DOI: 10.1002/ejic.200901141

Dendritic Zirconium-Peroxotungstosilicate Hybrids: Synthesis, Characterization, and Use as Recoverable and Reusable Sulfide Oxidation Catalysts

Claire Jahier,[a] Sib Sankar Mal,[b] Ulrich Kortz,*[b] and Sylvain Nlate*[a]

Keywords: Dendrimers / Polyoxometalates / Homogeneous catalysis / Oxidation / Catalyst recovery / Zirconium

A series of dendrimer-containing polyoxometalates (DENDRIPOMs) was synthesized by coupling zirconium-peroxotungstosilicate $[Zr_2(O_2)_2(SiW_{11}O_{39})_2]^{12-}$ with ammonium dendrons by electrostatic bonding. These DENDRIPOMs were successfully characterized by standard physicochemical techniques (e.g. IR and NMR spectroscopy and MS), and they represent the first examples of dendritic POMs based on zirconium-substituted polytungstates. The data obtained are consistent with structures in which the anionic POM is surrounded by cationic ammonium dendrons. In contrast to the potassium salt of $[Zr_2(O_2)_2(SiW_{11}O_{39})_2]^{12-}$, the dendritic counterparts are soluble in common organic solvents, an important feature for the use of DENDRIPOMs in homogeneous catalysis. Our DENDRIPOMs are stable, efficient, recoverable, and reusable catalysts for the oxidation of sulfides in aqueous/$CDCl_3$ biphasic media, with hydrogen peroxide as the oxidant, in contrast to their nondendritic *n*-butyl ammonium counterpart. Two cycles of catalytic reactions were performed without any appreciable loss of activity. We also discovered that the reaction kinetics and selectivity of the DENDRIPOMs are influenced by the structure of the countercation used.

Introduction

Research on dendritic catalysts has been developing during the last decade, because of the potential applications of such compounds in various areas.[1] The use of dendrimers in catalysis, pioneered by van Leeuwen,[2b,2d] has received considerable attention, because the large size of these compounds may allow for easy recovery of the catalyst, an essential feature for reaction efficiency, economy, and environmental compatibility.[2] In addition, by virtue of chemical and structural modifications, it is possible to design a variety of dendritic compounds with specific properties. Numerous dendrimers have been used in different domains such as supramolecular chemistry,[1d] nanoscience,[1c] drug delivery,[3] and catalysis.[2] Among them, a few examples based on polyoxometalates (POMs) have been reported.[4] POMs[5] are a large class of inorganic cage complexes with highly interesting properties that render them attractive for potential applications in a variety of fields such as catalysis, biology, magnetism, optics, and medicine.[6] The combination of POMs with appropriate organic molecules has resulted in a variety of inorganic–organic hybrids with specific properties.

An area of particular interest to us has been studying how the dendritic structures may alter the properties of the incorporated POMs. In this context, we designed and prepared various dendritic POM hybrids (DENDRIPOMs) based on electrostatic bonding between the triply charged Venturello ion $[PO_4\{WO(O_2)_2\}_4]^{3-}$ and dendritic cations, and then we used these materials as recoverable catalysts in the oxidation of organic substrates such as alkenes, alcohols, and sulfides.[4d–4j] The investigation of these DENDRIPOMs clearly indicated that the dendritic structure modulates the properties of the anionic POMs. For example, we have shown that the nature of the dendritic wedge is closely related to the catalytic efficiency, the stability, the solubility, and the recyclability of the POM clusters. More recently, we reported the first examples of optically active DENDRIPOMs, prepared by electrostatic interaction between an achiral POM and enantiopure dendritic cations, and by selecting an enantioselective reaction we demonstrated chirality transfer from dendritic wedges to a catalytically active POM unit.[4j] Thus, exploring the chemistry of DENDRIPOMs remains an interesting and challenging topic in POM chemistry and material science alike. Almost all DENDRIPOMs reported to date are based on the Venturello ion.

---

[a] ISM, UMR CNRS N° 5255, Université Bordeaux 1,
351 Cours de la liberation, 33405 Talence Cedex, France
Fax: +33-5-40006994
E-mail: s.nlate@ism.u-bordeaux1.fr
[b] Jacobs University, School of Engineering and Science,
P. O. Box 750 561, 28725 Bremen, Germany
E-mail: u.kortz@jacobs-university.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.200901141.

In this paper, we demonstrate that dendritic zirconium-peroxotungstosilicate hybrids can also be prepared, and we show their potential as efficient and recoverable sulfide oxidation catalysts.

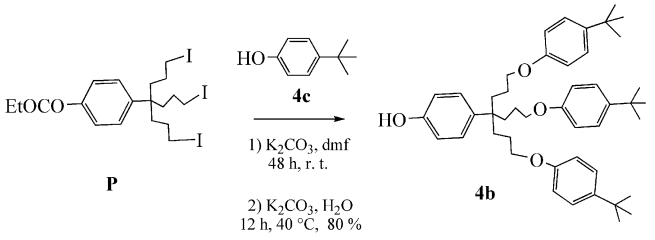
Results and Discussion

Synthesis and Characterization of Zirconium-Peroxo-Based DENDRIPOMs

The synthetic strategy used to incorporate the zirconium-peroxo-containing tungstosilicate[7] $[Zr_2(O_2)_2(SiW_{11}O_{39})_2]^{12-}$ into dendrimers involves the electrostatic coupling of designed dendritic cations with the anionic zirconium-peroxotungstosilicate in a biphasic mixture of water and methylene dichloride.

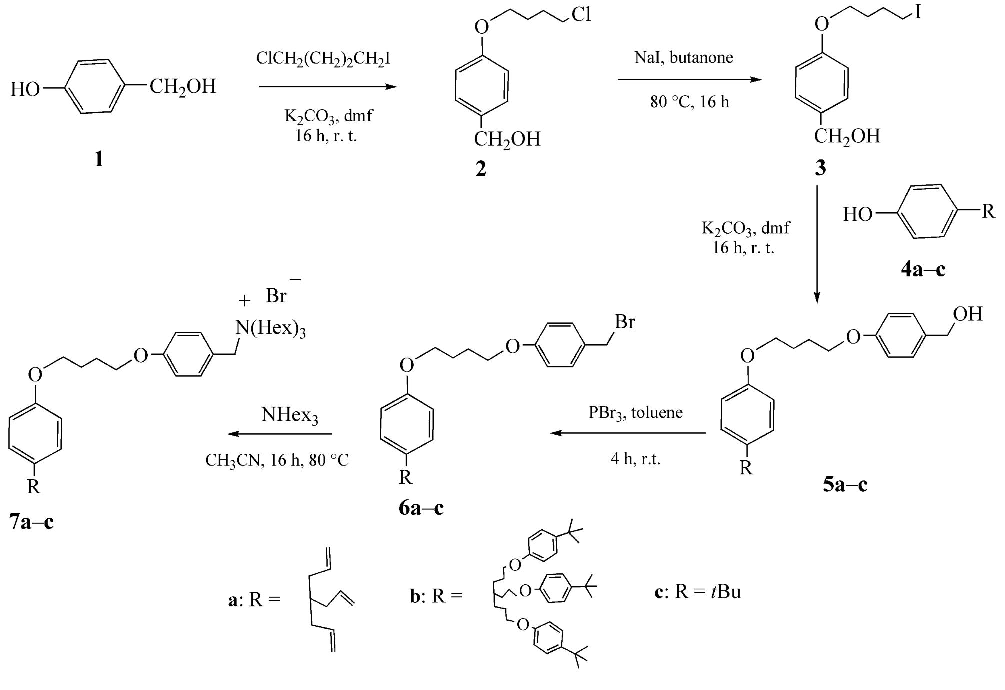
Synthesis of Dendritic Quaternary Ammonium Bromide Salts

