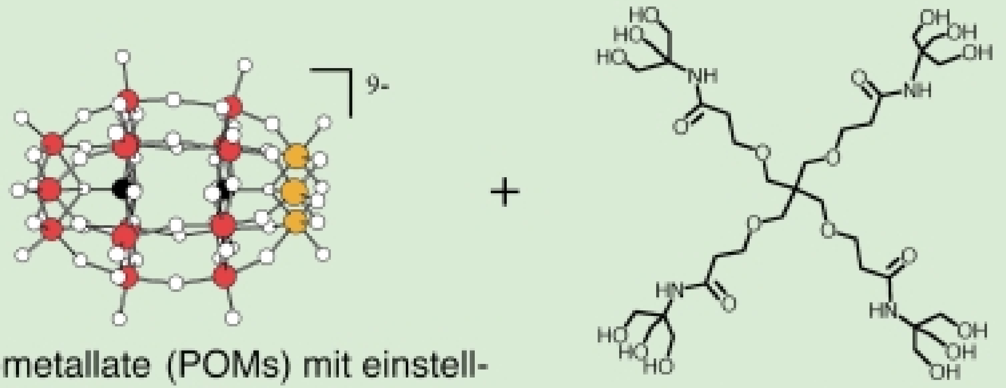
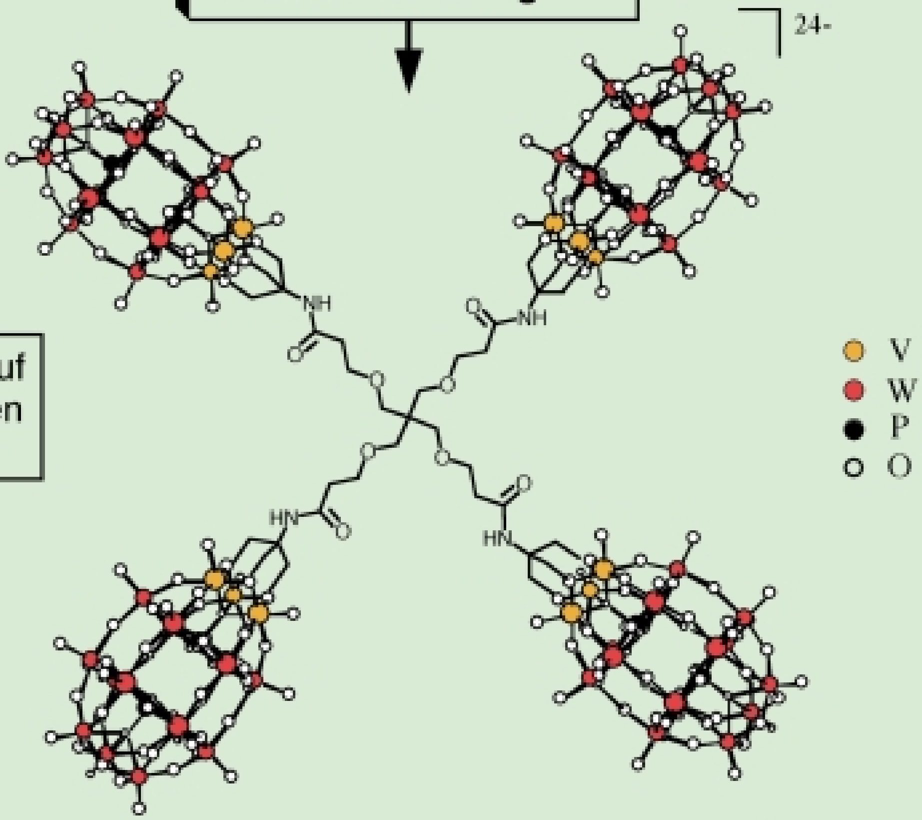
# Dendrimere mit katalytischen Polyoxometallaten als peripheren Substituenten



Polyoxometallate (POMs) mit einstellbaren katalytischen Eigenschaften

hydroxylierte Dendrimere

**Die einstufige, effiziente POM-Veresterung…**



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**…liefert Materialien, die die Vorteile von POMs und Dendrimeren vereinen.**

