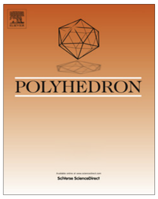
Polyhedron 57 (2013) 57–63

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



DENDRI-POM hybrids based on the Keggin, Dawson, Preyssler and Venturello polyanions and their catalytic evaluation in oxidation reactions

Claire Jahier [a], Sib Sankar Mal [b], Rami Al-Oweini [b], Ulrich Kortz [b,*], Sylvain Nlate [a,*]

[a] Institut Européen de Chimie et Biologies, IECB-CBMN, UMR 5248 CNRS, Université Bordeaux 1, 2 Rue Robert Escarpit, 33607 Pessac Cedex, France
[b] School of Engineering and Science, Jacobs University, P.O. Box 750 561, 28725 Bremen, Germany

ARTICLE INFO

Article history:
Received 13 February 2013
Accepted 4 April 2013
Available online 16 April 2013

Keywords:
Polyoxometalate
Dendrimer
^{183}W NMR spectroscopy
Oxidation-catalysis
Catalyst recovery

ABSTRACT

A series of four dendritic polyoxometalate hybrids (DENDRI-POMs) have been synthesized by electrostatic coupling of diallyl carbinol benzyl ammonium dendron with the Keggin $[PW_{12}O_{40}]^{3-}$, Dawson $[P_2W_{18}O_{62}]^{6-}$, Preyssler $[NaP_5W_{30}O_{110}]^{14-}$ and Venturello $[PO_4(WO(O_2)_2)_4]^{3-}$ polyanions, respectively. The structures of these DENDRI-POMs were examined in solution by standard physicochemical techniques such as IR and NMR spectroscopy as well as elemental analysis. Particular focus was devoted to ^{31}P and ^{183}W NMR spectroscopy of these hybrids, as these techniques offer evidence for the presence of the intact polyanion in the corresponding hybrids. The ^{183}W NMR spectrum of the Keggin-based DENDRI-POM showed the expected signal, whereas no signal was observed for the other hybrids. On the other hand, the expected ^{31}P NMR signal was observed for all four DENDRI-POMs. These POM-based dendrimers oxidized methyl phenyl sulfide to the corresponding sulfoxide and sulfone, with the Venturello-based DENDRI-POM being the most efficient catalyst. In addition, the latter catalyzed efficiently the oxidation of cyclooctene to the corresponding epoxide, whereas hybrids based on the other three polyanions were inert. Catalyst recovery experiments showed that, after two cycles of oxidation reactions, the activity of the Keggin- and Venturello-based DENDRI-POMs were not changed, whereas that of the Dawson-based hybrid decreased dramatically after the first cycle.

1. Introduction

Polyoxometalates (POMs) [1] are discrete, anionic metal-oxide clusters with a diverse range of properties that render them attractive candidates for potential applications in a variety of fields such as catalysis, medicine, analytical chemistry and material science [2]. Owing to their unique metal-oxo cage structure and reversible electron transformation abilities [3], POMs have been extensively investigated as catalysts in a variety of oxidation reactions, such as epoxidation and desulfurization [4].

However, in order to study the activity of POMs as homogenous catalysts in common organic solvents and due to the poor solubility of most alkali-POM salts in organic media, organic salts of these POM catalysts need to be prepared. This can usually be accomplished by cation exchange. Hence, to overcome the poor solubility problem of alkali-POM salts in organic solvents, a variety of cationic organic moieties have been used as countercations of polyanions [5], resulting in a wide range of hybrids soluble in organic media. Amongst these organic cations used with polyanions, dendritic cations have been recently reported. It has been shown that dendritic cations modify some properties of polyanions, such as solubility, catalytic efficiency, stability and recovery capacity [6]. Thus, by using an appropriate organic dendritic countercation, a variety of inorganic–organic hybrids with specific properties can be prepared.

For several years, we have been working on the preparation and characterization of POM-based dendritic hybrids, in order to evaluate the influence of the dendritic wedges on the properties of the polyanions. Accordingly, we have prepared various DENDRI-POM salts, based on electrostatic bonding between various POM polyanions and dendritic cations. These DENDRI-POMs have been used as recoverable catalysts in the oxidation of alkenes, alcohols and sulfides [6d–n]. These studies have clearly shown that a close relationship exists between the structure of the dendritic countercation and the properties of the hybrid polyanion. More recently, we have reported optically active DENDRI-POMs, prepared by electrostatic coupling of achiral polyanions with enantiopure dendritic cations [6j–l]. These optically active DENDRI-POMs catalyzed oxidation reactions with enantioselectivity, highlighting a chirality transfer from the dendritic wedges to the catalytically active polyanion. Recently, Musumeci et al. have also shown that the nature of the countercation can affect the self-assembly processes of hybrid polyoxometalates on surfaces [7]. Thus, due to the interest in dendritic materials on the one hand and POM chemistry on the other hand, exploring new DENDRI-POM hybrid materials remains an interesting and challenging topic for chemists. The

---

* Corresponding authors. Fax: +33 5 4000 2215 (S. Nlate).
E-mail addresses: u.kortz@jacobs-university.de (U. Kortz), s.nlate@iecb.u-bordeaux.fr (S. Nlate).

0277-5387/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.poly.2013.04.013

chemistry of DENDRI-POMs is not yet well understood, due to the difficulty of determining their real structure in solution. To date, the determination of the structure of DENDRI-POMs is usually based on solution NMR spectra (^{13}C, ^{1}H, ^{31}P), IR spectroscopy and elemental analysis. It would be desirable to also use ^{183}W NMR spectroscopy, which is a widely applied technique to investigate the solution stability of POMs [8], as well as X-ray diffraction to gain more information about the structure of DENDRI-POMs. A large number of polyoxotungstates have been characterized by solution ^{183}W NMR, whereas attempts to identify the structure of polytungstates in DENDRI-POM assemblies by solution ^{183}W NMR were unsuccessful. In ^{183}W NMR spectroscopy, the chemical shifts of the tungsten atoms are very sensitive to their surrounding environment, including electric charge, type of adjacent elements, counterions and solvent, which is reflected by a very large chemical shift range. Hence we decided to study the influence of the dendritic structure on the ^{183}W NMR chemical shifts of four structurally different tungstophosphates, compared to the free polyanions. Thus, using the diallyl carbinol benzyl ammonium dendron as the model countercation, we have prepared four DENDRI-POM hybrids based on the Keggin $[PW_{12}O_{40}]^{3-}$ [9], Dawson $[P_2W_{18}O_{62}]^{6-}$ [10], Preyssler $[NaP_5W_{30}O_{110}]^{14-}$ [11], and Venturello $[PO_4(WO(O_2)_2)_4]^{3-}$ [12] polyanions, respectively. We studied the solution ^{183}W NMR of these DENDRI-POMs, in order to demonstrate the presence of the intact polyanion. We also investigated the catalytic efficiency of these DENDRI-POMs in the oxidation of methyl phenyl sulfide and cyclohexene with H_2O_2, as well as their recovery capacities.

