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Peripheral functionalisation of dendrimers with polyoxotungstate complexes assembled by ionic bonding and their use as oxidation catalysts: Influence of the tether length†‡

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Two series of dendritic compounds functionalized at the periphery with polyoxometalate (POM) units were synthesized using two synthetic strategies. The first series involved the $[CpFe]^+$-induced functionalization of polymethylarenes, leading to dendrimers in which the dendronic tripod is directly bonded to the arene core. In the second procedure, dendrimers with a spacer group of six atoms between the arene core and the tripod units were synthesized through a coupling reaction between the phenol dendron and bromobenzyl derivatives. These polyallyl dendrimers were functionalized at the periphery to give quaternary poly-ammonium salts. Reactions of the latter with $H_3PW_{12}O_{40}$ in the presence of hydrogen peroxide led to dendrimers containing $\{PO_4[WO(O_2)_2]_4\}^{3-}$ species at the periphery. These compounds are efficient catalysts for the selective oxidation of alkenes, sulfides and alcohols in an aqueous–CDCl$_3$ biphasic system, using hydrogen peroxide as the primary oxidant. The complexes with dendritic wedges directly bonded to the arene core were found to be efficient, epoxidation catalysts that are stable if they are stored under an inert atmosphere, but they do not efficiently catalyze oxidation of alcohols. The dendritic POMs containing spacers, on the other hand, are shown to be more stable in air, they could be recycled and were efficient for the catalytic oxidation of alcohols. Recycling was carried out for the epoxidation reaction using both series of POM catalysts and yielded 50% to 85% of epoxides using the recovered catalysts, the best yields after recycling being obtained with the tris-POM catalyst built from mesitylene and containing spacers (100% conversion; yields in epoxide: first run: 90%; recycled catalyst: 85%). In the case of alcohol oxidation, the tris-POM catalyst was recycled with moderate success (92% conversion; ketone yields: first run: 75%; recycled catalyst: 50%). Among these POM catalysts, dendritic effects on the oxidation yields were found concerning the number of POM units.

Introduction

Dendrimers and metallodendrimers are generating much attention for their potential applications in various areas.[1,2] The increasing use of these macromolecules in catalysis, pioneered by van Leeuwen,[2b,d] is an emerging field, as the size of these macromolecules allows their easy recovery, an essential feature for reaction efficiency, economy and environmental concern.[2] In this context, a variety of dendrimers, cores, branches and end groups were assembled and used in different domains such as supramolecular chemistry,[3] nanosciences,[1c] drug delivery[4] and catalysis.[2] However, dendritic oxidation catalysts are relatively under-represented,[5] a few of them being based on

polyoxometalates (POMs). These POMs are a large class of inorganic transition metal–oxygen clusters that are the source of fascinating architectures[6] and rich redox chemistry[7] that is the basis of their catalytic activity in oxidation reactions.[8] Recently, a few heterogeneous[9] and homogeneous[10] dendritic polyoxometalate catalysts were reported and shown to be effective in oxidation reactions. In homogeneous catalysis, few reports concerning the use of dendritic polyoxometalate catalysts in oxidation reactions are known including POM-cored dendrimers and their application in catalytic oxidation reactions.[10e,f] The synthesis of dendritic tetra-POMs with $[HP_2V_3W_{15}O_{59}]^{5-}$ units covalently bonded to a tetra-armed core for their use as efficient and recoverable catalysts in the oxidation of tetrahydrothiophene to its sulfoxide by tBuOOH and H_2O_2 was described.[11a] Then, the structure and properties of a heteropolytungstate cluster encapsulated in a shell of dendritic branching surfactants was reported.[10b] Recently, the synthesis of two generations of dendritic catalysts based on the *in situ* assembly of dendritic phosphonates with diperoxotungstates, yielding peroxophosphonatotungstate mixtures that are efficient in the epoxidation of alkenes using hydrogen peroxide has been reported.[10d] In a preliminary communication,[10c] we

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published a series of dendritic POMs based on ionic bonding between dendritic ammonium wedges and the trianionic species $\{PO_4[WO(O_2)_2]_4\}^{3-}$, previously reported by Venturello.[11] In the present article, we now compare the syntheses, catalytic efficiencies and stabilities towards recycling of these POM dendrimers in which each methyl group can be transformed into three allyl groups using temporary complexation/activation by the CpFe$^+$ fragment,[12] with a new series of dendritic POMs in which a spacer group of six atoms was introduced between the dendritic wedges and the arene core. We were seeking, in this way, to investigate the influence of the neighbouring interactions of the POMs.