Dendritic quaternary ammonium salts **7a**,**b** and their nondendritic counterpart **7c** were prepared by the reaction of alcohol **3** with AB_3 phenol dendrons **4a**,[8] **4b** and 4-*tert*-butylphenol (**4c**), respectively (Scheme 1). The reaction of 1-chloro-4-iodobutane (in excess) with 4-hydroxybenzyl alcohol (**1**) led to alcohol **2** in 90% yield. The latter, in the presence of NaI in butanone, gave alcohol **3** in 96% yield. The reaction of iodo compound **3** with triallyl dendron **4a**, tri(4-*tert*-butylphenyl) dendron **4b**, and 4-*tert*-butylphenol (**4c**) led to the corresponding triallyl dendron **5a**,[4i] tri(4-*tert*-butylphenyl) dendron **5b**, and alcohol **5c**, respectively. The reaction was easily monitored by ^1H NMR spectroscopy by following the complete disappearance of the triplet at δ = 3.24 ppm, assigned to the CH_2I groups, and the appearance of a new triplet attributed to the CH_2O groups. Tri(4-*tert*-butylphenyl) dendron **4b** was prepared by the coupling reaction of protected dendron **P**[9] with 4-*tert*-butylphenol (**4c**) in the presence of K_2CO_3, as summarized in Scheme 2.



Scheme 2. Synthesis of tri(4-*tert*-butylphenyl) dendron **4b**.

Dendron **4b** was characterized by NMR spectroscopy, mass spectrometry, and elemental analysis before use. Its mass spectrum shows a prominent peak at *m*/*z* = 701.45 (calcd. 701.98) $[M + Na]^+$. The bromination of compounds **5a**–**c** with PBr_3 affords their bromobenzyl counterparts **6a**,[4i] **6b**, and **6c** in good to excellent yields. The reaction of trihexylamine with bromobenzyl compounds **6a**, **6b**, and **6c** leads to the corresponding ammonium salts **7a**, **7b**, and **7c** in 94, 98, and 97% yield, respectively. Ammonium salts **7b** and **7c** have been characterized by mass spectrometry, and their mass spectra show molecular peaks at *m*/*z* = 1109.59 $[M - Br]^+$ (calcd. 1109.73) and *m*/*z* = 580.51 $[M - Br]^+$ (calcd. 580.95), respectively.



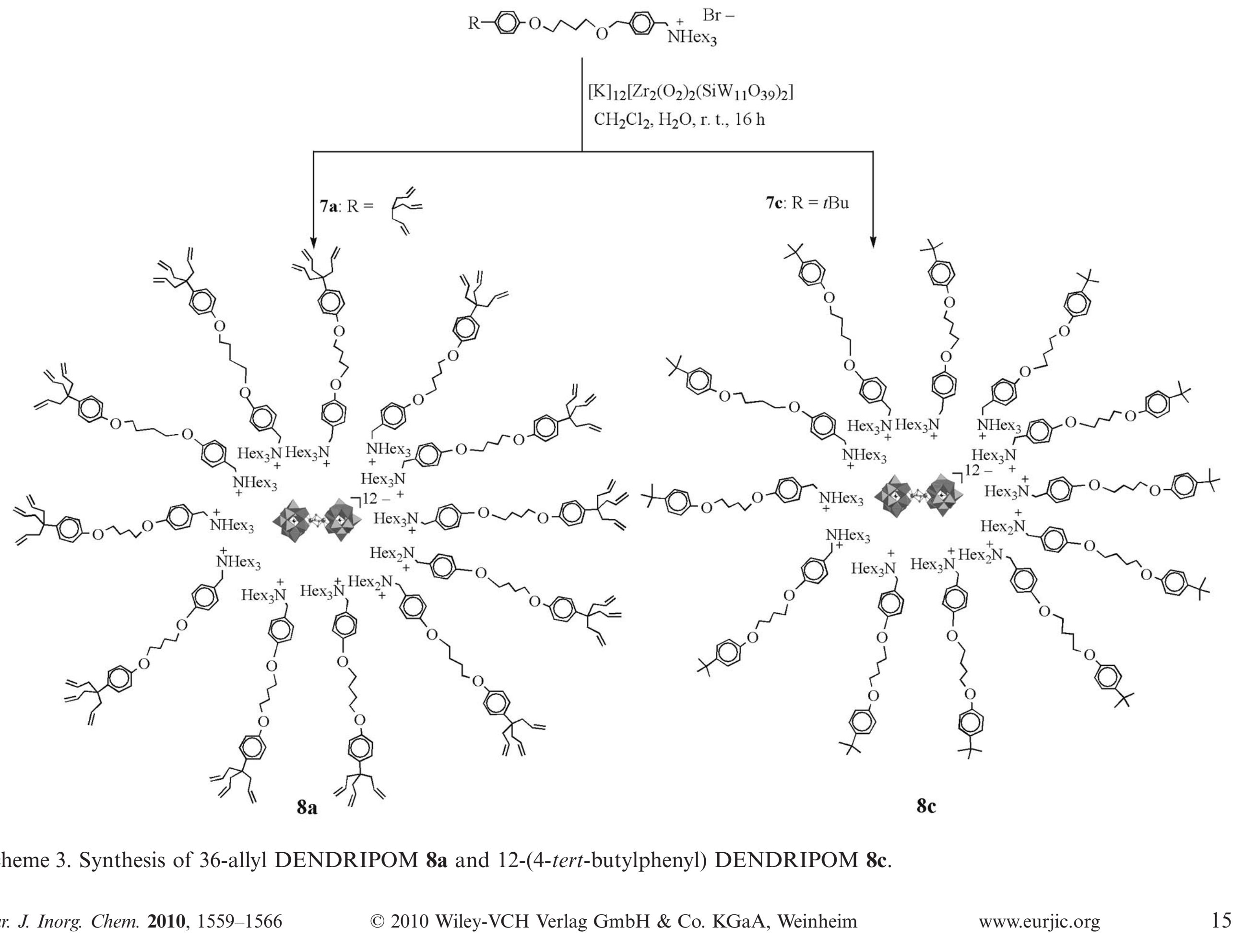
Scheme 1. Synthesis of ammonium bromide salts **7a**–**c**.