2. Experimental

2.1. General remarks

Reagent-grade tetrahydrofuran (THF) and diethyl ether were predried over Na foil and distilled from sodium-benzophenone under argon atmosphere immediately before use. Acetonitrile (CH_3CN) was stirred under argon atmosphere overnight over phosphorus pentoxide, distilled from sodium carbonate, and stored under argon atmosphere. Methylene chloride (CH_2Cl_2) was distilled from calcium hydride just before use. All other chemicals were used as received. The ^{1}H, ^{13}C, ^{31}P NMR spectra were recorded at 25 °C with a Bruker AC 250 FT spectrometer (^{1}H: 250.13, ^{13}C: 62.91 MHz) and a Bruker AC 200 FT spectrometer (^{1}H: 200.16, ^{13}C: 50.33, ^{31}P: 81.02 MHz) at CESAMO (Bordeaux, France). The ^{183}W NMR spectra were recorded on a 400 MHz JEOL ECX instrument and performed in 10 mm tubes (^{183}W: 16.67 MHz) at Jacobs University Bremen. Mass spectra were performed by the CESAMO on a QStar Elite mass spectrometer (Applied Biosystems). The instrument is required with an ESI source and spectra were recorded in the positive mode. The electrospray needle was maintained at 4500 V and operated at room temperature. Samples were introduced by injection through a 10 L sample loop into a 200 L/min flow of methanol from the LC pump. Elemental analyses were performed at the Vernaison CNRS center at Lyon-Villeurbanne (France). The infrared spectra were recorded in KBr pellets on a FT-IR Paragon 1000 Perkin–Elmer spectrometer, unless otherwise indicated. Organic oxidation products were identified by correlation to authentic samples.

2.2. Synthesis of diallyl carbinol benzyl ammonium dendron **3**

2.2.1. Synthesis of trihexylammonium benzoate **2**

In a Schlenk tube, a mixture of 4-(bromomethyl)benzoate **1** (1.67 g, 7.29 mmol) and 12 mL of tri-*n*-hexylamine (12 mL, 9.80 g, 36.40 mmol) in 3 mL of CH_3CN was stirred for 16 h at 80 °C. After removal of the solvent under vacuum, the residue was washed with petroleum ether (3 × 30 mL) and dried under vacuum, yielding the ammonium salt **2** with 95% yield (3.40 g). ^{1}H NMR (250.13 MHz, $CDCl_3$): $\delta = 7.80$ (d, 2H, Ar), 7.52 (d, 2H, Ar), 4.89 (s, 2H, CH_2–N), 3.72 (s, 3H, O–CH_3), 3.14 (broad, 6H, CH_2–N), 1.60 (broad, 6H, CH_2), 1.09 (broad, 18H, CH_2), 0.59 (broad, 9H, CH_3). ^{13}C NMR (62.91 MHz, $CDCl_3$): $\delta = 165.8$ (C=O), 132.8 (CH, Ar), 132.4 (Cq, Ar), 131.8 (Cq, Ar), 129.9 (CH, Ar), 62.3 (CH_2–N), 59.1 (CH_2–N), 52.3 (O–CH_3), 31.0 (CH_2), 25.9 (CH_2), 22.6 (CH_2), 22.3 (CH_2), 13.7 (CH_3). *Anal.* Calc. for $C_{27}H_{48}BrNO_2$: C, 65.04; H, 9.70. Found: C, 64.94; H, 9.76%.

2.2.2. Synthesis of diallyl carbinol benzyl ammonium **3**

In a Schlenk tube, allyl bromide (1.74 mL, 2.43 g, 20.06 mmol) was slowly added to a mixture of magnesium (0.54 g, 22.06 mmol) in anhydrous diethyl ether (15 mL) cooled to 0 °C. Then, a solution of trihexylammonium benzoate **2** (2.00 g, 4.01 mmol) in anhydrous diethyl ether (10 mL) was added to the reaction mixture at 0 °C. The mixture was stirred for 2 h at room temperature. Then solvent was removed under vacuum and the product was extracted with dichloromethane (3 × 20 mL) and dried over sodium sulfate. The solvent was removed under vacuum and the product **3** was obtained as colorless oil in 93% yield (2.05 g). ^{1}H NMR (250.13 MHz, $CDCl_3$, TMS): $\delta = 7.46$ (s, 4H, Ar), 5.59–5.46 (m, 2H, CH=CH_2), 5.08–5.02 (m, 4H, CH=CH_2), 4.83 (s, 2H, CH_2–N), 3.27 (broad, 6H, CH_2–N), 2.60 (dm, 4H, CH_2–CH=CH_2), 2.44 (s, 1H, OH), 1.73 (broad, 6H, CH_2), 1.29 (broad, 18H, CH_2), 0.85 (broad, 9H, CH_3). ^{13}C NMR (62.91 MHz, $CDCl_3$, TMS): $\delta = 149.0$ (Cq, Ar), 132.8 (CH, Ar), 132.2 (*C*H=CH_2), 126.6 (CH, Ar), 125.6 (Cq, Ar), 119.7 (CH=*C*H_2), 75.0 (Cq, C–OH), 62.9 (CH_2–N), 58.8 (CH_2–N), 46.6 (*C*H_2–CH=CH_2), 31.2 (CH_2), 26.1 (CH_2), 22.7 (CH_2), 22.4 (CH_2), 13.9 (CH_3). MS (ESI): Calc. for $C_{32}H_{56}NO$ $M-Br^+ = 470.80$, found 470.43. *Anal.* Calc. for $C_{32}H_{56}BrNO$: C, 69.79; H, 10.25. Found: C, 69.19; H, 10.23%.

