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Polyoxometalates

Synthesis of α-Dawson-Type Silicotungstate $[\alpha\text{-}Si_2W_{18}O_{62}]^{8-}$ and Protonation and Deprotonation Inside the Aperture through Intramolecular Hydrogen Bonds

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Abstract: The design of structurally well-defined anionic molecular metal–oxygen clusters, polyoxometalates (POMs), leads to inorganic receptors with unique and tunable properties. Herein, an α-Dawson-type silicotungstate, $TBA_8[\alpha\text{-}Si_2W_{18}O_{62}]\cdot 3H_2O$ (**II**) that possesses a −8 charge was successfully synthesized by dimerization of a trivacant lacunary α-Keggin-type silicotungstate $TBA_4H_6[\alpha\text{-}SiW_9O_{34}]\cdot 2H_2O$ (**I**) in an organic solvent. POM **II** could be reversibly protonated (in the presence of acid) and deprotonated (in the presence of base) inside the aperture by means of intramolecular hydrogen bonds with retention of the POM structure. In contrast, the aperture of phosphorus-centered POM $TBA_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot H_2O$ (**III**) was not protonated inside the aperture. The density functional theory (DFT) calculations revealed that the basicities and charges of internal μ_3-oxygen atoms were increased by changing the central heteroatoms from P^{5+} to Si^{4+}, thereby supporting the protonation of **II**. Additionally, **II** showed much higher catalytic performance for the Knoevenagel condensation of ethyl cyanoacetate with benzaldehyde than **I** and **III**.

Introduction

Polyoxometalates (POMs) are a large family of structurally well-defined anionic molecular metal–oxygen clusters, and their chemical and physical properties can be finely tuned by selecting constituent elements, charges, structures, or by introducing metal cations, and therefore they are of increasing interest in broad fields including catalytic chemistry, materials science, and medical science.[1,2] Based on the closely aligned oxygen donor ligands of the constituent M-O-M units and their negative charges, porous materials or apertures constructed by POMs can act as inorganic receptors for capturing various metal cations.[3] In particular, the accurate design of the sizes of apertures and the directions of the lone pair of oxygen donors enables selective metal-cation recognition in POM-based inorganic molecular receptors.[4] Herein, we explore the idea that POMs with basic small apertures would act as inorganic proton receptors through intramolecular hydrogen bonds by controlling the anion charges and local electron densities of the apertures.

We focused on rugby-ball-shaped α-Dawson-type POMs $[\alpha\text{-}X_2W_{18}O_{62}]^{n-}$ that possess a small aperture in which μ_3-oxygen donors are closely aligned. Initially, perchloric acid was added to a solution of phosphorus-centered POM $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ in acetonitrile, and the proton was delocalized on the anion surface (see the Experimental Section). DFT calculations showed that the highest-occupied molecular orbital (HOMO) of $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ consisted of orbitals on the terminal (W=O) and bridging (W-O-W) oxygen atoms of the anion surface, and no orbital was observed on the internal μ_3-oxygen atoms (Figure 1a). Therefore, to increase the affinity of the oxygen atoms of the aperture toward protons, we attempted to increase the negative charges by changing XO_4^{m-} units from PO_4^{3-} to SiO_4^{4-} because charges of the central XO_4^{m-} units in POMs largely affected those of the oxygen atoms of XO_4^{m-} units.[5] As expected, the natural bond orbital (NBO) charges of the six internal μ_3-oxygen atoms in $[\alpha\text{-}Si_2W_{18}O_{62}]^{8-}$

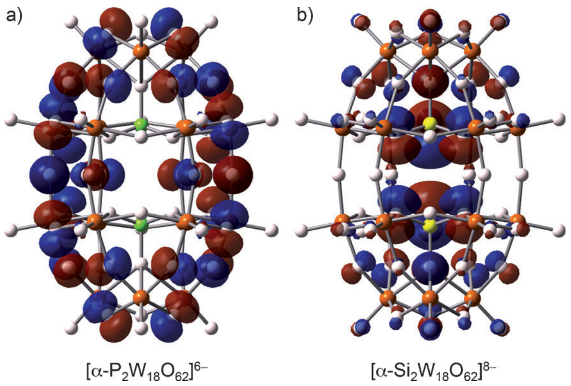

Figure 1. HOMOs of a) $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ and b) $[\alpha\text{-}Si_2W_{18}O_{62}]^{8-}$. The orbitals are represented by dark red and blue lobes (isosurface value 0.02). The atoms are represented by spheres: W, orange; P, green; Si, yellow; O, white.

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and $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ were −1.10 and −1.19, respectively, and the difference between $[\alpha\text{-}Si_2W_{18}O_{62}]^{8-}$and $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ (Δ) was 0.09 (Figure S1 in the Supporting Information). In contrast, the Δ values of the terminal oxygen atoms (W=O) and the bridging oxygen atoms (W-O-W) were less than 0.03 and small. Additionally, in the HOMO of $[\alpha\text{-}Si_2W_{18}O_{62}]^{8-}$, orbitals were observed at the μ_3-oxygen atoms within the aperture, thus suggesting that $[\alpha\text{-}Si_2W_{18}O_{62}]^{8-}$ can be protonated inside the aperture (Figure 1b; Figure S2 in the Supporting Information). However, the synthesis of silicon-centered α-Dawson-type POMs has been considered to be quite difficult because of the following three factors:[6–8] 1) trivacant lacunary $[\alpha\text{-}SiW_9O_{34}]^{10-}$, a precursor for $[\alpha\text{-}Si_2W_{18}O_{62}]^{8-}$, is metastable in an aqueous media and easily isomerizes to monovacant lacunary or fully occupied silicotungstates;[6] 2) dimerization is inhibited by the electrostatic repulsion because of the higher negative charges than those of $[\alpha\text{-}XW_9O_{34}]^{n-}$ (X = P, As, $n = 9$; X = S, Se, $n = 8$);[7] and 3) dimerization of alkali-metal salts of $[\alpha\text{-}SiW_9O_{34}]^{10-}$ in aqueous media is inhibited by strong coordination of alkali-metal cations to vacant sites of $[\alpha\text{-}SiW_9O_{34}]^{10-}$.[8,9] In this work, by utilizing an organic-solvent-soluble trivacant lacunary α-Keggin-type POM, $TBA_4H_6[\alpha\text{-}SiW_9O_{34}]\cdot 2H_2O$ (**I**), we successfully synthesized a −8-charged α-Dawson-type POM, $TBA_8[\alpha\text{-}Si_2W_{18}O_{62}]\cdot 3H_2O$ (**II**), in an organic solvent. POM **II** could be protonated (in the presence of acid) and deprotonated (in the presence of a base) inside the aperture through intramolecular hydrogen bonds with the retention of the POM structure, and **II** showed much higher catalytic performance for the Knoevenagel condensation of ethyl cyanoacetate with benzaldehyde than **I** and **III**.

