

## Supporting Information

### **Structural and Adsorption Features of Polyoxovanadate-Based Metal–Organic Clusters Controlled by Adjustable Template Effect**

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# 1. Experimental Details

## 1.1 Materials:

Unless otherwise indicated, all chemicals and reagents were purchased from commercial suppliers and used without further purification. The organic ligand used in this work was synthesized according to the published method with some modifications.

## 1.2 Physical measurements:

**FT-IR.** The Fourier transform infrared (FT-IR) spectra were recorded on KBr disk using a Shimadzu IRSpirit-T spectrometer between 400 and 4000  $\text{cm}^{-1}$ .

**Elemental Analyses.** CHNS microanalyses were performed on a Perkin-Elmer 240C elemental analyzer, and ICP-OES analyses were performed on a Perkin-Elmer Optima 8300 optical emission spectrometer.

**NMR.** The  $^1\text{H}$  and  $^{31}\text{P}$  nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III 400 MHz instrument at room temperature, using 5-mm tubes for  $^1\text{H}$  and  $^{31}\text{P}$  with respective resonance frequencies of 399.78 MHz ( $^1\text{H}$ ) and 162 MHz ( $^{31}\text{P}$ ).

**TGA.** Thermogravimetric analyses (TGA) were carried out on a TA Instruments SDT Q600 thermobalance with a 100  $\text{mL min}^{-1}$  flow of nitrogen; the temperature was ramped from 25 to 800  $^{\circ}\text{C}$  at a rate of 5  $^{\circ}\text{C min}^{-1}$ .

**Powder XRD.** Powder X-ray diffraction (Powder XRD) patterns were obtained using a Bruker D8 ADVANCE diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ).

**XPS.** For X-ray photoelectron spectroscopy (XPS), a 100-nm-thick Ag film was deposited by sputter-coating on a silicon substrate. The samples were then dispersed in acetone and drop-casted on the Ag coated silicon substrate. After sample preparation, they were introduced into the XPS vacuum chamber equipped with a photoelectron spectrometer consisting of a hemispherical analyzer (Spec Phoebos 100) and a Mg/Al X-ray source (Spec XR-50). For excitation, the Mg  $K\alpha$  ( $E = 1253.6 \text{ eV}$ ) anode was used. The shift in the binding energy due to surface charging was corrected with respect to the C 1s peak. The data evaluation was done by CASAXPS software.

**UV-vis Absorption.** The ultraviolet-visible (UV-vis) absorption spectra were measured at room temperature using a Shimadzu UV-1900i spectrophotometer.

**Raman Spectroscopy.** Raman spectra were recorded using a Raman microscope (Renishaw plc (invia-reflex)) with a 532 nm diode laser.

**EDX Spectroscopy.** The energy dispersive X-ray (EDX) spectra were acquired on a Hitachi Regulus 8100 instrument.

**X-ray Crystallography.** Single crystals of the seven compounds were mounted in a Hampton cryoloop with light oil to prevent efflorescence. The data collections for these compounds were performed at 150 K on a Bruker D8 Quest single-crystal diffractometer equipped with Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). All structures were solved with the ShelXT structure solution program using Intrinsic Phasing<sup>S1</sup> and refined with the ShelXL refinement package using Least Squares minimization<sup>S2</sup> operated in the OLEX2 interface.<sup>S3</sup> All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the organic groups were introduced in geometrically calculated positions. It was not possible to locate all counter cations by X-ray diffraction,

probably due to crystallographic disorder, which is a common problem in polyoxometalate crystallography. Thus, the SQUEEZE program<sup>S4</sup> or the Olex2 solvent mask function were further used to remove the contributions of weak reflections from the whole data. The newly generated hkl data were further used to refine the final crystal data. Therefore, the exact number of cations and solvent molecules was determined by elemental analysis and thermogravimetric diagrams. The resulting formula units were further used throughout the paper. In the Supporting Information, the crystal data and structure refinement for the seven compounds is summarized in Table S2. CCDC-2310865 (**DMA-V<sub>12</sub>P<sub>6</sub>**), CCDC-2310866 (**Na-V<sub>12</sub>P<sub>6</sub>**), CCDC-2310867 (**Mg-V<sub>12</sub>P<sub>6</sub>**), CCDC-2310868 (**Al-V<sub>12</sub>P<sub>6</sub>**), CCDC-2310869 (**Na-V<sub>10</sub>As<sub>8</sub>**), CCDC-2310870 (**TMA- $\alpha$ -VNC-1**) and CCDC-2310871 (**TMA- $\beta$ -VNC-1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Selective Uptake of Cations.** The equimolar (0.035 mmol) amount of Na<sup>+</sup> & K<sup>+</sup> as well as Mg<sup>2+</sup> & K<sup>+</sup> were respectively added into the reaction system of **DMA-V<sub>12</sub>P<sub>6</sub>** followed by hydrothermal treatment. Crystals were collected and analyzed by single-crystal X-ray diffraction, FT-IR, Powder XRD, and elemental analysis.

**Dye Adsorption.** The equimolar (0.030 mmol) freshly prepared crystals of **DMA-V<sub>12</sub>P<sub>6</sub>**, **Na-V<sub>12</sub>P<sub>6</sub>**, **TMA- $\alpha$ -VNC-1**, and **TMA- $\beta$ -VNC-1** were immersed in 3 mL of ethanol solution containing MB<sup>+</sup> ( $1.25 \times 10^{-5}$  M), SD<sup>0</sup> ( $5 \times 10^{-5}$  M), and AO<sup>-</sup> ( $5 \times 10^{-5}$  M), respectively. The mixture was stirred under dark condition to avoid photodegradation, then the supernatant was centrifuged and monitored periodically using UV-vis spectrophotometer.

**Iodine Adsorption.** The equimolar (0.030 mmol) freshly prepared crystals of **DMA-V<sub>12</sub>P<sub>6</sub>**, **Na-V<sub>12</sub>P<sub>6</sub>**, **TMA- $\alpha$ -VNC-1**, and **TMA- $\beta$ -VNC-1** were immersed in 3 mL of I<sub>2</sub>/n-hexane solution with a concentration of 2 mmol/L, respectively. The supernatant was then monitored periodically at room temperature using UV-vis spectrophotometer. Regarding the evaluation of reusability, **TMA- $\alpha$ -VNC-1** after iodine adsorption was re-activated in EtOH and air dried for the next run.

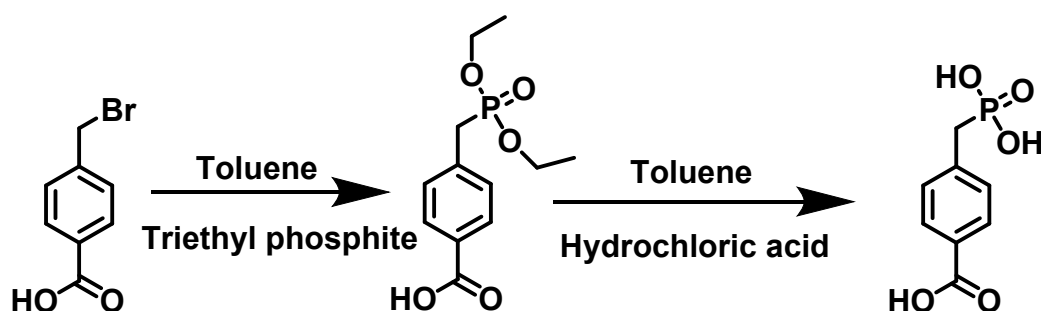
**Iodine Removal Efficiency.** The removal efficiency was calculated by using the following equation

$$Removal (\%) = (C_i - C_{e(or t)}) / C_i * 100$$

where  $C_i$  is the initial concentration of I<sub>2</sub> in n-hexane (mg/L) and  $C_e$  is the concentration at equilibrium (mg/L).

## 2. Synthesis of Organic Ligand

### 4-(phosphonomethyl) benzoic acid (*p*-PMBA):



*p*-PMBA was synthesized following a published procedure with minor modifications.<sup>S5</sup>

2.00 g (9.30 mmol) of 4-(bromomethyl) benzoic acid and 8 mL (46.37 mmol) of triethyl phosphite were dispersed in 40 mL of toluene in a round bottom flask. The solution was heated under reflux for 12 h. Afterwards, the solvent and an excess of triethyl phosphite were removed under vacuum and white solids dispersed in a colorless oil were obtained. The mixture was treated with 20 mL of toluene and 80 mL of concentrated hydrochloric acid, and then heated under reflux for another 24 h. After cooling the reaction solution, white crystals were filtered and washed with toluene. Yield: 1.83 g (91.04 %). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.85 (d, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 3.07 (s, 1H), 3.02 (s, 1H). <sup>31</sup>P NMR (162 MHz, DMSO-*d*<sub>6</sub>) δ 20.07. FT-IR (2% KBr pellet,  $\nu/\text{cm}^{-1}$ ): 1703, 1606, 1577, 1425, 1313, 1068, 992, 866, 758, 692, 641, 534  $\text{cm}^{-1}$ .

### 3. Synthesis of Compounds

#### Synthesis of $(\text{DMA})_6[\text{SO}_4(\text{V}^{\text{V}}\text{V}^{\text{IV}}_4\text{O}_9)_2\{\text{V}^{\text{IV}}_2(\text{OH})_2\text{O}_2\}(\text{PhPO}_3)_6]\cdot 2\text{CH}_3\text{OH}\cdot 3\text{DMF}$ (**DMA-V<sub>12</sub>P<sub>6</sub>**)

0.030 g (0.180 mmol) of  $\text{VOSO}_4$  and 0.010 g (0.060 mmol) of phenylphosphonic acid were suspended in a mixed solvent of DMF : MeOH (1 : 2 mL) and sonicated for 30 min. The mixture was sealed in a 25 mL Teflon-lined reactor, which was heated at 130 °C for 60 h. Upon cooling to room temperature at a rate of 10 °C h<sup>-1</sup>, light green block-shaped crystals were obtained. Yield: 0.011 g (43.02 % based on phenylphosphonic acid). Elemental analysis (%): Calcd: V 23.90, P 7.26, C 27.70, H 4.29, N 4.93, S 1.25; Found: V 23.77, P 7.21, C 28.01, H 4.54, N 4.72, S 1.17. FT-IR (2% KBr pellet, v/cm<sup>-1</sup>): 3416 (br), 3036 (w), 1633 (m), 1485 (s), 1439 (m), 1142 (w), 1097 (s), 1020 (w), 994 (s), 761 (w), 725 (w), 697 (w), 649 (s), and 552 (s).

#### Synthesis of $(\text{DMA})_7\text{Na}_3[\text{SO}_4(\text{V}^{\text{V}}\text{V}^{\text{IV}}_4\text{O}_9)_2\{\text{V}^{\text{IV}}_2(\text{OH})_2\text{O}_2\}(\text{PhPO}_3)_6]\cdot 2\text{SO}_4\cdot 2\text{H}_2\text{O}\cdot \text{CH}_3\text{OH}\cdot 2\text{DMF}$ (**Na-V<sub>12</sub>P<sub>6</sub>**)

**Na-V<sub>12</sub>P<sub>6</sub>** was synthesized by the same procedure as **DMA-V<sub>12</sub>P<sub>6</sub>** except that 0.005 g (0.035 mmol) of  $\text{Na}_2\text{SO}_4$  was added to the reaction system. Dark green block-shaped crystals were obtained. Yield: 0.008 g (28.61 % based on phenylphosphonic acid). Elemental analysis (%): Calcd: V 21.86, P 6.65, Na 2.47, C 24.49, H 3.97, N 4.51, S 3.44; Found: V 22.02, P 6.51, Na 2.43, C 25.16, H 4.54, N 4.77, S 3.32. FT-IR (2% KBr pellet, v/cm<sup>-1</sup>): 3436 (br), 3036 (w), 1631 (m), 1485 (s), 1437 (m), 1163 (w), 1138 (s), 1016 (w), 994 (s), 967 (w), 763 (m), 721 (m), 699 (m), 649 (s), and 554 (s).