2.3. Synthesis of DENDRI-POMs

2.3.1. Synthesis of Keggin-based DENDRI-POM **4**

To an aqueous solution (2 mL) of $Na_3[PW_{12}O_{40}]$ (0.429 g, 0.140 mmol) was added a solution of trihexylammonium diallyl carbinol salt **3** (0.253 g, 0.462 mmol) in dichloromethane (5 mL). The mixture was vigorously stirred at room temperature for 2 h. The dichloromethane layer was dried over sodium sulfate, filtered and evaporated under vacuum. The residue was washed three times with diethyl ether to provide the DENDRI-POM **4** as a light yellow solid (0.564 g, 94%). ^{1}H NMR (250.13 MHz, [D_6]acetone, TMS): $\delta = 7.57$ (m, 12H, Har), 5.65 (m, 6H, C*H*=CH_2), 4.95 (m, 12H, CH=CH_2), 4.67 (s, 6H, CH_2–N), 3.31 (m, 18H, CH_2–N), 2.60 (dd, 12H, CH_2–CH=CH_2), 1.95 (m, 18H, CH_2), 1.38 (m, 54H, CH_2), 0.88 (t, 27H, CH_3). ^{13}C NMR (62.91 MHz, [D_6]acetone, TMS): $\delta = 149.3$ (Cq, Ar), 133.8 (*C*H=CH_2), 131.8 (CH, Ar), 126.6 (CH, Ar), 125.3 (Cq, Ar), 117.5 (CH=*C*H_2), 75.1 (Cq, C–OH), 58.3 (CH_2–N), 53.4 (CH_2–N), 46.6 (*C*H_2–CH=CH_2), 31.0 (CH_2), 25.7 (CH_2), 23.7 (CH_2), 22.2 (CH_2), 21.7 (CH_2), 13.4 (CH_3). ^{31}P NMR (81.02 MHz, [D_6] acetone): $\delta = -15.1$ (PO_4). ^{183}W NMR (16.67 MHz, [D_6]acetone): $\delta = -88.6$; FTIR (KBr pellets), ν (cm^{-1}) = 1079 $(P–O)_{as}$, 978$(W–O)_{as}$, 894 $(W–O–W)_{as}$, 815 $(W–O–W)_{as}$. *Anal.* Calc. for $C_{96}H_{168}O_{43}N_3PW_{12}$: C, 26.88; H, 3.95; N, 0.98; P, 0.72; W, 51.43. Found: C, 26.22; H, 3.87; N, 1.07; P, 0.92; W, 52.23%.

2.3.2. Synthesis of Dawson-based DENDRI-POM **5**

To an aqueous solution (2 mL) of $K_6[P_2W_{18}O_{62}]$ (0.450 g, 0.098 mmol) was added a solution of trihexylammonium diallyl carbinol salt **3** (0.354 g, 0.647 mmol) in dichloromethane (5 mL). The mixture was vigorously stirred at room temperature for 2 h. The dichloromethane layer was dried over sodium sulfate, filtered and evaporated under vacuum. The residue was washed three times with diethyl ether to provide DENDRI-POM **5** as a light yellow solid (0.634 g, 92%). ^{1}H NMR (250.13 MHz, [D$_6$]acetone, TMS): δ = 7.55 (broad, 24H, Har), 5.65 (m, 12H, C*H*=CH$_2$), 4.95 (m, 24H, CH=CH$_2$), 4.83 (s, 12H, CH$_2$–N), 3.37 (broad, 36H, CH$_2$–N), 2.58 (broad, 24H, CH$_2$–CH=CH$_2$), 1.93 (broad, 36H, CH$_2$), 1.46–1.25 (broad, 108H, CH$_2$), 0.86 (broad, 54H, CH$_3$). ^{13}C NMR (62.91 MHz, [D$_6$]acetone, TMS): δ = 148.9 (Cq, Ar), 134.07 (*C*H=CH$_2$), 132.1 (CH, Ar), 126.3 (CH, Ar), 126.0 (Cq, Ar), 117.3 (CH=*C*H$_2$), 75.0 (Cq, C–OH), 59.5 (CH$_2$–N), 53.2 (CH$_2$–N), 46.3 (*C*H$_2$–CH=CH$_2$), 31.0 (CH$_2$), 25.7 (CH$_2$), 22.6 (CH$_2$), 22.2 (CH$_2$), 21.8 (CH$_2$), 13.5 (CH$_3$). ^{31}P NMR (81.02 MHz, [D$_6$]acetone): δ = −12.9 (PO$_4$). FTIR (KBr pellets), ν (cm^{-1}) = 1089 (P–O)$_{as}$, 955(W–O)$_{as}$, 908 (W–O–W)$_{as}$, 792 (W–O–W)$_{as}$. *Anal.* Calc. for $C_{192}H_{336}O_{68}N_6P_2W_{18}$: C, 32.08; H, 4.71; N, 1.17; P, 0.86; W, 46.04. Found: C, 32.20; H, 4.55; N, 1.22; P, 1.09; W, 45.12%.

2.3.3. Synthesis of Preyssler-based DENDRI-POM *6*

To an aqueous solution (2 mL) of $(NH_4)_{14}[NaP_5W_{30}O_{110}]$ (0.332 g, 0.040 mmol) was added a solution of trihexylammonium diallyl carbinol salt **3** (0.300 g, 0.548 mmol) in dichloromethane (5 mL). The mixture was vigorously stirred at room temperature for 4 h. The dichloromethane layer was dried over sodium sulfate, filtered and evaporated under vacuum. The residue was washed three times with diethyl ether to provide the DENDRI-POM **6** as a light yellow solid (0.337 g, 60%). ^{1}H NMR (250.13 MHz, [D$_6$]acetone, TMS): δ = 7.38 (broad, 56H, Har), 5.53 (m, 28H, C*H*=CH$_2$), 4.95 (m, 56H, CH=CH$_2$), 4.83 (s, 28H, CH$_2$–N), 3.20 (broad, 384H, CH$_2$–N), 2.50 (broad, 56H, CH$_2$–CH=CH$_2$), 1.70 (broad, 84H, CH$_2$), 1.22 (broad, 252H, CH$_2$), 0.79 (broad, 126H, CH$_3$). ^{13}C NMR (62.91 MHz, CDCl$_3$, TMS): δ = 142.9 (Cq, Ar), 128.0 (*C*H=CH$_2$), 127.2 (CH, Ar), 121.1 (CH, Ar), 120.8 (Cq, Ar), 113.6 (CH=*C*H$_2$), 69.6 (Cq, C–OH), 53.3 (CH$_2$–N), 40.9 (CH$_2$–N), 26.1 (*C*H$_2$–CH=CH$_2$), 25.6 (CH$_2$), 25.2 (CH$_2$), 24.2 (CH$_2$), 17.2 (CH$_2$), 8.7 (CH$_3$). ^{31}P NMR (81.02 MHz, [D$_6$]acetone): δ = −9.6 (PO$_4$); FTIR (KBr pellets), ν (cm^{-1}) = 1162 (P–O)$_{as}$, 1076 (W–O)$_{as}$, 910 (W–O–W)$_{as}$, 733 (W–O–W)$_{as}$, 571, 537. *Anal.* Calc. for $C_{448}H_{784}O_{124}N_{14}P_5NaW_{30}$: C, 38.31; H, 5.63; N, 1.40; P, 1.10; W, 39.27. Found: C, 37.99; H, 5.05; N, 1.32; P, 1.02; W, 38.12%.