# Poly(polyoxometalate) Dendrimers: Molecular Prototypes of New Catalytic Materials**

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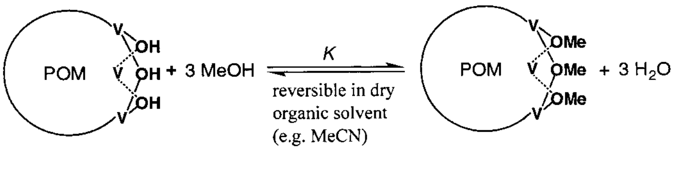
Craig L. Hill*

Metallodendrimers composed of tunable catalytic components could offer the selectivity advantages of homogeneous catalysts coupled with the recoverability and increased durability of heterogeneous catalysts. A variety of metal centers have been incorporated into dendritic structures,[1] but few of the resulting metallodendrimers have been effective catalysts and none have been catalysts for environmentally benign transformations, such as oxidations by peroxides.[2] The goal of this study was to assess the feasibility of incorporating redox-active polyoxometalates (POMs), a versatile class of homogeneous catalysts for oxidations and other reactions,[3] into polyhydroxylated polymers that include cotton, other cellulosics, and mass-produced polymers, such as polyvinyl alcohol. The few reports of POMs covalently incorporated in polymers do not involve POMs that possess either marked redox properties or demonstrable catalytic chemistry.[4] Herein we report the esterification of a representative redox and catalytically active POM, $[H_4P_2V_3W_{15}O_{62}]^{5-}$, first with MeOH (the sequential formation of the mono-, di-, and trimethyl esters is quantified) and then with two simple dendrimers each with four tris(hydroxymethyl) termini. These triol groups provide a useful handle for NMR spectroscopy, simulate the polyol surfaces of cellulosic materials, and are documented as structural components in POMs.[5, 6] The resulting tetra(POM) molecules are hydrolytically stable, catalyze peroxide oxidations, and represent the initial examples of a potentially very large class of new POM-containing catalytic materials.

The reaction of MeOH with $(n\mathrm{Bu_4N})_5[H_4P_2V_3W_{15}O_{62}]$ in dry organic polar aprotic solvents (for example, MeCN, dimethylacetamide (DMA), DMSO) results in replacement of the oxygen atoms bridging the vanadium atoms in the $V_3$ "cap" of this POM with methoxy groups, which are effectively methyl esters [Eq. (1)]. The hydrogen atoms of the POMs in this study most likely reside on the oxygen atoms bridging the vanadium atoms.[7]



(1)

Figure 1 illustrates the presence of the terminal $V_3$ unit and the mixture of mono-, di-, and trimethyl esters that form by the reaction of $[H_4P_2V_3W_{15}O_{62}]^{5-}$ with 4.2 equivalents of MeOH. These ester mixtures all exhibit single baseline-resolved peaks in both the $^1H$ and $^{31}P$ NMR spectra. Changes in both the $^1H$ and $^{31}P$ NMR spectra with time indicate that the monomethyl ester forms first, followed by the diester, and then the triester, all at the expense of the parent $[H_4P_2V_3W_{15}O_{62}]^{5-}$ ion, and that the same product distribution results starting with either the parent POM and MeOH or the independently prepared trimethyl POM, $[H(CH_3O)_3P_2V_3W_{15}O_{59}]^{5-}$, and three equivalents of $H_2O$. The esterification equilibrium is reached after approximately 48 h, and the reactions are highly selective (the only methyl groups detectable are those of the esters and MeOH and the only POM units detectable are those of the parent POM and the three esters). The equilibrium constants for Equations (2)–(4) ($K_1$, $K_2$, $K_3$ in $CD_3CN$, 20°C) evaluated by both $^1H$ and $^{31}P$ NMR are $2.0 \pm 0.2$, $1.3 \pm 0.2$, and $0.37 \pm 0.08$, respectively.