Results and discussion

Synthesis of dendrimers containing tetrakis(diperoxotungsto)phosphate units at the periphery

Dendritic POMs without a spacer between the dendritic wedge and the arene core. Dendritic polyoxometalate compounds with the tripod units directly bonded to the arene core were synthesized following the procedure summarized in Scheme 1 for the tris(POM) complex. In order to build the supramolecular assembly of the dendritic oxidation catalysts in which each POM trianion is connected to a trication unit, we have designed tricationic tripods consisting of triammonium groups. For this purpose, our synthetic strategy involved poly-methylarenes, in which each methyl group can be functionalized by three allyl groups, using temporary complexation/activation by the 12-electron fragment CpFe$^+$ (see Scheme 1 with the example of mesitylene).[12] Regioselective hydroboration of the nona-alkene **2**, which was synthesized from the mesitylene complex **1**, and oxidation of the nona-borane to give the nona-ol **3**, followed by treatment with SiMe$_3$Cl–NaI, provided the nona-iodo compound **4**.[13] Alkylation of tri-hexylamine using **4** gave the nona-ammonium salt **5** as an iodide salt that cannot be used as such for oxidation chemistry, because of the easy oxidation of the iodide anion.[14a] Treatment of **5** with AgBF$_4$ in ethanol gave the BF$_4$$^-$ ammonium salt **6** in 98% yield. The ammonium cations of **6** were then used as counter-cations for the tri-anionic POM complex $[PO_4\{WO(O_2)_2\}_4]^{3-}$, known for its catalytic efficiency in oxidation reactions. The tri-anionic species $[PO_4\{WO(O_2)_2\}_4]^{3-}$ was attached to the ammonium cation of **6** by electrostatic bonding. We used the synthetic procedure involving peroxide mediated decomposition of H$_3$PW$_{12}$O$_{40}$ that gave high yields and a good reproducibility.[10b–e,15] Using this procedure, the heteropolyacid H$_3$PW$_{12}$O$_{40}$ was decomposed in the presence of excess H$_2$O$_2$ to form the dinuclear peroxotungstate $[\{WO(O_2)_2(H_2O)\}_2O]^{2-}$ and the tri-anionic peroxophosphotungstate $[PO_4\{WO(O_2)_2\}_4]^{3-}$. The latter selectively reacted with the nona-ammonium salt **6** in a biphasic mixture of water and methylene chloride to give the dendritic POM **7** that contains three $[PO_4\{WO(O_2)_2\}_4]^{3-}$ units at the periphery in 70% yield. As for the dinuclear peroxotungstate decomposition by-product $[\{WO(O_2)_2(H_2O)\}_2O]^{2-}$, it remained in the aqueous phase of the reaction mixture, and was isolated as a potassium salt in the presence of potassium chloride. In previous studies,[10b–e,15] it was clearly established that

$[PO_4\{WO(O_2)_2\}_4]^{3-}$ was selectively transferred into the organic phase upon contact with the phase-transfer agent, whereas $[\{WO(O_2)_2(H_2O)\}_2O]^{2-}$ remained in the aqueous phase. The appropriate choice of counter-cations allowed the two peroxo salts to be selectively isolated. The tri(POM) dendrimer **7** was indeed isolated from the organic layer and fully characterized by ^{1}H, ^{13}C and ^{31}P NMR, elemental analysis and IR (see the experimental section).

This procedure was also applied to the hexaallyl dendrimer **8** and the triallyl dendrimer **9**, providing the bis(POM) derivative **10** and the mono(POM) derivative **11** in 52 and 73% yield, respectively. Standard characterizations by ^{1}H, ^{13}C, ^{31}P NMR and IR as well as elemental analysis were performed for these dendrimers, and these results are reported in the experimental section. The ^{31}P NMR spectra of the tri(POM) **7**, the bis(POM) **10** and the mono(POM) **11** show one signal at 3.44, 3.54 and 3.37 ppm, respectively.

Since the trifunctionalization of polymethylarenes used here requires that each methyl be free of methyl neighbours in the arene structure, it could not be extended to more than three methyl groups on a single arene ring. In order to extend our study to dendrimers with four POM units, we used the dodeca-allyl derivative **12**.[15] This synthetic strategy was successful and also provided the tetra(POM) derivative **17** according to Scheme 2.

