N_2 with a heating rate of 10 °C min^{-1}. C, H and N content analyses were obtained on a Vario Elementar instrument. Power X-ray diffraction (PXRD) was performed on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 1.54 Å) at a scanning rate of 5° min^{-1}. X-ray photoelectron spectroscopy (XPS) was performed by PHI 5000 Versa Probe III with a monochromatic Al Kα X-ray source with the beam size of 200 um. The binding energy was corrected by setting the binding energy of the hydrocarbon C 1s feature to 284.8 eV.

1.2 Synthesis

Synthesis of $V_{14}Nb_2P_8$: $VOSO_4 \cdot xH_2O$ (120 mg, 0.75 mmol), $NbCl_5$ (40 mg, 0.15 mmol), and phenylphosphonic acid (70 mg, 0.42 mmol) were dissolved in the mixture of DMF (N,N-dimethylformamide, 2 mL) and CH_3OH (methanol, 2 mL). The mixture was transferred to a Teflon-lined stainless steel vessel and heated to 130 °C for two days, and gradually cooled to room temperature. The green crystals were obtained by filtration, washed with ethanol, and dried in air. Yield: 13.4% based on V. Elemental analysis (%) cacld: V, 19.30; P, 6.71; C, 26.68; N, 4.93; H 4.40. Found: V, 18.94; P, 6.44; C, 25.80; N 4.13; H 3.88. IR spectrum (KBr, cm^{-1}): 3408 (m), 3055(m), 2967(w), 2802(w), 2454(w), 1971(w), 1914(w), 1814(w), 1653 (m), 1595 (m), 1486 (w), 1472 (m), 1435 (m), 1416(w), 1388(w), 1365(w), 1209(w), 1140 (s), 1065(s), 1035(s), 1017 (s), 998 (s), 980(s), 759 (m), 696(s), 624 (w), 615(m), 564 (s), 522 (s), 487(w).

Synthesis of Cs-$V_{14}Nb_2P_8$: $VOSO_4 \cdot xH_2O$ (180 mg, 1.13 mmol), $NbCl_5$ (40 mg, 0.15 mmol), phenylphosphonic acid (70 mg, 0.42 mmol), and CsCl (34 mg, 0.20 mmol) were dissolved in the mixture of DMF (2 mL) and CH_3OH (2 mL). The mixture was transferred to a Teflon-lined stainless steel vessel and heated to 130 °C for two days, and gradually cooled to room temperature. The green crystals were obtained by filtration, washed with ethanol, and dried in air. Yield: 29.2% based on V. Elemental analysis (%) cacld: V, 17.34; P, 6.02; Cs, 12.92; C, 21.02; N, 3.75; H, 3.31. Found: V, 17.49; P, 5.94; Cs, 12.71; C, 20.49; N, 2.93; H, 2.93. IR spectrum (KBr, cm^{-1}): 3429 (m), 3055(m), 2967(w), 2802(w), 2454(w), 1660 (m), 1597(m), 1574 (m), 1486 (m), 1472 (w), 1435 (m), 1416(w), 1388(w), 1365(w), 1140 (s), 1065(s), 1035(s), 1017 (s), 998 (s), 980(s), 908 (m), 759 (m), 696(s), 624 (w), 615(m), 564 (s), 522 (s), 455(w).

Synthesis of 3,5-pydc@$V_{14}Nb_2P_8$: $VOSO_4 \cdot xH_2O$ (120 mg, 0.75 mmol), $NbCl_5$ (40 mg, 0.15 mmol), phenylphosphonic acid (70 mg, 0.42 mmol), and 3,5-pyridinedicarboxylic acid (34 mg, 0.20 mmol) were dissolved in the mixture of DMF (2 mL) and CH_3OH (2 mL). The mixture was transferred to a Teflon-lined stainless steel vessel and heated to 130 °C for two days, and gradually cooled to room temperature. The green crystals were obtained by filtration, washed with ethanol, and dried in air. Yield: 15.2% based on V. Elemental analysis (%) cacld: V, 19.68; P, 6.84; C, 27.18; N, 4.25; H 4.23. Found: V, 19.34; P, 6.62; C, 26.30; N, 4.31; H, 3.75. IR spectrum (KBr, cm^{-1}): 3408 (m),

3055(m), 2967(w), 2802(w), 2454(w), 1653 (w), 1623(m), 1574 (m), 1486 (m), 1472 (w), 1435 (m), 1388(m), 1288(w), 1209(w), 1140 (s), 1065(s), 1035(s), 1017 (s), 998 (s), 980(s), 903(m), 824(w), 759 (m), 724(m), 696(s), 624 (w), 615(m), 564 (s), 513 (s), 439(w).

Synthesis of 2,5-fudc@$V_{14}Nb_2P_8$: $VOSO_4 \cdot xH_2O$ (180 mg, 1.13 mmol), $NbCl_5$ (40 mg, 0.15 mmol), phenylphosphonic acid (70 mg, 0.42 mmol), and 2,5-furandicarboxylic acid (32 mg, 0.20 mmol) in the mixture of DMF (2 mL) and CH_3OH (2 mL). The mixture was transferred to a Teflon-lined stainless steel vessel and heated to 130 °C for two days, and gradually cooled to room temperature. The green crystals were obtained by filtration, washed with ethanol, and dried in air. Yield: 39.0% based on V. Elemental analysis (%) cacld: V, 19.88; P, 6.91; C, 26.79; N, 4.69; H, 3.99. Found: V, 19.85; P, 7.28; C, 26.43; N, 4.00; H, 3.70. IR spectrum (KBr, cm^{-1}): 3408 (m), 3055(m), 2967(w), 2830(w), 2783(w), 2449(w), 1630 (m), 1576 (w), 1539 (w), 1463 (m), 1439 (m), 1416 (m), 1395 (m), 1370(m), 1212(w), 1145(s), 1112 (s), 1082(s), 1063(s), 1038 (m), 1017 (s), 1001 (s), 903(m), 815(w), 803(w), 773(w), 759 (m), 720(m), 701(m), 696(s), 627 (w), 615(m), 564 (s), 523 (s), 448(w).

1.3 Single-crystal X-Ray diffraction analyses.

Green crystals were mounted on a Hampton cryoloop with light oil. Single-crystal X-ray diffraction data were recorded on Rigaku XtaLAB Synergy R HyPix diffractometer equipped with graphitemonochromated Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were applied using multi-scan techniques. The structures were solved by direct methods and refined by the full-matrix least-squares method fitting on ($\Sigma w(|F_0|^2 - |F_c|^2)^2$)) using the SHELXTL program package (Bruker) and Olex-2 software.[1-3] The H atoms of the crystal waters were not located, and all heavy atoms were refined with anisotropic thermal parameters. The disordered solvent molecules and counter cations were treated by the Squeeze routine implemented in PLATON. The crystallographic data have been deposited to the Cambridge Crystallographic Data Centre (CCDC) as entries CCDC 2429482 (**$V_{14}Nb_2P_8$**), 2429483 (**3,5-pydc@ $V_{14}Nb_2P_8$**), 2429524 (**Cs-$V_{14}Nb_2P_8$**) and 2430715 (**2,5-fudc@ $V_{14}Nb_2P_8$**). The crystallographic data can be obtained from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The final molecular formulae were defined by single-crystal X-ray diffraction data combined with elemental analysis, TGA curve as well as BVS calculations.

2. Structure and Characterization

Table S1. Crystal data and structure refinements for **$V_{14}Nb_2P_8$**, **Cs-$V_{14}Nb_2P_8$**, **3,5-pydc@ $V_{14}Nb_2P_8$** and **2,5-fudc@ $V_{14}Nb_2P_8$**.