Table 1. Crystal data and structure refinement parameters for H_2·**II**, H_3·**II**, and H·**III**.

	H_2·**II**	H_3·**II**	H·**III**
formula	$C_{98}Cl_4N_6O_{65}Si_2W_{18}$	$C_{88}N_9O_{62}Si_2W_{18}$	$C_{88}N_9O_{62}P_2W_{18}$
M_r [g mol^{-1}]	5808.2	5540.3	5546.0
crystal system	orthorhombic	monoclinic	monoclinic
space group	$Pna2_1$ (no. 33)	$C2/c$ (no. 15)	$C2/c$ (no. 15)
a [Å]	34.6054(2)	26.15030(10)	26.0134(2)
b [Å]	22.6385(1)	15.50760(10)	15.45140(10)
c [Å]	19.9623(1)	35.9046(3)	36.1433(3)
α [°]	90	90	90
β [°]	90	105.6917(3)	105.6676(3)
γ [°]	90	90	90
V [Å^3]	15 638.75(14)	14 017.68(16)	13 987.79(19)
Z	4	4	4
T [K]	153(2)	123(2)	123(2)
ρ_{calcd} [g cm^{-3}]	2.467	2.625	2.634
GOF	0.904	1.099	1.100
R_1[a] ($I > 2\sigma(I)$)	0.0409	0.0468	0.0466
wR_2[a]	0.1364	0.1296	0.1302

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

Results and Discussion

Synthesis of α-Dawson-type silicotungstates

A tetra-*n*-butylammonium (TBA) salt of a trivacant lacunary Keggin-type silicotungstate **I** was synthesized by mixing $Na_{10}[\alpha\text{-}SiW_9O_{34}]\cdot 3H_2O$[6] and TBABr in an acetate buffer solution (pH 3.70) at 3 °C. The cold-spray ionization mass (CSI-MS) spectrum of **I** in dimethyl sulfoxide (DMSO) showed a signal set assignable to $[TBA_5SiW_9O_{31}]^+$ (m/z 3390.9). The ^{29}Si NMR spectrum of **I** in [D$_6$]DMSO showed a signal at $\delta = -83.2$ ppm, thus showing the presence of the single species. The ^{183}W NMR spectrum showed three signals at $\delta = -153.1$, −169.9, and −190.7 ppm with the respective ratio of 1:1:1, which suggests that the overall symmetry of the anion is C_3.

The CSI-MS spectrum of **I** in dichloromethane showed two new signal sets at m/z 3400.0 and 6575.5 assignable to $[TBA_{10}H_2Si_2W_{18}O_{63}]^{2+}$ and $[TBA_9H_4Si_2W_{18}O_{64}]^+$, respectively, thus indicating that dimerization of **I** proceeds (Figure S3 in the Supporting Information). The pale yellow single crystals were obtained by dimerization of **I** in a mixed solvent of dichloromethane and ethyl acetate. The X-ray crystallographic analysis revealed that the product was an α-Dawson-type POM (Table 1; Figure S4a in the Supporting Information). The bond valence sum (BVS) values of tungsten (5.95–6.21) and silicon (3.90 and 3.96) indicate that respective valences are +6 and +4. Six TBA cations per anion could crystallographically be assigned in accord with the elemental analysis data, thus indicating the existence of six TBA cations and two protons per anion (H_2·**II**). The CSI-MS spectrum of H_2·**II** in acetonitrile showed two signal sets at m/z 3149.5 and 6056.5 assignable to $[TBA_8H_2Si_2W_{18}O_{62}]^{2+}$ and $[TBA_7H_2Si_2W_{18}O_{62}]^+$, respectively (Figure S5a in the Supporting Information). The ^{1}H NMR spectrum of H_2·**II** in CD_3CN showed a signal at $\delta = 10.85$ ppm (2H per anion) assignable to hydrogen-bonded protons (Figure S6a in the Supporting Information).[10] The ^{29}Si NMR spectrum showed a signal at $\delta = -79.4$ ppm (Figure S7a in the Supporting Information), and the ^{183}W NMR spectrum showed five signals at $\delta = -118.5$, −134.1, −143.1, −145.0, and −151.8 ppm with the respective ratio of 1:2:2:2:2, thus suggesting that the overall symmetry of the anion is C_{2v} (Figure 2a). These NMR spectroscopic data indicate that two protons in H_2·**II** are located within the aperture without delocalization (H_2·**II** = $TBA_6[\alpha\text{-}H_2Si_2W_{18}O_{62}]\cdot 3H_2O$). The BVS values of bridging oxygen atoms (W-O-W) are 1.92–2.13. In contrast, the BVS values of internal μ_3-oxygen atoms (O19, O47, O20, O48, O21, O49: 1.38–1.71; average: 1.59) and terminal oxygen atoms (W=O; O13–O18, O32–O34, O41–O46, O60–O62: 1.59–1.81; average: 1.70) are lower than those of other oxygen atoms of H_2·**II** (Table S1 in the Supporting Information). The BVS values of internal μ_3-oxygen atoms of H_2·**II** are lower than those of other α-Dawson-type POMs (Table S2 in the Supporting Information; 1.75–2.12), whereas the values of terminal oxygen atoms of H_2·**II** are almost equal to those of other non-protonated α-Dawson-type POMs (Table S3 in the Supporting Information; average 1.67–1.95). Additionally, the distances between μ_3-oxygen atoms (O19···O47, O20···O48, O21···O49) are in the range of 2.72–2.79 Å and shorter than those of other