2.3.4. Synthesis of Venturello-based DENDRI-POM *7*

H_2O_2 (5.2 mL, 35% in water) was added to a solution of the commercial heteropolyacid $H_3PW_{12}O_{40}$ (0.303 g, 0.105 mmol) in water. The mixture was stirred at room temperature for 30 min. A solution of trihexylammonium diallyl carbinol salt **3** (0.150 g, 0.274 mmol) in CH$_2$Cl$_2$ (3 mL) was added, and the mixture was stirred for 90 min. The CH$_2$Cl$_2$ layer was washed with water and dried over sodium sulfate. The product was obtained by removing the solvent under vacuum to provide DENDRI-POM **7** as a white solid (0.245 g, 91%). ^{1}H NMR (250.163 MHz, CDCl$_3$, TMS): δ = 7.48 (br, 12H, Har), 4.59 (br, 6H, CH$_2$–N), 3.08–2.92 (mbr, 30H, CH$_2$–N, CH$_2$–O), 2.63 (br, 8H, CH–O, CH$_2$), 1.73 (br, 18H, CH$_2$), 1.31 (br, 54H, CH$_2$), 0.88 (br, 27H, CH$_3$). ^{13}C NMR (62.91 MHz, CDCl$_3$, TMS): δ = 149.0 (Cq, Ar), 131.4 (CH, Ar), 126.7 (Cq, Ar), 126.2 (CH, Ar), 74.4 (Cq–OH), 74.1 (CH–N), 60.4 (CH$_2$–N), 54.9 (CH$_2$–N), 45.2 (*C*H–O), 45.1 (CH$_2$–O), 38.2 (CH$_2$), 37.4 (CH$_2$), 26.4 (CH$_2$), 23.6 (CH$_2$), 16.6 (CH$_2$), 14.2 (CH$_3$). ^{31}P NMR (121.49 MHz, CDCl$_3$): δ = 2.72 (PO$_4$). FTIR (KBr pellets), ν (cm^{-1}) = 3414.1 (s), 2955.6 (s), 1467.0 (s), 1086.9 (m, P–O), 1053.5 (m, P–O), 968.3 (s, W=O), 845.5 (m, O–O), 729 (m), 649 (m), 573 (w, W(O$_2$))$_{s,as}$, 549 (w, W(O$_2$))$_{s,as}$. *Anal.* Calc. for $C_{96}H_{168}N_3O_{33}PW_4$: C, 43.37; H, 6.37; P, 1.16; W, 27.66. Found: C, 43.22; H, 6.26; P, 1.10; W, 26.71%.

2.4. General procedure for the catalytic oxidation reactions with DENDRI-POMs and catalyst recovery experiments

The DENDRI-POM catalyst and the substrate (250 equiv.) were dissolved in 1 mL of CDCl$_3$. 800 equiv of an aqueous solution of H_2O_2 (35% in water) was added to the reaction mixture at 35 °C. The latter was stirred and monitored by ^{1}H NMR. Upon reaction completion, the organic layer was separated and concentrated under vacuum to about 0.2 mL. The catalyst was precipitated by addition of Et$_2$O (5 mL). The solid was filtered, washed with diethyl ether (3 × 1 mL) and dried under vacuum to yield the DENDRI-POM catalyst, which was analyzed by ^{1}H and ^{31}P NMR spectroscopy, before a new catalytic experiment was performed. The diethyl ether solution was evaporated under vacuum and the oxidized product was purified by chromatography on a silica gel column (petroleum ether/diethyl ether 1:9; v/v. The catalyst was recovered following the typical procedure and conditions described above for the first cycle, the organic solvent and the reactants being adjusted to the amount of catalyst used.

3. Results and discussion

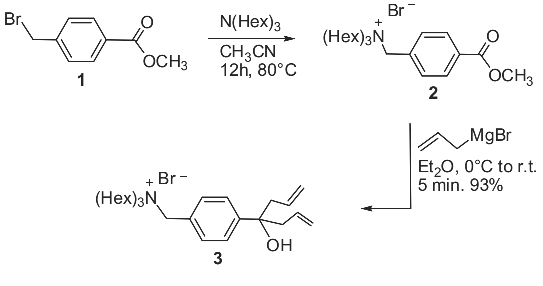
3.1. Synthesis and characterization of DENDRI-POM hybrids *4–7*

3.1.1. Synthesis of *4–7*

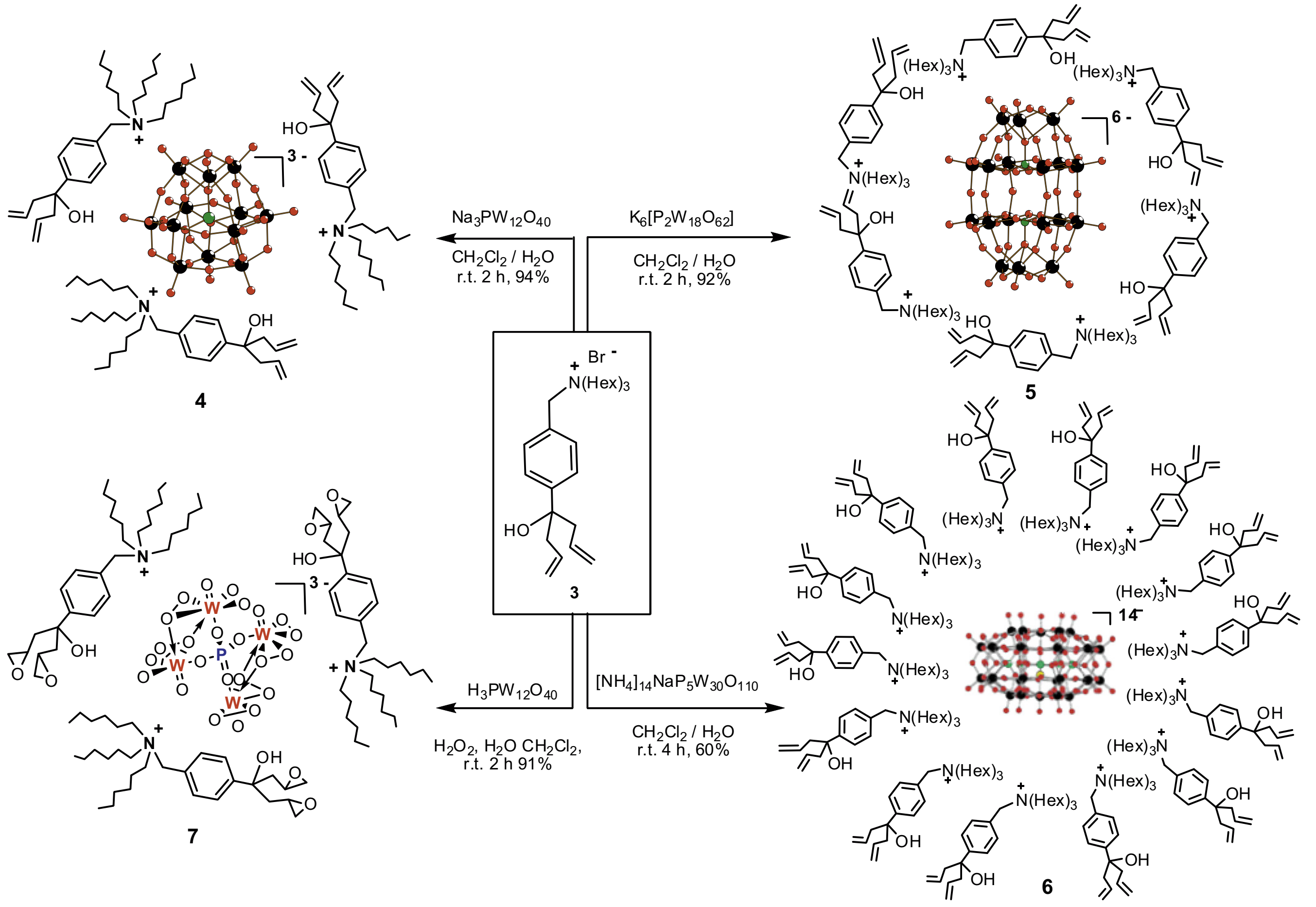
DENDRI-POM salts of the various polyanions were obtained by electrostatic coupling of diallyl carbinol benzyl ammonium dendron **3**, prepared in two steps as summarized in Scheme 1, with the Keggin $[PW_{12}O_{40}]^{3-}$, Dawson $[P_2W_{18}O_{62}]^{6-}$, Preyssler $[NaP_5W_{30}O_{110}]^{14-}$, and Venturello $[PO_4(WO(O_2)_2)_4]^{3-}$ ions respectively.