Compound	**$V_{14}Nb_2P_8$**	**Cs-$V_{14}Nb_2P_8$**	**3,5-pydc@ $V_{14}Nb_2P_8$**	**2,5-fudc@ $V_{14}Nb_2P_8$**
Empirical Formula	$C_{82}N_{13}Nb_2O_{72}P_8S_2$	$C_{72}N_{11}Nb_2O_{72}P_8$	$C_{80}N_{11}Nb_2O_{70}$	$C_{80}N_{12}Nb_2O_{69}P_8$
	$V_{14}H_{161}$	$S_4V_{14}Cs_4H_{135}$	$P_8S_2V_{14}H_{152}$	$S_2V_{14}H_{142}$
Formula weight	3692.09	4113.52	3598.98	3586.91
Temperature (K)	293(2)	150(0)	150(0)	150(0)
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$Pnma$	$P2_1/n$	$P2_1/n$
a (Å)	18.4212(4)	26.0643(4)	18.0624(3)	18.1749(3)
b (Å)	25.9376(5)	31.9841(7)	25.9485(4)	25.9752(4)
c (Å)	29.3062(6)	16.5506(3)	29.2392(5)	29.0297(4)
α (°)	90	90	90	90
β (°)	92.117(2)	90	90.2780(10)	90.1190(10)
γ (°)	90	90	90	90
V (Å^3)	13993.0(5)	13797.3(4)	13704.0(4)	13704.8(4)
Z	4	16	4	4
D_{calcd} (g·m^{-3})	1.753	7.921	1.744	1.738
μ (mm^{-1})	1.265	9.400	1.287	1.287
F(000)	7504.0	32448.0	7300.0	7256.0
Index ranges	$-25 \le h \le 24$, $-37 \le$	$-29 \le h \le 31$, $-38 \le$	$-20 \le h \le 21$, $-30 \le$	$-21 \le h \le 21$, $-30 \le$
	$k \le 32$, $-34 \le l \le 40$	$k \le 32$, $-19 \le l \le 18$	$k \le 30$, $-29 \le l \le 34$	$k \le 30$, $-34 \le l \le 29$
Reflns coll.	105343	69343	72059	70213
Independent reflns	35067	12365	23827	23641
GOF	1.031	0.974	1.057	1.026
R_{int}	0.0342	0.0435	0.0427	0.0600
R_1 [$I > 2\sigma(I)$][a]	0.0722	0.1161	0.0842	0.0762
wR_2 [$I > 2\sigma(I)$][b]	0.1908	0.3388	0.2470	0.2123
R_1 (all data)	0.1039	0.1327	0.1042	0.0975
wR_2 (all data)	0.2129	0.3531	0.2638	0.2234

[a] $R_1 = \Sigma||F_0| - |F_c|| / \Sigma|F_0|$; [b] $wR_2 = \Sigma[w(F_0^2-F_c^2)^2]/ \Sigma[w(F_0^2)^2]^{1/2}$

Table S2. Selected bond lengths and angles for $V_{14}Nb_2P_8$.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Nb1−O1	2.076(4)	V2−O7	1.617(4)	V5−O5	1.930(4)
Nb1−O2	2.056(4)	V2−O14	1.972(4)	V5−O10	1.604(5)
Nb1−O3	2.077(4)	V2−O15	1.961(4)	V5−O20	1.971(4)
Nb1−O4	2.057(4)	V3−O2	1.936(4)	V5−O21	1.993(5)
Nb1−O5	2.093(4)	V3−O3	1.961(4)	V11−O28	1.976(4)
Nb1−O11	1.814(4)	V3−O8	1.601(4)	V11−O32	1.578(4)
Nb1−O12	2.346(5)	V3−O16	1.993(4)	V11−O34	1.962(4)
V1−O1	1.944(4)	V3−O17	1.985(4)	V11−O36	1.970(5)
V1−O5	1.914(4)	V4−O3	1.933(4)	V11−O61	1.981(4)
V1−O6	1.616(5)	V4−O4	1.912(4)	V12−O27	1.963(4)
V1−O13	1.976(5)	V4−O9	1.625(4)	V12−O31	1.583(4)
V1−O22	2.005(5)	V4−O18	1.964(4)	V12−O34	1.967(5)
V2−O1	1.926(4)	V4−O19	1.989(4)	V12−O36	1.956(5)
V2−O2	1.927(4)	V5−O4	1.925(4)	V12−O62	1.975(4)

Bond	Angle (°)	Bond	Angle (°)	Bond	Angle (°)
O1−Nb1−O2	71.84(16)	O1−V2−O2	77.98(17)	O4−V5−O5	77.91(17)
O1−Nb1−O3	142.71(15)	O1−V2−O7	108.7(2)	O4−V5−O20	90.61(18)
O1−Nb1−O5	70.98(16)	O1−V2−O14	89.86(19)	O4−V5−O21	149.3(2)
O1−Nb1−O12	85.03(19)	O1−V2−O15	144.32(18)	O5−V5−O20	144.7(2)
O2−Nb1−O3	71.30(15)	O2−V2−O7	108.3(2)	O5−V5−O21	90.7(2)
O2−Nb1−O4	141.15(16)	O2−V3−O3	76.38(16)	O28−V11−O31	106.3(2)
O2−Nb1−O5	140.68(16)	O2−V3−O16	90.48(16)	O28−V11−O61	85.39(19)
O2−Nb1−O12	82.96(19)	O2−V3−O17	145.26(18)	O32−V11−O34	107.0(2)
O3−Nb1−O5	142.17(15)	O3−V3−O16	148.54(16)	O32−V11−O36	107.5(3)
O3−Nb1−O12	85.06(18)	O3−V3−O17	90.83(16)	O32−V11−O61	105.8(2)
O1−V1−O5	77.72(17)	O3−V4−O4	78.16(16)	O27−V12−O34	89.93(18)
O1−V1−O13	90.21(19)	O3−V4−O9	104.6(2)	O27−V12−O62	84.51(18)
O1−V1−O22	150.8(2)	O3−V4−O18	90.20(16)	O31−V12−O27	106.6(2)
O5−V1−O13	142.1(2)	O3−V4−O19	151.05(17)	O31−V12−O34	107.0(2)
O5−V1−O22	90.10(19)	O4−V4−O18	145.52(17)	O31−V12−O62	106.4(2)