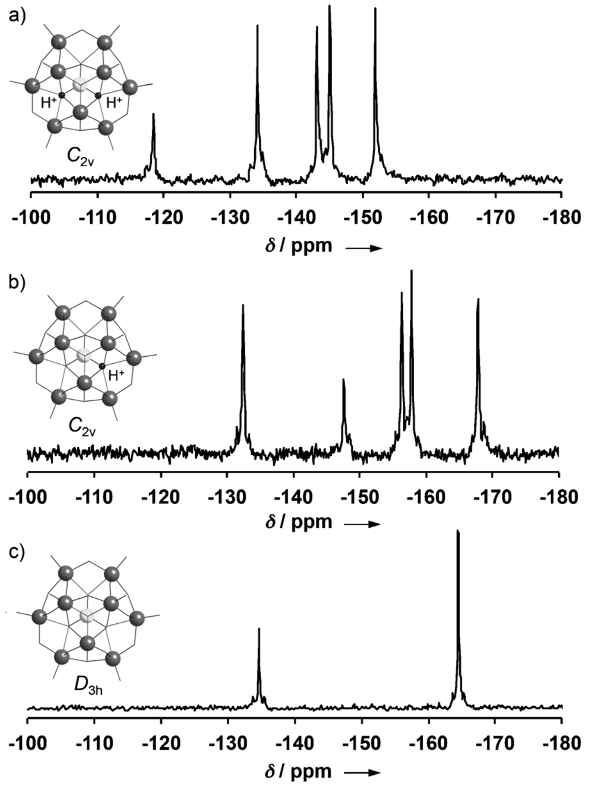


Figure 2. ^{183}W NMR spectra of a) **H_2·II**, b) **H·II**, and c) **II** in CD_3CN. Insets: Top views of a) **H_2·II**, b) **H·II**, and c) **II**, and the atoms are represented by spheres: W, dark gray; Si, light gray; H, black.

α-Dawson-type POMs (W-based POMs, 2.83–3.10 Å; Mo-based POMs, 2.93–3.26 Å; Table S4 in the Supporting Information). These results show that two protons are sandwiched between two pairs of oxygen atoms among the six internal μ_3-oxygen atoms with intramolecular hydrogen bonds.[11]

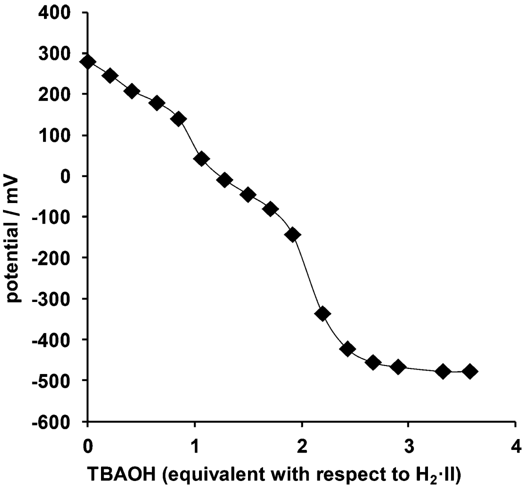


Figure 3. Profiles for the potentiometric titration of **H_2·II** in a mixed solvent of acetonitrile and water (9:1 v/v) with 1 M aqueous TBAOH as titrant. The potentials are relative to a standard Ag/AgCl electrode.

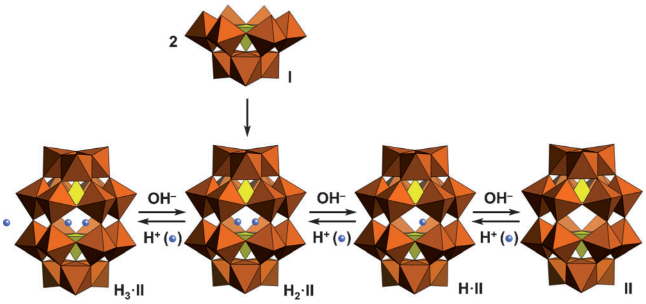


Figure 4. Schematic representation of condensation of **I** and reversible extraction and insertion of protons. The atoms are represented by polyhedrals and spheres: W, orange; Si, yellow; H, blue.

Reversible protonation and deprotonation inside the aperture of α-Dawson-type silicotungstates

The potentiometric titration of **H_2·II** with TBAOH showed inflection points at 1 and 2 equivalents of TBAOH with respect to **H_2·II** (Figure 3). Singly protonated **H·II** (TBA_7[α-$HSi_2W_{18}O_{62}$]·H_2O) was formed by the addition of 1 equivalent of TBAOH to the solution of **H_2·II** in acetonitrile and was characterized by CSI-MS and ^{1}H, ^{29}Si, and ^{183}W NMR spectra (Figures S5b, S6b, and S7b in the Supporting Information; Figures 2b and 4). Upon further addition of 1 equivalent of TBAOH to the solution of **H·II** in CD_3CN, the ^{1}H NMR spectrum showed no signal assignable to a hydrogen-bonded proton (Figure S6c in the Supporting Information). The product (**II**) was precipitated by the addition of diethyl ether to the solution. The ^{183}W NMR spectrum showed two signals at $\delta = -134.6$ and -164.6 ppm with the respective ratio of 1:2 (Figure 2c), thereby suggesting that the overall symmetry of the anion is D_{3h} and that the proton is released from **H·II** (**II** = TBA_8[α-$Si_2W_{18}O_{62}$]·3 H_2O).[12]

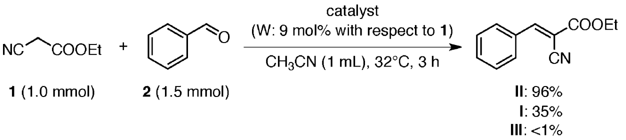
A proton-free **II** can capture two protons within the aperture. Upon addition of 2 equivalents of nitric acid to the solution of **II** in CD_3CN, the ^{29}Si and ^{183}W NMR spectra showed the same signals as those of **H_2·II** (Table 2). The ^{1}H signals of **H_2·II** and **H·II** were observed at much lower fields than those of the previously reported POMs that contain protons inside their structures ($\delta = 2.1$–8.1 ppm), thus indicating the stronger hydrogen bonds of **H_2·II** and **H·II** (Table S5 in the Supporting Information).[13] Proton sponges are a class of compounds with unusually high basicity and can capture protons through strong intramolecular hydrogen bonds.[14] Upon addition of the proton sponge (1,8-bis(dimethylamino)naphthalene (DMAN)) to the solution of **H·II** in CD_3CN (20 equivalents with respect to **H·II**), the signal intensity of **H·II** did not change and no signal of $DMANH^+$ ($\delta = 8.02$, 7.88, 7.67, and 3.04 ppm) was observed (Figure S8 in the Supporting Information). These results suggest that **II** is more basic than DMAN and the pK_a value of the conjugated acid of **II** is higher than that of $DMANH^+$ (18.18 in acetonitrile).[15] The Knoevenagel condensation of ethyl cyanoacetate with benzaldehyde in the presence of **II** efficiently proceeded to give ethyl *trans*-α-cyanocinnamate in 96% yield. The yield of ethyl *trans*-α-cyanocinnamate was about three times higher than that with **I** [Eq. (1)]. The reaction rate of **II** (1.1×10^4 mM min^{-1}) was approximately 2000 times higher than that of **I** (5.6 mM min^{-1}). In addition, the reaction did not pro-