#### Synthesis of $(\text{DMA})_6\text{Mg}_2[\text{SO}_4(\text{V}^{\text{V}}\text{V}^{\text{IV}}_4\text{O}_9)_2\{\text{V}^{\text{IV}}_2(\text{OH})_2\text{O}_2\}(\text{PhPO}_3)_6]\cdot 2\text{SO}_4\cdot 2\text{H}_2\text{O}\cdot \text{CH}_3\text{OH}\cdot 4\text{DMF}$ (**Mg-V<sub>12</sub>P<sub>6</sub>**)

**Mg-V<sub>12</sub>P<sub>6</sub>** was synthesized by the same procedure as **DMA-V<sub>12</sub>P<sub>6</sub>** except that 0.004 g (0.035 mmol) of  $\text{MgSO}_4$  was added to the reaction system. Dark green block-shaped crystals were obtained. Yield: 0.007 g (24.35 % based on phenylphosphonic acid). Elemental analysis (%): Calcd: V 21.26, P 6.46, Mg 1.69, C 25.48, H 4.07, N 4.87, S 3.34; Found: V 21.37, P 6.29, Mg 1.57, C 26.11, H 4.13, N 5.22, S 3.12. FT-IR (2% KBr pellet, v/cm<sup>-1</sup>): 3506 (br), 3028 (w), 1648 (w), 1485 (s), 1437 (w), 1140 (s), 1107 (s), 985 (s), 725 (m), 701 (m), 651 (w), and 556 (w).

#### Synthesis of $(\text{DMA})_4\text{Al}_2[\text{SO}_4(\text{V}^{\text{V}}\text{V}^{\text{IV}}_4\text{O}_9)_2\{\text{V}^{\text{IV}}_2(\text{OH})_2\text{O}_2\}(\text{PhPO}_3)_6]\cdot 2\text{SO}_4\cdot 2\text{H}_2\text{O}\cdot 2\text{CH}_3\text{OH}\cdot 6\text{DMF}$ (**Al-V<sub>12</sub>P<sub>6</sub>**)

**Al-V<sub>12</sub>P<sub>6</sub>** was synthesized by the same procedure as **DMA-V<sub>12</sub>P<sub>6</sub>** except that 0.023 g (0.035 mmol) of  $\text{Al}_2(\text{SO}_4)_3\cdot 18\text{H}_2\text{O}$  was added to the reaction system. Dark green block-shaped crystals were obtained. Yield: 0.008 g (26.96 % based on phenylphosphonic acid). Elemental analysis (%): Calcd: V 20.60, P 6.26, Al 1.82, C 25.91, H 4.00, N 4.72, S 3.24; Found: V 20.36, P 6.25, Al 1.74, C 25.97, H 3.14, N 4.84, S 2.89. FT-IR (2% KBr pellet, v/cm<sup>-1</sup>): 3407 (br), 3032 (w), 1631 (w), 1487 (s), 1437 (m), 1142 (s), 1016 (m), 998 (s), 761 (m), 721 (m), 701 (m), 649 (s), and 562 (s).

#### Synthesis of $(\text{DMA})\text{Na}_3[\text{SO}_4(\text{NH}_2\text{PhAs}^{\text{V}}\text{V}^{\text{IV}}_4\text{O}_8)_2\{\text{V}^{\text{IV}}_2(\text{OH})_2\text{O}_2\}(\text{NH}_2\text{PhAsO}_3)_6]\cdot 2\text{H}_2\text{O}\cdot 4\text{CH}_3\text{OH}\cdot 4\text{DMF}$ (**Na-V<sub>10</sub>As<sub>8</sub>**)

**Na-V<sub>10</sub>As<sub>8</sub>** was synthesized by the same procedure as **Na-V<sub>12</sub>P<sub>6</sub>**, except using 0.040 g (0.184 mmol) of *p*-Arsanic acid instead of phenylphosphonic acid. Green block-shaped crystals were obtained. Yield: 0.023 g (40.91 % based on V). Elemental analysis (%): Calcd: V 16.31, As 19.19, Na 2.21, C 25.38, H 3.42, N 5.83, S 1.03; Found: V 16.03, As 19.04, Na 2.34, C 24.86, H 3.47, N 6.22, S 1.08. FT-IR (2% KBr pellet, v/cm<sup>-1</sup>): 3354 (br), 3224 (w), 1629 (w), 1592 (s), 1507 (s), 1481 (w), 1303 (m), 1190 (m), 1095 (s), 996 (s), 868 (s), 651 (m), and 525 (m).

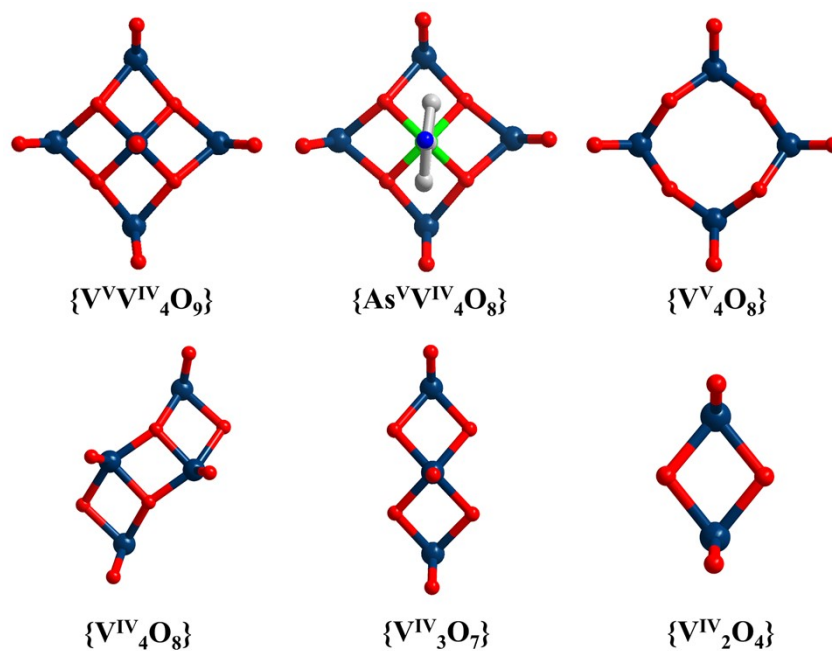
**Synthesis of  $\text{TMA}_{10}\{\text{V}^{\text{IV}}_6\text{O}_6(\text{OMe})_9(p\text{-PMBA})\}_2\{\text{V}^{\text{IV}}_4\text{O}_6(\text{OMe})_2\}_2\{\text{V}^{\text{IV}}_4\text{O}_6(p\text{-PMBA})_6\}\cdot 16\text{CH}_3\text{OH}\cdot 5\text{DMF}$  (TMA- $\alpha$ -VNC-1)**

0.040 g (0.246 mmol) of  $\text{VO}_2\text{SO}_4$  and 0.015 g (0.069 mmol) of *p*-PMBA were suspended in a mixed solvent of DMF : MeOH (1.5 : 4 mL) and sonicated for 30 min. The mixture was sealed in a 25 mL Teflon-lined reactor, which was heated at 130 °C for 60 h. Upon cooling to room temperature at a rate of 10 °C h<sup>-1</sup>, green block-shaped crystals were obtained. Yield: 0.024 g (48.88 % based on *p*-PMBA). Elemental analysis (%): Calcd: V 21.41, P 4.34, C 33.03, H 5.88, N 3.68; Found: V 21.09, P 4.29, C 33.19, H 6.03, N 3.53. FT-IR (2% KBr pellet,  $\nu/\text{cm}^{-1}$ ): 3438 (br), 2923 (w), 2809 (w), 1590 (s), 1549 (s), 1487 (m), 1425 (s), 1247 (w), 1070 (s), 996 (w), 944 (s), 800 (w), 707 (w), 649 (w), and 546 (m).

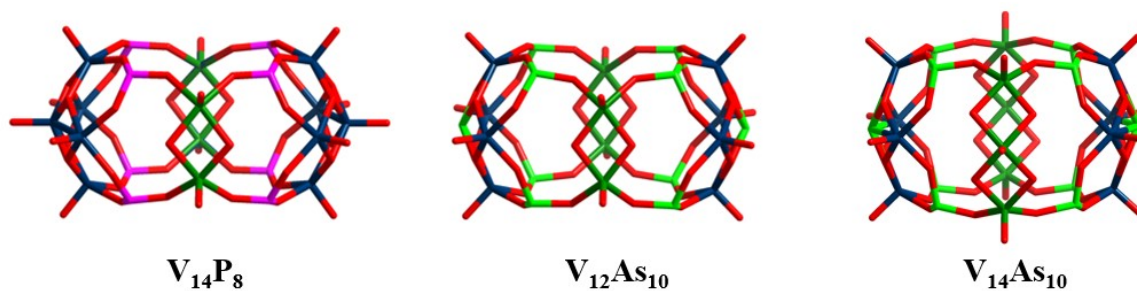
**Synthesis of  $\text{TMA}_{10}\{\text{V}^{\text{IV}}_6\text{O}_6(\text{OMe})_9(p\text{-PMBA})\}_2\{\text{V}^{\text{IV}}_4\text{O}_6(\text{OMe})_2\}_2\{\text{V}^{\text{IV}}_4\text{O}_6(p\text{-PMBA})_6\}\cdot 24\text{CH}_3\text{OH}\cdot 6\text{DMAc}$  (TMA- $\beta$ -VNC-1)**

TMA- $\beta$ -VNC-1 was synthesized by the same procedure as TMA- $\alpha$ -VNC-1 except using 1.5 mL DMAc instead of DMF. Green rod-shaped crystals were obtained. Yield: 0.031 g (58.70 % based on *p*-PMBA). Elemental analysis (%): Calcd: V 19.97, P 4.05, C 34.13, H 6.32, N 3.66; Found: V 20.05, P 4.14, C 33.68, H 6.19, N 3.50. FT-IR (2% KBr pellet,  $\nu/\text{cm}^{-1}$ ): 3453 (br), 2925 (w), 2815 (w), 1596 (s), 1557 (s), 1419 (s), 1243 (w), 1153 (w), 1082 (s), 994 (s), 954 (s), 791 (w), 703 (w), 653 (w), and 556 (s).