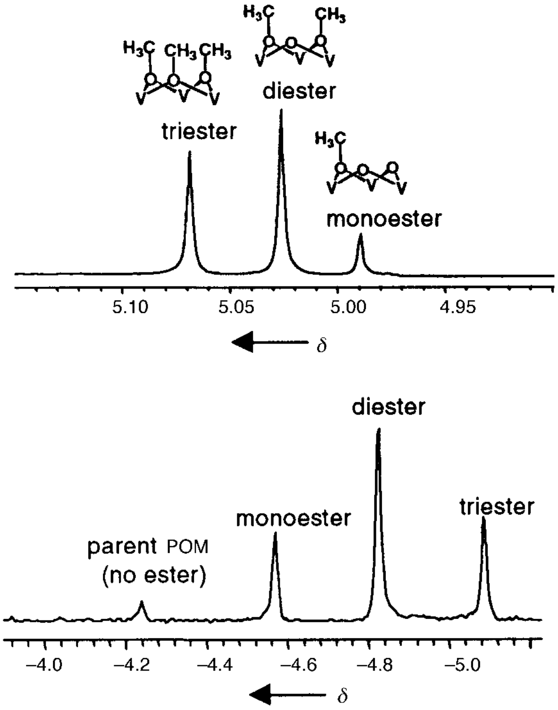


Figure 1. $^1H$ (top) and $^{31}P$ (bottom) NMR spectra of an equilibrated $CD_3CN$ solution of MeOH and $[H_4P_2V_3W_{15}O_{62}]^{5-}$ (20 °C, after 120 h). Only the resonances of the P atom proximal to the $V_3$ unit in these compounds are shown for clarity.

$$[H_4P_2V_3W_{15}O_{62}]^{5-} + CH_3OH \overset{K_1}{\rightleftharpoons} [H_3(CH_3O)P_2V_3W_{15}O_{61}]^{5-} + H_2O \quad (2)$$

$$[H_3(CH_3O)P_2V_3W_{15}O_{61}]^{5-} + CH_3OH \overset{K_2}{\rightleftharpoons} [H_2(CH_3O)_2P_2V_3W_{15}O_{60}]^{5-} + H_2O \quad (3)$$

$$[H_2(CH_3O)_2P_2V_3W_{15}O_{60}]^{5-} + CH_3OH \overset{K_3}{\rightleftharpoons} [H(CH_3O)_3P_2V_3W_{15}O_{59}]^{5-} + H_2O \quad (4)$$

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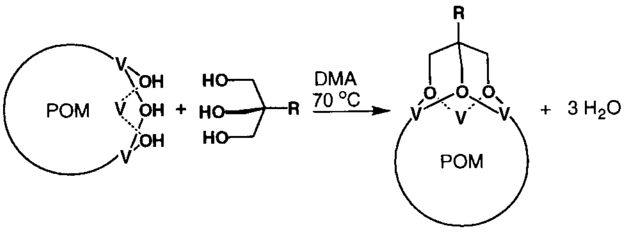
By analogy with Equations (1)–(4), simple representative dendrimers each bearing four tris(hydroxymethyl) groups react with four equivalents of $[H_4P_2V_3W_{15}O_{62}]^{5-}$ in dry polar aprotic organic solvents to form the corresponding tetra(POM) molecules (**1** and **2** in Figure 2). A kinetic product mixture of triester linkages (the product in Equation (5)) plus diester/free-$CH_2OH$ linkages forms initially. The fully $H^+$-exchanged forms of **1** and **2** (H-**1** and H-**2**) can be prepared, and both the ion-exchange process ($Bu_4N^+$ by $H^+$) and heating (<100°C) cause the diester/free-$CH_2OH$ linkages to rearrange to the thermodynamically more stable triester linkages. However, while **1** and **2** are pure by elemental analysis, NMR spectroscopy shows that some diester/free-$CH_2OH$ linkages remain (<5%) even after ion exchange and heating. No monoesters are observed, but this is consistent with the apparent thermodynamic control operable in this system and the clear order of relative stabilities (triester > diester/free-$CH_2OH$ > monoester). Unlike the nonchelating methyl esters (for example, Equations (2)–(4)), these chelating triesters are so stable to hydrolysis that the corresponding equilibrium constants for hydrolysis could not be assessed experimentally as noted (NMR) by the lack of evidence even after heating in 40/60 $D_2O$/[$D_6$]DMSO at 80°C for two days.



(5)