Table 2. Chemical shifts [ppm] of **I**, **II**, **H·II**, **H_2·II**, **H_3·II**, **III**, and **H·III** in CD_3CN.[a]

	^{1}H	^{29}Si	^{183}W
I[b]	–[c]	−83.17	−151.3(1), −169.9(1), −190.7(1)
II	–[d]	−87.97	−134.6(1), −164.6(2)
H·II	10.35 (1 H)	−83.49	−132.4(2), −147.6(1), −156.3(2), −157.8(2), −167.8(2)
H·II[b]	10.27 (1 H)	−83.61	–[c]
H_2·II	10.85 (2 H)	−79.44	−118.5(1), −134.1(2), −143.1(2), −145.0(2), −151.8(2)
H_2·II[b]	10.76 (2 H)	−78.99	–[c]
II + 2 HNO_3	10.85 (2 H)	−79.61	−120.2(1), −135.9(2), −144.8(2), −147.6(2), −153.3(2)
H_3·II[b]	10.75 (2 H)	−79.13	−120.3(1), −136.1(2), −144.1(2), −145.7(2), −152.9(2)
II + 3 HNO_3	–[c]	−79.48	−120.0(1), −135.7(2), −144.6(2), −147.6(2), −152.9(2)
	^{1}H	^{31}P	^{183}W
III	–[d]	−12.50	−113.6(1), −157.7(2)
III[b]	–[c]	−12.35	−115.5(1), −158.6(2)
H·III[b]	–[d]	−12.33	−113.9(1), −156.9(2)
III + HNO_3	–[d]	−12.40	–[c]

[a] The numbers in parentheses are integrated intensity ratios. [b] Chemical shifts in [D_6]DMSO (**H_3·II** and **H·III** are insoluble in acetonitrile). [c] The spectra were not measured. [d] No signal assignable to a hydrogen-bonded proton was observed.

ceed in the presence of **III**. These results support the stronger basicity of **II**.



(1)

Upon further addition of 1 equivalent of nitric acid or trifluoromethanesulfonic acid to the solution of **H_2·II** in acetonitrile, the CSI-MS and ^{29}Si and ^{183}W NMR spectra did not change and no crystal was obtained (Table 2). In contrast, upon addition of 1 equivalent of perchloric acid to the solution of **H_2·II** in acetonitrile, pale yellow single crystals were obtained. Five TBA cations per anion could crystallographically be assigned in accord with the elemental analysis data, thus indicating that five TBA and three protons are contained in the anion (**H_3·II**) (Table 1; Table S6 and Figure S4b in the Supporting Information). The ^{1}H and ^{29}Si NMR spectra of **H_3·II** in [D_6]DMSO showed almost the same signals as those of **H_2·II** in [D_6]DMSO (Table 2). The ^{183}W NMR spectrum of **H_3·II** showed five signals with the respective ratio of 1:2:2:2:2, thereby suggesting that the overall symmetry of the anion is C_{2v} and the same as that of **H_2·II** (Figure S9 in the Supporting Information). These data indicate that two of three protons are located within the aperture and the other one is delocalized on the surface of the anion, which shows that **II** can capture up to two protons (Figure 4).

Finally, we examined protonation of **II** in the presence of various metal cations. Upon the addition of a mixture of 1 equivalent of $Co(OAc)_2$, $Zn(acac)_2$, LiOTf, NaOTf, AgOTf, $Pb(OTf)_2$, KOTf (OTf = trifluoromethane sulfonate, acac = acetylacetonate), and nitric acid to the solution of **II** in [D_6]DMSO, the ^{1}H NMR spectrum showed a signal at $\delta = 10.22$ ppm assignable to the hydrogen-bonded proton of H·II (Figure S10a in the Supporting Information). The ^{29}Si NMR spectrum of the solution showed a signal at $\delta = -83.4$ ppm assignable to **H·II**, thus indicating that **II** is protonated upon coexistence of various metal cations with protons (Figure S10b in the Supporting Information). These results are in sharp contrast with the selective metal encapsulation within a closed dimer $TBA_8[Si_2W_{20}O_{68}]$.[4g] The distances between three pairs of six internal μ_3-oxygen atoms of the Si-O-W bonding of **II** (2.73–2.79 Å) were significantly shorter than those of $TBA_8[Si_2W_{20}O_{68}]$ (3.98 Å). In addition, the entrance of the aperture of **II** (height: 3.07–3.08 Å; width: 4.27–4.30 Å) was also smaller than that of $TBA_8[Si_2W_{20}O_{68}]$ (height: 3.89–3.90 Å; width: 3.98–5.14 Å). These results indicate that the aperture of **II** is too small to capture the metal cations, and only protonation proceeds.

DFT calculations supported the protonation behavior. In contrast to the orbitals on the internal μ_3-oxygen atoms of HOMOs of **II** and **H·II**, those of **H·II** and **III** possessed orbitals only on the surface oxygen atoms. Additionally, the energies of HOMOs decreased with increase in the anion charges (**II** > **H·II** > **H_2·II**, **III**) and basicities decrease in this order (Figure S2 in the Supporting Information). These results support that only the aperture of **II** and **H·II** can be protonated.

Conclusion

In conclusion, α-Dawson-type silicotungstates $TBA_6[\alpha\text{-}H_2Si_2W_{18}O_{62}]\cdot3H_2O$ (**H_2·II**), $TBA_7[\alpha\text{-}HSi_2W_{18}O_{62}]\cdot H_2O$ (**H·II**), and $TBA_8[\alpha\text{-}Si_2W_{18}O_{62}]\cdot3H_2O$ (**II**) were successfully synthesized by dimerization of a trivacant lacunary α-Keggin-type silicotungstate $TBA_4H_6[\alpha\text{-}SiW_9O_{34}]\cdot2H_2O$ (**I**) in an organic solvent under mild conditions. Silicon-centered **II** that possessed a −8 charge could reversibly be protonated (in the presence of acid) and deprotonated (in the presence of base) inside the aperture through intramolecular hydrogen bonds with the retention of the POM structure.