#### 4. Characterization on Compounds and Ligands

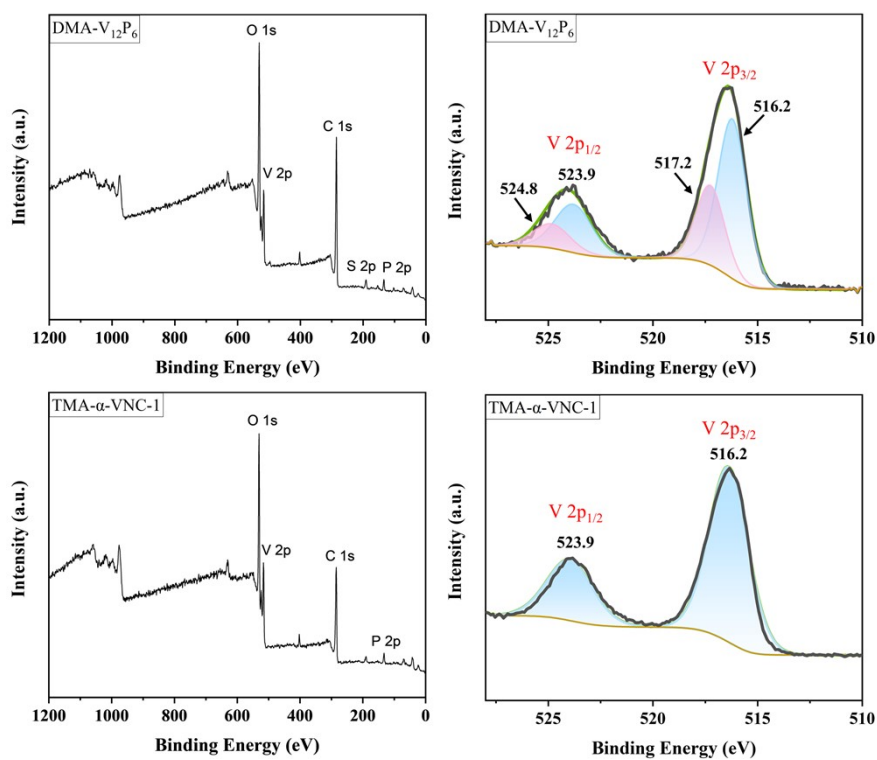


**Figure S1.** Ball-and-stick representation of the basic building blocks for POV-P/As-MOCs. Color code: V, dark blue; As, light green; O, red balls.

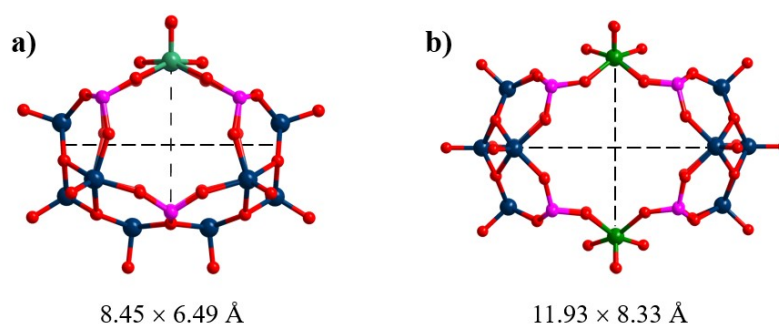


**Figure S2.** Typical examples of annular POV-P/As-MOCs. Color code: V, dark blue or green; As, light green; P, pink; O, red.

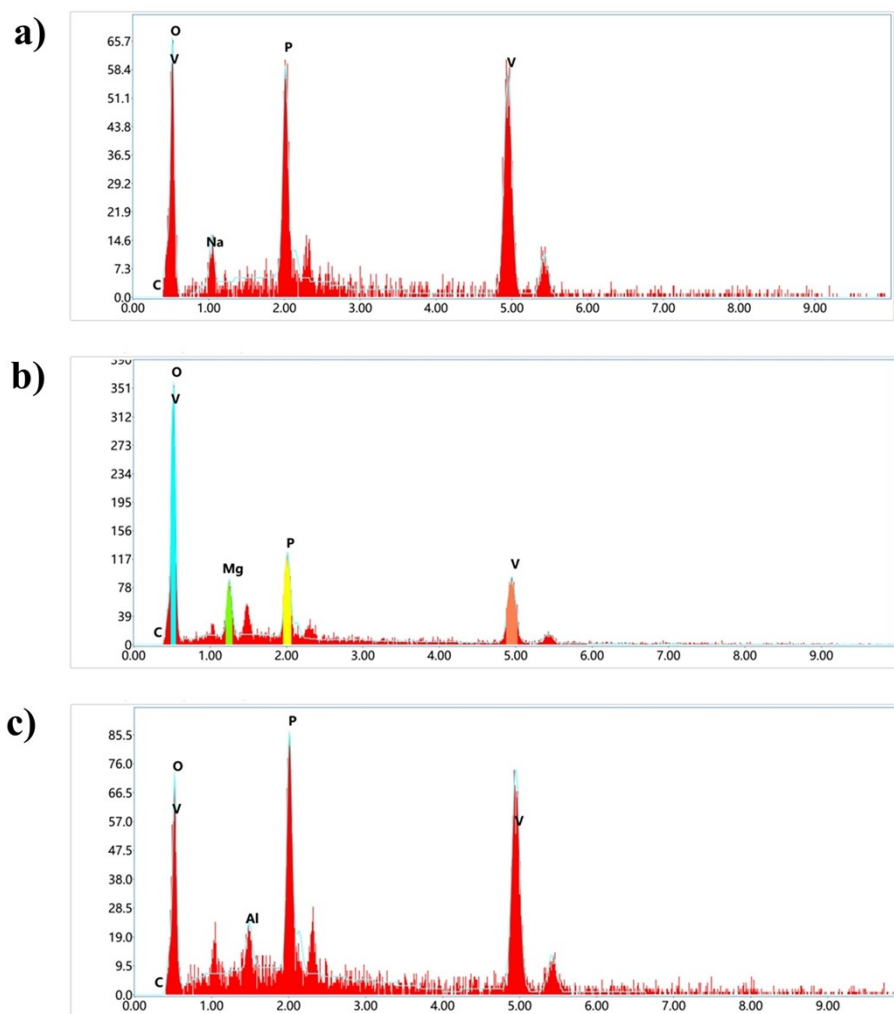




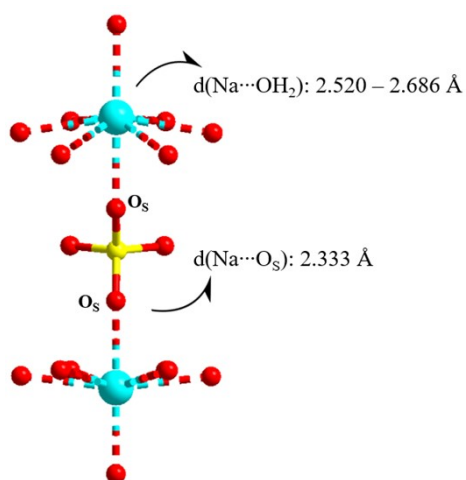
**Figure S3.** XPS spectra and fits for V 2p of **DMA-V<sub>12</sub>P<sub>6</sub>** (top) and **TMA- $\alpha$ -VNC-1** (bottom).



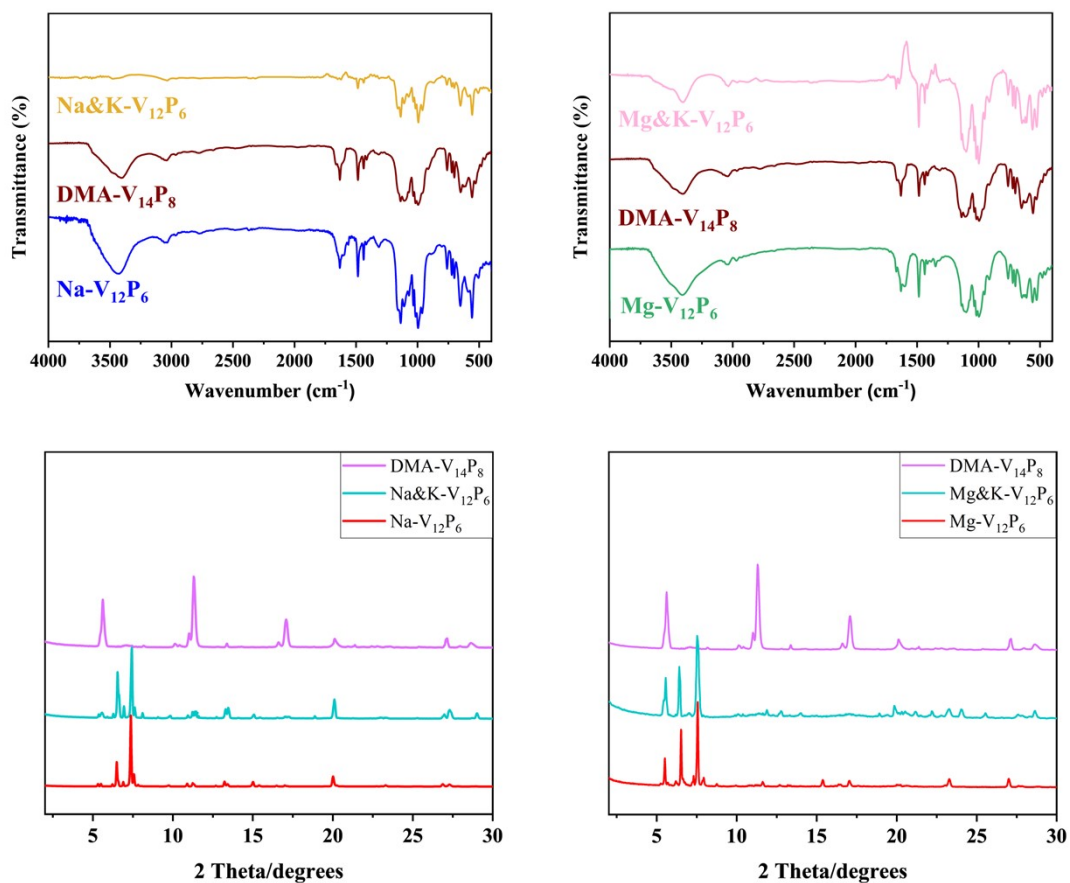
**Figure S4.** The size of the elliptical cavity in a) **V<sub>12</sub>P<sub>6</sub>** and b) **V<sub>14</sub>P<sub>8</sub>**.



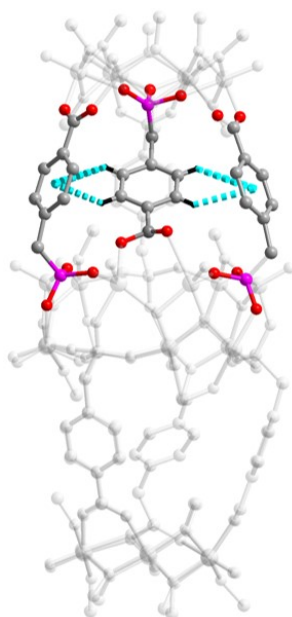
**Figure S5.** EDX spectra of Na-V<sub>12</sub>P<sub>6</sub> (a), Mg-V<sub>12</sub>P<sub>6</sub> (b), and Al-V<sub>12</sub>P<sub>6</sub> (c).



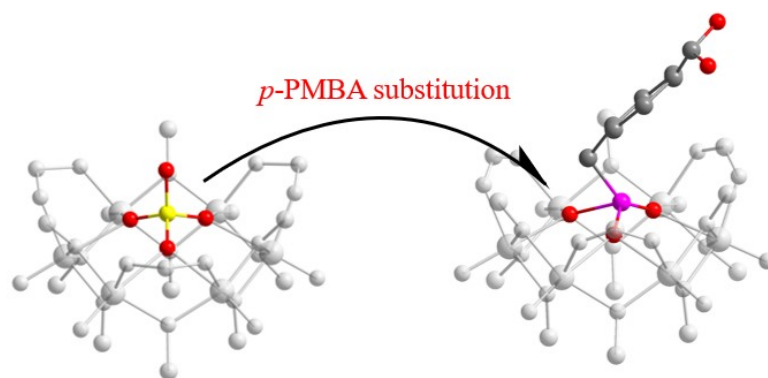
**Figure S6.** The distance of Na...O<sub>s</sub> and Na...OH<sub>2</sub> bonds in Na-V<sub>12</sub>P<sub>6</sub>.