Dendritic POMs **7**, **10**, **11** and **17** were slightly air sensitive; it was noticed that if they were left in air for several days, they became less soluble in CDCl$_3$ or CH$_2$Cl$_2$, and their ^{31}P NMR spectrum changed (peak shift from 3.44 to 1.11 ppm for tris(POM) **7**). However, if the POM catalysts were kept under an inert atmosphere, they did not decompose, as could be checked by the observation of the ^{31}P NMR peak at 3.44 ppm that remained unchanged.

Dendritic POMs containing a spacer between the dendritic wedges and the arene core. The tris(POM) complex **25** and bis(POM) complex **32** were prepared from commercially available 2,4,6-tri(bromomethyl)mesitylene and *p*-dibromoxylene, respectively, following the procedure[14] described in Scheme 3 for compound **25**. The nona-allyl derivative **19** and hexa-allyl dendrimers **26** were synthesized in 80 and 90% yield, respectively, after chromatography, by reaction of the phenol dendron *p*-HO-C$_6$H$_4$C(allyl)$_3$ **18** with the appropriate bromobenzyl derivative in the presence of K$_2$CO$_3$. The tris-(POM) complex **25** and bis(POM) complex **32** were obtained as white solids in 90 and 85% yield by conversion of the allyl dendrimers **19** and **26**, respectively to the nona-ol dendrimer **20** and hexa-ol dendrimer **27**. The nona-mesylate dendrimer **21** and hexa-mesylate dendrimer **28** were then prepared, respectively by reaction of **20** and **27** with chloromethylsulfonate at –5 °C. The reaction of **21** and **28** with sodium iodide gave the nona-iodo dendrimer **22** and the hexa-iodo dendrimer **29** in 95 and 90% yield, respectively. The nona-ammonium iodide salt **23** and the hexa-ammonium iodide salt **30** were then prepared by alkylation of tri-hexylamine, respectively with the nona-iodo dendrimer **22** and the hexa-iodo dendrimer **29**. Treatment of **23** and **30** with AgBF$_4$ in ethanol gave the nona-ammonium BF$_4$$^-$ salt **24** and hexa-ammonium BF$_4$$^-$ salt **31**. The nona-ammonium salt **24** and the hexa-ammonium salt **31** were then
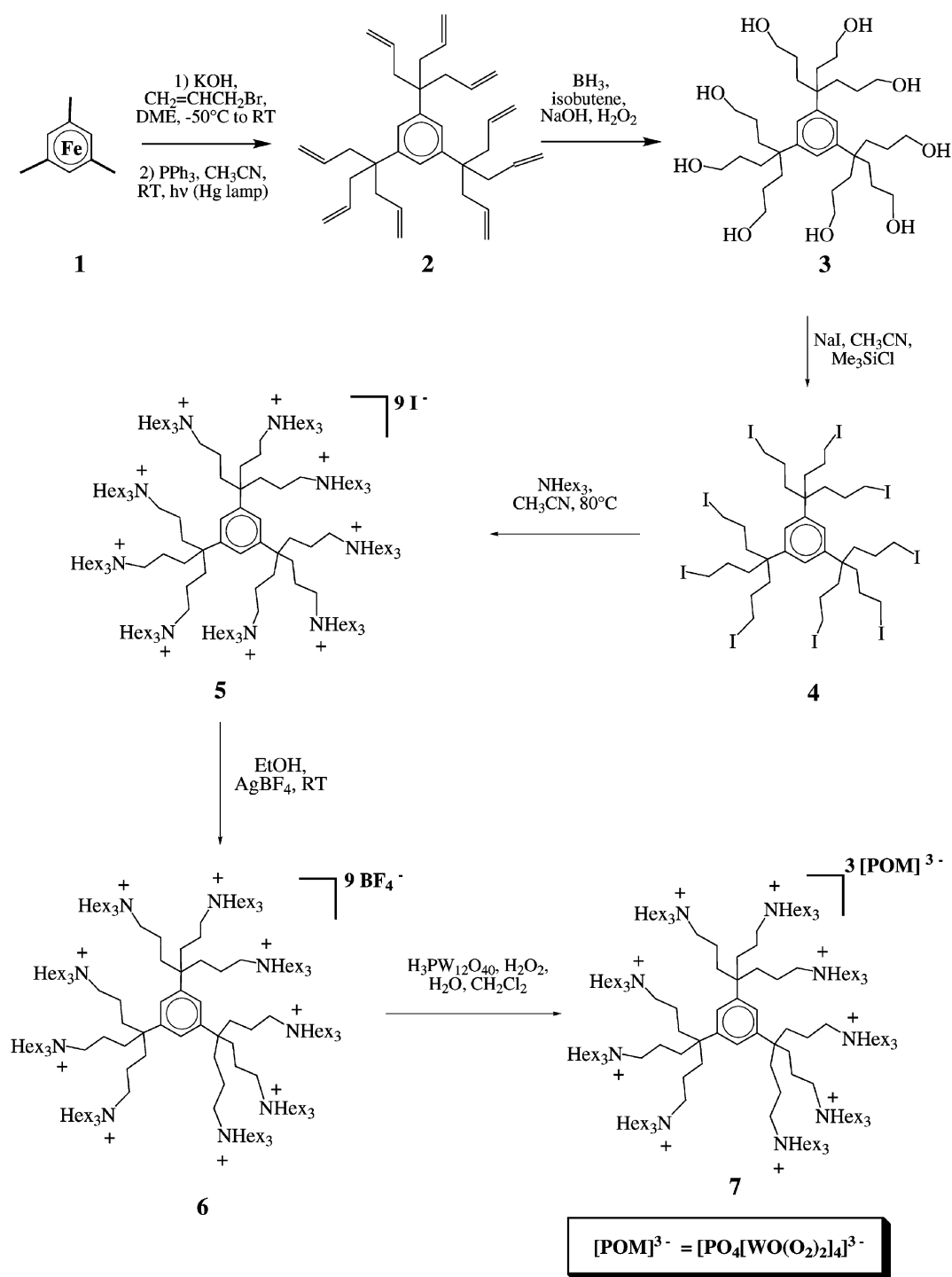
Scheme 1 Synthesis of the tris(POM) **7**.