Table S3. Selected bond lengths and angles for **Cs-$V_{14}Nb_2P_8$**

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Nb1−O1	2.096(8)	V4#2−O32	1.979(9)	Cs1−O42	3.10(2)
Nb1−O2	2.108(8)	V5−O4	1.945(8)	Cs2−O17	3.589(14)
Nb1−O3	2.145(8)	V5−O5	1.951(9)	Cs2−O17#2	3.589(14)
Nb1−O4	2.094(9)	V5−O10	1.576(9)	Cs2−O30	3.093(11)
Nb1−O5	2.075(8)	V5−O17	2.027(13)	Cs2−O30#2	3.093(11)
Nb1−O35	2.327(11)	V5#2−O31	1.981(9)	Cs2−O31	3.310(10)
Nb1−O39	1.742(9)	V6−O22	2.002(10)	Cs2−O31#2	3.310(10)
V1−O1	1.931(8)	V6−O24	1.601(13)	Cs2−O33	3.840(15)
V1−O6	1.592(9)	V6−O25	1.977(10)	Cs2−O38	3.547(14)
V1−O11	1.958(10)	V7−O21	1.955(11)	Cs2−O38#2	3.547(14)
V2−O1	1.926(8)	V7−O23	1.562(15)	Cs2−O41	2.61(2)
V2−O2	1.919(9)	V7−O25	1.974(10)	Cs3#3−O23	2.878(16)
V2−O7	1.659(9)	V8−O28	2.015(10)	Cs3#3−O24	3.336(14)
V2−O12	1.974(9)	V8−O29	1.608(14)	Cs3#3−O25	3.495(11)
V2−O13	1.974(8)	V8−O30	1.977(10)	Cs3−O29	2.915(14)
V3−O2	1.949(8)	V8−O33	2.428(15)	Cs3−O30	3.697(10)
V3−O3	1.941(9)	V9−O26	1.994(9)	Cs4−O1	3.206(8)
V3−O8	1.646(8)	V9−O27	1.552(14)	Cs4#1−O4	3.195(9)
V3−O14	1.981(10)	V9−O28	2.015(10)	Cs4−O6	3.113(9)
V3−O15	1.971(9)	Cs1−O14	3.273(10)	Cs4−O7	3.219(9)
V4−O3	1.907(9)	Cs1−O15	3.401(9)	Cs4#1−O9	3.367(9)
V4−O4	1.914(8)	Cs1−O22	3.440(10)	Cs4#1−O10	3.167(9)
V4−O9	1.660(9)	Cs1−O26	3.436(9)	Cs4−O39	3.351(8)
V4−O16	1.983(9)	Cs1−O40	2.923(11)	Cs4#1−O39	3.105(8)

Symmetry code: #1 1-X,1-Y,1-Z; #2 +X,1/2-Y,+Z; #3 +X,+Y,-1+Z

Bond	Angle (°)	Bond	Angle (°)	Bond	Angle (°)
O1−Nb1−O2	71.6(3)	O2−V3−O15	152.8(4)	O24−V6−O25#2	104.7(5)
O1−Nb1−O3	139.9(3)	O2−V3−O14	91.4(4)	O21−V7−O25	151.4(5)
O1−Nb1−O5	71.4(3)	O2−V3−O3	77.7(4)	O21−V7−O25#2	93.1(4)
O1−Nb1−O4	141.6(3)	O3−V3−O15	89.7(4)	O21−V7−O21#2	83.4(7)
O1−Nb1−O35	81.1(3)	O3−V4−O16	90.7(4)	O21#2−V7−O25	93.1(4)
O2−Nb1−O3	70.1(3)	O3−V4−O32#2	152.9(4)	O21#2−V7−O25#2	151.4(5)
O2−Nb1−O4	139.5(3)	O3−V4−O4	80.1(4)	O14−Cs1−O15	48.2(2)
O2−Nb1−O35	82.1(3)	O4−V4−O16	148.9(4)	O30#2−Cs2−O33	50.0(3)
O3−Nb1−O4	70.9(3)	O4−V4−O32#2	91.7(4)	O31−Cs2−O33	81.15(18)
O3−Nb1−O35	82.6(3)	O9−V4−O16	106.5(4)	O31#2−Cs2−O17	44.6(3)
O3−Nb1−O39	98.0(3)	O9−V4−O32#2	102.5(4)	O41−Cs2−O31	96.0(2)
O1−V1−O6	104.0(4)	O4−V5−O31#2	91.2(4)	O24#4−Cs3−O25#5	49.1(3)
O1−V1−O11	89.8(4)	O4−V5−O17	150.5(5)	O24#4−Cs3−O30	109.2(3)
O6−V1−O11	108.1(4)	O5−V5−O31#2	146.1(4)	O29−Cs3−O30	48.8(3)
O1−V2−O13	151.7(4)	O5−V5−O17	92.1(5)	O1−Cs4−O9#1	140.7(2)

O1−V2−O12	90.2(4)	O5−V5−O4	77.5(4)	O1−Cs4−O7	52.8(2)
O2−V2−O1	79.4(4)	O22−V6−O22#2	83.2(6)	O39#1−Cs4−O9#1	76.7(2)
O2−V2−O12	149.2(4)	O22#2−V6−O24	104.6(5)	O39#1−Cs4−O1	98.6(2)
O2−V2−O13	90.7(4)	O24−V6−O25	104.7(5)		

Symmetry code: #1 1-X,1-Y,1-Z; #2 +X,1/2-Y,+Z; #3 +X,+Y,-1+Z; #4 +X,+Y,1+Z; #5 +X,1/2-Y,1+Z

Table S4. Selected bond lengths and angles for **3,5-pydc@$V_{14}Nb_2P_8$**.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Nb1−O1	2.088(6)	V2−O13	1.978(7)	V5−O5	1.937(6)
Nb1−O2	2.065(5)	V2−O14	2.014(6)	V5−O10	1.603(6)
Nb1−O3	2.071(6)	V3−O3	1.957(6)	V5−O19	1.959(7)
Nb1−O4	2.110(6)	V3−O4	1.957(6)	V5−O20	1.997(6)
Nb1−O5	2.089(5)	V3−O8	1.611(6)	V11−O24	1.972(7)
Nb1−O11	1.826(6)	V3−O15	1.982(6)	V11−O28	1.589(7)
Nb1−O63	2.129(6)	V3−O16	1.981(6)	V11−O32	1.974(7)
V1−O1	1.930(6)	V4−O4	1.929(5)	V11−O34	1.966(6)
V1−O2	1.932(6)	V4−O5	1.942(6)	V11−O36	1.978(7)
V1−O6	1.602(7)	V4−O9	1.681(5)	V12−O25	1.980(6)
V1−O12	1.978(6)	V4−O17	1.997(6)	V12−O29	1.590(6)
V1−O21	2.002(7)	V4−O18	1.986(6)	V12−O32	1.967(6)
V2−O2	1.950(6)	V4−O65	2.455(12)	V12−O34	1.954(6)
V2−O3	1.924(6)	V5−O1	1.940(6)	V12−O37	1.995(6)
V2−O7	1.629(6)				

Bond	Angle (°)	Bond	Angle (°)	Bond	Angle (°)
O1−Nb1−O2	71.0(2)	O2−V2−O7	104.4(3)	O5−V4−O65	81.6(3)
O1−Nb1−O3	141.2(2)	O2−V2−O13	92.3(3)	O1−V5−O10	105.3(3)
O1−Nb1−O4	141.0(2)	O2−V2−O14	156.5(2)	O1−V5−O19	147.2(3)
O1−Nb1−O5	71.2(2)	O3−V2−O7	109.3(3)	O1−V5−O20	92.0(3)
O1−Nb1−O11	100.6(2)	O3−V2−O13	146.3(3)	O1−V5−O5	77.7(2)
O1−Nb1−O63	81.3(2)	O3−V3−O4	76.2(2)	O5−V5−O10	105.4(3)
O2−Nb1−O3	72.3(2)	O3−V3−O8	107.1(3)	O24−V11−O28	106.5(4)
O2−Nb1−O4	141.6(2)	O3−V3−O15	90.8(2)	O24−V11−O32	90.2(3)
O2−Nb1−O5	140.8(2)	O3−V3−O16	147.7(3)	O24−V11−O34	147.5(3)
O2−Nb1−O11	98.5(2)	O4−V3−O8	107.6(3)	O24−V11−O36	85.7(3)
O2−Nb1−O63	83.2(2)	O4−V4−O5	78.4(2)	O28−V11−O32	107.4(4)
O1−V1−O2	77.2(2)	O4−V4−O17	93.1(2)	O25−V12−O29	105.8(3)
O1−V1−O6	106.8(3)	O4−V4−O18	151.8(3)	O25−V12−O32	89.7(3)
O1−V1−O12	145.8(3)	O4−V4−O65	79.1(3)	O25−V12−O34	147.1(3)
O1−V1−O21	90.7(3)	O5−V4−O17	155.3(2)	O25−V12−O37	88.8(2)
O2−V1−O6	107.1(3)	O5−V4−O18	91.9(2)	O29−V12−O32	106.2(3)