Synthesis of DENDRIPOMs 8a–c

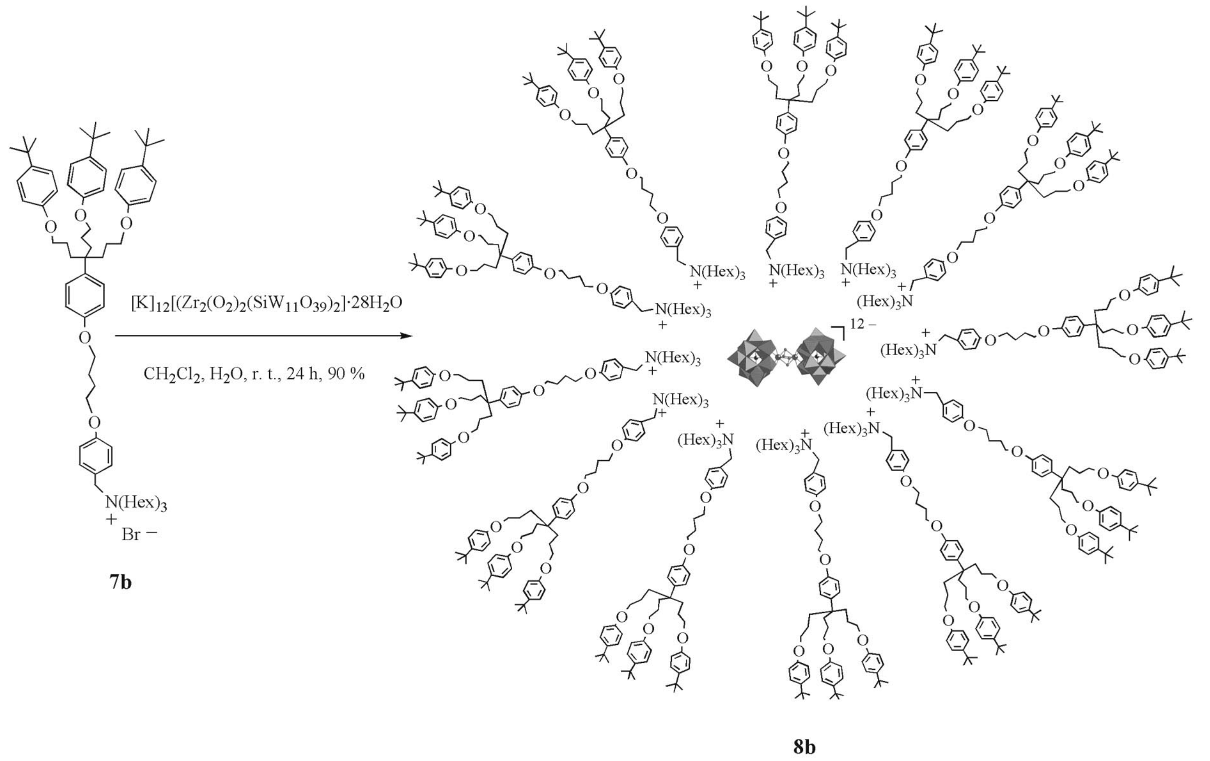
The potassium salt of the anionic zirconium-peroxo-containing tungstosilicate $[Zr_2(O_2)_2(SiW_{11}O_{39})_2]^{12-}$ reacts with ammonium compounds **7a**, **7b**, and **7c** in a biphasic mixture of water and methylene dichloride to give the corresponding DENDRIPOMs **8a**, **8b**, and **8c**, which contain the polyanion at the core. These compounds were obtained in 98, 95, and 95% yield, respectively. The syntheses of 36-allyl DENDRIPOM **8a** and 12-(4-*tert*-butylphenyl) DENDRIPOM **8c** are summarized in Scheme 3, whereas that of 36-(4-*tert*-butylphenyl) DENDRIPOM **8b** is shown in Scheme 4. The NMR and IR spectroscopic and elemental analysis data reported for DENDRIPOMs **8a–c** were in agreement with the structures shown in Schemes 3 and 4 (see the Experimental Section and the Supporting Information for the spectra). Furthermore, in contrast to the potassium salt of polyanion $[Zr_2(O_2)_2(SiW_{11}O_{39})_2]^{12-}$, DENDRIPOMs **8a–c** are soluble in common organic solvents, indicating transfer of the polyanion into the organic phase. In addition, the ^1H NMR signals of DENDRIPOMs **8a–c** are broad compared to the ^1H NMR signals of the ammonium bromide salts of dendrons **7a–c**, probably due to substitution of the bromide ions by the polyanion. We have tried very hard to crystallize our DENDRIPOMs, but up to now all attempts to obtain single crystals suitable for XRD studies have failed. Some ^{29}Si and ^{183}W NMR spectroscopic data would be a good line of evidence for the presence of the polyanion in these systems. Unfortunately, all attempts to perform ^{29}Si and ^{183}W NMR spectroscopy were futile. We have not been able to observe any signal in the ^{29}Si and ^{183}W NMR spectra yet, probably because of the low receptivity of Si and W in dilute systems. In certain POM systems we have observed ^{29}Si and ^{183}W NMR spectra, but this has become increasingly difficult with dendritic POM frameworks. However, efforts have been devoted to the characterization of these hybrids by NMR (^1H and ^{13}C) and IR spectroscopy and especially by elemental analysis (see the Experimental Section and the Supporting Information). The data reported in this manuscript agree with the proposed structures for these DENDRIPOMs. To the best of our knowledge, DENDRIPOMs **8a–c** represent the first examples of dendritic POM salts based on a zirconium-containing polytungstate.

Catalytic Oxidation Tests with DENDRIPOMs 8a and 8c

To evaluate the catalytic efficiency of our DENDRIPOMs **8a** and **8c** in oxidation reactions, we tested the oxidation of thioanisole (**9a**), 4-bromothioanisole (**9b**), and diphenyl sulfide (**9c**), as well as cyclooctene (**10**) and cyclohexanol (**11**), with H_2O_2 (35%) in a biphasic mixture of water and $CDCl_3$ (0.4%, Scheme 5). The properties of **8a** and **8c** were

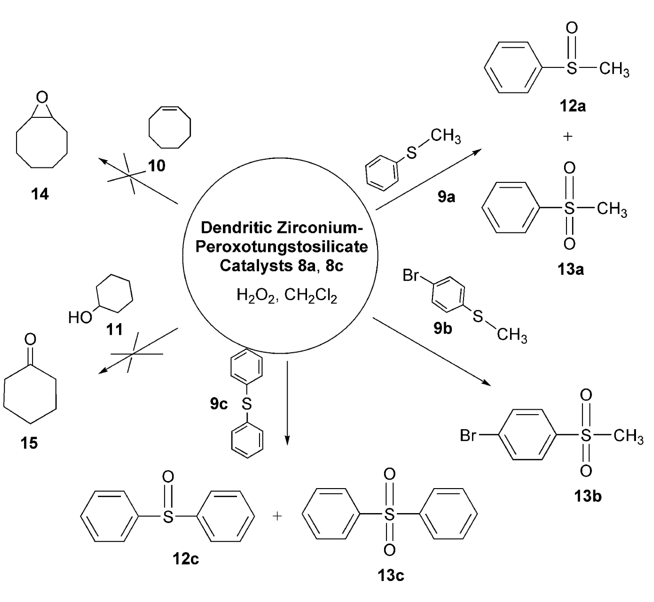


Scheme 3. Synthesis of 36-allyl DENDRIPOM **8a** and 12-(4-*tert*-butylphenyl) DENDRIPOM **8c**.