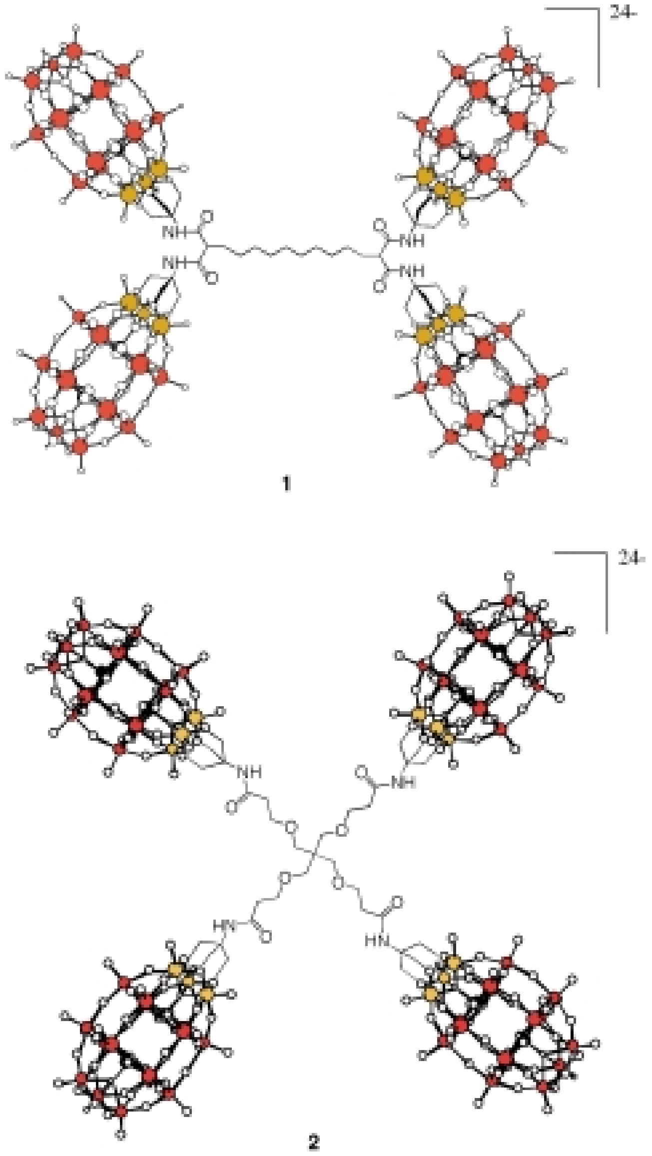


Figure 2. Representative structures of two dendritric tetra(POM) molecules (**1** and **2**). Each has a charge of 24 – countered by 24 cations that are not shown for clarity. The V, W, P, and O atoms are colored orange-yellow, red, black, and white (open circles), respectively.

Both **1** and H-**1**, a representative mixed ($nBu_4N^+/H^+$) and $H^+$ salt, respectively, of these POM ester-bearing molecules, catalyze the oxidation of the thioether tetrahydrothiophene (THT) by both *t*BuOOH and $H_2O_2$. Figure 3 shows the time course of exemplary *t*BuOOH oxidations and control reactions. The order of catalytic reactivity is H-**1** > **1** + $p$-$C_7H_7SO_3H$ (a strong MeCN-soluble Brønsted acid) > $p$-$C_7H_7SO_3H$ alone > **1** ($Bu_4N^+$ salt) alone ≫ no catalyst. Both calculated and measured pH values indicate that $p$-$C_7H_7SO_3H$ is a stronger acid than H-**1**. Two points are clear: the reaction is catalyzed by strong acids, and the POM imparts considerable activity in addition to its acidity (H-**1** > **1** + $p$-$C_7H_7SO_3H$ and **1** alone ≫ no catalyst). Significantly, these catalysts (**1** and H-**1**) can be easily recovered ($Et_2O$ precipitation and filtration) and reused without loss in catalytic activity. Similar catalysis is seen for THT oxidation by $H_2O_2$. In this case the catalytic effect (rate with catalyst/rate without catalyst) is lower because the rate without catalyst ($H_2O_2$ + THT alone) is substantial.

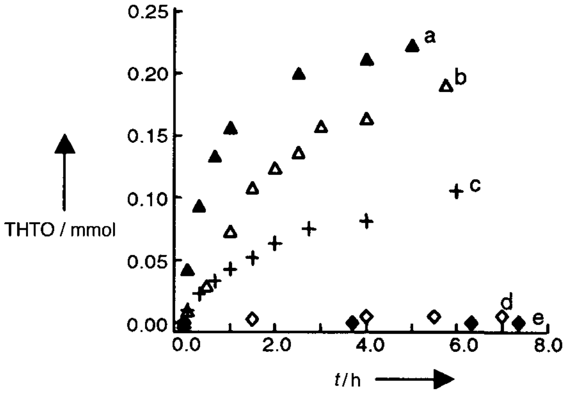


Figure 3. Relative formation rates of tetrahydrothiophene oxide (THTO) in the oxidation of THT by *t*BuOOH catalyzed by a) H-**1**, b) **1** + $p$-$C_7H_7SO_3H$, c) $p$-$C_7H_7SO_3H$, d) **1**, and e) nothing (control without catalyst). The conditions for all reactions are otherwise identical (see Experimental Section).