The first step involves benzylation of trihexylamine by 4-(bromomethyl)-benzoate **1** to give the corresponding trihexyl-ammonium benzoate **2**. The allylation of **2** with allylmagnesium bromide gives the diallyl carbinol benzyl ammonium dendron **3** in 93% yield. NMR and mass spectrometry as well as elemental analysis of compound **3** are consistent with the proposed structure.

The reaction of **3** with the sodium salt of the Keggin ion $Na_3[PW_{12}O_{40}]$, the potassium salt of the Dawson ion $K_6[P_2W_{18}O_{62}]$ and the ammonium salt of the Preyssler ion $(NH_4)_{14}[NaP_5W_{30}O_{110}]$ in a biphasic medium of water and CH$_2$Cl$_2$ led to the corresponding polyallyl DENDRI-POM hybrids **4**, **5** and **6**, respectively (Scheme 2). These DENDRI-POMs were isolated from the organic layer and obtained in good to excellent yields. In the ^{1}H NMR spectra of hybrids **4**, **5** and **6**, the signals attributed to the CH$_2$N groups of diallyl cation were shifted from 4.83 to 3.27 ppm for the free cation (see the Supporting information, Fig. S3) to 4.67 and 3.31, 4.83 and 3.37, 4.83 and 3.20 ppm, for hybrids **4**, **5** and **6**, respectively (see the Supporting information, Figs. S5, S10 and S14 respectively). In addition to the spectroscopy data and elemental analysis of hybrids **4**, **5** and **6** reported in the Section 2, this ^{1}H NMR modification further supports the existence of an interaction between the cation and the POM species. DENDRI-POM **7** based on the Venturello ion $[PO_4(WO(O_2)_2)_4]^{3-}$ was prepared from the heteropolyacid $H_3PW_{12}O_{40}$, in a biphasic mixture of water and dichloromethane, in the presence of H$_2$O$_2$ [13,6d–6m]. As shown in Scheme 2, all the peripheral allyl groups of the dendrons were oxidized giving the corresponding 6-epoxy DENDRI-POM **7**. ^{1}H NMR spectra of **7**



Scheme 1. Synthesis of diallyl carbinol benzyl ammonium dendron **3**.



Scheme 2. Synthesis of DENDRI-POMs **4**–**7**.

(see the Supporting information, Fig. S17) showed the complete disappearance of the signals at 5.53, 5.06 and 2.60 ppm attributed to $CH_2CH{=}CH_2$ groups of compound **3** (Supporting information, Fig. S3), and the appearance of broad signals at 2.92–2.38 ppm assigned to the terminal epoxide groups. In addition, the signals attributed to the CH_2N groups of diallyl cation were shifted from 4.83 to 3.27 ppm for the free cation to 4.59 and 3.06 ppm for the POM hybrid **7**.

3.1.2. Characterization of 4–7

3.1.2.1. ^{31}P NMR spectroscopy on 4–7. The ^{31}P NMR spectra of DENDRI-POMs **4**–**7** showed a single sharp peak for each hybrid at $\delta = -15.1$ (Keggin), -12.9 (Dawson), -9.6 (Preyssler), and 2.7 (Venturello) ppm, respectively, which can be assigned to the phosphate groups of the respective polyanion. The chemical shifts of these singlets are comparable to those of the free POM precursors ($[PW_{12}O_{40}]^{3-}$ at -14.9 ppm, $[P_2W_{18}O_{62}]^{6-}$ at -12.7 ppm, and $[NaP_5W_{30}O_{110}]^{14-}$ at -9.9 ppm) [14] and the ammonium salts of the Venturello anion [6d,l–m,12,13] already reported by our group. These results imply that the starting polyanions are present in the respective DENDRI-POMs, and that they are magnetically and hence structurally equivalent. As expected, substitution of sodium or ammonium countercations by dendritic cations did not show any significant change in the ^{31}P NMR chemical shifts of the Keggin, Dawson and Preyssler polyanion-based DENDRI-POMs (Table 1).

These results can be explained by the fact that the central PO_4 group is surrounded and protected by WO_6 subunits, and thus cannot interact directly with peripheral cations. This feature was also observed by Massart et al. [14], when they studied the ^{31}P NMR spectroscopy of the Keggin anion $[PW_{12}O_{40}]^{3-}$ by varying parameters such as countercations of the POM salt and the NMR solvent. They did not observe any significant variation of the ^{31}P NMR chemical shifts of POMs by varying the cation or the NMR solvent. In the case of the Venturello anion, one signal was obtained at $\delta = 2.7$ ppm in chloroform for hybrid **7**. This value is similar to those obtained for $[PO_4(WO(O_2)_2)_4]^{3-}$ based hybrids and different to that of the Keggin anion precursor. The ^{31}P NMR spectroscopy of all the DENDRI-POMs studied confirms the presence of the corresponding polyanion in their structure.

3.1.2.2. ^{183}W NMR spectroscopy on 4. ^{183}W NMR spectroscopy was used to identify the polyanions in the DENDRI-POM hybrids, and to obtain information about the interaction between the dendritic structure and the polyanion. The ^{183}W NMR spectrum of the Keggin-based DENDRI-POM **4** consists of one peak at $\delta = -88.6$ ppm

Table 1
^{31}P NMR chemical shifts of DENDRI-POM hybrids and their polyanion precursors [8,13,6d–m].

Hybrid	Solvent	(δ)	POM precursor	(δ)[a]
4	$[D_6]$acetone	−15.1	$Na_3[PW_{12}O_{40}]$	−14.9
5	$[D_6]$acetone	−12.9	$Na_6[P_2W_{18}O_{62}]$	−12.7
6	$[D_6]$acetone	−9.6	$(NH_4)_{14}[NaP_5W_{30}O_{110}]$	−9.9
7	$CDCl_3$	2.7	$(cation)_3[PW_4O_{24}]$	2.08–3.2[b]

[a] ^{31}P NMR performed in D_2O at room temperature.
[b] ^{31}P NMR performed in $CDCl_3$ at room temperature.

in [D_6]-acetone, indicating that all tungsten atoms are equivalent (Fig. 1).