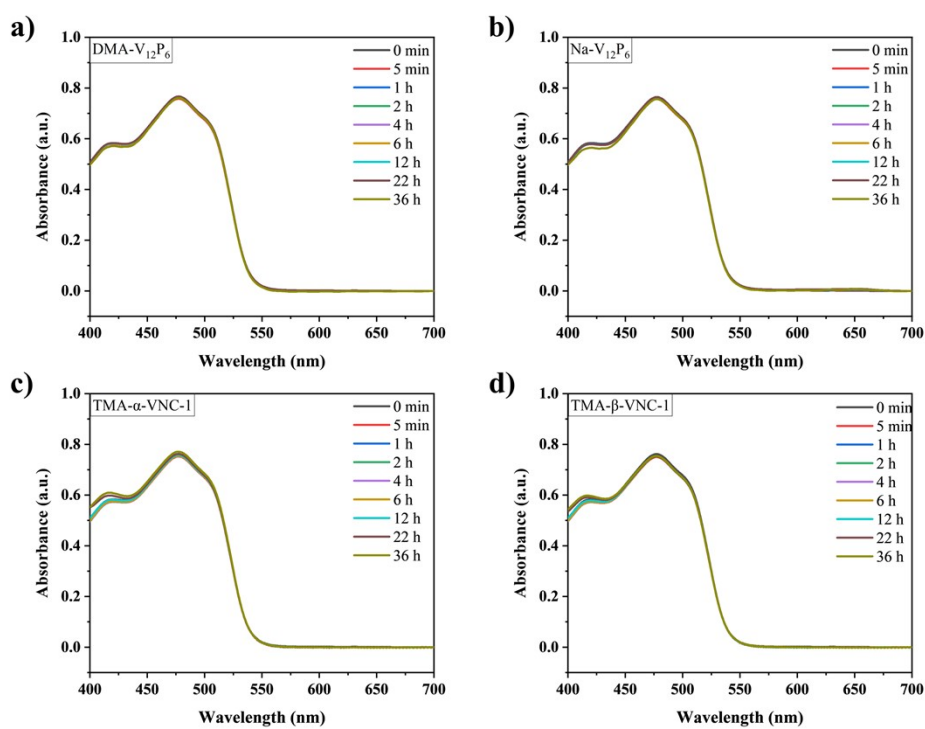
**Figure S7.** FT-IR spectra (top) and Powder XRD patterns (bottom) of the compounds from the system of Na & K-V<sub>12</sub>P<sub>6</sub> and Mg & K-V<sub>12</sub>P<sub>6</sub>.



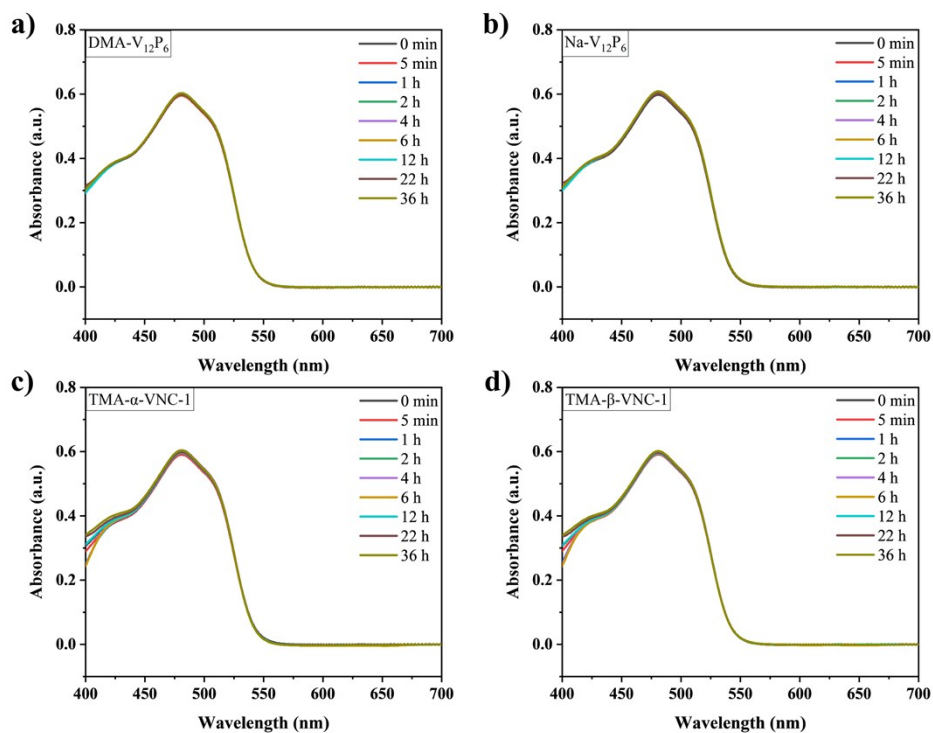
**Figure S8.** C-H... $\pi$  interactions among *p*-PMBA ligands inside the cavity of VNC-1.



**Figure S9.** Ligand substitution of  $\text{SO}_4^{2-}$  ( $\text{V}_6\text{-SO}_4$ ) by  $p\text{-PMBA}$  ( $\text{V}_6\text{-PMBA}$ ).



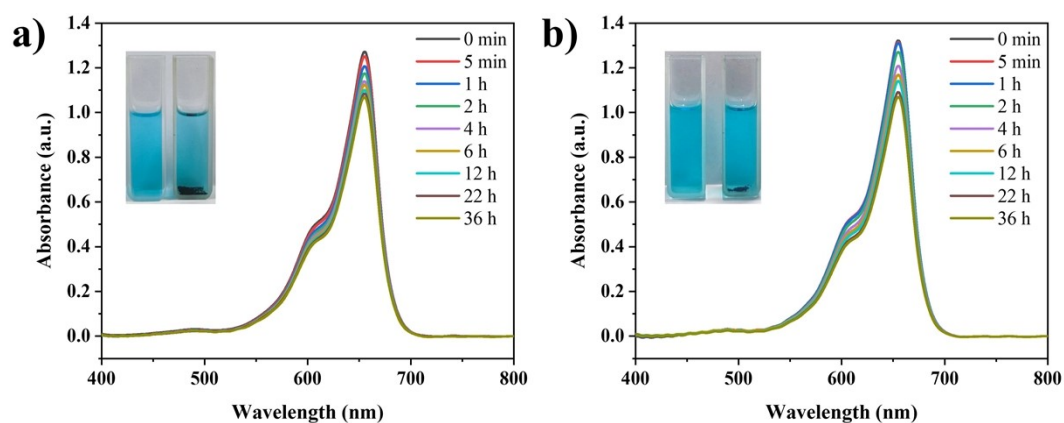
**Figure S10.** The UV-vis spectra of  $\text{SD}^0$  in ethanol in the presence of a)  $\text{DMA-V}_{12}\text{P}_6$ , b)  $\text{Na-V}_{12}\text{P}_6$ , c)  $\text{TMA-}\alpha\text{-VNC-1}$  and d)  $\text{TMA-}\beta\text{-VNC-1}$  at various time intervals.



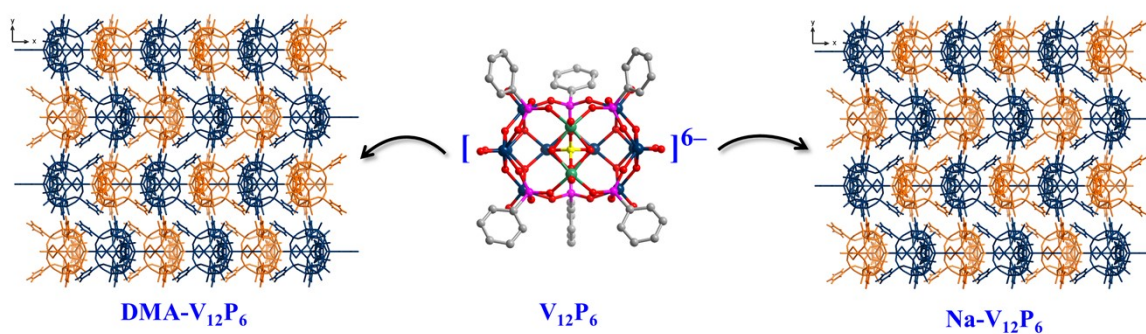
**Figure S11.** The UV-vis spectra of  $\text{AO}^-$  in ethanol in the presence of a)  $\text{DMA-V}_{12}\text{P}_6$ , b)  $\text{Na-V}_{12}\text{P}_6$ , c)  $\text{TMA-}\alpha\text{-VNC-1}$  and d)  $\text{TMA-}\beta\text{-VNC-1}$  at various time intervals.

	<b>Methylene Blue (<math>\text{MB}^+</math>)</b>	<b>Sudan I (<math>\text{SD}^0</math>)</b>	<b>Acid Orange (<math>\text{AO}^-</math>)</b>
<b>X(Å)</b>	<b>4.59</b>	<b>4.13</b>	<b>5.19</b>
<b>Y(Å)</b>	<b>8.01</b>	<b>9.57</b>	<b>9.66</b>
<b>Z(Å)</b>	<b>16.75</b>	<b>14.09</b>	<b>15.49</b>

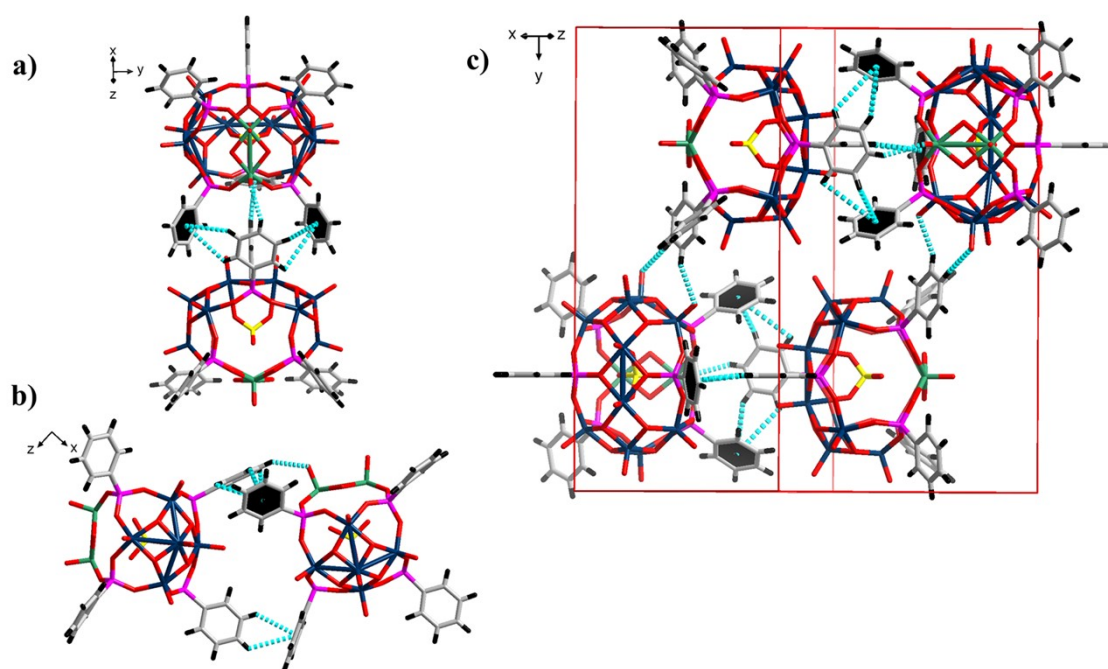
**Figure S12.** Molecular structures and dimensions of dye molecules used in this study.