Given the number of redox-active POMs with two or more vanadium atoms and the large number of polyhydroxylated polymers, including cellulosics, the prospects for making POM-bound polymer materials with catalytic oxidation activity are considerable.

## Experimental Section

Methylation of $[H_4P_2V_3W_{15}O_{62}]^{5-}$: MeOH (2.5 µL, 0.061 mmol, 4.2 equiv) was added to $[(n\text{-}C_4H_9)_4N]_5[H_4P_2V_3W_{15}O_{62}]$[8] (0.0746 g, 0.0144 mmol) in $CD_3CN$ (0.60 mL), and the reaction was followed by $^1H$ and $^{31}P$ NMR spectroscopy. Effective equilibrium at 20 °C was achieved after 48 h. $^1H$ NMR (400 MHz, 0.024 M, $CD_3CN$, TMS) for the mono-, di-, and trimethyl esters: $\delta = 4.99$, 5.03, and 5.08, respectively; $^{31}P$ NMR (162 MHz, 0.024 M, $CD_3CN$, 85 % $H_3PO_4$, only the chemical shifts of the P atom close to the $V_3$ cap are given) for these isomers: $\delta = -4.56$, $-4.81$, and $-5.07$, respectively.

Trimethyl ester of $[H_4P_2V_3W_{15}O_{62}]^{5-}$: Excess MeOH (1 mL) and $[(n\text{-}C_4H_9)_4N]_5[H_4P_2V_3W_{15}O_{62}]$ (1.347 g, 0.26 mmol) dissolved in MeCN (10 mL) was stirred at 40 °C for 24 h. The solution was then added to diethyl ether (20 mL), and the resulting yellow powder was dried under vacuum for 4 h to give 1.30 g (yield 96 % based on POM). Selected data: $^1H$ NMR (400 MHz, 0.010 M, $CD_3CN$, TMS): $\delta = 5.08$ ($CH_3O$); $^{31}P$ NMR (162 MHz. 0.010 M, $CD_3CN$, 85 % $H_3PO_4$): $\delta = -5.07$, $-9.89$. Elemental analysis calcd for $[(n\text{-}C_4H_9)_4N]_5[H(CH_3O)_3P_2V_3W_{15}O_{59}]$: C 19.09, H 3.67, N 1.34, P 1.19, V 2.93, W 52.80; found: C 19.07, H 3.52, N 1.52, P 1.18, V 2.94 W 52.61.

**1**: $[(n\text{-}C_4H_9)_4N]_5[H_4P_2V_3W_{15}O_{62}]$ (0.743 g) was added to a solution of $N,N',N'',N'''$-tetrakis[1,3-dihydroxy-2-(hydroxymethyl)prop-2-yl]-$\alpha,\alpha,\omega,\omega$-dodecane tetracarboxamide[9] (0.99 equiv, 28.3 mg) in DMA (10 mL). After heating the solution to 70 °C for 7 d under argon, it was cooled, added dropwise at 25 °C to stirred $Et_2O$ (100 mL), and the resulting yellow solid collected and redissolved in the minimum volume of MeCN. After filtration, the product was re-precipitated by addition of $Et_2O$ (30 mL). This procedure was repeated twice, and the resulting yellow powder was washed with $Et_2O$ and dried under vacuum at 50 °C for 24 h (yield 90 % based on ligand). The acid form, H-**1**, was obtained by cation exchange using $H^+$-loaded Amberlyst 15 resin in DMF solution. **1**: $^1H$ NMR (500 MHz, 0.015 M, $[D_6]$DMSO, TMS): $\delta = 5.52$ and 5.24 (s, 15 H, relative ratio 95:5, $CH_2$-O-V), 4.78 (s, 4H), 3.59 and 3.82 (s, 9 H), 1.26 (broad, 24 H); $^{31}P$ NMR (202 MHz, 0.015 M, $[D_6]$DMSO, 85 % $H_3PO_4$): $\delta = -6.78$, $-6.96$, $-13.08$, $-13.45$, $-13.67$; $^{51}V$ NMR (132 MHz, 0.015 M, $[D_6]$DMSO, neat $VOCl_3$): $\delta = -490.2$, $-516.7$ with two small peaks at $-459$ and $-560$ (< 5 %). Elemental analysis calcd for $[(n\text{-}C_4H_9)_4N]_{20}H_4[(C_{34}H_{54}O_{16})(P_2V_3W_{15}O_{59})_4]$: C 19.97, H 3.68, N 1.58, P 1.16, V 2.87, W 51.8; found: C 19.77, H 3.73, N 1.94, P 1.16, V 2.46, W 51.92. H-**1**: $^1H$ NMR (500 MHz, 0.019 M, $[D_6]$DMSO, TMS): $\delta = 5.52$, 1.26; $^{31}P$ NMR (202 MHz, 0.019 M, $[D_6]$DMSO, 85 % $H_3PO_4$): $\delta = 7.97$, $-13.06$ and two small peaks at $-5.50$ and $-11.84$ (< 5 %); $^{51}V$ NMR (132 MHz, 0.019 M, $[D_6]$DMSO, neat $VOCl_3$): $\delta = -542.9$. C,H,N analysis calcd for $H_{24}[(C_{34}H_{54}O_{16})(P_2V_3W_{15}O_{59})_4] \cdot 41\,DMF$: C 9.69, H 1.89, N 3.24; found: C 9.80; H 2.08, N 2.96.