Experimental Section

General methods

IR spectra were measured using a JASCO FT/IR-460 instrument using KBr disks. UV/Vis spectra were measured by using a JASCO V-570DS instrument. CSI-MS spectra were recorded using a JEOL JMS-T100CS instrument. NMR spectra were recorded using a JEOL JNM EX-270 or JMN ECA-500 spectrometer (^{1}H, 269.60 or 495.13 MHz; ^{29}Si, 53.45 or 98.37 MHz; ^{31}P, 109.05 MHz; ^{183}W, 11.20 or 20.84 MHz) by using 5 mm (for ^{1}H and ^{29}Si (98.37 MHz)) or 10 mm (for ^{29}Si (53.45 MHz), ^{31}P, and ^{183}W) tubes. Chemical shifts (δ) were reported in parts per million (ppm) downfield from $SiMe_4$ (solvent, $CDCl_3$) for ^{1}H and upfield for ^{29}Si NMR spectra, H_3PO_4 (solvent, D_2O) for ^{31}P NMR spectra, and 1 M Na_2WO_4 (solvent, D_2O) for ^{183}W NMR spectra. GC analyses were performed by using a Shimadzu GC-2014 instrument with a flame ionization detector equipped with an RTX-1 capillary column (internal diameter = 0.25 mm; length = 30 m). Mass spectra were recorded using a Shimadzu GCMS-QP2010 equipped with a TC-5HT capillary column at an ionization voltage of 70 eV. Thermogravimetric and differential thermal analyses (TG-DTA) were performed by using a Rigaku Thermo Plus TG 8120. Inductively coupled plasma (ICP) atomic emission spectroscopy (AES) analyses were performed by using a Shimadzu ICPS-8100 instrument. Elemental analyses for C, H, and N were performed by using a Yanaco MT-6 at the Elemental Analysis Center of School of Science of the University of Tokyo. Acetonitrile (Kanto Chemical) was purified by The Ultimate Solvent System (Glass Contour Company) prior to use.[16] Substrates and other solvents were purified according to the reported procedures.[17] $Na_2WO_4{\cdot}2\,H_2O$ (Nippon Inorganic Colour and Chemical), $Na_2SiO_3{\cdot}9\,H_2O$ (Wako Chemical), Na_2CO_3 (Nacalai Tesque), NaCl (Kanto Chemical), tetra-*n*-butylammonium bromide (TCI), tetra-*n*-butylammonium hydroxide (37 % methanol solution) (TCI), nitric acid (Kanto Chemical), acetic acid (Kanto Chemical), sodium acetate (Kanto Chemical), phosphoric acid (Kanto Chemical), trifluoromethanesulfonic acid (TCI), perchloric acid (Wako Chemical), $Fe(OTf)_2$ (Wako Chemical), $Co(OAc)_2{\cdot}4\,H_2O$ (Wako Chemical), $Ni(acac)_2{\cdot}2\,H_2O$ (Kanto Chemical), $Cu(OTf)_2$ (TCI), $Zn(acac)_2$ (Kanto Chemical), LiOTf (TCI), NaOTf (TCI), Agacac (Aldrich), KOTf (Kanto Chemical), Br_2 (Kanto Chemical), NH_4Cl (Kanto Chemical), KCl (Nacalai Tesque), TBACl (TCI), $PbCl_2$ (Kanto Chemical), AgOTf (Aldrich), $CaCl_2$ (Kanto Chemical), naphthalene (Wako Chemical), and deuterated solvents (CD_3CN and $[D_6]$DMSO) (ACROS) were used as received. $Na_{10}[\alpha\text{-}SiW_9O_{34}]$ was synthesized according to the reported procedures.[6]

X-ray crystallography

Diffraction measurements were carried out by using a Rigaku MicroMax-007 Saturn 724 charge-coupled device (CCD) detector with graphic-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) at 153 or 123 K. The data were collected and processed using CrystalClear software[18] for Windows and HKL2000[19] for Linux. Neutral scattering factors were obtained from the standard source. In the reduction of data, Lorentz and polarization corrections were made. The structural analyses were performed by using CrystalStructure,[20] WinGX,[21] and Yadokari-XG.[22] All structures were solved by SHELXS-97 (direct methods) and refined by SHELXH-97.[23] The metal atoms (Si, P, and W) and oxygen atoms in the POM frameworks were refined anisotropically.

CCDC-974406 ($\mathbf{H_2{\cdot}II}$), -974407 ($\mathbf{H_3{\cdot}II}$), and -974408 ($\mathbf{H{\cdot}III}$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Quantum chemical calculations

The calculations were performed with Gaussian 09 software.[24] Anionic parts of $\mathbf{H_2{\cdot}II}$, **H·II**, **II**, and **III** were optimized at the B3LYP level of theory[25] with 6-31++G** (for H and O), 6-31G** (for Si and P), and LanL2DZ (for W)[26] by using the conductor-like polarizable continuum model (CPCM)[27] with the parameters of the United Atom Topological Model (UAHF) for acetonitrile.

Experimental details for addition of acids to $TBA_6[\alpha\text{-}P_2W_{18}O_{62}]{\cdot}H_2O$ (III)

Upon addition of 1 equivalent of nitric acid or trifluoromethanesulfonic acid with respect to $TBA_6[\alpha\text{-}P_2W_{18}O_{62}]{\cdot}H_2O$ (**III**) in acetonitrile, the CSI-MS spectrum showed only two signal sets assignable to $[TBA_8P_2W_{18}O_{62}]^{2+}$ (*m/z* 3151.4) and $[TBA_7P_2W_{18}O_{62}]^{+}$ (*m/z* 6060.3). The ^{31}P NMR spectrum of the resulting solution in CD_3CN showed a signal at $\delta = -12.40$ ppm, and the chemical shift was the same as that ($\delta = -12.50$ ppm) of **III** (Table 2). No ^{1}H signal assignable to a hydrogen-bonded proton was observed in the range of $\delta = 10$–11 ppm. The pale yellow single crystals (**H·III**) were obtained by addition of 1 equivalent of perchloric acid with respect to **III** to the solution of **III** in acetonitrile. Five TBA cations per anion could crystallographically be assigned in accord with the result of elemental analysis, thus indicating the existence of five TBA cations and one proton per anion (Table 1; Table S6 and Figure S4c in the Supporting Information). The ^{31}P NMR spectrum of **H·III** in $[D_6]$DMSO showed a signal at $\delta = -12.33$ ppm, and the chemical shift was the same as that ($\delta = -12.35$ ppm) of **III** (Table 2; Figure S11a in the Supporting Information). The ^{183}W NMR spectrum showed two signals at $\delta = -113.9$ and -156.9 ppm with the respective ratio of 1:2 (Figure S11b in the Supporting Information), thus suggesting that the overall symmetry of the anion is D_{3h}. The ^{1}H NMR spectrum of **H·III** in $[D_6]$DMSO showed no signal assignable to a hydrogen-bonded proton in the range of $\delta = 10$–11 ppm (Figure S11c in the Supporting Information). These NMR spectroscopic data indicated that **III** cannot be protonated inside the aperture and the proton was delocalized on the surface of the anion ($\mathbf{H{\cdot}III} = TBA_5H[\alpha\text{-}P_2W_{18}O_{62}]{\cdot}H_2O$).