This chemical shift is comparable to that obtained for the sodium salt of the Keggin ion $Na_3[PW_{12}O_{40}]$ ($\delta = -99.4$ ppm) in D_2O [15]. Our result represents the first successful ^{183}W NMR spectrum of a DENDRI-POM hybrid, showing a clear-cut signal. The small chemical shift variation in the spectrum of **4** and that of the $Na_3[PW_{12}O_{40}]$ sodium precursor indicates no structural change of the polyanion, but rather reflects substitution of the sodium cations by a dendritic ammonium structure, as well as solvent effects. Analogous studies were also carried out with the DENDRI-POMs **5**–**7**, containing the Dawson, Preyssler and Venturello ions, respectively. We obtained ^{183}W NMR spectra for the Dawson precursor salt $Na_6[P_2W_{18}O_{62}]$ (two singlets at $\delta = -169.9$ and -124.5 ppm) and the Preyssler salt $(NH_4)_{14}[NaP_5W_{30}O_{110}]$ (four singlets at $\delta = -287.8$, -275.5, -209.7 and -207.6 ppm), but the solution ^{183}W NMR measurements on the DENDRI-POMs **5**–**7** were unsuccessful. The ^{183}W NMR spectra of the *n*-tetrabutyl ammonium and the Arquad (n-$C_{18}H_{37}(75\%) + [n$-$C_{16}H_{33}(25\%)]_2N(CH_3)_2$) salts of the Venturello anion were reported by Brégeault and co-workers [16]. In the case of *n*-tetrabutyl ammonium salt, a well-resolved doublet at −593 ppm was obtained, whereas a broad resonance was obtained with a solution of the Arquad salt at −586 ppm. This result indicates that the ^{183}W NMR measurement of the Venturello anion becomes more difficult with the bulky Arquad versus *n*-tetrabutyl cation. Furthermore, in our earlier studies, all attempts to obtain ^{183}W NMR spectra of a series of Venturello-based DENDRI-POMs ion were unsuccessful.

3.1.2.3. IR spectroscopy on 4–6. Infrared spectroscopy was used to obtain information on the interaction between the dendritic structures and the polyanions. Thus, the IR spectra of DENDRI-POMs **4**–**6** were acquired and compared to those of their POM salt precursors (Table 2). The data summarized in Table 2 indicate that the IR spectra of DENDRI-POMs **4**–**6** are very similar to those of their respective POM precursor salts, suggesting that the polyanions retain their structures in the DENDRI-POM hybrids.

The spectra of **4**–**6** exhibit prominent bands from 400 to 1200 cm^{-1} for the polyanions and from 2000 to 3400 cm^{-1} for the dendrimer. A comparison with the POM precursor indicates a slight difference in the stretching vibrations of the W–O–W and the W=O bonds, whereas the P–O bands are essentially unchanged. This is not unexpected, as the phosphate groups are located inside the polyanions, and hence not very sensitive to a change of the countercations. On the other hand, the differences in the tungsten-oxo vibrations indicate an interaction between the polyanions and the dendrimer.

In addition to IR and NMR, we also obtained good elemental analysis data for the DENDRI-POM hybrids (see Section 2). However, all attempts to crystallize the DENDRI-POMs in a variety of organic solvents failed. In general, amorphous materials were obtained in pure or mixed solvents. Crystallization of **4** by slow vapor diffusion resulted in small crystals after about three weeks, but they were not suitable for single-crystal X-ray analysis.

In order to evaluate the stability of **4**, **5** and **7** under catalytic conditions, and their catalytic efficiency and recovery potential, we decided to study the oxidation of methyl phenyl sulfide and cyclooctene in the presence of H_2O_2.

3.2. Catalytic oxidation of methyl phenyl sulfide and cyclooctene with DENDRI-POMs 4, 5 and 7 using H_2O_2

We tested the catalytic performance of DENDRI-POMs **4**, **5** and **7** in the oxidation of methyl phenyl sulfide and cyclooctene in an aqueous/$CDCl_3$ biphasic mixture containing 0.4 mol-% of the selective DENDRI-POM, 250 equiv of the appropriate substrate and 800 equiv of aqueous hydrogen peroxide (35%). The reaction was accomplished by vigorous stirring at 35 °C. The reaction kinetics

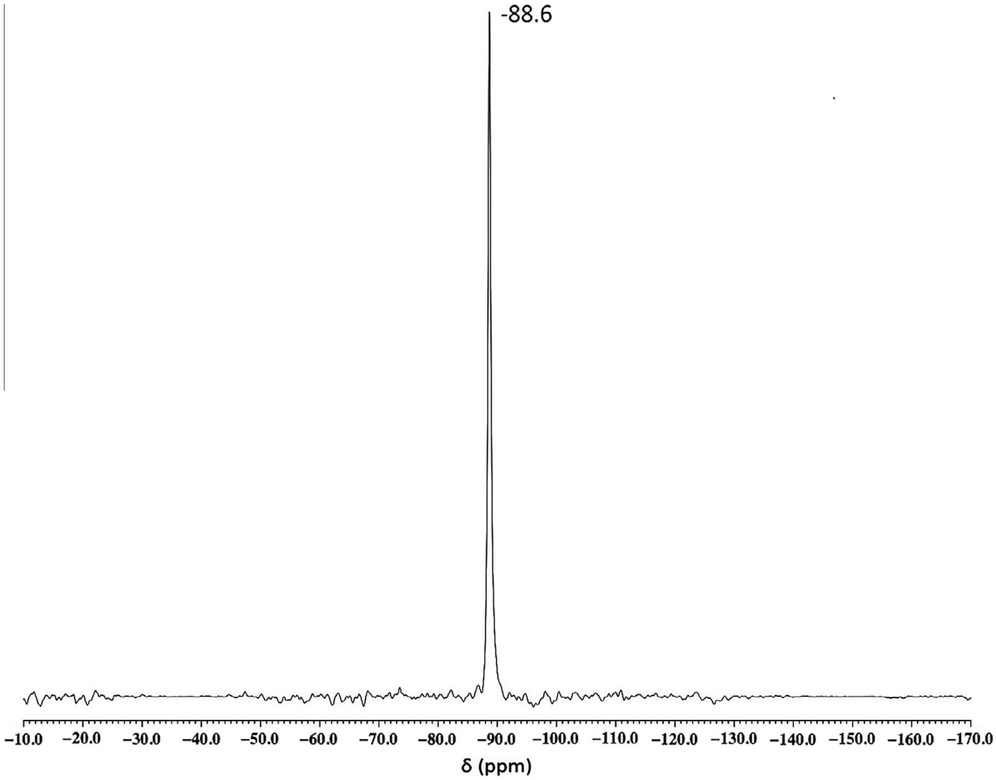


Fig. 1. ^{183}W NMR spectrum of **4**.