**2**: The procedure for **1** (above) was used except that $C[CH_2OCH_2CH_2CONHC(CH_2OH)_3]_4$, prepared from 6,6-bis(carboxy-2-oxabutyl)-4,8-dioxaundecane-1,11-dicarboxylic acid,[10] followed by methanolysis and treatment with tris(hydroxymethyl)aminomethane (Tris), was used in place of the arborol precursor. $^1H$ NMR (500 MHz, 0.012 M, $[D_6]$DMSO, TMS): $\delta = 5.70$ and 5.65 (s, 24 H in 82:18 ratio), 3.62 (broad, 8 H), 3.56 (broad, 8 H), 2.49 (s, 8 H); $^{31}P$ NMR (202 MHz, 0.012 M, $[D_6]$DMSO, 85 % $H_3PO_4$): $\delta = -3.94$, $-4.07$, $-9.81$; $^{51}V$ NMR(132 MHz, 0.012 M, $[D_6]$DMSO, neat $VOCl_3$): $\delta = -542.4$. C,H,N analysis calcd for $[(n\text{-}C_4H_9)_4N]_{20}H_4\{(C_{33}H_{52}O_{20})[P_2V_3W_{15}O_{59}]_4\}$: C 19.86, H 3.66, N 1.57; found: C 20.15, H 3.62, N 1.80.

Catalytic oxidation of THT: In a typical reaction the catalyst **1**, or H-**1** (5.0 µmol of the $[P_2V_3W_{15}O_{62}]$ unit), THT substrate (0.281 mmol), and decane (internal standard, 5.0 µL) were dissolved in solvent (MeCN or $C_6H_5CH_3$, 5.0 mL) containing $[(n\text{-}C_4H_9)_4N]HSO_4$ (50.0 mmol) under argon. For the reactions with $p\text{-}C_7H_7SO_3H$, this acid (30 µmol, equaling the $[H^+]$ from 5.0 µmol of H-**1**) was added. The reactions were initiated by addition of 90 % aqueous *t*BuOOH (0.295 mmol) using a gas-tight syringe. The organic products were identified by GC-MS and quantified by GC using a 5 % methyl siloxane column with a gradient temperature program. Aliquots of the solution (approximately 0.1 mL) were withdrawn at the time intervals shown in Figure 3.

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[7] The hydrogen atoms of the POMs in this study most likely reside on the oxygen atoms bridging the vanadium centers for three reasons: these oxygen atoms are the most basic of the POM anion, they are also the most basic in the entire system (POM anion, cations, and solvent), and the one study involving a mixed $nBu_4N^+/H^+$ salt of a polyvanadium-containing POM where the protons were structurally located indicated they were on these oxygen atoms in MeCN, see V. W. Day, W. G. Klemperer, D. J. Maltbie, *J. Am. Chem. Soc.* **1987**, *109*, 2991–3002. In consequence, the hydrogen atoms in both formulas and equations of the POMs here have been written to indicate that they are on these POM oxygen atoms.

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