Synthesis and characterization of $[(n\text{-}C_4H_9)_4N]_4H_6[\alpha\text{-}SiW_9O_{34}]{\cdot}2\,H_2O$ (I)

$Na_{10}[\alpha\text{-}SiW_9O_{34}]{\cdot}3\,H_2O$ (20.0 g, 7.97 mmol) was dissolved in acetate buffer solution kept at 3 °C (300 mL, 1 M, pH 3.70), and TBABr (100 g, 0.310 mol) was added. After vigorous stirring for 2 min, the white precipitate formed was isolated by filtration and washed with water (10 °C, 1 L) (7.01 g, 28 % yield). ^{29}Si NMR (53.45 MHz, $[D_6]$DMSO, 298 K, $SiMe_4$): $\delta = -83.17$ ppm ($\Delta\nu_{1/2} = 3.4$ Hz); ^{183}W NMR (11.20 MHz, $[D_6]$DMSO, 298 K, Na_2WO_4): $\delta = -153.1$ ($\Delta\nu_{1/2} = 22.3$ Hz), -169.9 ($\Delta\nu_{1/2} = 32.3$ Hz), -190.7 ppm ($\Delta\nu_{1/2} = 21.5$ Hz) with the respective integrated intensity ratio of 1:1:1; IR (KBr pellet): $\tilde{\nu} = 2961$, 2873, 1634, 1485, 1470, 1381, 1347, 1153, 1106, 1065, 1004, 952, 901, 819, 738, 565, 515, 454, 376, 361, 352, 337, 287, 257, 251 cm^{-1}; MS^{+} (CSI, DMSO): *m/z*: calcd: 3390.9; found: 3390.9 $[TBA_5SiW_9O_{31}]^{+}$; MS^{+} (CSI, dichloromethane): *m/z*: calcd: 3400.0; found: 3400.0 $[TBA_{10}H_2Si_2W_{18}O_{63}]^{2+}$; calcd: 6575.5; found: 6575.5 $[TBA_9H_4Si_2W_{18}O_{64}]^{+}$; elemental analysis calcd (%) for $TBA_4H_6[SiW_9O_{34}]{\cdot}2\,H_2O$ ($C_{64}H_{154}N_4O_{36}SiW_9$): C 23.74, H 4.79, N 1.73, Si 0.87, W 51.09; found: C 23.42, H 4.75, N 1.67, Si 0.89, W 51.05.

Synthesis and characterization of $[(n\text{-}C_4H_9)_4N]_6[\alpha\text{-}H_2Si_2W_{18}O_{62}]{\cdot}3\,H_2O$ ($H_2{\cdot}II$)

Ethyl acetate (4 mL) was added to a solution of **I** (186 mg, 57.4 μmol) in dichloromethane (12 mL). The pale yellow single crystals of $\mathbf{H_2{\cdot}II}$ suitable for X-ray crystallographic analysis were obtained (47.0 mg, 28 % yield). ^{1}H NMR (269.60 MHz, CD_3CN, 298 K, $SiMe_4$): $\delta = 10.85$ (2 H), 3.15 (m, 48 H), 1.64 (m, 48 H), 1.41 (m, 48 H), 0.98 ppm (t, 72 H); ^{1}H NMR (269.60 MHz, $[D_6]$DMSO, 298 K, $SiMe_4$): $\delta = 10.76$ (s, 2 H), 3.18 (m, 48 H), 1.58 (m, 48 H), 1.33 (m, 48 H), 0.94 ppm (t, 72 H); ^{29}Si NMR (53.45 MHz, CD_3CN, 298 K, $SiMe_4$): $\delta = -79.44$ ppm ($\Delta\nu_{1/2} = 2.1$ Hz); ^{29}Si NMR (98.37 MHz, $[D_6]$DMSO, 298 K, $SiMe_4$): $\delta = -78.99$ ppm ($\Delta\nu_{1/2} = 8.7$ Hz); ^{183}W NMR (11.20 MHz, CD_3CN, 298 K, Na_2WO_4): $\delta = -118.5$ ($\Delta\nu_{1/2} = 2.7$ Hz), -134.1 ($\Delta\nu_{1/2} = 2.8$ Hz), -143.1 ($\Delta\nu_{1/2} = 2.7$ Hz), -145.0 ($\Delta\nu_{1/2} = 3.0$ Hz), -151.8 ppm ($\Delta\nu_{1/2} = 3.0$ Hz) with the respective integrated intensity ratio of 1:2:2:2:2; IR (KBr pellet): $\tilde{\nu} = 2961$, 2933, 2872, 1735, 1631, 1483, 1382, 1267, 1230, 1153, 1031, 1007, 957, 936, 915, 899, 799, 770, 533, 513, 484, 446, 420, 379, 328, 303, 294, 253 cm^{-1}; UV/Vis (acetonitrile): λ (ε) = 369 (2.07×10^{3}), 285 (4.42×10^{4}), 242 nm (6.10×10^{4} M^{-1} cm^{-1}); MS^{+} (CSI, acetonitrile): *m/z*: calcd: 3149.5; found: 3149.5 $[TBA_8H_2Si_2W_{18}O_{62}]^{2+}$; calcd: 6056.5; found: 6056.5 $[TBA_7H_2Si_2W_{18}O_{62}]^{+}$; elemental analysis calcd (%) for $TBA_6[H_2Si_2W_{18}O_{62}]{\cdot}3\,H_2O$ ($C_{96}H_{224}N_6O_{65}Si_2W_{18}$): C 19.65, H 3.85, N 1.43, Si 0.96, W 56.39; found: C 19.63, H 3.84, N 1.44, Si 0.95, W 56.35.