**Figure S13.** The UV-vis spectra of  $\text{MB}^+$ /ethanol in the presence of  $\text{Mg-V}_{12}\text{P}_6$  (a) and  $\text{Al-V}_{12}\text{P}_6$  (b) at various time intervals (inset, photographs of the color of dye solutions before and after adsorption).

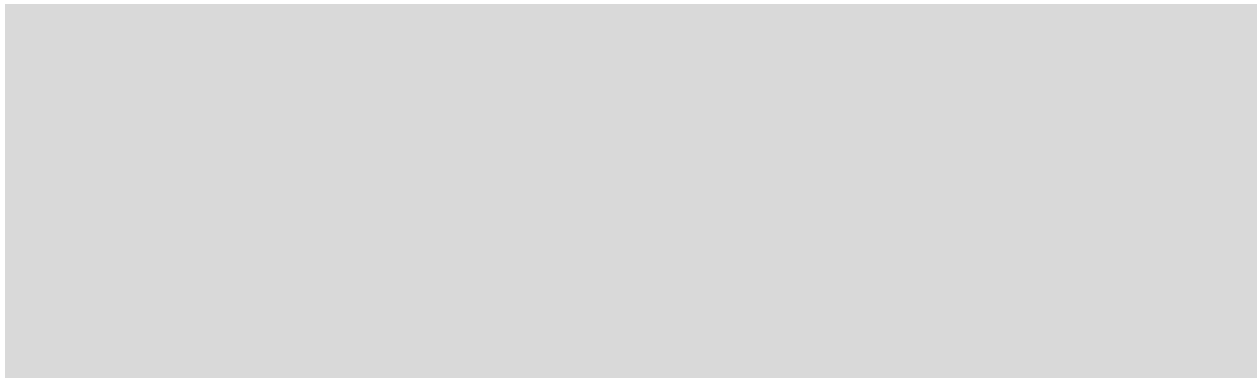


**Figure S14.** The crystal packing diagrams of  $\text{DMA-V}_{12}\text{P}_6$  and  $\text{Na-V}_{12}\text{P}_6$ .

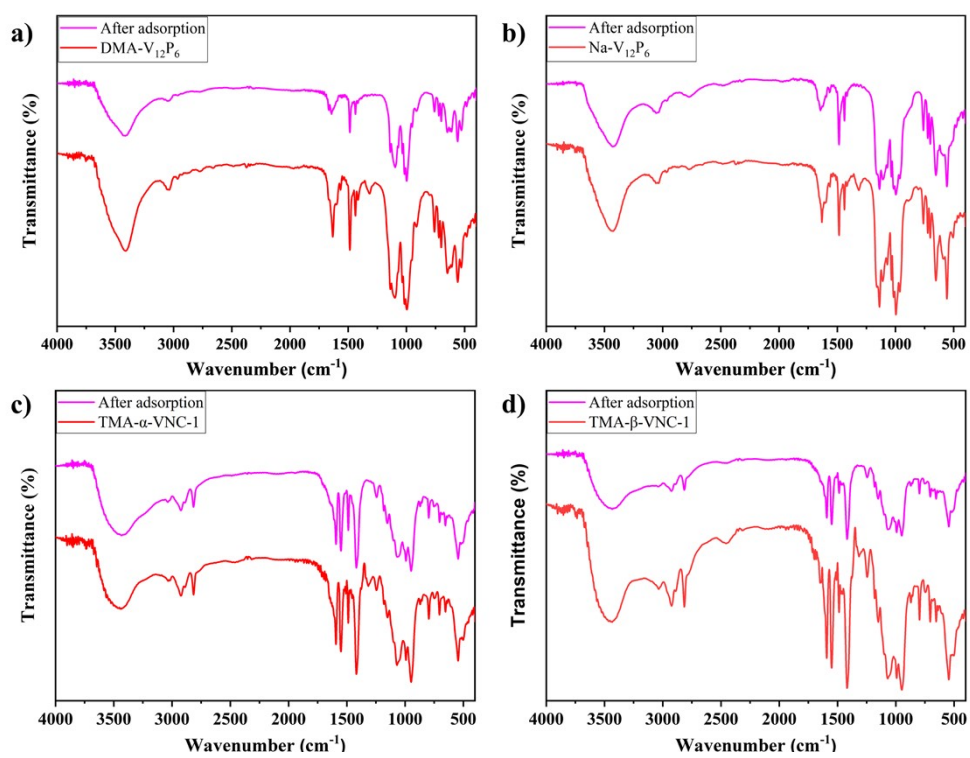


**Figure S15.** Diagrams of the intermolecular  $\text{C-H}\cdots\pi$  interactions among cages in  $\text{DMA-V}_{12}\text{P}_6$ .

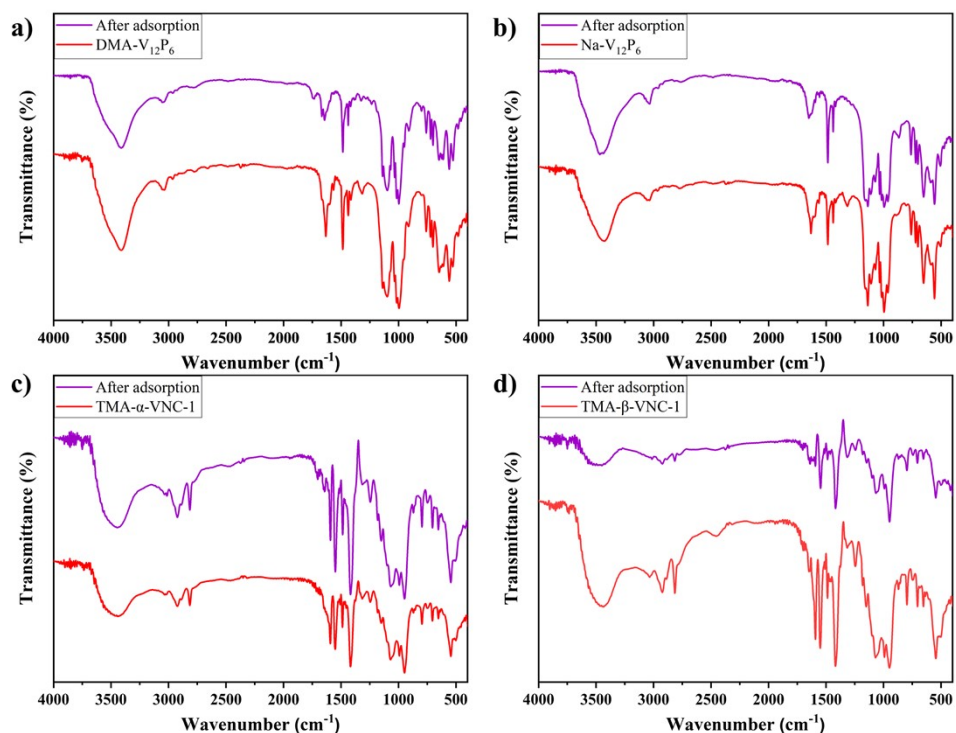




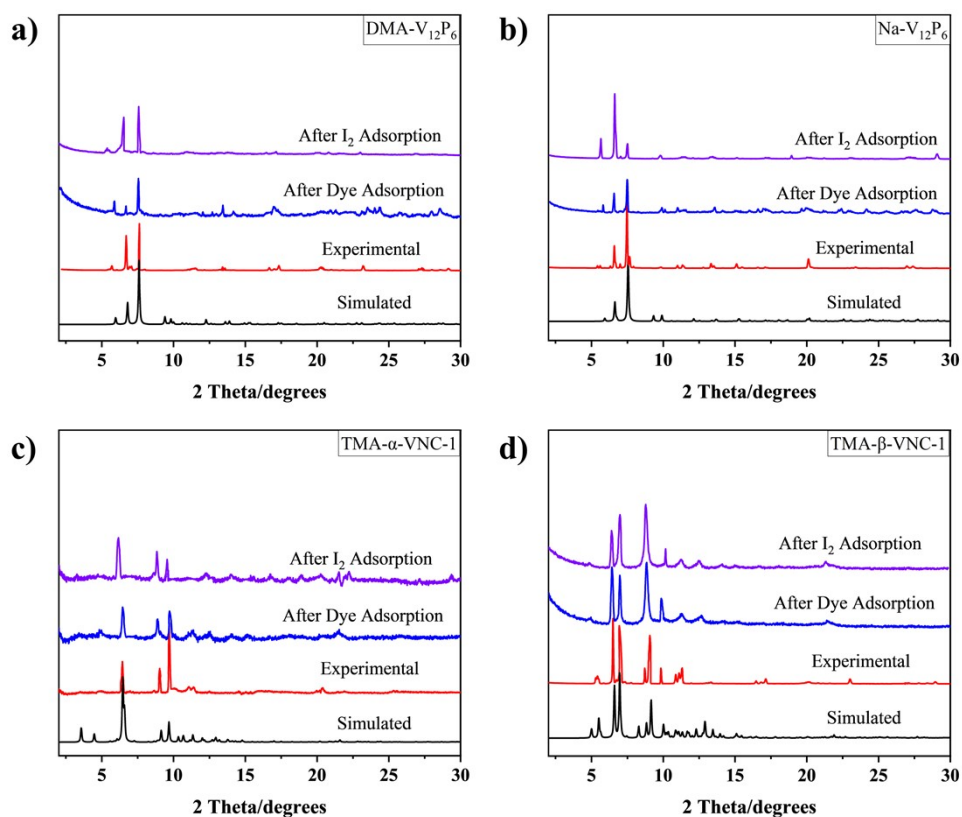
**Figure S16.** The crystal packing diagrams of TMA- $\alpha$ -VNC-1 and TMA- $\beta$ -VNC-1.



**Figure S17.** FT-IR spectra of a) DMA- $\text{V}_{12}\text{P}_6$ , b) Na- $\text{V}_{12}\text{P}_6$ , c) TMA- $\alpha$ -VNC-1 and d) TMA- $\beta$ -VNC-1 before and after dye adsorption.