Scheme 4. Synthesis of 36-(4-*tert*-butylphenyl) DENDRIPOM **8b**.

compared to those of their nondendritic *n*-butyl ammonium counterpart **8d** (see Supporting Information for IR and NMR spectra of **8d**). The results reported in Table 1 clearly show that DENDRIPOMs **8a** and **8c** oxidize thioanisole (**9a**) to the corresponding sulfoxide **12a** and sulfone **13a**, with 87% conversion for **8a** and 76% conversion for **8c**, after 15 min reaction time, whereas only 6% of **12a** was obtained with nondendritic POM **8d**. In addition, **8a** and **8c** do not react with diphenyl sulfide (**9c**). The comparison between the catalytic activity of the nondendritic POM **8d** and DENDRIPOM catalysts **8a** and **8c** indicated that DENDRIPOMs were more active. Within the DENDRIPOM series, **8a** was more active than **8c** (87 vs. 76% conversion, Table 1, entries 1 and 6) and slightly more selective for sulfone **13a** (78 vs. 73%).



Scheme 5. Catalytic oxidation of **9a**–**c**, **10**, and **11** with **8a** and **8c**.

Table 1. Catalytic oxidation of sulfides with DENDRIPOMs **8a** and **8c** and nondendritic *n*-butyl ammonium salt **8d**, as well as the oxidation of cyclooctene (**10**) and cyclohexanol (**11**) with **8a** and **8c**, by using H_2O_2.[a]

Entry	Catalyst	Substrate	Time[b]	% Conversion[c]	Product[c] (% yield)	
1	**8a**	**9a**	15 min	87	**12a** (22)	**13a** (78)
2		**9b**	15 min	100		**13b** (100)
3		**9c**	24 h	100	**12c** (32)	**13c** (68)
4		**10**	48 h	–	**14** (0)	
5		**11**	48 h	–	**15** (0)	
6	**8c**	**9a**	15 min	76	**12a** (27)	**13a** (73)
7		**9b**	15 min	100		**13b** (100)
8		**9c**	24 h	100	**12c** (39)	**13c** (61)
9		**10**	48 h	–	**14** (0)	
10		**11**	48 h	–	**15** (0)	
11	**8d**	**9a**	15 min	6	**12a** (6)	**13a** (0)
12			30 min	10	**12a** (10)	**13a** (0)
13		**9c**	24 h	–	**12c** (0)	**13c** (0)

[a] Catalytic conditions: in $CDCl_3$ at 35 °C under vigorous stirring; reactants were added as follows: catalyst (0.4 mol-%), H_2O_2 (35% in H_2O, 800 equiv.), $CDCl_3$, and substrate (250 equiv.). [b] Nonoptimized reaction times. [c] Conversion determined from the relative intensities of the ^1H NMR signals of the substrate and the product.

After the first 15 min, the reaction became extremely slow, without any appreciable activity (2 to 5% conversion), even upon lengthening the reaction time up to 6 h or raising the temperature up to 50 °C. In contrast to thioanisole (**9a**), DENDRIPOMs **8a** and **8c** selectively oxidize 4-bromothioanisole (**9b**) to the corresponding sulfone **13b** with 100% conversion after 15 min (Table 1, entries 2 and 7). Under analogous reaction conditions, no trace of sulfoxide was observed. In the case of the diphenyl sulfide (**9c**), the reaction kinetics was low with DENDRIPOMs and gave quantitatively sulfoxide **12c** in 32 to 39% conversion (Table 1, entries 3 and 8) and sulfone **13c** in 68 to 61% conversion. No trace of sulfoxide **12c** or sulfone **13c** was observed when using *n*-butyl salt **8d**. It is interesting to note that these reactions did not proceed in the absence of DENDRIPOMs **8a** and **8c**, when carried out under similar conditions. The catalyst was easily recovered by precipitation with diethyl ether and checked by ^{1}H NMR and IR spectroscopy before a new catalytic cycle was conducted. Two reaction cycles were performed in order to test the stability of **8a**, **8c**, and **8d** under catalytic reaction conditions. Thioanisole (**9a**) was used as a model substrate and was oxidized with DENDRIPOMs without any appreciable loss in activity and selectivity, whereas the activity decreased significantly after the first cycle with *n*-butyl salt **8d**: only 3% of **12a** was obtained after 4 h reaction time. In the case of cyclooctene (**10**) and cyclohexanol (**11**), DENDRIPOMs do not display any appreciable reactivity, and epoxide **14** and ketone **15** were not observed (Scheme 4 and Table 1, entries 9, 10).

Conclusions

We have synthesized and characterized dendritic zirconium-peroxo-containing tungstosilicate salts (DENDRIPOMs) and used them as recoverable catalysts in the oxidation of sulfides to the corresponding sulfoxides and sulfones, with hydrogen peroxide as the oxidant, with good to excellent conversion. These compounds represent the first examples of DENDRIPOMs based on a zirconium-containing polytungstate. A study of the countercation effects revealed that the dendritic structure modifies the solubility, reactivity, and selectivity of the polyanion. These results highlight that some key parameters important in catalysis can be tuned by modifying the local environment of the polyanion. We believe that an appropriate design of dendritic structures will enable the use of a large variety of POM species in catalysis. Hence DENDRIPOMs represent a promising and elegant approach with respect to catalytic activity, selectivity (including enantioselectivity), and catalyst recovery. We are currently working in this area.

Experimental Section

General Remarks: Reagent-grade tetrahydrofuran (thf) and diethyl ether were predried with Na foil and distilled from sodium benzophenone under argon immediately prior to use. Acetonitrile (CH_3CN) was stirred under argon overnight over phosphorus pentoxide, distilled from sodium carbonate, and stored under argon. Methylene chloride (CH_2Cl_2) was distilled from calcium hydride just before use. All other chemicals were used as received. The ^{1}H and ^{13}C NMR spectra were recorded at 25 °C with a Bruker AC, 250 FT spectrometer (250.13 MHz for ^{1}H and 62.91 MHz for ^{13}C) and a Bruker AC 200 FT spectrometer (200.16 MHz for ^{1}H and 50.33 MHz for ^{13}C) at the CESAMO (Bordeaux, France). All chemical shifts are referenced to Me_4Si (TMS). Mass spectrometry was performed by the CESAMO with a QStar Elite mass spectrometer (Applied Biosystems) equipped 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 µL sample loop into a 200 µL/min flow of methanol from the LC pump. Elemental analyses were carried out at the Vernaison CNRS center. The infrared spectra were recorded in KBr pellets with a FTIR Paragon 1000 Perkin–Elmer spectrometer, unless otherwise indicated. Organic oxidation products were identified by correlation to authentic samples.