O2−V2−O3	78.0(2)				

Table S5. Selected bond lengths and angles for **2,5-fudc@$V_{14}Nb_2P_8$**.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Nb1−O1	2.060(5)	V2−O7	1.643(6)	V5−O5	1.937(5)
Nb1−O2	2.076(5)	V2−O13	1.990(7)	V5−O10	1.595(6)
Nb1−O3	2.107(5)	V2−O14	2.008(6)	V5−O19	1.961(6)
Nb1−O4	2.075(5)	V3−O2	1.961(6)	V5−O20	1.996(6)
Nb1−O5	2.080(5)	V3−O3	1.954(5)	V11−O24	1.975(7)
Nb1−O11	1.829(5)	V3−O8	1.607(6)	V11−O28	1.593(6)
Nb1−O63	2.134(5)	V3−O15	1.986(6)	V11−O32	1.961(6)
V1−O1	1.929(6)	V3−O16	1.986(6)	V11−O34	1.946(6)
V1−O5	1.931(5)	V4−O3	1.937(5)	V11−O36	1.971(7)
V1−O6	1.606(6)	V4−O4	1.940(5)	V12−O25	1.981(6)
V1−O12	1.971(6)	V4−O9	1.669(5)	V12−O29	1.589(6)
V1−O21	2.001(6)	V4−O17	1.985(6)	V12−O32	1.969(6)
V2−O1	1.951(6)	V4−O18	1.988(6)	V12−O34	1.959(6)
V2−O2	1.925(6)	V5−O4	1.941(5)	V12−O37	1.995(6)

Bond	Angle (°)	Bond	Angle (°)	Bond	Angle (°)
O1−Nb1−O2	70.7(2)	O1−V2−O13	92.6(2)	O4−V5−O5	77.3(2)
O1−Nb1−O3	140.7(2)	O1−V2−O14	156.8(2)	O4−V5−O10	105.8(3)
O1−Nb1−O4	141.8(2)	O2−V2−O7	107.8(3)	O4−V5−O19	92.2(2)
O1−Nb1−O5	83.9(2)	O2−V3−O15	91.0(2)	O4−V5−O20	149.7(2)
O1−Nb1−O63	72.2(2)	O2−V3−O16	147.7(2)	O5−V5−O10	106.4(3)
O2−Nb1−O3	141.2(2)	O3−V3−O2	76.6(2)	O24−V11−O28	105.6(3)
O2−Nb1−O5	70.9(2)	O3−V3−O15	144.2(2)	O24−V11−O32	107.4(3)
O2−Nb1−O63	82.9(2)	O3−V3−O16	91.4(2)	O24−V11−O34	106.6(3)
O3−Nb1−O63	82.4(2)	O3−V4−O4	78.2(2)	O24−V11−O36	108.0(3)
O6−V1−O12	107.2(3)	O3−V4−O17	92.7(2)	O28−V11−O32	90.5(3)
O6−V1−O5	106.7(3)	O3−V4−O18	152.9(2)	O25−V12−O29	106.3(3)
O6−V1−O1	107.0(3)	O3−V4−O66	81.1(3)	O25−V12−O32	89.5(2)
O6−V1−O21	104.3(3)	O4−V4−O17	153.3(2)	O25−V12−O34	145.6(3)
O12−V1−O21	81.8(3)	O4−V4−O18	91.6(2)	O25−V12−O37	88.1(2)
O1−V2−O2	77.9(2)	O4−V4−O66	81.1(3)	O29−V12−O32	107.1(3)
O1−V2−O7	103.9(3)				

Table S6. Bond valence sum (BVS) values for Nb, V and O atoms in $\mathbf{V_{14}Nb_2P_8}$.

Atom	BVS Value	Atom	BVS Value	Atom	BVS Value
Nb1	4.848	O12	0.309	O39	2.028
Nb2	4.935	O13	1.897	O40	2.053
V1	4.073	O14	1.914	O41	1.959
V2	4.153	O15	1.871	O42	1.635
V3	4.072	O16	1.882	O43	1.484
V4	4.102	O17	1.890	O44	1.640
V5	4.155	O18	1.925	O45	1.579
V6	4.108	O19	1.888	O46	1.541
V7	4.065	O20	1.882	O47	1.129
V8	4.088	O21	2.001	O48	0.398
V9	4.134	O22	2.058	O49	1.920
V10	4.069	O23	1.472	O50	1.926
V11	4.150	O24	1.662	O51	1.884
V12	4.173	O25	1.903	O52	1.918
V13	4.182	O26	1.860	O53	1.922
V14	4.152	O27	1.883	O54	1.872
O1	1.970	O28	1.891	O55	1.938
O2	2.018	O29	1.708	O56	1.889
O3	1.927	O30	1.726	O57	1.959
O4	2.068	O31	1.722	O58	1.944
O5	1.991	O32	1.745	O59	1.354
O6	1.579	O33	1.263	O60	1.698
O7	1.570	O34	1.228	O61	1.844
O8	1.644	O35	1.233	O62	1.893
O9	1.533	O36	1.233	O63	1.895
O10	1.627	O37	2.048	O64	1.936
O11	1.303	O38	2.001		

Table S7. Bond valence sum (BVS) values for Nb, V and O atoms in **Cs-$V_{14}Nb_2P_8$**.

Atom	BVS Value	Atom	BVS Value	Atom	BVS Value
Nb1	4.881	O6	1.627	O20	1.750
V1	4.119	O7	1.436	O21	1.861
V2	4.011	O8	1.444	O22	1.857
V3	3.917	O9	1.406	O23	1.754
V4	3.996	O10	1.740	O24	1.649
V5	4.141	O11	1.913	O25	1.208
V6	4.004	O12	1.878	O26	1.934
V7	4.229	O13	1.868	O27	1.740
V8	4.032	O14	1.855	O28	1.116
V9	4.030	O15	1.843	O29	1.600
O1	1.967	O16	1.895	O30	1.843
O2	1.912	O17	1.956	O31	1.848
O3	1.906	O18	1.915	O32	1.838
O4	1.963	O19	1.476	O39	1.562
O5	1.956				

Table S8. Bond valence sum (BVS) values for Nb, V and O atoms in **3,5-pydc@ $V_{14}Nb_2P_8$**.

Atom	BVS Value	Atom	BVS Value	Atom	BVS Value
Nb1	4.944	O11	1.255	O37	1.860
Nb2	4.964	O12	1.906	O38	1.869
V1	4.118	O13	1.879	O39	1.815
V2	4.110	O14	1.818	O40	1.886
V3	4.014	O15	1.903	O41	1.901
V4	3.950	O16	1.921	O42	1.814
V5	4.132	O17	1.845	O43	1.948
V6	4.106	O18	1.890	O44	1.978
V7	3.955	O19	1.928	O45	1.703
V8	4.088	O20	1.948	O46	1.372
V9	4.092	O21	2.007	O47	1.703
V10	4.067	O22	1.570	O48	1.468
V11	4.102	O23	1.635	O49	1.562
V12	4.088	O24	1.870	O50	1.452
V13	4.100	O25	1.901	O51	1.912
V14	3.987	O26	1.918	O52	1.857
O1	1.950	O27	1.836	O53	1.803
O2	1.966	O28	1.694	O54	1.885
O3	1.959	O29	1.689	O55	1.893
O4	1.886	O30	1.698	O56	1.886
O5	1.934	O31	1.722	O57	1.862
O6	1.631	O32	1.210	O58	1.873
O7	1.524	O33	1.257	O59	2.095
O8	1.592	O34	1.243	O60	2.406
O9	1.321	O35	1.157	O61	1.960
O10	1.631	O36	1.884	O62	1.512

Table S9. Bond valence sum (BVS) values for Nb, V and O atoms in **2,5-fudc@ $V_{14}Nb_2P_8$**.