used to prepare the tris(POM) complex **25** and the bis(POM) complex **32** in a way similar to that described for the mono-(POM) **11**, bis(POM) **10**, tris(POM) **7** and tetra(POM) **17**. Standard characterization techniques (^{1}H and ^{13}C NMR, and elemental analysis) are consistent with the proposed structures. Only one ^{31}P NMR signal was observed for **25** (3.12 ppm) and **32** (3.21 ppm). These values are similar to those obtained for the mono(POM) complex **11**, bis(POM) complex **10**, tris(POM) complex **7** and tetra(POM) complex **17** (see experimental section).

This synthetic strategy was also attempted in the synthesis of the tetra(POM) derivative, starting from the dodeca-allyl dendrimer **33**, prepared in 75% yield by reaction of the phenol dendron **18** with the commercially available 1,2,4,5-tetra(bromomethyl)benzene, in the presence of K_2CO_3 (See supplementary information‡). Regioselective hydroboration of the dodeca-allyl dendrimer **33**, followed by oxidation of the dodeca-borane, led to the dodeca-ol dendrimer **34** in 85% yield. Many attempts to prepare the dodeca-mesylate from the dodeca-ol dendrimer **34** and chloromethylsulfonate at –5 °C
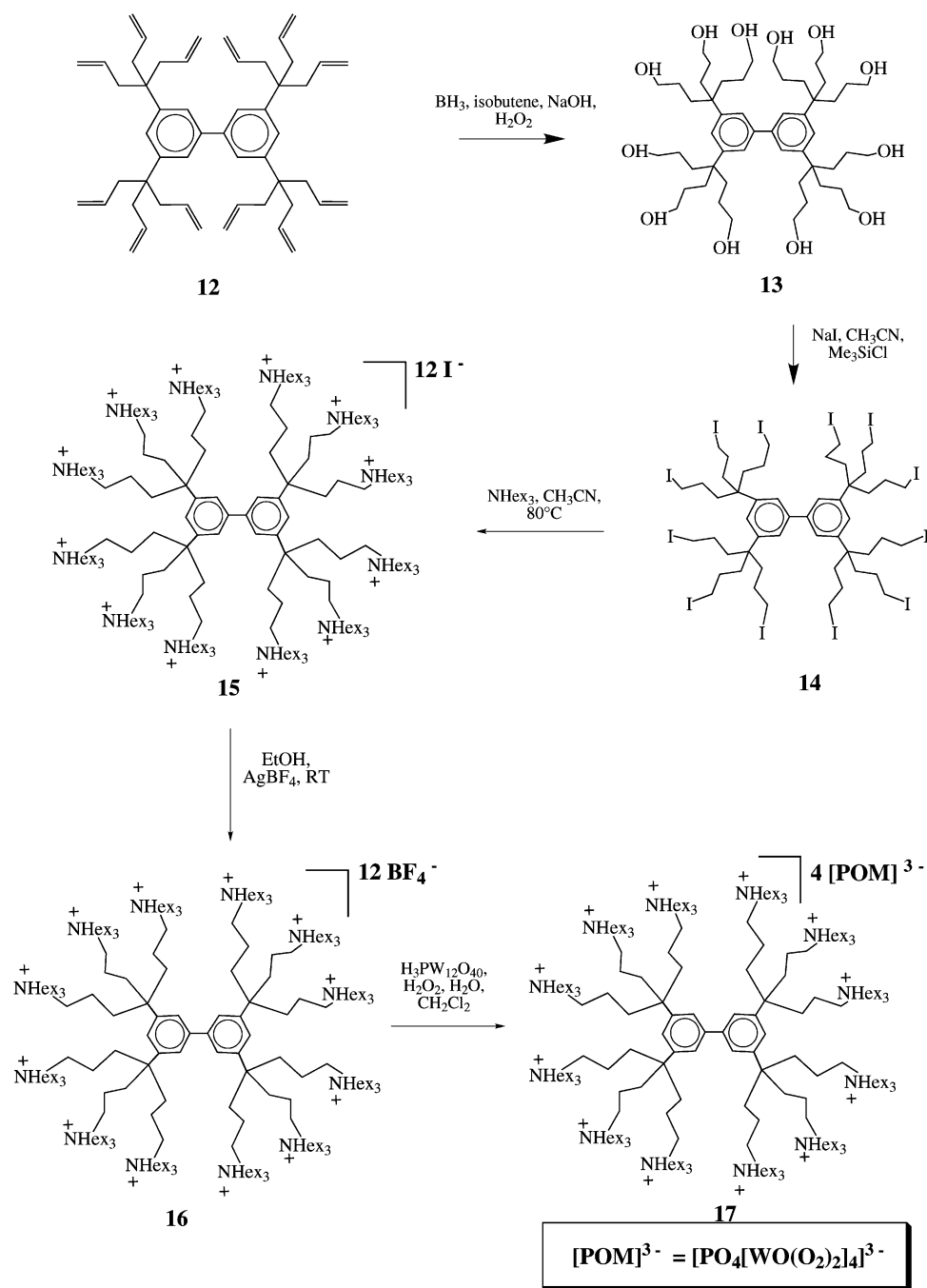
Scheme 2 Synthesis of the tetra(POM) **17**.

were unsuccessful. Indeed, the reaction was not complete, and the ^{1}H NMR spectra showed the two triplets, respectively attributed to SO_3Me (4.15 ppm) and CH_2OH (3.48 ppm) groups. This unsatisfied result to the dodeca-mesylate **35** is probably due to the increased bulk at the dendrimer periphery.

Oxidation of sulfides, alkenes and alcohols with hydrogen peroxide using dendritic POM catalysts 7, 10, 11, 17, 25 and 32