Dendritic Zirconium-Peroxotungstosilicate Hybrids

Alcohol 2: To a solution of 4-hydroxybenzyl alcohol (**1**) (5.00 g, 40.27 mmol) in dmf (20 mL) were added 1-chloro-4-iodobutane (6.4 mL, 11.44 g, 52.36 mmol) and K_2CO_3 (14.09 g, 100.67 mmol). The mixture was stirred overnight at room temperature and extracted with diethyl ether (3 × 30 mL). The resulting solution was washed with water and dried with sodium sulfate. After removal of the solvent under vacuum, the product was purified by chromatography on a silica gel column with a 9:1 petroleum ether/diethyl ether mixture to provide 7.78 g (90%) of **2** as a white solid. ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ = 7.27 (d, 2 H, Ar), 6.88 (d, 2 H, Ar), 4.62 (d, 2 H, CH_2OH), 3.99 (t, 2 H, OCH_2), 3.60 (t, 2 H, $ClCH_2$), 1.96 (broad, 2 H, CH_2), 1.55 (broad, 2 H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 158.4 (C_q, ArO), 133.2 (C_q, Ar), 128.7 (CH, Ar), 114.4 (CH, Ar), 66.7 (OCH_2), 64.8 (OCH_2), 44.7 ($ClCH_2$), 31.5 (CH_2), 30.2 (CH_2) ppm. $C_{11}H_{15}ClO_2$ (214.69): calcd. C 61.54, H 7.04; found C 61.69, H 6.98.

Alcohol 3: A mixture of alcohol **2** (3.00 g, 13.97 mmol) and NaI (4.20 g, 28.00 mmol) in 2-butanone (20 mL) was stirred for 24 h at 80 °C. After removal of the solvent under vacuum, the residue was extracted with dichloromethane (3 × 30 mL). Then the organic layer was washed with a saturated aqueous solution of $Na_2S_2O_3$. The solvent was removed under vacuum to provide 4.10 g (96%) of **3** as a white solid. ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ = 7.25 (d, 2 H, Ar), 6.85 (d, 2 H, Ar), 4.55 (broad, 2 H, CH_2OH), 3.96 (t, 2 H, OCH_2), 3.24 (t, 2 H, ICH_2), 2.07–1.82 (m, 4 H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 158.4 (C_q, ArO), 133.3 (C_q, Ar), 128.7 (CH, Ar), 114.3 (CH, Ar), 66.7 (OCH_2), 64.9 (OCH_2), 31.5 (CH_2), 30.2 (CH_2), 6.7 (ICH_2) ppm. $C_{11}H_{15}IO_2$ (306.13): calcd. C 43.16, H 4.94; found C 42.77, H 4.64.

Dendron 4b: In a Schlenk tube, a mixture of protected triiodophenol dendron **P**[9] (2.00 g, 2.99 mmol), 4-*tert*-butyl phenol (**4c**), (2.03 g, 13.51 mmol), and K_2CO_3 (3.80 g, 27.14 mmol) in dmf (20 mL) was stirred for 48 h at room temperature. K_2CO_3 (2.14 g, 15.28 mmol) and water (4 mL) were added, and the reaction mixture was stirred at 40 °C for 48 h. The mixture was then extracted with CH_2Cl_2 (3 × 30 mL), and the resulting solution was washed with water and dried with sodium sulfate. After removal of the solvent under vacuum, the product was purified by chromatography on a silica gel column with a 9:1 pentane/diethyl ether mixture to provide 1.62 g (80%) of **4b** as a white solid. ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ = 7.27 (d, 8 H, Ar), 6.79 (d, 8 H, Ar), 4.66 (broad, 1 H, OH), 3.87 (t, 6 H, OCH_2), 1.82 (broad, 6 H, CH_2), 1.60 (broad, 6 H, CH_2), 1.30 (s, 27 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 156.7 (C_q, ArO), 153.3 (C_q, ArO), 143.2

(C_q, Ar), 138.7 (C_q, Ar), 127.7 (CH, Ar), 126.2 (CH, Ar), 115.0 (CH, Ar), 113.9 (CH, Ar), 68.3 (OCH_2), 42.1 (C_q-CH_2), 34.07 (C_q-CH_3), 33.7 (CH_2), 31.6 (CH_3), 23.7 (CH_2) ppm. ESI-MS: calcd. for $[M + Na]^+$ 701.98; found 701.45. $C_{46}H_{62}O_4$ (678.99): calcd. C 81.37, H 9.20; found C 81.28, H 9.08.

Dendron 5b: A mixture of tri(4-*tert*-butylphenyl) dendron **4b** (1.00 g, 1.47 mmol), alcohol **3** (0.408 g, 1.33 mmol), and K_2CO_3 (0.617 g, 4.41 mmol) in dmf (10 mL) was stirred for 48 h at room temperature. The reaction mixture was then extracted with CH_2Cl_2 (3 × 20 mL), and the resulting solution was washed with water and dried with sodium sulfate. The solvent was removed under vacuum, and the product was purified by chromatography on a silica gel column with a 6:4 petroleum ether/diethyl ether mixture to provide 0.855 g (75%) of **5b** as a yellow solid. ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.27–7.25 (m, 10 H, Ar), 6.90–6.76 (m, 10 H, Ar), 4.61 (d, 2 H, CH_2-OH), 4.01 (m, 4 H, CH_2-O), 3.86 (t, 6 H, CH_2-O), 1.98 (broad, 4 H, CH_2-CH_2), 1.80 (broad, 6 H, CH_2-CH_2), 1.57 (broad, 6 H, CH_2-CH_2), 1.28 (s, 27 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 156.7 (C_q, Ar-O), 143.1 (C_q, Ar), 138.2 (C_q, Ar), 129.4 (CH, Ar), 127.5 (CH, Ar), 126.2 (CH, Ar), 114.4 (CH, Ar), 113.9 (CH, Ar), 68.3 (CH_2-O), 64.9 (CH_2-OH), 42.1 (C_q-CH_2), 34.1 (C_q-CH_3), 33.8 (CH_2), 31.2 (CH_3), 23.8 (CH_2) ppm. $C_{57}H_{76}O_6$ (857.22): calcd. C 79.87, H 8.94; found C 79.00, H 8.68.

Alcohol 5c: This compound was synthesized according to the same procedure as described above for **5b**, but with 4-*tert*-butylphenol (**4c**) instead of tri(4-*tert*-butylphenyl) dendron **4b**. Alcohol **5c** was obtained in 95% yield as a white solid, after chromatography on a silica gel column with a 7:3 petroleum ether/diethyl ether mixture. ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.30 (m, 4 H, Ar), 6.86 (m, 4 H, Ar), 4.61 (s, 2 H, CH_2-OH), 4.02 (broad, 4 H, CH_2-O), 1.97 (broad, 4 H, CH_2-CH_2), 1.30 (s, 9 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 158.9 (C_q, Ar-O), 156.8 (C_q, Ar-O), 138.8 (C_q, Ar), 132.9 (C_q, Ar), 129.4 (CH, Ar), 127.5 (CH, Ar), 114.4 (CH, Ar), 114.0 (CH, Ar), 67.9 (CH_2-O), 67.6 (CH_2-O), 64.9 (CH_2-OH), 34.1 (C_q-CH_3), 31.5 (CH_3), 26.0 (CH_2) ppm. $C_{21}H_{28}O_3$ (328.45): calcd. C 76.79, H 8.59; found C 76.29, H 8.52.