Atom	BVS Value	Atom	BVS Value	Atom	BVS Value
Nb1	4.968	O11	1.248	O37	1.858
Nb2	4.947	O12	1.907	O38	1.899
V1	4.125	O13	1.890	O39	1.831
V2	4.080	O14	1.825	O40	1.935
V3	4.023	O15	1.879	O41	1.918
V4	4.025	O16	1.911	O42	1.827
V5	4.166	O17	1.846	O43	1.953
V6	4.150	O18	1.904	O44	1.978
V7	4.031	O19	1.902	O45	1.689
V8	4.088	O20	1.951	O46	1.368
V9	4.046	O21	1.993	O47	1.667
V10	4.177	O22	1.562	O48	1.440
V11	4.141	O23	1.596	O49	1.662
V12	4.076	O24	1.925	O50	1.376
V13	4.126	O25	1.897	O51	1.921
V14	4.065	O26	1.890	O52	1.866
O1	1.981	O27	1.862	O53	1.809
O2	1.943	O28	1.676	O54	1.879
O3	1.882	O29	1.694	O55	1.899
O4	1.952	O30	1.717	O56	1.885
O5	1.967	O31	1.708	O57	1.822
O6	1.618	O32	1.226	O58	1.888
O7	1.464	O33	1.272	O59	2.247
O8	1.613	O34	1.269	O60	2.266
O9	1.365	O35	1.175	O61	2.453
O10	1.667	O36	1.910	O62	1.653

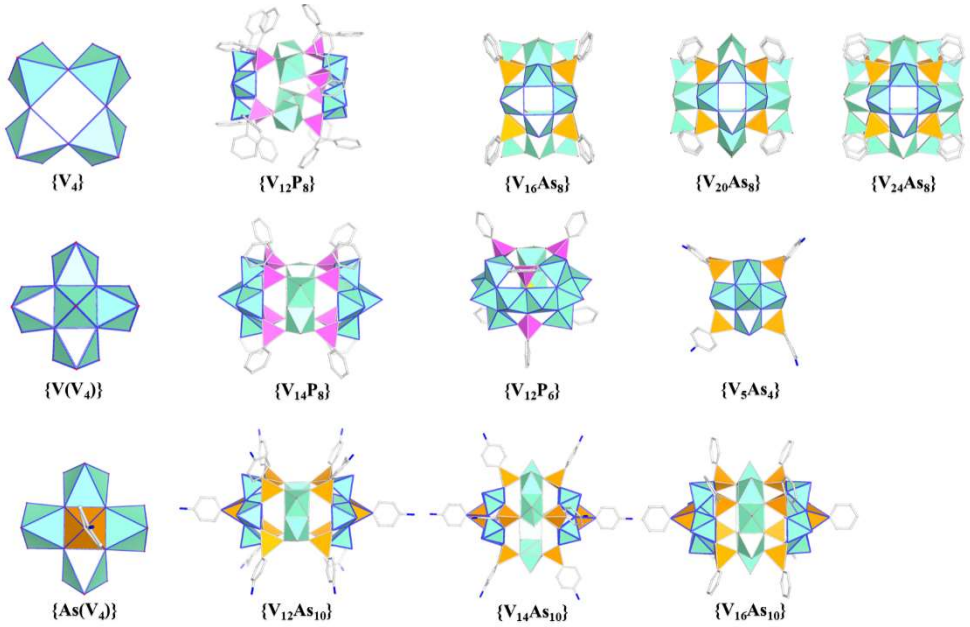


Figure S1. The representative POVs built from square SBBs.[4-9] Color code: V, cyan; P, pink; As, orange; C, grey; O, red; N, blue.

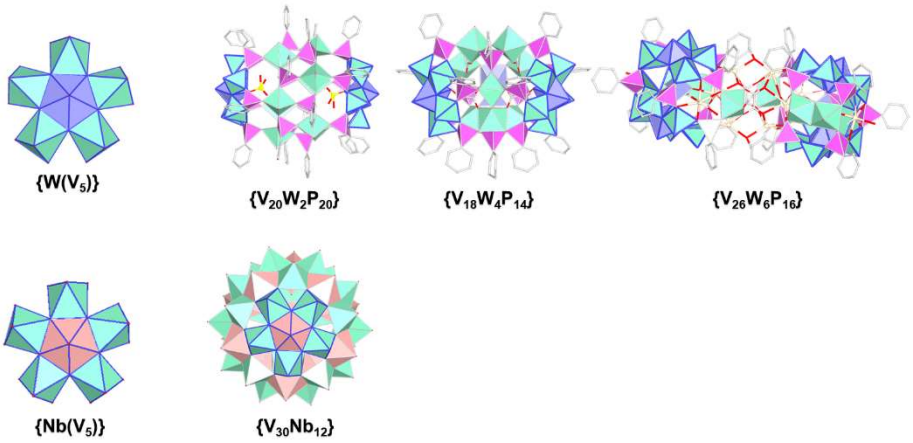


Figure S2. The representative POVs built from pentagonal SBBs.[10,11] Color code: V, cyan; W, lavender; Nb, apricot; P, pink; S, yellow; Na, tan; C, grey; O, red.

Figure S3. Crystal morphologies of $\mathbf{V_{14}Nb_2P_8}$ under an optical microscope.

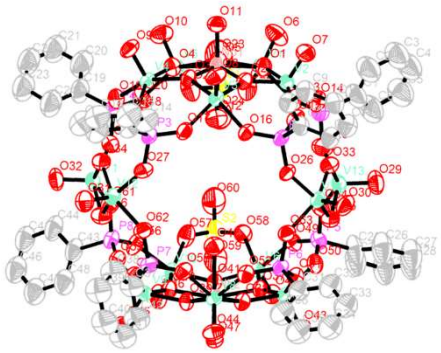


Figure S4. The asymmetric unit of $\mathbf{V_{14}Nb_2P_8}$ (probability ellipsoids drawn at 50%).

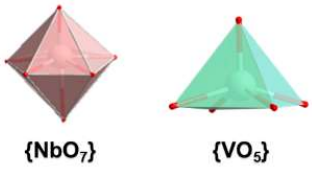


Figure S5. The geometric coordination of Nb and V atoms in $\mathbf{V_{14}Nb_2P_8}$.

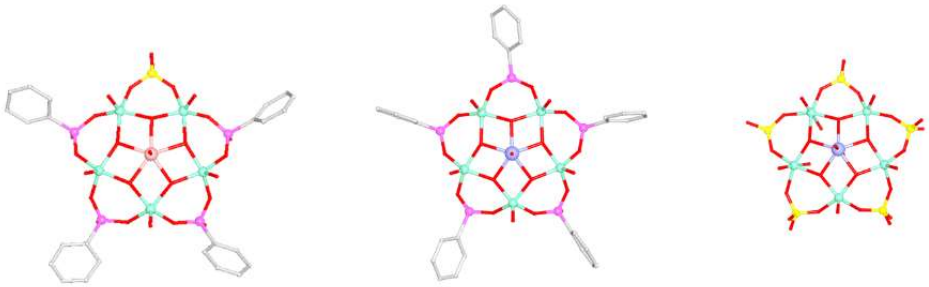


Figure S6. Ball-and-stick representations of {Nb(V_5)} SBB in $\mathbf{V_{14}Nb_2P_8}$ and previously reported {W(V_5)} SBBs.[10,12] Color code: V, cyan; W, lavender; Nb, apricot; P, pink; S, yellow; C, grey; O, red.