Table 2
Infrared data of DENDRI-POMs **4**–**6** and their POM precursors.[a]

Hybrid	$(P{-}O)_{as}$	$(W{=}O)_{as}$	$(W{-}O{-}W)_{as}$
DENDRI-POM **4**	1079	978	895–814
$Na_3[PW_{12}O_{40}]$	1081	995–982	900–805
DENDRI-POM **5**	1080	958	910–792
$K_6[P_2W_{18}O_{62}]$	1081	983	913–788
DENDRI-POM **6**	1183–1081	–	918–783
$(NH_4)_{14}[NaP_5W_{30}O_{110}]$	1184–1078	960	938–784

[a] IR measurements performed in KBr pellets, ν (cm^{-1}).

was monitored over time by plotting the ratio between the intensity of the disappearing ^1H NMR signals of the substrate and the new peaks of the product. The results summarized in Table 3 show that the hybrids **4**, **5** and **7** catalyzed the oxidation of methyl phenyl sulfide to the corresponding methyl phenyl sulfoxide and methyl phenyl sulfone, with **7** being the most active DENDRI-POM catalyst. As shown in Table 3, methyl phenyl sulfide is oxidized by DENDRI-POM **4** with 74% conversion after 24 h (Table 3, entry 1), giving 66% and 8% of the corresponding sulfoxide and sulfone, respectively. A similar conversion rate (77%) and product distribution (sulfoxide 69% and sulfone 8%) were obtained after 72 h, indicating a deactivation of the catalyst. In the case of the Dawson-based DENDRI-POM **5**, a conversion of 77% was obtained after 24 h with 69% sulfoxide and 8% sulfone (Table 3, entry 2). In this case, the reaction kinetics is very slow, compare to that of the Keggin-based DENDRI-POM **4**. In contrast to DENDRI-POMs **4** and **5**, the DENDRI-POM **7** bearing the Venturello ion is more active. It catalyzes the oxidation of sulfide with 98% conversion within 30 min, whereas 24 h were needed in the case of **4** and **5** to reach 74% and 77%, respectively. However, DENDRI-POM **7** was less selective than **4** and **5** under similar reaction conditions.

Studies on the amount of oxidant used in the oxidation of methyl phenyl sulfide with the DENDRI-POMs showed a significant change in both the reaction kinetics and the selectivity in the case of hybrids **4** and **5**. We discovered that decreasing the amount of H_2O_2 with DENDRI-POM hybrids **4** and **5** decreases the reaction kinetics. The use of 2 equiv of H_2O_2 versus 3.2 equiv at the initial conditions with hybrids **4** and **5** led to 8% versus 30% and 6% versus 23% conversion, respectively, after 2 h. At such conditions, no trace of sulfone was observed. For the Venturello-based DENDRI-POM **7**, decreasing the concentration of H_2O_2 from 3.2 to 2 equiv increased the selectivity for sulfoxide from 56% to 75% after 30 min reaction, without affecting the reaction kinetics.

The catalytic efficiency of DENDRI-POMs **4**, **5** and **7** was also evaluated in the oxidation of cyclooctene using similar catalytic conditions. Amongst these catalysts, only the hybrid **7** was active in the oxidation of cyclooctene to the corresponding epoxide, with 100% conversion after 4 h (Table 3). The DENDRI-POMs **4** and **5** do not show any reactivity towards cyclooctene, under similar conditions. Interestingly, when methyl phenyl sulfide (**8**) was treated with H_2O_2, in similar conditions without a POM catalyst, only 4% of sulfoxide was obtained after 6 days (Table 3, entry 4). In the case of cyclooctene (**9**), no reaction was observed.

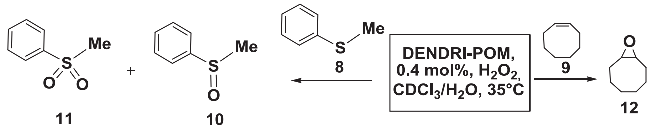
3.3. Catalyst recovery and recycling

In order to check the stability of the DENDRI-POMs at catalytic conditions, two catalytic cycles were performed with hybrids **4**, **5** and **7** in the oxidation of sulfide and cyclooctene. The catalyst was recovered by precipitation after each catalytic cycle and checked by ^1H and ^{31}P NMR before the second catalytic experiment. The Keggin- and Venturello-based DENDRI-POMs **4** and **7** oxidized methyl phenyl sulfide without any obvious loss in activity and selectivity over two cycles. In contrast, the activity and isolated yield of the Dawson-based dendritic hybrid **5** in the oxidation of sulfide decreased significantly after the first cycle. This was observed in the drop in conversion rate from 74% to 54% as well as the isolated yield from 72% to 43% after the first cycle. The deactivation of catalyst **5** is probably due to the decomposition of the POM structure in acidic medium. This feature could be attributed to the size of the ammonium dendron **3** used for these studies, which is probably not sufficiently dendritic to protect the Dawson ion against external acidic attack under these reaction conditions, in contrast to the smaller Keggin and Venturello ions, which are easily stabilized. According to our previous studies [6], it has clearly been established that the dendritic structures around the POM increase their stability in solution, allowing the facile recovery and reuse of the catalyst.

4. Conclusions

We have synthesized four DENDRI-POMs based on the diallyl carbinol benzyl ammonium dendron **3** and tungstophosphates

Table 3
Catalytic oxidation of methyl phenyl sulfide (**8**) and cyclooctene (**9**) with DENDRI-POMs **4**, **5** and **7**, using H_2O_2.[a]



Entry	Catalyst	Substrate	Time (h)[b]	Conversion (%)[c]	Products (yield, %)
1	**4**	**8**	24	74	**10**(66)/**11**(8)
2	**5**		24	77	**10**(69)/**11**(8)
3	**7**		0.5	98	**10**(54)/**11**(44)
4	–		144	4	**10**
5	**4**	**9**	72	0	**12**
6	**5**		72	0	**12**
7	**7**		4	100	**12**

[a] Reaction conditions: catalyst (0.4 mol-%), substrate (250 equiv), 35% H_2O_2 (800 equiv), $CDCl_3$ (1 mL).
[b] Reactions were monitored by ^1H NMR.
[c] Conversions were determined by integration of the ^1H NMR signals of substrate and product.

with the Keggin, Dawson, Preyssler and Venturello structure. The DENDRI-POMs **4**–**7** were fully characterized by IR and multinuclear (^{1}H, ^{13}C, ^{31}P) NMR spectroscopy as well as elemental analysis. We also performed catalytic studies on these DENDRI-POMs for the homogeneous oxidation of methyl phenyl sulfide and cyclooctene using H_2O_2 as oxidant. Our work has demonstrated that DENDRI-POMs are highly attractive catalysts, which can be recovered and reused. We also report an example of a DENDRI-POM characterized by solution ^{183}W NMR.