Synthesis and characterization of $[(n\text{-}C_4H_9)_4N]_7[\alpha\text{-}HSi_2W_{18}O_{62}]\cdot H_2O$ (H·II)

TBAOH (37% methanol solution, 0.6 μL, 2 μmol, 1 equivalent with respect to **H_2·II**) was added to a solution (1 mL) of **H_2·II** (50.0 mg, 8.60 μmol) in acetonitrile. Diethyl ether (10 mL) was added to the solution and a white precipitate formed and was isolated by filtration and washed with diethyl ether (2 mL) (32.2 mg, 62% yield). ^{1}H NMR (269.60 MHz, CD_3CN, 298 K, $SiMe_4$): $\delta = 10.35$ (1 H), 3.18 (m, 56 H), 1.65 (m, 56 H), 1.41 (m, 56 H), 0.98 ppm (t, 84 H); ^{1}H NMR (495.13 MHz, [D$_6$]DMSO, 298 K, $SiMe_4$): $\delta = 10.27$ (1 H), 3.15 (m, 56 H), 1.55 (m, 56 H), 1.30 (m, 56 H), 0.90 ppm (t, 84 H); ^{29}Si NMR (53.45 MHz, CD_3CN, 298 K, $SiMe_4$): $\delta = -83.49$ ppm ($\Delta\nu_{1/2} = 2.8$ Hz); ^{29}Si NMR (98.37 MHz, [D$_6$]DMSO, 298 K, $SiMe_4$): $\delta = -83.61$ ppm ($\Delta\nu_{1/2} = 2.4$ Hz); ^{183}W NMR (11.20 MHz, CD_3CN, 298 K, Na_2WO_4): $\delta = -132.4$ ($\Delta\nu_{1/2} = 3.2$ Hz), -147.6 ($\Delta\nu_{1/2} = 3.3$ Hz), -156.3 ($\Delta\nu_{1/2} = 2.9$ Hz), -157.8 ($\Delta\nu_{1/2} = 3.3$ Hz), -167.8 ppm ($\Delta\nu_{1/2} = 3.2$ Hz) with the respective integrated intensity ratio of 2:1:2:2:2; IR (KBr pellet): $\tilde{\nu} = 2961$, 2933, 2871, 1636, 1483, 1384, 1254, 1152, 1120, 1034, 1013, 946, 915, 899, 843, 795, 768, 556, 529, 452, 421, 383, 331, 295, 288, 253 cm^{-1}; MS$^+$ (CSI, acetonitrile): *m/z*: calcd: 3270.2; found: 3270.2 $[TBA_9HSi_2W_{18}O_{62}]^{2+}$; calcd: 6298.0; found: 6298.0 $[TBA_8HSi_2W_{18}O_{62}]^+$; elemental analysis calcd (%) for $TBA_7[HSi_2W_{18}O_{62}]\cdot H_2O$ ($C_{112}H_{255}N_7O_{63}Si_2W_{18}$): C 22.15, H 4.23, N 1.61, Si 0.92, W 54.48; found: C 22.52, H 4.62, N 1.57, Si 0.91, W 54.42.

Synthesis and characterization of $[(n\text{-}C_4H_9)_4N]_8[\alpha\text{-}Si_2W_{18}O_{62}]\cdot 3H_2O$ (II)

TBAOH (37% methanol solution, 75 μL, 5.5×10^2 μmol, 2 equivalents with respect to **H_2·II**) was added to a solution (2 mL) of **H_2·II** (1.60 g, 275 μmol) in acetonitrile. Diethyl ether (400 mL) was added to the solution and a white precipitate formed and was isolated by filtration and washed with diethyl ether (10 mL) (1.49 g, 93% yield). ^{1}H NMR (269.60 MHz, CD_3CN, 298 K, $SiMe_4$): $\delta = 3.15$ (m, 64 H), 1.64 (m, 64 H), 1.40 (m, 64 H), 0.98 ppm (t, 96 H); ^{29}Si NMR (53.45 MHz, CD_3CN, 298 K, $SiMe_4$): $\delta = -87.97$ ppm ($\Delta\nu_{1/2} = 1.6$ Hz); ^{183}W NMR (11.20 MHz, CD_3CN, 298 K, Na_2WO_4): $\delta = -134.6$ ($\Delta\nu_{1/2} = 2.3$ Hz, ^2J(W-O-W) = 18.6 Hz), -164.6 ppm ($\Delta\nu_{1/2} = 2.3$ Hz, ^2J(W-O-W) = 19.4 Hz) with the respective integrated intensity ratio of 1:2; IR (KBr pellet): $\tilde{\nu} = 2961$, 2932, 2872, 1635, 1484, 1384, 1152, 1107, 1008, 946, 900, 844, 770, 563, 514, 475, 454, 421, 386, 328, 303, 293, 282, 254 cm^{-1}; MS$^+$ (CSI, acetonitrile): *m/z*: calcd: 3390.9; found: 3390.9 $[TBA_{10}Si_2W_{18}O_{62}]^{2+}$; calcd: 6539.4; found: 6539.4 $[TBA_9Si_2W_{18}O_{62}]^+$; elemental analysis calcd (%) for $TBA_8[Si_2W_{18}O_{62}]\cdot 3H_2O$ ($C_{128}H_{293}N_8O_{65}Si_2W_{18}$): C 24.21, H 4.67, N 1.76, Si 0.88, W 52.10; found: C 24.14, H 4.89, N 1.91, Si 0.84, W 52.01.

Synthesis and characterization of $[(n\text{-}C_4H_9)_4N]_5H[\alpha\text{-}H_2Si_2W_{18}O_{62}]\cdot 4H_2O$ (H_3·II)

$HClO_4$ (70% aqueous solution, 25 μL, 172 μmol, 1 equivalent with respect to **H_2·II**) was added to a solution (1.5 mL) of **H_2·II** (1.00 g, 172 μmol) in acetonitrile. The pale yellow single crystals of **H_3·II** suitable for X-ray crystallographic analysis were obtained after 1 d (737 mg, 77% yield). ^{1}H NMR (269.60 MHz, [D$_6$]DMSO, 298 K, $SiMe_4$): $\delta = 10.75$ (s, 2 H), 3.18 (m, 40 H), 1.58 (m, 40 H), 1.33 (m, 40 H), 0.94 ppm (t, 60 H); ^{29}Si NMR (98.37 MHz, [D$_6$]DMSO, 298 K, $SiMe_4$): $\delta = -79.13$ ppm ($\Delta\nu_{1/2} = 7.7$ Hz); ^{183}W NMR (20.84 MHz, [D$_6$]DMSO, 298 K, Na_2WO_4): $\delta = -120.3$ ($\Delta\nu_{1/2} = 11.7$ Hz), -136.1 ($\Delta\nu_{1/2} = 12.4$ Hz), -144.1 ($\Delta\nu_{1/2} = 12.0$ Hz), -145.7 ($\Delta\nu_{1/2} = 12.5$ Hz), -152.9 ppm ($\Delta\nu_{1/2} = 9.8$ Hz) with the respective integrated intensity ratio of 1:2:2:2:2; IR (KBr pellet): $\tilde{\nu} = 2962$, 2933, 2873, 1629, 1483, 1380, 1240, 1152, 1103, 1029, 972, 920, 802, 778, 530, 486, 444, 379, 329, 291, 281, 256 cm^{-1}; MS$^+$ (CSI, acetonitrile): *m/z*: calcd: 3028.8; found: 3028.8 $[TBA_7H_3Si_2W_{18}O_{62}]^{2+}$; calcd: 3149.5; found: 3149.5 $[TBA_8H_2Si_2W_{18}O_{62}]^{2+}$; calcd: 5815.1; found: 5815.1 $[TBA_6H_3Si_2W_{18}O_{62}]^+$; elemental analysis calcd (%) for $TBA_5H[H_2Si_2W_{18}O_{62}]\cdot 4H_2O$ ($C_{80}H_{191}N_5O_{66}Si_2W_{18}$): C 17.02, H 3.41, N 1.24, Si 1.00, W 58.62; found: C 17.27, H 3.74, N 1.04, Si 1.01, W 58.98.