Dendron 6b: PBr_3 (0.05 mL, 0.53 mmol) was added to a cooled mixture (0 °C) of dendron **5b** (1.00 g, 1.16 mmol) in toluene (5 mL). The resulting solution was stirred at room temperature for 4 h. After removal of the solvent, the residue was extracted with Et_2O, washed with water, and dried with sodium sulfate. The solvent was removed under vacuum to provide 1.05 g (99%) of **6b** as a yellow oil. ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.33–7.26 (m, 8 H, Ar), 6.88–6.77 (m, 8 H, Ar), 4.50 (s, 2 H, Br-CH_2), 4.04 (broad, 4 H, CH_2-O), 3.87 (broad, 6 H, CH_2-O), 1.98 (m, 4 H, CH_2-CH_2), 1.82 (m, 6 H, CH_2-CH_2), 1.58 (m, 6 H, CH_2-CH_2), 1.34 (s, 27 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 159.1 (C_q, Ar-O), 156.7 (C_q, Ar-O), 143.1 (C_q, Ar), 138. 8 (C_q, Ar), 134.1 (C_q, Ar), 130.5 (C_q, Ar), 127.5 (CH, Ar), 126.2 (CH, Ar), 114.7 (CH-CH_2), 114.0 (CH, Ar), 113.9 (CH, Ar), 68.3 (CH_2-O), 67.6 (CH_2-O), 67.3 (CH_2-O), 42.1 (C_q-CH_2), 34.1 (CH_2-Br), 34.0 (C_q-CH_3), 33.7 (CH_2), 31.6 (CH_3), 26.1 (CH_2), 23.7 (CH_2) ppm. $C_{57}H_{75}BrO_5$ (920.12): calcd. C 74.41, H 8.22; found C 74.41, H 7.50.

Bromobenzyl Compound 6c: This compound was synthesized according to the same procedure as described above for **6b**, but with alcohol **5c** instead of tri(4-*tert*-butylphenyl) dendron **5b**. Bromobenzyl compound **6c** was obtained in 93% yield (2.0 g) as a white solid. ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.33–7.26 (m, 4 H, Ar), 6.87–6.82 (m, 4 H, Ar), 4.51 (s, 2 H, $BrCH_2$), 4.02 (broad, 4 H, CH_2-O), 1.97 (broad, 4 H, CH_2-CH_2), 1.30 (s, 9 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 63 MHz): δ = 156.7 (C_q, Ar-O), 143.3 (C_q, Ar), 130.5 (CH, Ar), 129.9 (C_q, Ar), 126.3 (CH, Ar), 114.8 (CH, Ar), 113.9 (CH, Ar), 67.6 (CH_2-O), 67.3 (CH_2-O), 34.1 ($BrCH_2$), 34.1 (C_q-CH_3), 33.7 (CH_2), 31.5 (CH_3), 26.0 (CH_2) ppm. $C_{21}H_{27}BrO_2$ (391.34): calcd. C 64.45, H 6.95; found C 64.62, H 7.17.

Ammonium Bromide Dendron 7a: A mixture of triallylphenyl bromobenzyl compound **6a**[4i] (0.76 g, 1.66 mmol) and tri-*n*-hexylamine (1.6 mL, 4.98 mmol) in CH_3CN (3 mL) 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 to provide ammonium salt **7a** with 94% yield (1.10 g). ^1H NMR ($CDCl_3$, 200.16 MHz): δ = 7.40 (d, 2 H, Ar), 7.17 (d, 2 H, Ar), 6.90 (d, 2 H, Ar), 6.82 (d, 2 H, Ar), 5.49 (m, 3 H, $CH=CH_2$), 4.96 (m, 6 H, $CH=CH_2$), 4.59 (s, 2 H, NCH_2), 4.09 (m, 4 H, CH_2-O), 3.20 (m, 6 H, NCH_2), 2.37 (d, 6 H, $CH_2CH=CH_2$), 2.01 (broad, 4 H, CH_2), 1.74 (m, 18 H, CH_2), 0.88 (m, 9 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 160.4 (C_q, ArO), 156.6 (C_q, ArO), 143.3 (C_q, Ar), 133.9 (C_q, Ar), 132.7 ($CH=CH_2$), 126.2 (CH, Ar), 118.9 (CH, Ar), 117.59 ($CH=CH_2$), 115.0 (CH, Ar), 113.8 (CH, Ar), 67.7 (CH_2O), 67.2 (CH_2O), 58.4 (CH_2N), 41.2 (CH_2), 31.5 (CH_2), 31.2 (CH_2), 26.6 (CH_2), 26.1 (CH_2), 25.9 (CH_2), 22.6 (CH_2), 22.5 (CH_2), 13.9 (CH_3) ppm. $C_{45}H_{72}BrNO_2$ (738.97): calcd. C 73.14, H 9.82; found C 74.15, H 9.89.

Ammonium Bromide Dendron 7b: This compound was synthesized according to the same procedure as described above for **7a**, but with tri(4-*tert*-butylphenyl)bromobenzyl compound **6b** instead of triallylphenyl bromobenzyl compound **6a**. Ammonium salt **7b** was obtained as a yellow solid in 98% (0.46 g) yield. ^1H NMR ($CDCl_3$, 200.16 MHz): δ = 7.42 (d, 2 H, Ar), 7.25 (m, 6 H, Ar), 6.94 (d, 2 H, Ar), 6.79 (m, 6 H, Ar), 4.81 (s, 2 H, NCH_2), 4.01 (m, 4 H, CH_2-O), 3.84 (broad, 6 H, CH_2-O), 3.24 (broad, 6 H, NCH_2), 1.97 (broad, 4 H, CH_2), 1.78 (broad, CH_2), 1.56 (broad, CH_2), 1.32 (broad, CH_2), 1.27 (broad, CH_2), 0.88 (broad, 9 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 160.8 (C_q, ArO), 156.7 (C_q, ArO), 143.1 (C_q, Ar), 133.9 (CH, Ar), 127.5 (C_q, Ar), 126.2 (CH, Ar), 118.8 (C_q, Ar), 115.2 (CH, Ar), 113.9 (CH, Ar), 68.3 (CH_2O), 67.8 (CH_2O), 67.2 (CH_2O), 58.5 (CH_2N), 42.0 (CH_2), 34.0 (CH_2), 33.7 (CH_2), 31.5 (C_q-CH_3), 31.2 (CH_2), 26.1 (CH_2), 26.0 (CH_2), 23.7 (CH_2), 22.7 (CH_2), 22.5 (CH_2), 13.9 (CH_3) ppm. MALDI-TOF: calcd. for $[M - Br]^+$ 1109.73; found 1109.59. $C_{75}H_{114}BrNO_5$ (1189.63): calcd. C 75.72, H 9.66; found C 75.89, H 9.22.