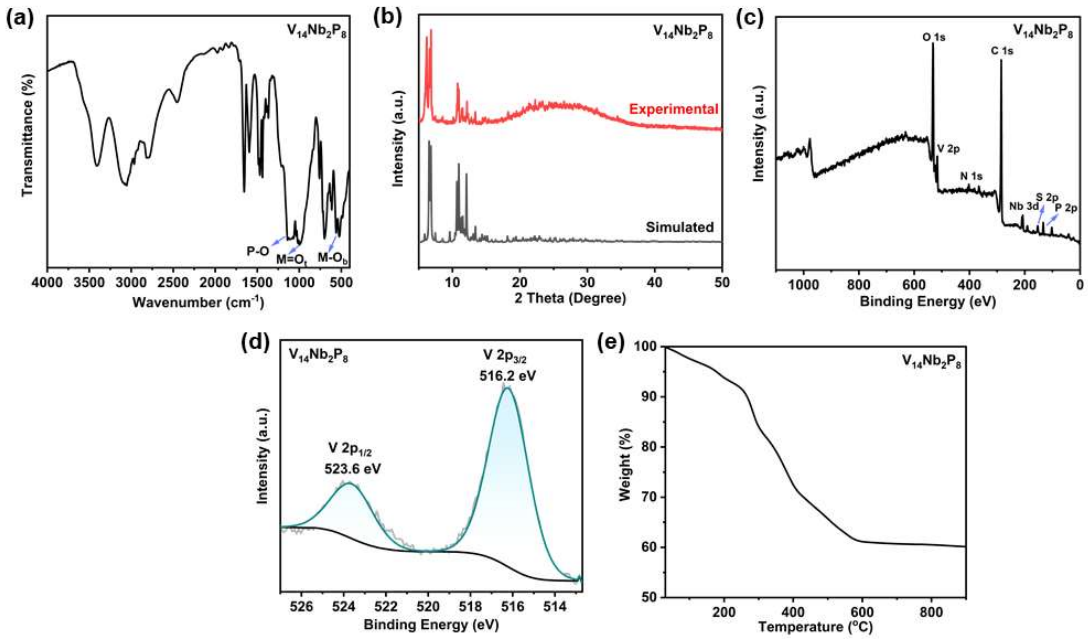


Figure S7. (a) IR spectra of $\mathbf{V_{14}Nb_2P_8}$. The characteristic absorption peak at 1140 cm^{-1} corresponds to the vibration of P−O bond. The characteristic peaks at 1017 and 998 cm^{-1} are associated with the vibrations of M=O$_t$ (M= V or Nb, O$_t$ = terminal oxygen atom). Meanwhile, the peaks at 699, 613, 562 and 525 cm^{-1} are attributed to the ν(M-O$_b$-M) stretching vibrations (M = V or Nb, O$_b$ = bridging oxygen atom). Additionally, the peaks in the range of 1595-1435 cm^{-1} correspond to the skeletal vibration of the benzene ring. (b) Experimental and simulated PXRD patterns of $\mathbf{V_{14}Nb_2P_8}$. (c) Survey XPS spectrum of $\mathbf{V_{14}Nb_2P_8}$. (d) High-resolution V 2p XPS spectrum of $\mathbf{V_{14}Nb_2P_8}$. All the V atoms in $\mathbf{V_{14}Nb_2P_8}$ are in the +4 oxidation state. (e) TGA curve of $\mathbf{V_{14}Nb_2P_8}$.

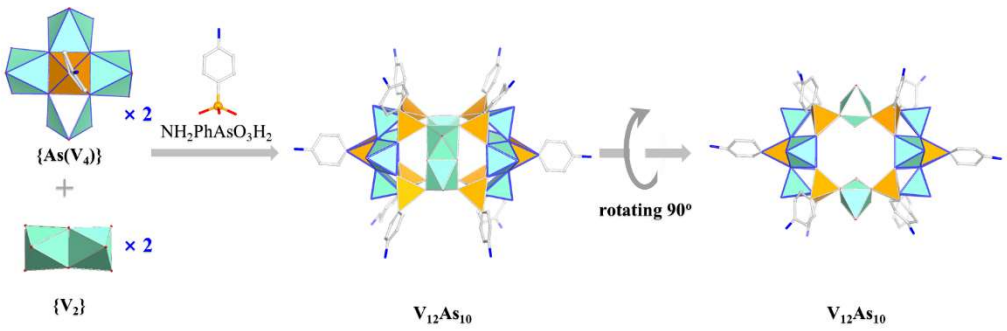


Figure S8. Self-assembly of $\mathbf{V_{12}As_{10}}$. Color code: V, cyan; As, orange; C, grey; O, red; N, blue. When substituting phenylphosphonic acid with p-arsanilic acid yielded $[(PhAsV_4O_8)_2\{V_2(OH)_2(H_2O)_2O_2\}_2(NH_2PhAsO_3)_8]^{4-}$ ($\mathbf{V_{12}As_{10}}$), a previously reported POV cage constructed from {As(V$_4$)} squares.

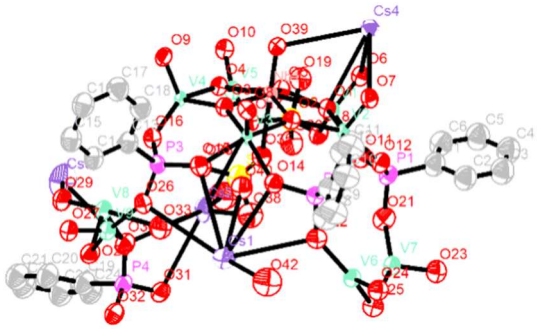


Figure S9. The asymmetric unit of **Cs-$V_{14}Nb_2P_8$** (probability ellipsoids drawn at 50%).

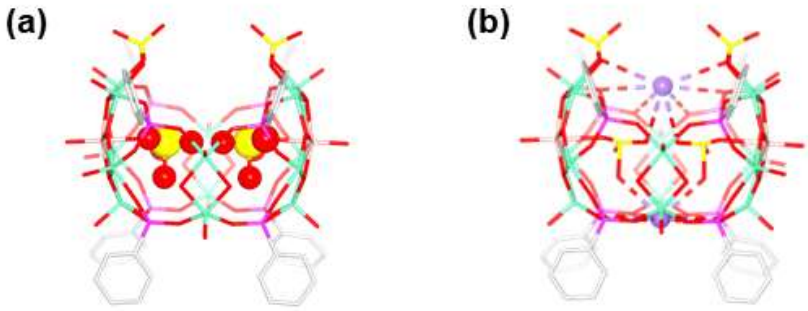


Figure S10. The structure of **Cs-$V_{14}Nb_2P_8$**. Color code: Nb, apricot; V, cyan; P, pink; S, yellow; C, grey; O, red; Cs, purple.

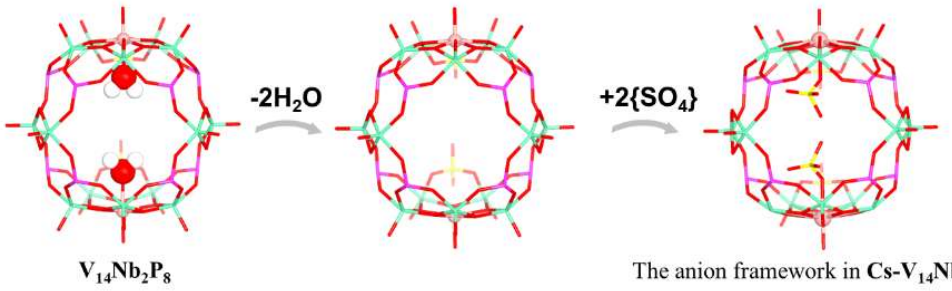


Figure S11. The conversion of the anion framework from **$V_{14}Nb_2P_8$** to **Cs-$V_{14}Nb_2P_8$**. Color code: V, cyan; Nb, apricot; P, pink; S, yellow; O, red; H, white.