Acknowledgments

S. N. and C. J. thank the Agence National de la Recherche (grant ANR-06-BLAN-0215), the University Bordeaux 1 and the CNRS for financial support. C. J. thanks ESF COST D40 action for a STSM grant, allowing for a research visit at Jacobs University. U. K. thanks Jacobs University and the Fonds der Chemischen Industrie for research support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2013.04.013.

References

[1] (a) M.T. Pope, A. Müller, Angew. Chem., Int. Ed. Engl. 30 (1991) 34;
(b) J.T. Rhule, C.L. Hill, D.A. Rud, R.F. Schinazi, Chem. Rev. 98 (1998) 327;
(c) Dimitris E. Katsoulis, Chem. Rev. 98 (1998) 359;
(d) M.T. Pope, A. Müller (Eds.), Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications, Kluwer Academic, Dordrecht, 2001.

[2] (a) Chem. Rev. Special Thematic Issues, Polyoxometalates. 98 (1998) pp. 1–389.;
(b) A. Proust, R. Thouvenot, P. Gouzerh, Chem. Commun. 16 (2008) 1837–1852;
(c) D.L. Long, E. Burkholder, L. Cronin, Chem. Soc. Rev. 36 (2007) 105–121;
(d) D. Long, R. Tsunashima, L. Cronin, Angew. Chem. Int. Ed. 49 (2010) 1736–1758;
(e) P. Mialane, A. Dolbecq, F. Sécheresse, Chem. Commun. (2006) 3477–3485;
(f) A. Dolbecq, E. Dumas, C.R. Mayer, P. Mialane, *Chem. Rev*. 110 (2010) 6009–6048.

[3] (a) D.A. Judd, J.H. Nettles, N. Nevins, J.P. Snyder, D.C. Liotta, J. Tang, J. Ermolieff, R.F. Schinazi, C.L. Hill, J. Am. Chem. Soc. 123 (2001) 886;
(b) S. Shigeta, S. Mori, E. Kodama, J. Kodama, K. Takahashi, T. Yamase, Antiviral Res. 58 (2003) 265;
(c) X. Wang, J. Liu, M.T. Pope, Dalton Trans. 5 (2003) 957;
(d) Y. Tajima, Microbiol. Immunol. 47 (2003) 207.

[4] (a) M. Sadakane, E. Steckhan, Chem. Rev. 98 (1998) 219;
(b) C. Fleming, D.-L. Long, N. McMillan, J. Johnston, N. Bovet, V. Dhanak, N. Gadegaard, P. Kögerler, L. Cronin, M. Kadodwala, Nat. Nanotechnol. 3 (2008) 229.

[5] (a) N. Mizuno, K. Yamaguchi, K. Kamata, Coord. Chem. Rev. 249 (2005) 1944;
(b) W. Zhu, H. Li, X. Jiang, Y. Yan, J. Lu, L. He, J. Xia, Green Chem. 10 (2008) 641.

[6] (a) H. Zeng, G.R. Newkome, C.L. Hill, Angew. Chem., Int. Ed. 39 (2000) 1771;
(b) D. Volkmer, B. Bredenkötter, J. Tellenbröker, P. Kögerler, D.G. Kurth, P. Lehmann, H. Schnablegger, D. Schwahn, M. Piepenbrink, B. Krebs, J. Am. Chem. Soc. 124 (2002) 10489;
(c) M.C. Rogers, B. Adisa, D.A. Bruce, Catal. Lett. 98 (2004) 29;
(d) L. Plault, A. Hauseler, S. Nlate, D. Astruc, J. Ruiz, S. Gatard, R. Neumann, Angew. Chem., Int. Ed. 43 (2004) 2924;
(e) M.V. Vasylyev, D. Astruc, R. Neumann, Adv. Synth. Catal. 347 (2005) 39;
(f) S. Nlate, D. Astruc, R. Neumann, R. Adv, Synth. Catal. 346 (2004) 1445;
(g) S. Nlate, L. Plault, D. Astruc, Chem. Eur. J. 12 (2006) 903;
(h) S. Nlate, L. Plault, D. Astruc, New J. Chem. 31 (2007) 1264;
(i) C. Jahier, L. Plault, S. Nlate, Isr. J. Chem. 49 (2009) 109;
(j) C. Jahier, M. Cantuel, N.D. McClenaghan, T. Buffeteau, D. Cavagnat, F. Agbossou, M. Carraro, M. Bonchio, S. Nlate, Chem. Eur. J. 15 (2009) 8703;
(k) C. Jahier, S.S. Mal, U. Kortz, S. Nlate, Eur. J. Inorg. Chem. (2010) 1559;
(l) C. Jahier, M.-F. Coustou, M. Cantuel, N.D. McClenaghan, T. Buffeteau, D. Cavagnat, M. Carraro, S. Nlate, Eur. J. Inorg. Chem. (2011) 727;
(m) C. Jahier, S. Nlate, Eur. J. Inorg. Chem. (2012) 833;
(n) S. Nlate, C. Jahier, Eur. J. Inorg. Chem. (2013) 1606.

[7] C. Musumeci, M.H. Rosnes, F. Giannazzo, M.D. Symes, L. Cronin, B. Pignataro, ACS Nano 5 (2011) 9992.

[8] Y.-G. Chen, J. Gong, L.-Y. Qu, Coord. Chem. Rev. 248 (2004) 245.

[9] (a) J.F. Keggin, Nature 13 (1933) 908;
(b) J.W. Illingworth, J.F. Keggin, J. Chem. Soc. (1935) 575.

[10] (a) B. Dawson, Acta Crystallogr. 6 (1953) 113;
(b) I.-M. Mbomekalle, Y.W. Lu, B. Keita, L. Nadjo, Inorg. Chem. Commun. 7 (2004) 86.

[11] (a) C. Preyssler, Bull. Soc. Chim. Fr. (1970) 30;
(b) M.H. Alizadeh, S.P. Harmalker, Y. Jeannin, J. Martin-Frère, M.T. Pope, J. Am. Chem. Soc. 107 (1985) 2662.

[12] C. Venturello, R. D'Aloisio, J.C.J. Bart, M. Ricci, J. Mol. Catal. 32 (1985) 107.

[13] D.C. Duncan, R.C. Chambers, E. Hecht, C. Hill, J. Am. Chem. Soc. 117 (1995) 1681.

[14] R. Massart, R. Constant, J.-M. Fruchart, J.-P. Ciabrini, M. Fournier, Inorg. Chem. 16 (1977) 2916.

[15] R. Acerete, C.F. Hammer, L.C.W. Baker, J. Am. Chem. Soc. 104 (1982) 5384.

[16] C. Aubry, G. Chottard, N. Platzer, J.-M. Brégeault, R. Thouvenot, F. Chauveau, C. Huet, H. Ledon, Inorg. Chem. 30 (1991) 4409.