Ammonium Bromide Salt 7c: This compound was synthesized according to the same procedure as described above for **7a**, but with bromobenzyl compound **6c** instead of triallylphenyl bromobenzyl compound **6a**. Ammonium salt **7c** was obtained as a light orange oil in 97% (2.9 g) yield. ^1H NMR ($CDCl_3$, 200.16 MHz): δ = 7.43 (d, 2 H, Ar), 7.28 (d, 2 H, Ar), 6.87 (d, 2 H, Ar), 6.83 (d, 2 H, Ar), 4.84 (s, 2 H, NCH_2), 4.02 (broad, 4 H, CH_2-O), 3.28 (broad, 6 H, NCH_2), 1.97 (broad, 4 H, CH_2), 1.76 (broad, 6 H, CH_2), 1.33 (broad, CH_2) 1.29 (s, 9 H, CH_3), 0.89 (broad, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 160.7 (C_q, ArO), 156.6 (C_q, ArO), 143.3 (C_q, Ar), 133.9 (C_q, Ar), 126.2 (CH, Ar), 119.0 (CH, Ar), 115.1 (CH, Ar), 113.8 (CH, Ar), 67.7 (CH_2O), 67.2 (CH_2O), 58.4 (CH_2N), 41.2 (C_q-CH_3), 34.0 (CH_2), 31.5 (CH_2), 31.2 (CH_2), 26.1 (CH_2), 26.0 (CH_2), 22.6 (CH_2), 22.5 (CH_2), 13.9 (CH_3) ppm. ESI-MS: calcd. for $[M - Br]^+$ 580.95; found 580.51. $C_{39}H_{66}BrNO_2$ (660.86): calcd. C 70.88, H 10.07; found C 71.34, H 10.24.

36-Allyl Dendritic Zirconium-Peroxotungstosilicate Hybrid 8a: To a water solution (0.5 mL) of POM $K_{12}[Zr_2(O_2)_2(SiW_{11}O_{39})_2]\cdot 28H_2O$ (189 mg, 0.029 mmol) was added a solution of ammonium bromide dendron **7a** (300 mg, 0.406 mmol) in CH_2Cl_2 (3 mL). The mixture was vigorously stirred at room temperature for 24 h. The CH_2Cl_2 layer was with dried with sodium sulfate. After evaporation under vacuum, the residue was washed with diethyl ether to provide dendritic POM **8a** as a yellow solid (398 mg, 98%). ^{1}H NMR ($CDCl_3$, 200.16 MHz): δ = 7.43 (broad, 24 H, Ar), 7.19 (broad, 24 H, Ar), 6.83 (broad, 48 H, Ar), 5.52 (m, 36 H, $CH=CH_2$), 5.01–4.94 (m, 96 H, $CH=CH_2$ and NCH_2), 4.12 (broad, 48 H, CH_2-O), 3.19 (broad, 72 H, NCH_2), 2.40 (d, 72 H, $CH_2CH=CH_2$), 2.24 (broad, 48 H, CH_2), 1.81 (broad, 72 H, CH_2), 1.29 (broad, 216 H, CH_2), 0.86 (broad, 108 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 160.1 (C_q, ArO), 156.7 (C_q, ArO), 137.7 (C_q, Ar), 134.6 ($CH=CH_2$), 134.3 (C_q, Ar), 127.6 (CH, Ar), 119.9 (CH, Ar), 117.6 ($CH=CH_2$), 114.8 (CH, Ar), 113.8 (CH, Ar), 64.5 (CH_2O), 64.1 (CH_2O), 58.1 (CH_2N), 42.7 (C_q-CH_2), 41.9 (CH_2), 31.2 (CH_2), 29.3 (CH_2), 26.0 (CH_2), 22.5 (CH_2), 22.3 (CH_2), 14.0 (CH_3) ppm. FTIR (KBr pellets): $\tilde{\nu}$ = 1469 (s), 1378 (w), 957 (s), 909 (vs), 879 (m), 825 (m), 793 (vs) cm^{-1}. $C_{540}H_{920}N_{12}O_{134}Si_2W_{22}Zr_2$ (14008.52): calcd. C 46.30, H 6.62, N 1.20, W 28.87; found C 46.52, H 6.42, N 1.23, W 29.15.

36-(4-*tert*-Butylphenyl) Dendritic Zirconium-Peroxotungstosilicate Hybrid 8b: This compound was synthesized according to the same procedure as described above for **8a**, but with tri(4-*tert*-butylphenyl) ammonium bromide dendron **7b** instead of triallylphenyl ammonium bromide dendron **7a**. Dendritic POM salt **8b** was obtained as a light yellow solid in 95% (0.416 g) yield. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.37 (d_{broad}, 24 H, Ar), 7.18 (m_{broad}, 96 H, Ar), 6.84–6.69 (m_{broad}, 120 H, Ar), 6.79 (m, 6 H, Ar), 4.81 (s_{broad}, 24 H, NCH_2), 3.93 (broad, 48 H, CH_2-O), 3.78 (t_{broad}, 72 H, CH_2-O), 3.14 (broad, 72 H, NCH_2), 1.90 (broad, 48 H, CH_2), 1.74 (broad, CH_2), 1.50 (broad, 72 H, CH_2), 1.36 (broad, CH_2), 1.20 (broad, 324 H, CH_3), 0.80 (broad, 108 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 160.5 (C_q, ArO), 156.9 (C_q, ArO), 156.7 (C_q, ArO), 143.2 (C_q, Ar), 143.1 (CH, Ar), 138.5 (C_q, Ar), 134.2 (C_q, Ar), 127.5 (CH, Ar), 126.2 (CH, Ar), 119.6 (C_q, Ar), 115.2 (CH, Ar), 114.0 (CH, Ar), 113.9 (CH, Ar), 68.3 (CH_2O), 67.6 (CH_2O), 67.4 (CH_2O), 58.3 (CH_2N), 42.0 (C_q-CH_2), 34.0 (C_q-CH_3), 33.7 (CH_2), 33.5 (CH_2), 31.5 (CH_3), 31.2 (CH_2), 27.5 (CH_2), 26.0 (CH_2), 23.7 (CH_2), 22.4 (CH_2), 13.9 (CH_3) ppm. FTIR (KBr pellets): $\tilde{\nu}$ = 1469 (s), 1378 (w), 957 (s), 909 (vs), 879 (m), 825 (m), 793 (vs) cm^{-1}. $C_{900}H_{1424}N_{12}O_{170}Si_2W_{22}Zr_2$ (19416.44): calcd. C 55.67, H 7.39, W 20.83; found C 55.04, H 7.48, W 20.07.

12-(4-*tert*-Butylphenyl) Dendritic Zirconium-Peroxotungstosilicate Hybrid 8c: This compound was synthesized according to the same procedure as described above for **8a**, but with 4-*tert*-butylphenyl ammonium dendron **7c** instead of triallylphenyl ammonium bromide dendron **7a**. Dendritic POM salt **8c** was obtained as a light yellow solid in 95% (0.374 g). ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ = 7.44 (broad, 24 H, Ar), 7.28 (d, 24 H, Ar), 6.88–6.81 (m, 48 H, Ar), 4.92 (broad, 24 H, CH_2N), 4.00 (broad, 48 H, CH_2-O), 3.20 (broad, 72 H, CH_2N), 1.94 (broad, 48 H, CH_2), 1.79 (broad, CH_2), 1.40 (broad, CH_2), 1.28 (s, 108 H, CH_3), 0.86 (broad, 108 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 160.1 (C_q, ArO), 156.7 (C_q, ArO), 143.2 (C_q, Ar), 134.2 (CH, Ar), 126.1 (CH, Ar), 119.9 (C_q, Ar), 114.6 (CH, Ar), 113.8 (CH, Ar), 67.4 (CH_2O), 62.8 (CH_2O), 58.1 (CH_2N), 33.9 (C_q-CH_2), 31.5 (CH_3), 31.2 (CH_2), 26.0 (CH_2), 25.9 (CH_2), 22.4 (CH_2), 22.2 (CH_2), 13.9 (CH_3) ppm. FTIR (KBr pellets): $\tilde{\nu}$ = 1469 (s), 1378 (w), 957 (s), 909 (vs), 880 (m), 827 (m), 793 (vs) cm^{-1}. $C_{468}H_{848}N_{12}O_{134}Si_2W_{22}Zr_2$ (13071.16): calcd. C 43.00, H 6.54, N 1.29, W 30.94; found C 42.24, H 6.30, N 1.29, W 29.92.