Synthesis and characterization of $[(n\text{-}C_4H_9)_4N]_6[\alpha\text{-}P_2W_{18}O_{62}]\cdot H_2O$ (III)

$TBA_6[\alpha\text{-}P_2W_{18}O_{62}]$ was synthesized according to the reported procedures.[13a,28] Ethyl acetate (3.5 mL) was added to a solution (30 mL) of $TBA_6[\alpha\text{-}P_2W_{18}O_{62}]$ (500 mg, 85.9 μmol) in dichloromethane. The pale yellow single crystals of **III** suitable for X-ray crystallographic analysis were obtained (357.7 mg, 71% yield). ^{1}H NMR (269.60 MHz, CD_3CN, 298 K, $SiMe_4$): $\delta = 3.15$ (m, 48 H), 1.64 (m, 48 H), 1.40 (m, 48 H), 0.98 ppm (t, 72 H); ^{31}P NMR (109.05 MHz, CD_3CN, 298 K, H_3PO_4): $\delta = -12.50$ ppm ($\Delta\nu_{1/2} = 3.4$ Hz); ^{31}P NMR (109.05 MHz, [D$_6$]DMSO, 298 K, H_3PO_4): $\delta = -12.35$ ppm ($\Delta\nu_{1/2} = 2.5$ Hz); ^{183}W NMR (20.84 MHz, CD_3CN, 298 K, Na_2WO_4) $\delta = -113.6$ ($\Delta\nu_{1/2} = 6.4$ Hz), -157.7 ppm ($\Delta\nu_{1/2} = 5.7$ Hz) with the respective integrated intensity ratio of 1:2; ^{183}W NMR (20.84 MHz, [D$_6$]DMSO, 298 K, Na_2WO_4): $\delta = -115.5$ ($\Delta\nu_{1/2} = 19.9$ Hz), -158.6 ppm ($\Delta\nu_{1/2} = 13.3$ Hz) with the respective integrated intensity ratio of 1:2; IR (KBr pellet): $\tilde{\nu} = 2961$, 2933, 2872, 1631, 1483, 1380, 1153, 1090, 1019, 991, 955, 913, 790, 598, 565, 527 cm^{-1}; MS$^+$ (CSI, acetonitrile): *m/z*: calcd: 3151.4; found: 3151.4 $[TBA_8P_2W_{18}O_{62}]^{2+}$; calcd: 6060.3; found: 6060.3 $[TBA_7P_2W_{18}O_{62}]^+$; elemental analysis calcd (%) for $TBA_6[P_2W_{18}O_{62}]\cdot H_2O$ ($C_{96}H_{218}N_6O_{63}P_2W_{18}$): C 19.76, H 3.77, N 1.44; found: C 19.61, H 3.69, N 1.28.

Synthesis and characterization of $[(n\text{-}C_4H_9)_4N]_5H[\alpha\text{-}P_2W_{18}O_{62}]\cdot H_2O$ (H·III)

$HClO_4$ (70% aqueous solution, 33 μL, 447 μmol, 1 equivalent with respect to **III**) was added to a solution (1.5 mL) of **III** (1.30 g, 223 μmol) in acetonitrile. Pale yellow single crystals of **H·III** suitable for X-ray crystallographic analysis were obtained after 1 d (1.10 g, 88% yield). ^{1}H NMR (269.60 MHz, [D$_6$]DMSO, 298 K, $SiMe_4$): $\delta = 3.18$ (m, 40 H), 1.59 (m, 40 H), 1.32 (m, 40 H), 0.95 ppm (t, 60 H); ^{31}P NMR (109.05 MHz, [D$_6$]DMSO, 298 K, H_3PO_4): $\delta = -12.33$ ppm ($\Delta\nu_{1/2} = 3.3$ Hz); ^{183}W NMR (11.20 MHz, [D$_6$]DMSO, 298 K, Na_2WO_4): $\delta = -113.9$ ($\Delta\nu_{1/2} = 10.1$ Hz), -156.9 ppm ($\Delta\nu_{1/2} = 8.0$ Hz) with the respective integrated intensity ratio of 1:2; IR (KBr pellet): $\tilde{\nu} = 2962$, 2933, 2874, 1631, 1483, 1382, 1152, 1091, 1025, 962, 910, 801, 597, 563, 530, 472, 389, 372, 332, 321, 303, 292, 287, 281, 256 cm^{-1}; MS$^+$ (CSI, acetonitrile): *m/z*: calcd: 3030.7; found: 3030.7 $[TBA_7HP_2W_{18}O_{62}]^{2+}$; calcd: 3151.4; found: 3151.4 $[TBA_8P_2W_{18}O_{62}]^{2+}$; calcd: 6060.3; found: 6060.3 $[TBA_7P_2W_{18}O_{62}]^+$; elemental analysis calcd (%) for $TBA_5H[P_2W_{18}O_{62}]\cdot H_2O$ ($C_{80}H_{183}N_5O_{63}P_2W_{18}$): C 17.18, H 3.30, N 1.25; found: C 17.08, H 3.34, N 1.22.

Procedure for catalytic Knoevenagel condensation

Catalytic reactions were carried out with a glass tube (15 mL) containing a magnetic stir bar. The procedure for the catalytic reaction was as follows: ethyl cyanoacetate (**1**, 1.0 mmol), benzaldehyde (**2**, 1.5 mmol), acetonitrile (1 mL), and internal standard (naphthalene, ≈0.2 mmol) were charged in the reaction vessel. The reaction was initiated by the addition of **II** (5 μmol), **I** (10 μmol), or **III** (5 μmol) and the reaction solution was periodically analyzed by GC and GC-MS.

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