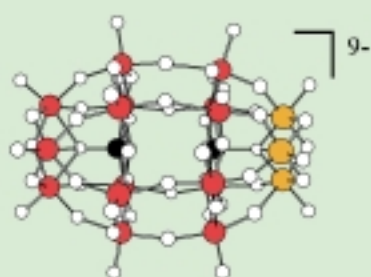
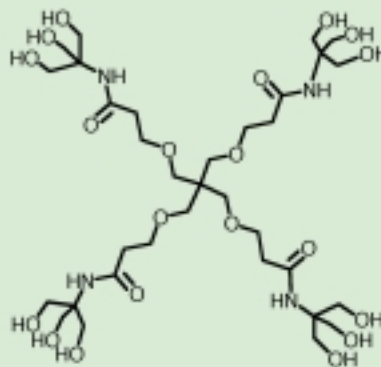


Catalytic Polyoxometalate Terminated Dendrimers



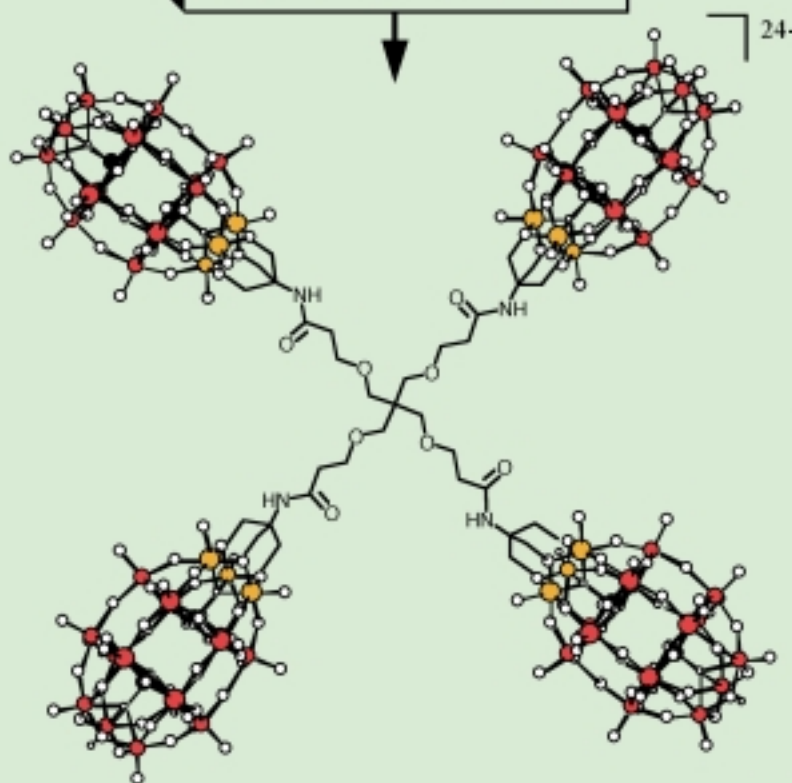
polyoxometalates (POMs) with tunable catalytic properties

+



hydroxylated dendrimers

one-step high-yield
POM esterification...



See next
pages for
details.

● V
● W
● P
○ O

...yields materials with the advantages of
both POMs and dendrimers

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

Huadong Zeng, George R. Newkome,* and 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 cellulose, 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, $[\text{H}_4\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]^{5-}$, 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 $(n\text{Bu}_4\text{N})_5[\text{H}_4\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]$ 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]

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 $[\text{H}_4\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]^{5-}$ with 4.2 equivalents of