The catalytic performances in oxidation reactions of all the POM dendrimers described herein were examined under mild conditions. The experimental results summarized in Scheme 4 and Table 1 indicate that all these dendritic POMs are efficient catalysts. In accord with our previous studies, the reaction was accomplished with vigorous stirring of an aqueous–CDCl₃ biphasic mixture containing 284 equivalents of the appropriate substrate, 800 equivalents of hydrogen peroxide per POM unit and 0.3 mol% of dendritic POM, at 30 °C. The reaction kinetics were monitored over time by plotting the ratio between the intensity of the disappearing ^{1}H NMR signals substrate *vs.* TMS and the rising peaks of the product.
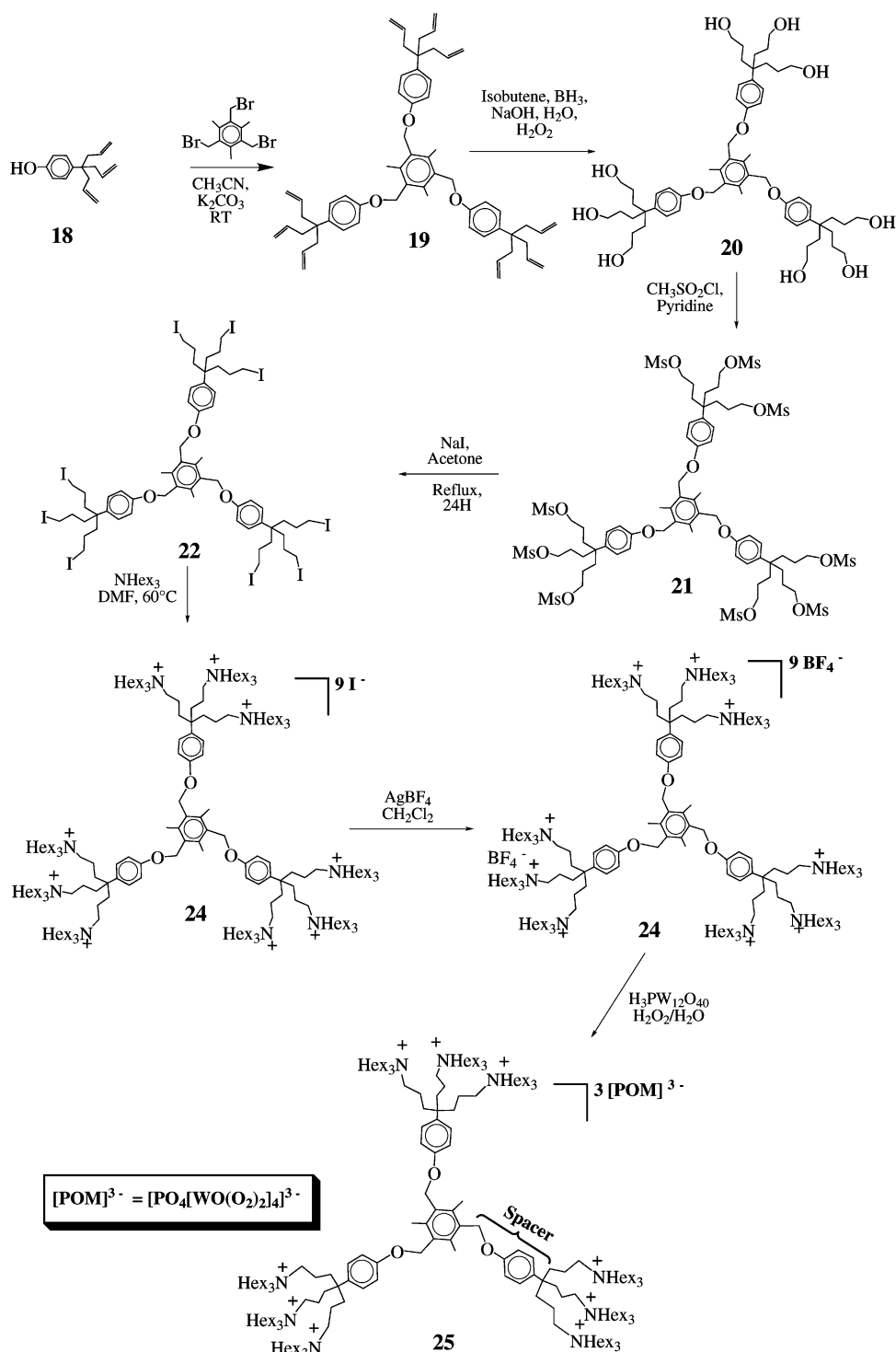
Scheme 3 Synthesis of the tris(POM) **25**.

All the polyoxometalate dendrimers oxidized alkenes quantitatively to their corresponding epoxides, and sulfides to their corresponding sulfones. The dendritic POMs that do not contain a spacer were ineffective in catalyzing the oxidation of secondary alcohols to ketones, whereas their homologues bearing a spacer were efficient in the oxidation of cyclohexanol to cylohexanone. The oxidation of cyclooctene **36** was moni-