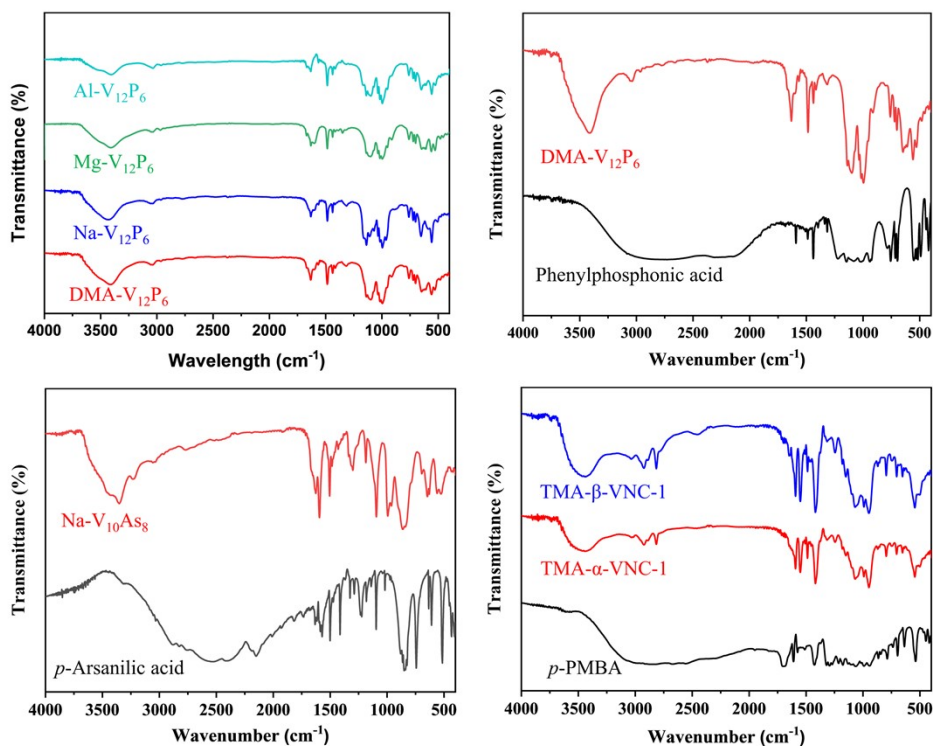


**Figure S18.** FT-IR spectra of a)  $\text{DMA-V}_{12}\text{P}_6$ , b)  $\text{Na-V}_{12}\text{P}_6$ , c)  $\text{TMA-}\alpha\text{-VNC-1}$  and d)  $\text{TMA-}\beta\text{-VNC-1}$  before and after  $\text{I}_2$  adsorption.

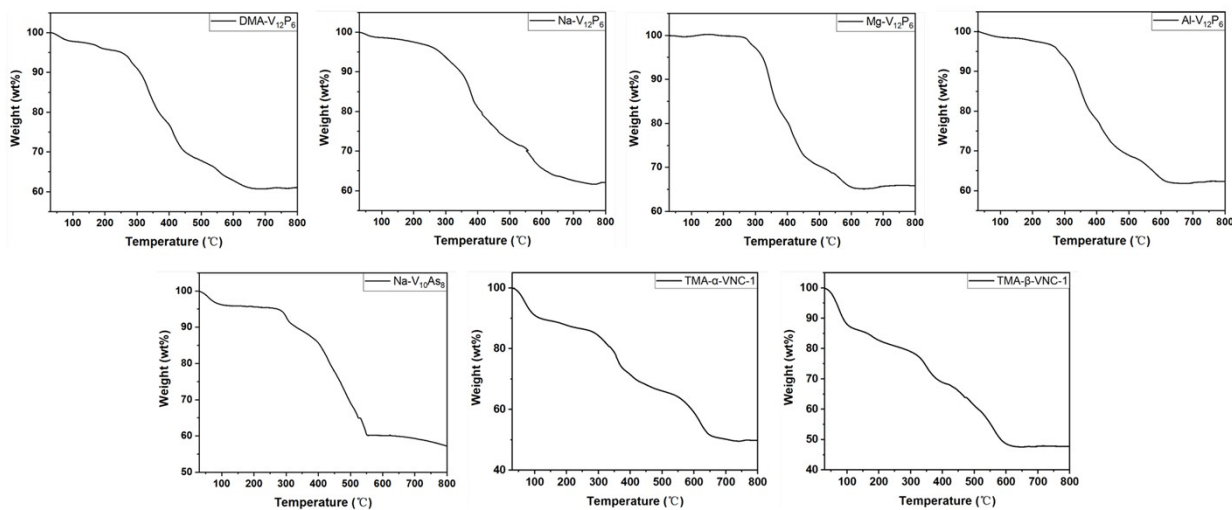


**Figure S19.** Powder XRD patterns of a)  $\text{DMA-V}_{12}\text{P}_6$ , b)  $\text{Na-V}_{12}\text{P}_6$ , c)  $\text{TMA-}\alpha\text{-VNC-1}$  and d)  $\text{TMA-}\beta\text{-VNC-1}$  before and after dye and  $\text{I}_2$  adsorption.

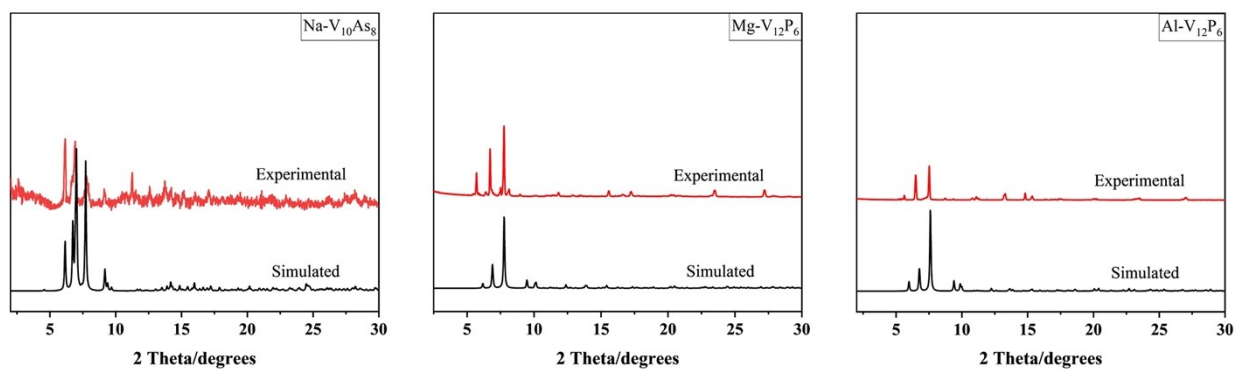




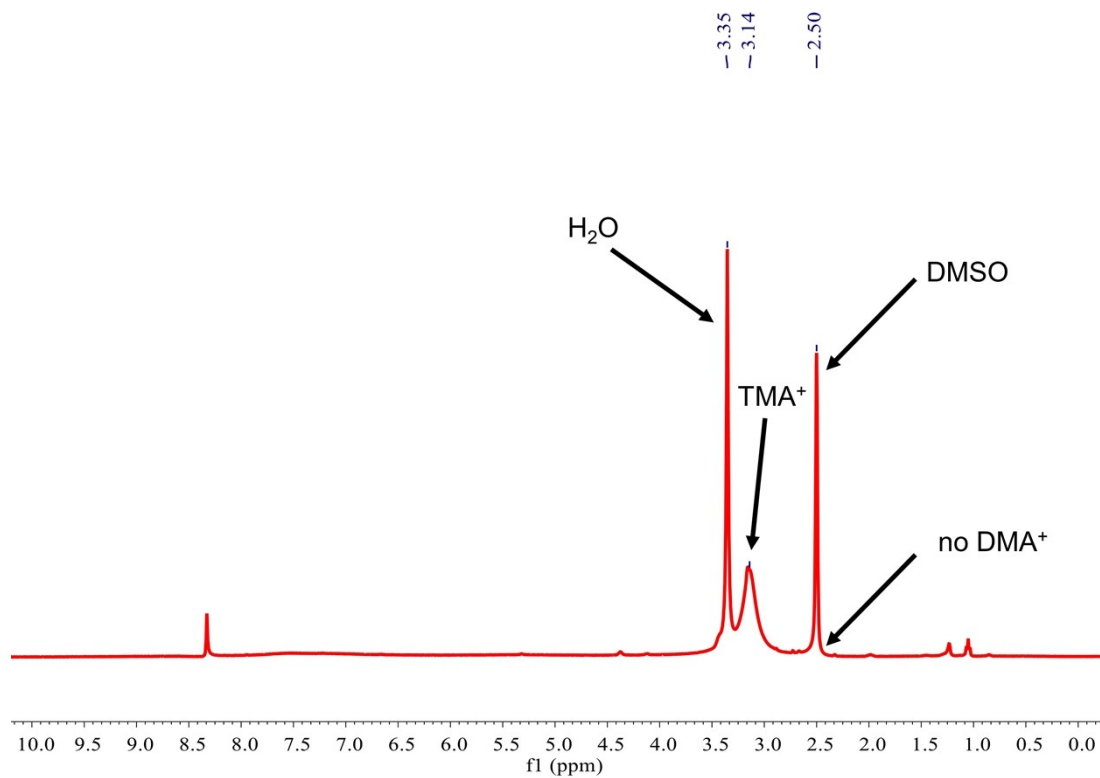
**Figure S20.** FT-IR spectra of the as-synthesized compounds.



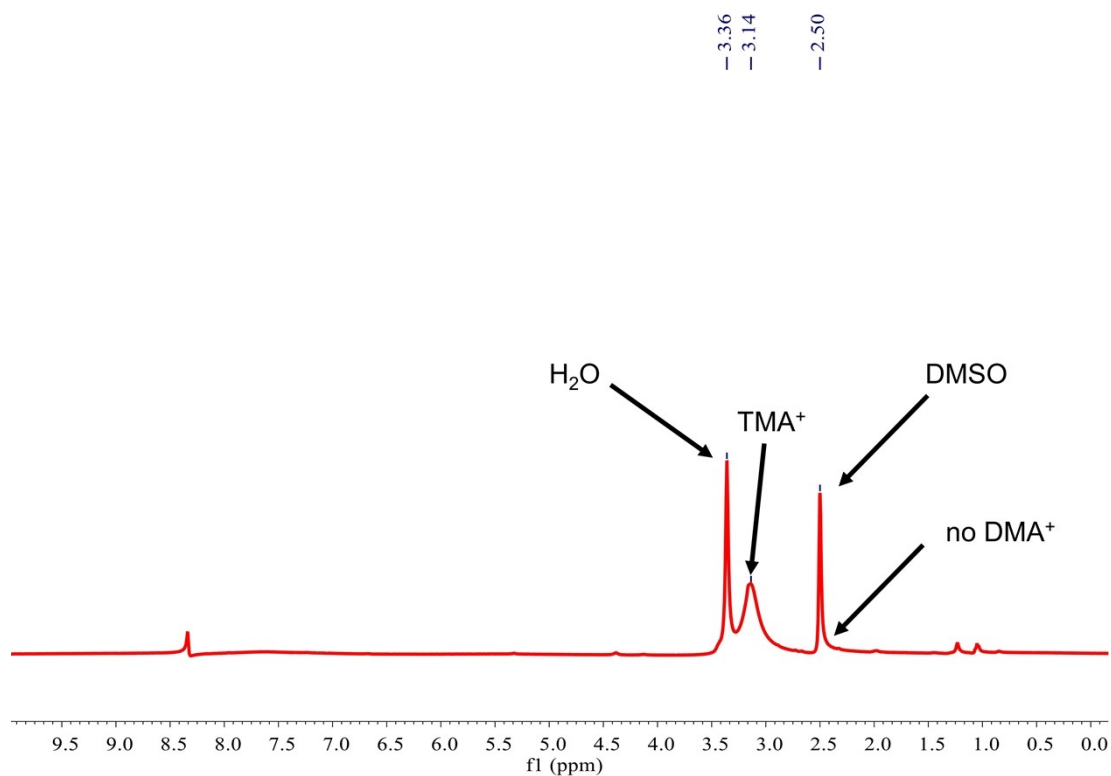
**Figure S21.** Thermogram of the as-synthesized compounds from 25 to 800 °C under N<sub>2</sub> atmosphere.