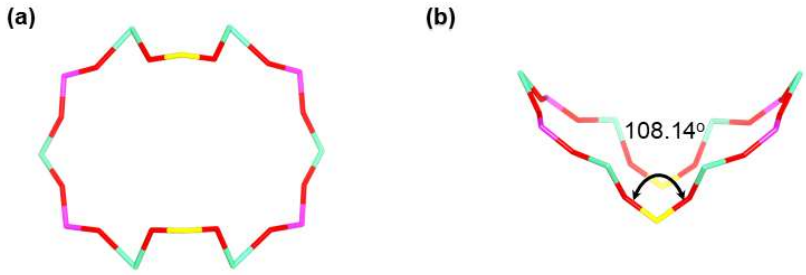


Figure S12. Two views of the two half-crown-ether-like $V_3P_2O_6$ units from different perspectives. The angle between the two $V_3P_2O_6$ units is 108.14°. Color code: V, cyan; Nb, apricot; P, pink; S, yellow; O, red.

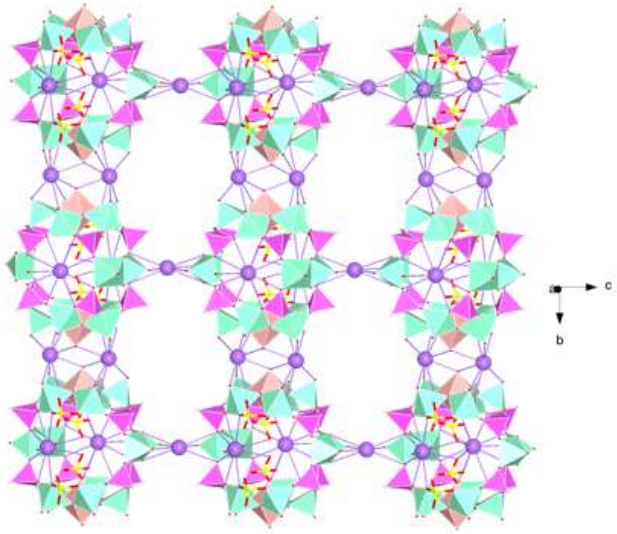


Figure S13. The 2D structure of **Cs-$V_{14}Nb_2P_8$**. Phenyl rings are omitted for clarity. Color code: Nb, apricot; V, cyan; P, pink; S, yellow; C, grey; O, red; Cs, purple.

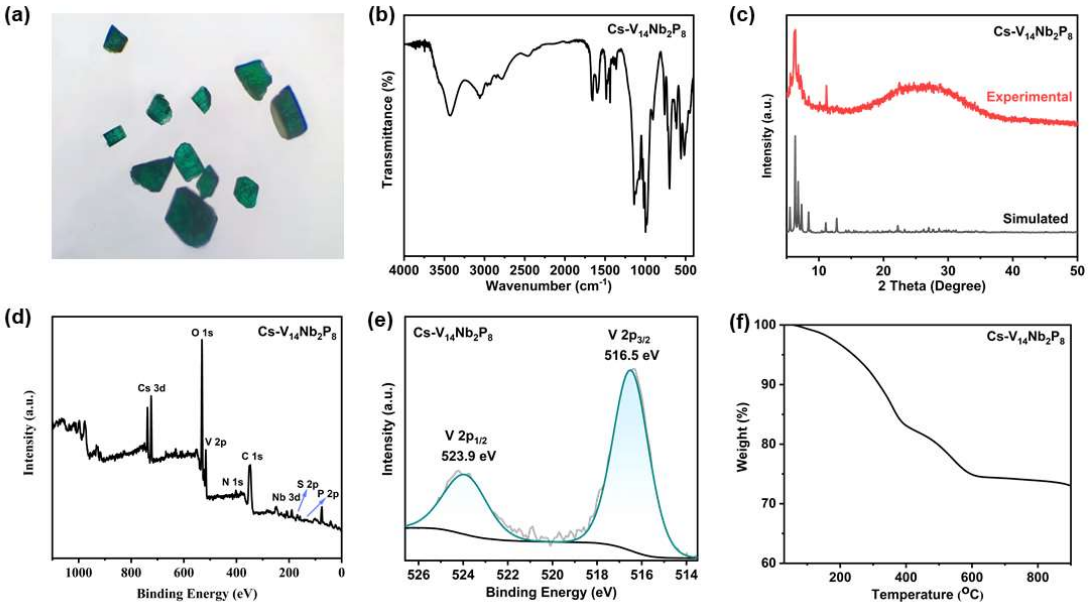


Figure S14. (a) Crystal morphologies of **Cs-$V_{14}Nb_2P_8$** under an optical microscope. (b) IR spectrum of **Cs-$V_{14}Nb_2P_8$**. (c) Experimental and simulated PXRD patterns of **$V_{14}Nb_2P_8$**. (d) Survey XPS spectrum of **Cs-$V_{14}Nb_2P_8$**. (e) High-resolution V 2p XPS spectrum of **Cs-$V_{14}Nb_2P_8$**. All the V atoms in **Cs-$V_{14}Nb_2P_8$** are in the +4 oxidation state. (f) TGA curve of **Cs-$V_{14}Nb_2P_8$**.

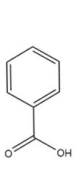
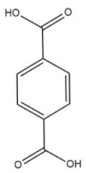
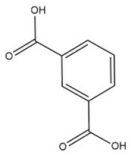
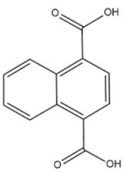
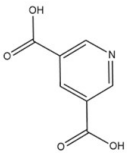
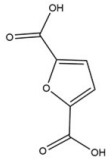
	benzoic acid	terephthalic acid	isophthalic acid	1,4-naphthalenedicarbo-xylic acid	3,5-pyridinedicarbo-xylic acid	2,5-furandicarboxylic acid
						
pKa	4.2	3.49	3.53	2.82	2.60	2.28

Figure S15. The pKa value of different carboxylic acid ligands. It is found that the ligands (3,5-pyridinedicarbo-xylic acid and 2,5-furandicarboxylic acid) with lower pKa values can be encapsulated into the **$V_{14}Nb_2P_8$** cage. The ligands with lower pKa value are more prone to deprotonation, exposing bare oxygen atoms that subsequently coordinate within the POV cage. 1,4-naphthalenedicarbo-xylic acid cannot be encapsulated in the POV cage probably due to the steric hindrance.

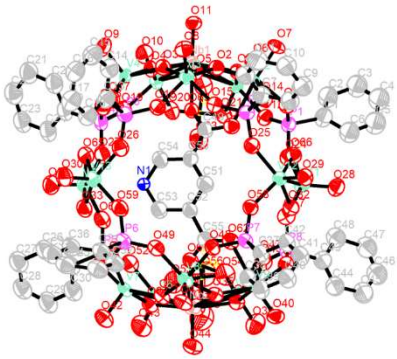


Figure S16. The asymmetric unit of **3,5-pydc@$V_{14}Nb_2P_8$** (probability ellipsoids drawn at 50%). The disordered pyridine ring inside the cage is omitted here for clarify.