tored over time by plotting the ratio between the intensity of the disappearance of the ¹H NMR signal of cyclooctene at 5.6 ppm attributed to cyclooctene and the new peak of the epoxide at 2.9 ppm. As shown in Table 2 (entries 1–6), the POM dendrimers **7–32** oxidized cyclooctene with 100% conversion within the limits of ¹H NMR detection, with reaction times between 3.5 to 6 hours. High conversion and good
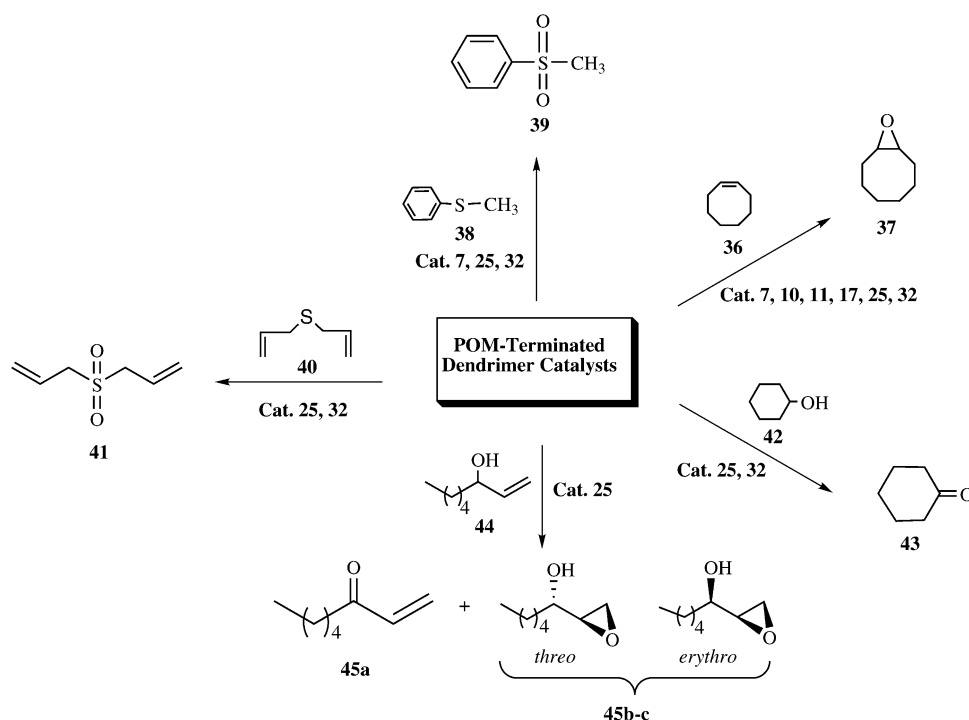
Scheme 4 Catalytic oxidation reactions using 0.3 mol% of POM dendrimers, 284 equiv. of substrate, 800 equiv. H_2O_2 and 3 mL $CDCl_3$.

Table 1 Oxidation of representative alkenes, sulfides and alcohols using H_2O_2, catalyzed by **7**, **10**, **11**, **17**, **25**, and **32**[a]

Entry	Substrate	Catalyst	T (°C)	Time[b] (h)	Product	Conversion (%)[c]
1	**36**	**7**	30	4.8	**37**	100
2		**10**	30	5		100
3		**11**	30	4.6		100
4		**17**	30	6		100
5		**25**	30	4.0		100
6		**32**	30	3.5		100
7	**38**	**7**	30	1.4	**39**	100
8	CH_3–S–	**25**	30	0.2	CH_3–S(O)$_2$–	100
9		**32**	30	0.2		100
						100
10	**40**	**25**	30	1	**41**	100
11		**32**	30	1.1		100
12	**42**	**7**	30	36	**43**	2
13		**25**	30	36		92
15		**32**	30	36		79
15	**44**	**25**	30	34	**45**	95
					45a	7
					45b-*threo*	53
					45c-*erythro*	35

[a] Reaction conditions: catalyst (0.3 mol%), substrate (284 equiv.), H_2O_2 (800 equiv.), $CDCl_3$ (3 mL). [b] Reactions were monitored by ^{1}H NMR. [c] Conversion determined from the relative intensities of the ^{1}H NMR signals of the substrate and product.

Table 2 Isolated yields of recovered POM dendrimer catalysts **7–32**, after the first and second runs, in the oxidation of cyclooctene **36** and cyclohexanol **42**, using H_2O_2