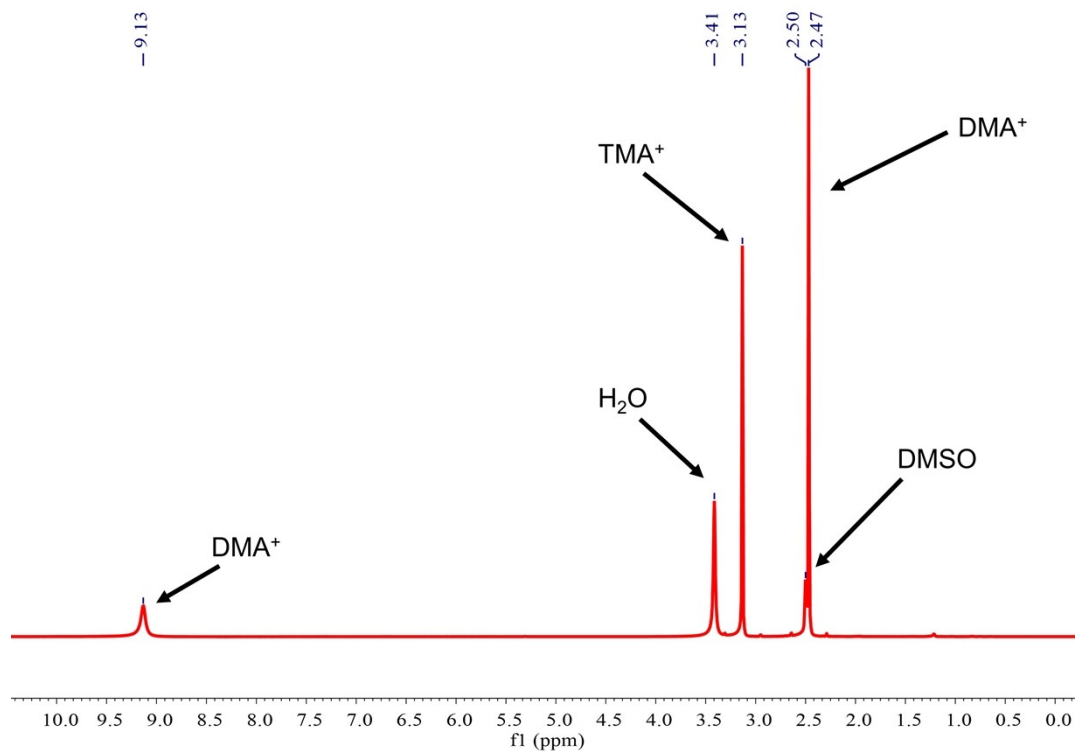
**Figure S22.** Powder XRD patterns of  $\text{Na-V}_{10}\text{As}_8$ ,  $\text{Mg-V}_{12}\text{P}_6$ , and  $\text{Al-V}_{12}\text{P}_6$ .



**Figure S23.**  $^1\text{H}$  NMR spectrum of **TMA- $\alpha$ -VNC-1** dissolved in  $d_6$ -DMSO to confirm the presence of TMA cations.



**Figure S24.**  $^1\text{H}$  NMR spectrum of **TMA- $\beta$ -VNC-1** dissolved in  $d_6$ -DMSO to confirm the presence of TMA cations.



**Figure S25.**  $^1\text{H}$  NMR spectrum of  $\text{TMA}^+\text{Cl}^-$  and  $\text{DMA}^+\text{Cl}^-$  dissolved in  $d_6$ -DMSO as reference for identifying counter cations.

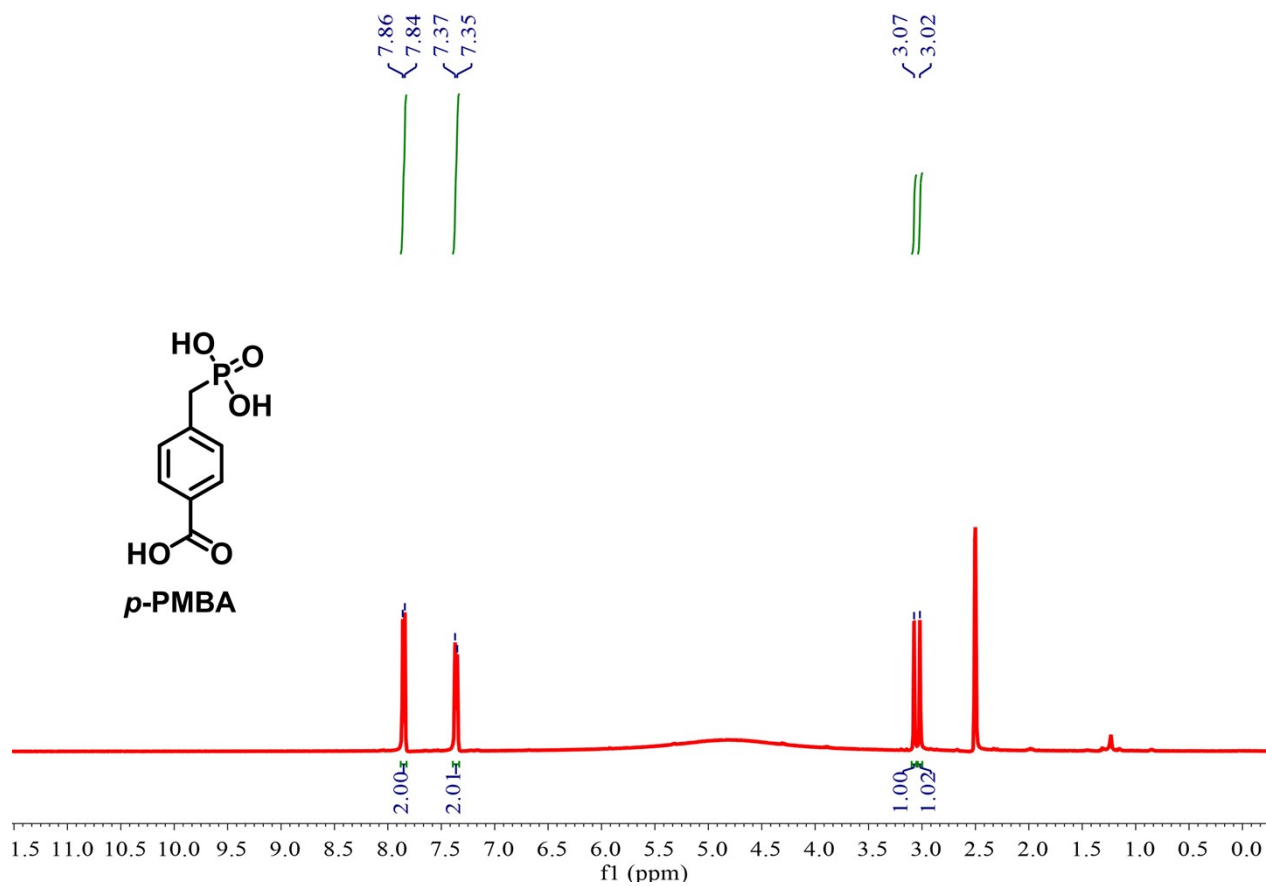


Figure S26. <sup>1</sup>H NMR spectrum of *p*-PMBA.

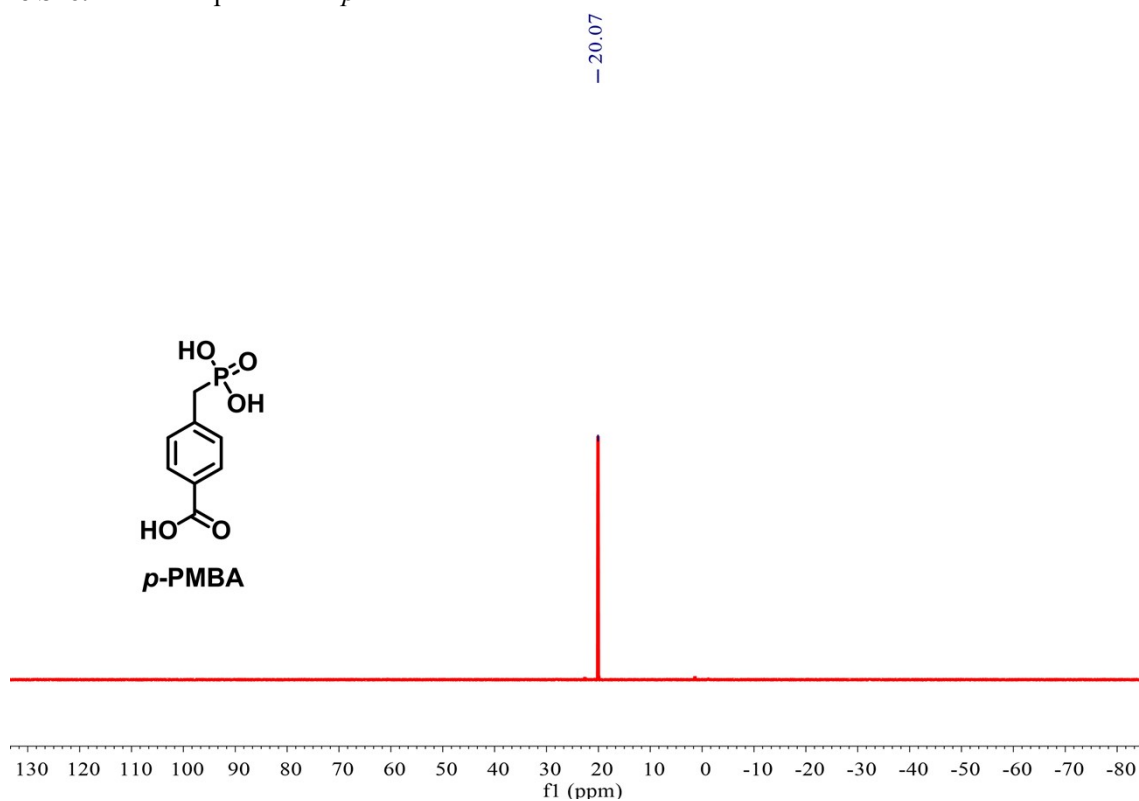


Figure S27. <sup>31</sup>P NMR spectrum of *p*-PMBA.

**Table S1.** BVS values for **DMA-V<sub>12</sub>P<sub>6</sub>**, **Na-V<sub>10</sub>As<sub>8</sub>** and **TMA-β-VNC-1**.