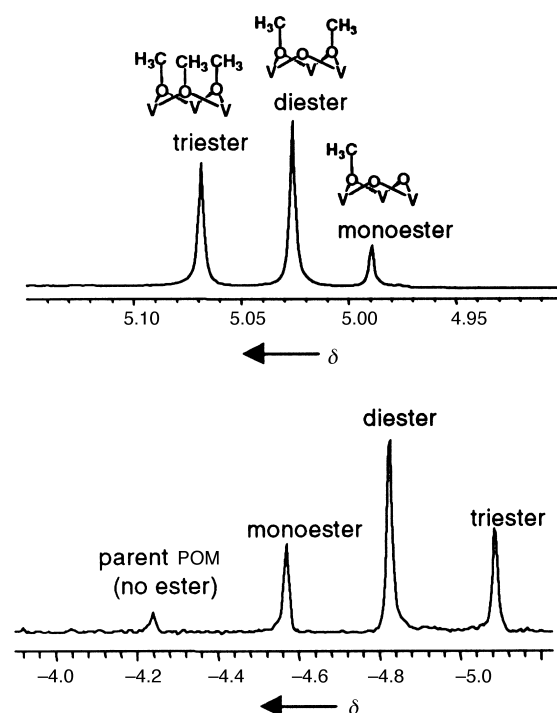
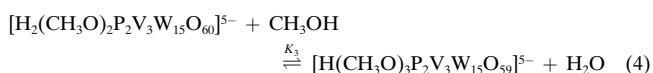
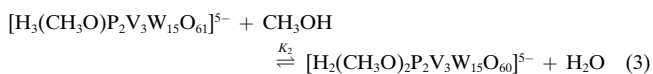
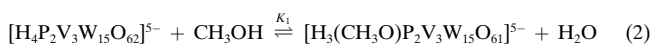


Figure 1. ^1H (top) and ^{31}P (bottom) NMR spectra of an equilibrated CD_3CN solution of MeOH and $[\text{H}_4\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]^{5-}$ (20°C , after 120 h). Only the resonances of the P atom proximal to the V_3 unit in these compounds are shown for clarity.

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 $[\text{H}_4\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]^{5-}$ ion, and that the same product distribution results starting with either the parent POM and MeOH or the independently prepared trimethyl POM, $[\text{H}(\text{CH}_3\text{O})_3\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{59}]^{5-}$, 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 ± 0.2 , 1.3 ± 0.2 , and 0.37 ± 0.08 , respectively.



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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

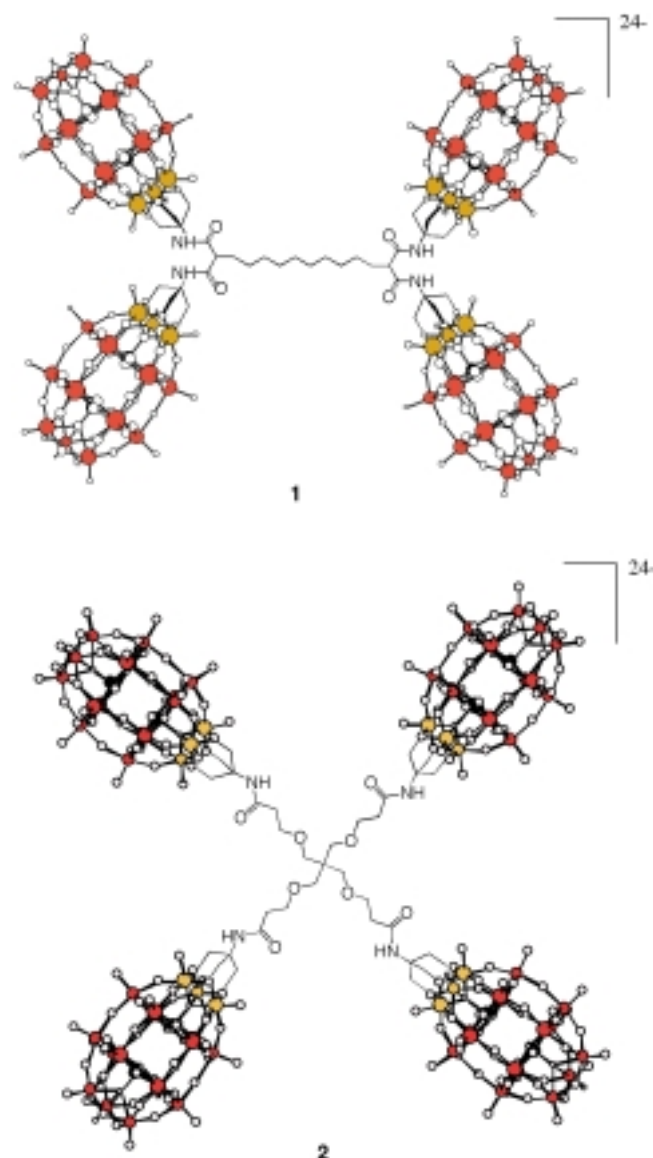
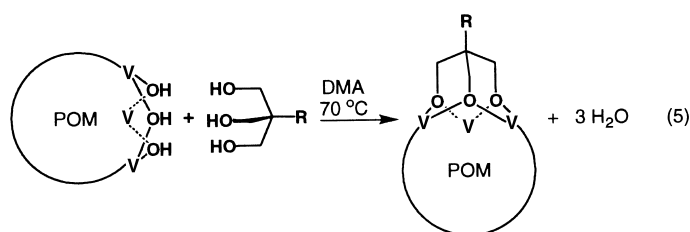