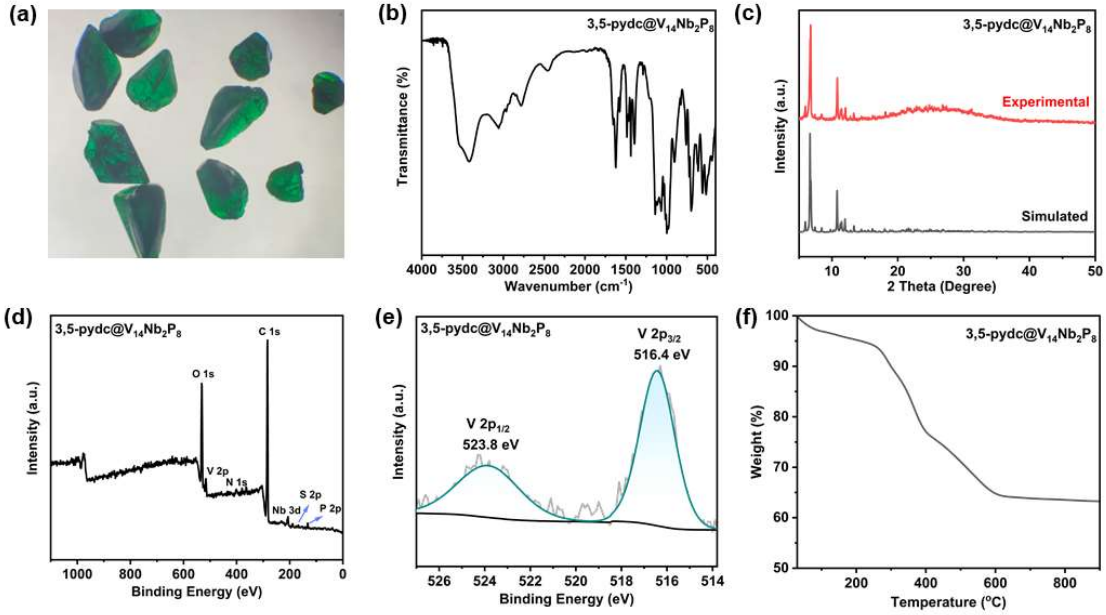


Figure S17. (a) Crystal morphologies of **3,5-pydc@$V_{14}Nb_2P_8$** under an optical microscope. (b) IR spectrum of **3,5-pydc@$V_{14}Nb_2P_8$**. (c) Experimental and simulated PXRD patterns of **$V_{14}Nb_2P_8$**. (d) Survey XPS spectrum of **3,5-pydc@$V_{14}Nb_2P_8$**. (e) High-resolution V 2p XPS spectrum of **3,5-pydc@$V_{14}Nb_2P_8$**. All the V atoms in **3,5-pydc@$V_{14}Nb_2P_8$** are in the +4 oxidation state. (f) TGA curve of **3,5-pydc@$V_{14}Nb_2P_8$**.

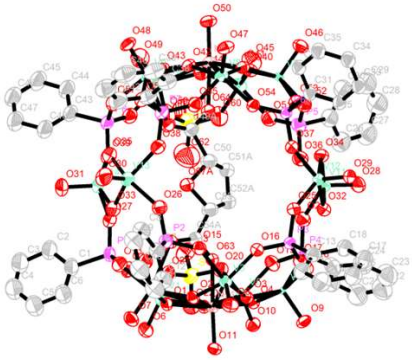


Figure S18. The asymmetric unit of **2,5-fudc@$V_{14}Nb_2P_8$** (probability ellipsoids drawn at 50%). The disordered furan ring inside the cage is omitted here for clarify.

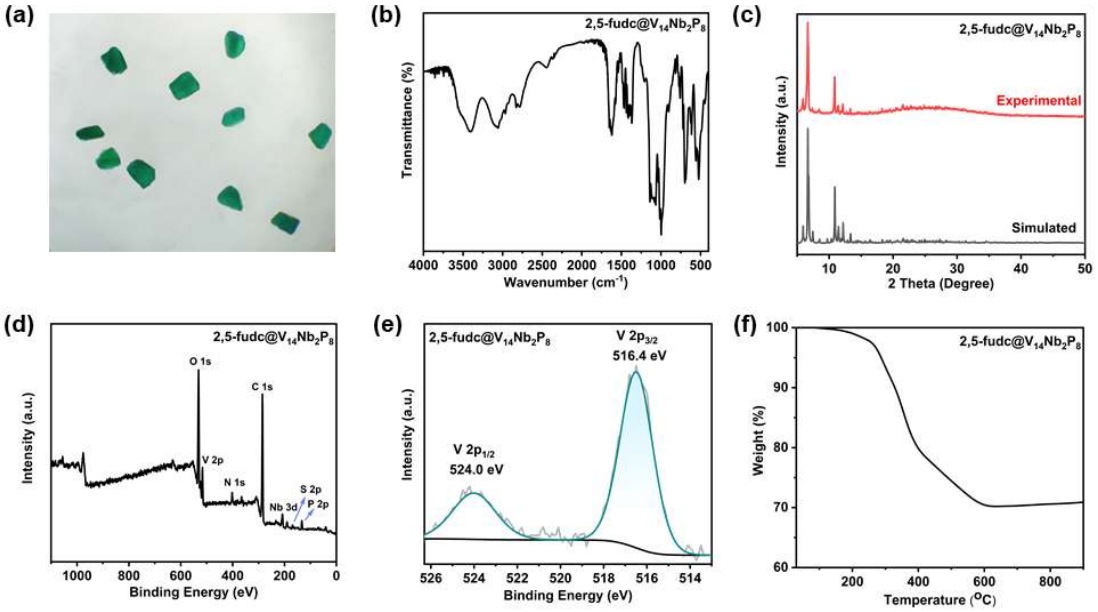


Figure S19. (a) Crystal morphologies of **2,5-fudc@$V_{14}Nb_2P_8$** under an optical microscope. (b) IR spectrum of **2,5-fudc@$V_{14}Nb_2P_8$**. (c) Experimental and simulated PXRD patterns of **2,5-fudc@$V_{14}Nb_2P_8$**. (d) Survey XPS spectrum of **2,5-fudc@$V_{14}Nb_2P_8$**. (e) High-resolution V 2p XPS spectrum of **2,5-fudc@$V_{14}Nb_2P_8$**. All the V atoms in **2,5-fudc@$V_{14}Nb_2P_8$** are in the +4 oxidation state. (f) TGA curve of **2,5-fudc@$V_{14}Nb_2P_8$**.

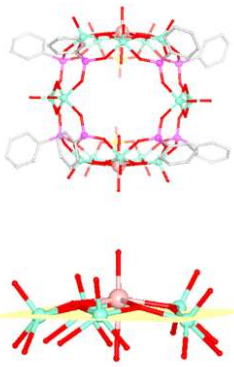
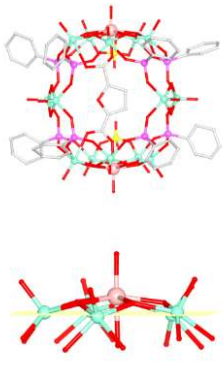
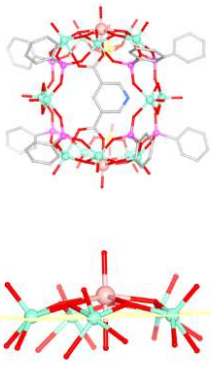
	$V_{14}Nb_2P_8$	2,5-fudc@$V_{14}Nb_2P_8$	3,5-pydc@$V_{14}Nb_2P_8$
			
distance of Nb to V atoms plane (Å)	0.59	0.72	0.81

Figure S20. The distances from the Nb atom to the plane of V atoms in **$V_{14}Nb_2P_8$**, **2,5-fudc@$V_{14}Nb_2P_8$** and **3,5-pydc@$V_{14}Nb_2P_8$**.

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