***n*-Butyl Zirconium-Peroxotungstosilicate Hybrid 8d:** This compound was synthesized according to the same procedure as described above for **8a**, but with *n*-butylammonium iodide instead of triallylphenyl ammonium bromide dendron **7a**. Dendritic POM salt **8d** was obtained as a light yellow solid in 96% (0.125 g) yield. ^{1}H NMR ($CDCl_3$, 200.16 MHz): δ = 3.26 (broad, 96 H, CH_2-N), 1.60 (broad, 96 H, CH_2), 1.37 (broad, 96 H, CH_2), 0.90 (broad, 144 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 58.8 (CH_2-N), 24.0 (CH_2), 19.5 (CH_2), 13.5 (CH_3) ppm. FTIR (KBr pellets): $\tilde{\nu}$ = 1473 (s), 1382 (w), 955 (s), 914 (s), 877 (m), 805 (m), 741 (s) cm^{-1}.

Supporting Information (see footnote on the first page of this article): IR spectra of $K_{12}[Zr_2(O_2)_2(SiW_{11}O_{39})_2]^{12-}\cdot 28H_2O$, **7a**, **7c**, **8a–d**, and *n*-butylammonium iodide salt; NMR spectra of **8a**, **8b**, and **8d**.

Acknowledgments

S. N. and C. J. thank the Agence National de la Recherche (grant ANR-06-BLAN-0215), the University Bordeaux 1, and the Centre national de la recherche scientifique (CNRS) for financial support. C. J. thanks the European Science Foundation (ESF) European Cooperation in Science and Technology (COST) D40 action for a Short Term Scientific Missions (STSM) grant, allowing for a research visit at Jacobs University Bremen. U. K. and S. S. M. thank Jacobs University Bremen and the Fonds der Chemischen Industrie for research support. We also thank Dr. Bassem Bassil and Dr. Nadeen Nsouli for assistance in the lab.

---

[1] a) G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendrimers and Dendrons, Concepts, Synthesis and Applications*, VCH-Wiley, Weinheim, **2001**; b) D. Tomalia, J. M. J. Fréchet (Eds.), *Dendrimers and Other Dendritic Polymers*, Wiley-VCH, New York, **2002**; c) D. Astruc (Ed.), "Dendrimers and Nanoscience", special triple issue of *C. R. Chimie*, *Vol. 6, Issues 8–10*, Elsevier, Paris, **2003**; d) J.-M. Lehn *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, **1995**; e) F. Zeng, S. C. Zimmerman, *Chem. Rev.* **1997**, *97*, 1681.

[2] a) D. Astruc, F. Chardac, *Chem. Rev.* **2001**, *101*, 2991–3024; b) G. E. Oosterom, J. N. H. Reek, P. C. J. Kramer, P. W. N. M. van Leeuwen, *Angew. Chem. Int. Ed.* **2001**, *40*, 1828–1849; c) R. Kreiter, A. Kleij, R. J. M. Klein Gebbink, G. van Koten, *Top. Curr. Chem.* **2001**, *217*, 163–199; d) R. van Heerbeek, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. N. H. Reek, *Chem. Rev.* **2002**, *102*, 3717–3756.

[3] G. R. Newkome, E. He, C. N. Moorefield, *Chem. Rev.* **1999**, *99*, 1689–1746; H. M. Janssen, E. W. Meijer, *Chem. Rev.* **1999**, *99*, 1665–1688; I. Cuadrado, M. Moran, C. M. Casado, B. Alonso, J. Losada, *Coord. Chem. Rev.* **1999**, *193–195*, 395–445; M. A. Hearshaw, J. R. Moss, *Chem. Commun.* **1999**, *1*,1–8.

[4] a) M. C. Rogers, B. Adisa, D. Bruce, *Catal. Lett.* **2004**, *98*, 29–36; b) H. Zeng, G. R. Newkome, C. L. Hill, *Angew. Chem. Int. Ed.* **2000**, *39*, 1771–1774; c) D. Volkmer, B. Bredenkötter, J. Tellenbröker, P. Kögerler, D. G. Kurth, P. Lehmann, H. Schnableggen, D. Schwahn, M. Piepenbrink, B. Krebs, *J. Am. Chem. Soc.* **2002**, *124*, 10489–10496; d) L. Plault, A. Hauseler, S. Nlate, D. Astruc, J. Ruiz, S. Gatard, R. Neumann, *Angew. Chem. Int. Ed.* **2004**, *43*, 2924–2928; e) M. V. Vasylyev, D. Astruc, R. Neumann, *Adv. Synth. Catal.* **2005**, *347*, 39–44; f) S. Nlate, D. Astruc, R. Neumann, *Adv. Synth. Catal.* **2004**, *346*, 1445–1448; g) S. Nlate, L. Plault, D. Astruc, *Chem. Eur. J.* **2006**, *12*, 903–914; h) S. Nlate, L. Plault, D. Astruc, *New J. Chem.* **2007**, *31*, 1264–1274; i) C. Jahier, L. Plault, S. Nlate, *Isr. J. Chem.* **2009**, *49*, 109–118; j) C. Jahier, M. Cantuel, N. D. McClenaghan, T. Buffeteau, D. Cavagnat, F. Agbossou, M. Carraro, M. Bonchio, S. Nlate, *Chem. Eur. J.* **2009**, *15*, 8703–8708.

[5] a) M. T. Pope, A. Müller, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34–48; b) J. T. Rhule, C. L. Hill, D. A. Rud, R. F. Schinazi, *Chem. Rev.* **1998**, *98*, 327–358; c) D. E. Katsoulis, *Chem. Rev.* **1998**, *98*, 359–388; d) M. T. Pope, A. Müller, *Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications*, Kluwer Academic, Dordrecht, **2001**.

[6] For the multiple facets of POM chemistry, see ref.[5] and the special issue dedicated to POMs: *Chem. Rev.* **1998**, *98*, 1–390.
[7] a) S. S. Mal, N. H. Nsouli, M. Carraro, A. Sartorel, G. Scorrano, H. Oelrich, L. Walder, M. Bonchio, U. Kortz, *Inorg. Chem.* **2010**, *49*, 7–9; b) B. S. Bassil, S. S. Mal, M. H. Dickman, U. Kortz, H. Oelrich, L. Walder, *J. Am. Chem. Soc.* **2008**, *130*, 6696–6697.
[8] S. Nlate, L. Plault, F.-X. Felpin, D. Astruc, *Adv. Synth. Catal.* **2008**, *350*, 1419–1424.
[9] V. Sartor, S. Nlate, J. L. Fillaut, L. Djakovitch, F. Moulines, V. Marvaud, F. Neveu, J. C. Blais, J. F. Létard, D. Astruc, *New J. Chem.* **2000**, *24*, 351–370.

Received: November 24, 2009