Figure 2. Representative structures of two dendritic tetra(POM) molecules (**1** and **2**). Each has a charge of 24[−] counteracted by 24 cations that are not shown for clarity. The V, W, P, and O atoms are colored orange-yellow, red, black, and white (open circles), respectively.

triester linkages (the product in Equation (5)) plus diester/free-CH₂OH 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 (Bu₄N⁺ by H⁺) and heating (<100°C) cause the diester/free-CH₂OH 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-CH₂OH 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-CH₂OH > 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 D₂O/[D₆]DMSO at 80°C for two days.

Both **1** and H-**1**, a representative mixed (*n*Bu₄N⁺/H⁺) and H⁺ salt, respectively, of these POM ester-bearing molecules, catalyze the oxidation of the thioether tetrahydrothiophene (THT) by both *t*BuOOH and H₂O₂. Figure 3 shows the time

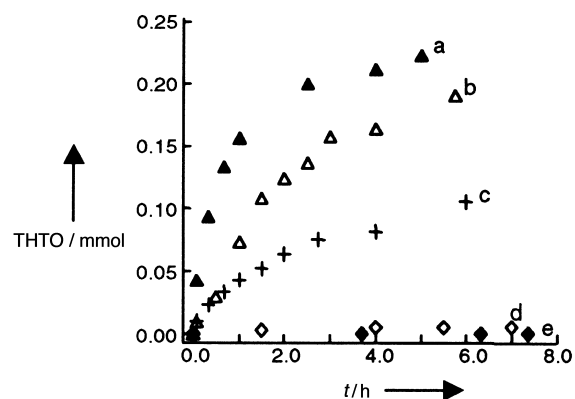


Figure 3. Relative formation rates of tetrahydrothiophene oxide (THTO) in the oxidation of THT by *t*BuOOH catalyzed by a) H-**1**, b) **1** + *p*-C₇H₇SO₃H, c) *p*-C₇H₇SO₃H, d) **1**, and e) nothing (control without catalyst). The conditions for all reactions are otherwise identical (see Experimental Section).

course of exemplary *t*BuOOH oxidations and control reactions. The order of catalytic reactivity is H-**1** > **1** + *p*-C₇H₇SO₃H (a strong MeCN-soluble Brønsted acid) > *p*-C₇H₇SO₃H alone > **1** (Bu₄N⁺ salt) alone ≫ no catalyst. Both calculated and measured pH values indicate that *p*-C₇H₇SO₃H 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*-C₇H₇SO₃H and **1** alone ≫ no catalyst). Significantly, these catalysts (**1** and H-**1**) can be easily recovered (Et₂O precipitation and filtration) and reused without loss in catalytic activity. Similar catalysis is seen for THT oxidation by H₂O₂. In this case the catalytic effect (rate with catalyst/rate without catalyst) is lower because the rate without catalyst (H₂O₂ + THT alone) is substantial.