<b>DMA-V<sub>12</sub>P<sub>6</sub></b>			
<b>V</b>	<b>BVS value</b>	<b>μ<sub>2</sub>-O (V-O-P)</b>	<b>BVS value</b>
V1	4.128	O8	1.911
V2	5.092	O10	1.911
V3	4.142	O13	1.929
V4	4.194	O14	1.893
V5	4.176	O15	1.982
V6	4.161	O16	1.946
V7	4.031	O18	1.877
<b>μ<sub>3</sub>-O</b>	<b>BVS value</b>	O20	1.911
O1	2.214	<b>Terminal O (V)</b>	<b>BVS value</b>
O6	2.196	O5	1.669
O4	2.080	O9	1.573
O7	2.070	O11	1.688
O12	2.092	O19	1.599
O22	2.070	O21	1.815
<b>μ<sub>2</sub>-O (V-O-V)</b>	<b>BVS value</b>	O24	1.638
O2	1.168	O25	1.660
<b>μ<sub>2</sub>-O (V-O-S)</b>	<b>BVS value</b>		
O17	1.795		
O23	1.754		
<b>Na-V<sub>10</sub>As<sub>8</sub></b>			
<b>V</b>	<b>BVS value</b>	<b>μ<sub>2</sub>-O (V-O-S)</b>	<b>BVS value</b>
V1	4.122	O8	1.810
V3	4.126	O10	1.732
V4	3.862	<b>Terminal O (V)</b>	<b>BVS value</b>
V6	4.167	O13	1.644
V9	3.977	O23	1.689
V10	4.137	O28	1.644
<b>μ<sub>2</sub>-O (V-O-V)</b>	<b>BVS value</b>	O33	1.689
O25	1.116	O37	1.689
O30	1.212	O41	1.644
<b>μ<sub>2</sub>-O (V-O-As)</b>	<b>BVS value</b>	<b>μ<sub>3</sub>-O</b>	<b>BVS value</b>
O7	1.940	O1	2.045
O12	1.992	O4	2.251
O15	2.070	O6	2.037
O18	1.938	O14	2.303
O24	2.010	O16	2.028
O26	1.910	O42	2.022
O35	2.021		
O36	1.957		

<b>TMA-<math>\beta</math>-VNC-1</b>			
<b>V</b>	<b>BVS value</b>	<b>Terminal O (V)</b>	<b>BVS value</b>
V1	4.194	O5	1.644
V2	4.192	O13	1.644
V3	4.566	O17	1.558
V4	3.995	O19	1.498
V5	4.070	O21	1.689
V6	4.354	O37	1.882
V7	3.914	O39	1.516
V8	4.007	O41	1.558
V9	4.181	O42	1.558
V10	4.455	O44	1.736
V11	4.349	O45	1.736
V12	4.336	O46	1.516
<b><math>\mu_3</math>-O</b>	<b>BVS value</b>	<b><math>\mu_2</math>-O (V-O-P)</b>	<b>BVS value</b>
O7	1.918	O1	2.017
O9	1.815	O2	2.084
O10	1.871	O16	1.998
O12	1.988	O33	1.845
O15	1.960	O35	1.818
O23	1.803	O38	1.772

**Table S2.** Crystal data and structure refinement for the as-synthesized compounds.

Compound	DMA-V <sub>12</sub> P <sub>6</sub>	Na-V <sub>12</sub> P <sub>6</sub>	Mg-V <sub>12</sub> P <sub>6</sub>
Empirical formula	V <sub>12</sub> P <sub>6</sub> SC <sub>59</sub> N <sub>9</sub> O <sub>49</sub> H <sub>109</sub>	V <sub>12</sub> P <sub>6</sub> S <sub>3</sub> Na <sub>3</sub> C <sub>57</sub> N <sub>9</sub> O <sub>57</sub> H <sub>110</sub>	V <sub>12</sub> P <sub>6</sub> S <sub>3</sub> Mg <sub>2</sub> C <sub>61</sub> N <sub>10</sub> O <sub>59</sub> H <sub>116</sub>
Formula weight, g/mol	2557.73	2795.82	2875.55
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>
<i>a</i> , Å	18.799(4)	18.7492(6)	18.9438(12)
<i>b</i> , Å	25.986(6)	26.2464(8)	26.1533(14)
<i>c</i> , Å	18.008(5)	17.6616(6)	17.6647(11)
$\alpha$ , °	90	90	90
$\beta$ , °	90	90	90
$\gamma$ , °	90	90	90
Volume, Å <sup>3</sup>	8797(4)	8691.3(5)	8751.8(9)
<i>Z</i>	4	4	4
<i>D</i> <sub>calc</sub> , g/cm <sup>3</sup>	1.542	1.712	1.612
Absorption coefficient, mm <sup>-1</sup>	1.423	1.503	1.461
<i>F</i> (000)	4028	4416	4182
Theta range for data collection, °	4.432 to 50.336	4.92 to 56.654	5.122 to 55.844
Completeness to $\Theta_{\max}$	99.5 %	99.5 %	99.4 %
Index ranges	-22 ≤ <i>h</i> ≤ 22 -30 ≤ <i>k</i> ≤ 31 -21 ≤ <i>l</i> ≤ 21	-24 ≤ <i>h</i> ≤ 25 -35 ≤ <i>k</i> ≤ 35 -21 ≤ <i>l</i> ≤ 23	-22 ≤ <i>h</i> ≤ 24 -30 ≤ <i>k</i> ≤ 34 -21 ≤ <i>l</i> ≤ 23
Reflections collected	77577	96833	87724
Independent reflections	8039	10998	10637
<i>R</i> (int)	0.1144	0.0340	0.0335
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Data / restraints / parameters	8039 / 498 / 496	10998 / 528 / 664	10637 / 494 / 569
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.039	1.025	1.025
<i>R</i> <sub>1</sub> , <sup>[a]</sup> <i>wR</i> <sub>2</sub> <sup>[b]</sup> ( <i>I</i> > 2σ( <i>I</i> ))	<i>R</i> <sub>1</sub> = 0.0657 <i>wR</i> <sub>2</sub> = 0.1843	<i>R</i> <sub>1</sub> = 0.0417 <i>wR</i> <sub>2</sub> = 0.1231	<i>R</i> <sub>1</sub> = 0.0509 <i>wR</i> <sub>2</sub> = 0.1526
<i>R</i> <sub>1</sub> , <sup>[a]</sup> <i>wR</i> <sub>2</sub> <sup>[b]</sup> (all data)	<i>R</i> <sub>1</sub> = 0.0956 <i>wR</i> <sub>2</sub> = 0.2119	<i>R</i> <sub>1</sub> = 0.0481 <i>wR</i> <sub>2</sub> = 0.1292	<i>R</i> <sub>1</sub> = 0.0578 <i>wR</i> <sub>2</sub> = 0.1607
Largest diff. peak and hole, e/Å <sup>3</sup>	1.04 and -1.16	1.48 and -0.85	2.17 and -1.42

Compound	Al-V <sub>12</sub> P <sub>6</sub>	Na-V <sub>10</sub> As <sub>8</sub>	TMA- $\alpha$ -VNC-1
Empirical formula	V <sub>12</sub> P <sub>6</sub> S <sub>3</sub> Al <sub>2</sub> C <sub>64</sub> N <sub>10</sub> O <sub>62</sub> H <sub>118</sub>	V <sub>10</sub> As <sub>8</sub> SNa <sub>3</sub> C <sub>66</sub> N <sub>13</sub> O <sub>52</sub> H <sub>106</sub>	V <sub>24</sub> P <sub>8</sub> C <sub>157</sub> N <sub>15</sub> O <sub>113</sub> H <sub>333</sub>
Formula weight, g/mol	2966.95	3123.43	5709.74
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>Pnma</i>	<i>Pna2</i> <sub>1</sub>	<i>Fddd</i>
<i>a</i> , Å	18.8119(17)	26.192(4)	31.7556(12)
<i>b</i> , Å	26.116(2)	28.694(4)	53.665(2)
<i>c</i> , Å	17.9103(19)	14.197(2)	58.241(3)
$\alpha$ , °	90	90	90
$\beta$ , °	90	90	90
$\gamma$ , °	90	90	90
Volume, Å <sup>3</sup>	8799.0(15)	10670(3)	99252(7)
<i>Z</i>	4	4	16
<i>D</i> <sub>calc</sub> , g/cm <sup>3</sup>	1.548	1.636	1.087
Absorption coefficient, mm <sup>-1</sup>	1.389	3.400	0.969
<i>F</i> (000)	4043	5104	32320
Theta range for data collection, °	4.602 to 56.664	4.464 to 52.746	4.366 to 35.48
Completeness to $\Theta$ <sub>max</sub>	99.7 %	97.6 %	99.2 %
Index ranges	-25 ≤ <i>h</i> ≤ 23 -34 ≤ <i>k</i> ≤ 31 -23 ≤ <i>l</i> ≤ 23	-31 ≤ <i>h</i> ≤ 32 -34 ≤ <i>k</i> ≤ 35 -17 ≤ <i>l</i> ≤ 16	-27 ≤ <i>h</i> ≤ 25 -45 ≤ <i>k</i> ≤ 45 -49 ≤ <i>l</i> ≤ 49
Reflections collected	88935	93610	39200
Independent reflections	11132	20349	8120
<i>R</i> (int)	0.0391	0.0912	0.0643
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Data / restraints / parameters	11132 / 1423 / 521	20349 / 7 / 1081	8120 / 3701 / 1004
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.020	0.991	1.709
<i>R</i> <sub>1</sub> , <sup>[a]</sup> <i>wR</i> <sub>2</sub> <sup>[b]</sup> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	<i>R</i> <sub>1</sub> = 0.0477 <i>wR</i> <sub>2</sub> = 0.1361	<i>R</i> <sub>1</sub> = 0.0491 <i>wR</i> <sub>2</sub> = 0.1138	<i>R</i> <sub>1</sub> = 0.1237 <i>wR</i> <sub>2</sub> = 0.3613
<i>R</i> <sub>1</sub> , <sup>[a]</sup> <i>wR</i> <sub>2</sub> <sup>[b]</sup> (all data)	<i>R</i> <sub>1</sub> = 0.0585 <i>wR</i> <sub>2</sub> = 0.1451	<i>R</i> <sub>1</sub> = 0.0625 <i>wR</i> <sub>2</sub> = 0.1196	<i>R</i> <sub>1</sub> = 0.1481 <i>wR</i> <sub>2</sub> = 0.3985
Largest diff. peak and hole, e/Å <sup>3</sup>	1.62 and -1.54	0.79 and -1.26	1.27 and -0.65



Compound	<b>TMA-<math>\beta</math>-VNC-1</b>		
Empirical formula	V <sub>24</sub> P <sub>8</sub> C <sub>174</sub> N <sub>16</sub> O <sub>122</sub> H <sub>384</sub>		
Formula weight, g/mol	6036.21		
Crystal system	Monoclinic		
Space group	<i>C2/c</i>		
<i>a</i> , Å	23.6879(12)		
<i>b</i> , Å	26.7644(14)		
<i>c</i> , Å	35.2346(17)		
$\alpha$ , °	90		
$\beta$ , °	92.2100(10)		
$\gamma$ , °	90		
Volume, Å <sup>3</sup>	22321.9(19)		
<i>Z</i>	4		
<i>D</i> <sub>calc</sub> , g/cm <sup>3</sup>	1.217		
Absorption coefficient, mm <sup>-1</sup>	1.078		
<i>F</i> (000)	8152		
Theta range for data collection, °	4.106 to 49.998		
Completeness to $\Theta_{\max}$	99.5 %		
Index ranges	-28 ≤ <i>h</i> ≤ 27 -31 ≤ <i>k</i> ≤ 31 -41 ≤ <i>l</i> ≤ 40		
Reflections collected	95276		
Independent reflections	19553		
<i>R</i> (int)	0.1312		
Absorption correction	Semi-empirical from equivalents		
Data / restraints / parameters	19553 / 2655 / 897		
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.440		
<i>R</i> <sub>1</sub> , <sup>[a]</sup> <i>wR</i> <sub>2</sub> <sup>[b]</sup> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	<i>R</i> <sub>1</sub> = 0.1578 <i>wR</i> <sub>2</sub> = 0.4215		
<i>R</i> <sub>1</sub> , <sup>[a]</sup> <i>wR</i> <sub>2</sub> <sup>[b]</sup> (all data)	<i>R</i> <sub>1</sub> = 0.2499 <i>wR</i> <sub>2</sub> = 0.4976		
Largest diff. peak and hole, e/Å <sup>3</sup>	2.52 and -1.58		

<sup>[a]</sup>  $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ . <sup>[b]</sup>  $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ .

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