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

Experimental Section

Methylation of $[\text{H}_4\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]^{5-}$: MeOH (2.5 μL , 0.061 mmol, 4.2 equiv) was added to $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5[\text{H}_4\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]^{18}$ (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 $[\text{H}_4\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]^{5-}$: Excess MeOH (1 mL) and $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5[\text{H}_4\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]$ (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 $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5[\text{H}(\text{CH}_3\text{O})_3\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{59}]$: 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: $[(n\text{-C}_4\text{H}_9)_4\text{N}]_5[\text{H}_4\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]$ (0.743 g) was added to a solution of N,N',N'',N''' -tetrakis[1,3-dihydroxy-2-(hydroxymethyl)prop-2-yl]- $\alpha,\omega,\omega,\omega$ -dodecane tetracarboxamide⁹¹ (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, $[\text{D}_6]\text{DMSO}$, TMS): $\delta = 5.52$ and 5.24 (s, 15H, relative ratio 95:5, $\text{CH}_2\text{-O-V}$), 4.78 (s, 4H), 3.59 and 3.82 (s, 9H), 1.26 (broad, 24H); ^{31}P NMR (202 MHz, 0.015 M, $[\text{D}_6]\text{DMSO}$, 85 % H_3PO_4): $\delta = -6.78, -6.96, -13.08, -13.45, -13.67$; ^{51}V NMR (132 MHz, 0.015 M, $[\text{D}_6]\text{DMSO}$, neat VOCl_3): $\delta = -490.2, -516.7$ with two small peaks at -459 and -560 (< 5 %). Elemental analysis calcd for $[(n\text{-C}_4\text{H}_9)_4\text{N}]_{20}\text{H}_4[(\text{C}_{34}\text{H}_{54}\text{O}_{16})_4(\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{59})_4]$: 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, $[\text{D}_6]\text{DMSO}$, TMS): $\delta = 5.52, 1.26$; ^{31}P NMR (202 MHz, 0.019 M, $[\text{D}_6]\text{DMSO}$, 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, $[\text{D}_6]\text{DMSO}$, neat VOCl_3): $\delta = -542.9$. C,H,N analysis calcd for $\text{H}_{24}[(\text{C}_{34}\text{H}_{54}\text{O}_{16})_4(\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{59})_4] \cdot 41\text{DMF}$: 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 $\text{C}[\text{CH}_2\text{OCH}_2\text{CH}_2\text{CONHC}(\text{CH}_2\text{OH})_3]_4$, prepared from 6,6-bis(carboxy-2-oxabutyl)-4,8-dioxaundecane-1,11-dicarboxylic acid,¹⁰⁰ 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, $[\text{D}_6]\text{DMSO}$, TMS): $\delta = 5.70$ and 5.65 (s, 24H in 82:18 ratio), 3.62 (broad, 8H), 3.56 (broad, 8H), 2.49 (s, 8H); ^{31}P NMR (202 MHz, 0.012 M, $[\text{D}_6]\text{DMSO}$, 85 % H_3PO_4): $\delta = -3.94, -4.07, -9.81$; ^{51}V NMR (132 MHz, 0.012 M, $[\text{D}_6]\text{DMSO}$, neat VOCl_3): $\delta = -542.4$. C,H,N analysis calcd for $[(n\text{-C}_4\text{H}_9)_4\text{N}]_{20}\text{H}_4[(\text{C}_{33}\text{H}_{52}\text{O}_{20})_4(\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{59})_4]$: 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 $[\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]$ unit), THT substrate (0.281 mmol), and decane (internal standard, 5.0 μL) were dissolved in solvent (MeCN or $\text{C}_6\text{H}_5\text{CH}_3$, 5.0 mL) containing $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{HSO}_4$ (50.0 mmol) under argon. For the reactions with $p\text{-C}_6\text{H}_4\text{SO}_3\text{H}$, this acid (30 μmol , equaling the $[\text{H}^+]$ from 5.0 μmol of **H-1**) was added. The reactions were initiated by addition of 90 % aqueous $t\text{BuOOH}$ (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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