Substrate	Catalyst	First cycle yield (%)	Second cycle yield (%)
Cyclooctene **36**	**7**	81	68
	10	87	50
	11	74	20
	17	98	55
	25	90	85
	32	95	80
Cyclohexanol **42**	**25**	75	50
	32	70	40

selectivity were observed in the oxidation of phenyl methyl sulfide **38** and diallyl sulfide **40** to the corresponding sulfones **39** and **41**, with dendritic POM catalysts **7**, **25** and **32** (Table 2, entries 7–9). The dendritic POM catalysts **25** and **32** containing spacer groups oxidized cyclohexanol **42** to cyclohexanone **43** with conversion up to 92% after a reaction time of 36 hours (Table 2, entries 12–15), in contrast to compound **7** that does not contain spacer groups, which gave only traces of cyclohexanone **43** (Table 2, entry 12). In addition, the tris(POM) **25** oxidized 1-octen-3-ol **44** with excellent conversion rates after 34 hours (Table 2, entry 15), leading to a diastereoisomeric mixture of *threo*:*erythro*-1,2-epoxy-3-octanol **45b and c** as major products, together with 1-octen-3-one **45a**. On the other hand, no trace of conversion was observed using the periphery-congested tris(POM) **7**. The reaction was easily monitored in the ^1H NMR spectrum using the disappearance of the three multiplets at 5.84, 5.15 and 4.10 ppm attributed to the CHOHCH=CH$_2$ group, and the appearance of two multiplets at 3.80 and 3.40 ppm, respectively assigned to the CHOH group of (2S,3R)-1,2-epoxy-3-octanol (**45b** *threo*) and (2S,3S)-1,2-epoxy-3-octanol (**45c** *erythro*). The signals attributed to the epoxy group appear as a multiplet between 3.01 and 2.75 ppm. The α,β-unsaturated 1-octen-3-one **45a** was identified by a new triplet at 2.57 ppm assigned to the CH$_2$CO group. The chemoselectivity of the olefin epoxidation predominated over the alcohol ketonization. Table 1, entries 7–9 and 12–15. This clearly shows that the oxidation of phenyl methyl sulfide **38** and cyclohexanol **42** proceeded more rapidly with POM dendrimers containing spacer groups between the arene core and the POM units, than with their homologues that did not contain spacer groups.

The relationship between the dendritic structure and the catalyst properties is complex, and the question as to what is responsible for this difference in activity and selectivity between the two series of dendrimers is not easy to answer. However, the decreased steric constraints around the POM units in the dendrimers containing spacers compared to the ones that do not contain spacers may provide a possible explanation for the dramatically increased catalytic efficiency in the oxidation of alcohols by dendritic POMs containing spacer groups. The POM units may also interact more easily with one another in the series of compounds without spacer groups, due to the proximity among the POM units. As a result, the decomposition of the catalyst might occur more rapidly for the series that does not contain spacers than in the case of compounds **25** and **32**, each of which contains spacer groups. Unlike the dendritic compounds functionalized at the

periphery with POM units studied in the present work, we have recently found that POM-cored dendrimers (with only one POM unit) are air stable and highly effective catalysts in oxidation reactions.[10f] This indicates that the microenvironment of the catalytic species in dendritic catalysts largely determines their properties.

Recovery and reutilization of dendritic POMs 7–32

Two reaction cycles were performed in order to investigate the stability of the dendritic POMs **7–32** under catalytic reaction conditions. Cyclooctene **36** and cyclohexanol **42** were used as model substrates for catalyst recycling experiments. The dendritic POM catalyst was recovered by precipitation from the organic layer with pentane (isolated yields varied between 74 and 95% for the first cycle and between 20 and 85% for the second cycle as shown in Table 2). The quality of the recovered catalyst was checked by ^1H and ^{31}P NMR before the second catalytic experiment.

Cyclooctene **36** and cyclohexanol **42** were oxidized with conversion between 79 and 100%, over the two cycles. In the case of tris(POM) complex **25** and bis(POM) complex **32**, only one signal, respectively at 3.12 and 3.21 ppm was obtained in the ^{31}P NMR spectrum of the recovered catalyst, indicating the presence of the active species for reaction times of up to 24 hours. In addition, the reaction kinetics showed no discernable loss of activity over the two catalytic cycles, contrary to tris(POM) **7**, bis(POM) **10**, mono(POM) **11** and tetra(POM) **17**, which slowly decomposed in solution (yields ranged from 20 to 68% after the second cycle). The results obtained in these experiments reveal that all the POM dendrimers with a spacer group are more stable and easier to recover and to handle than their homologues without a spacer. However, compared to non-dendritic POMs, both series of dendritic POMs with and without spacers are more stable and reusable. Indeed, it has been shown that precipitation of the alkyl ammonium POMs > n-(C$_8$H$_{17}$)$_3$NCH$_3$]$^+_3$[PO$_4$\{WO(O$_2$)$_2$\}$_4$]$^{3-}$ **46** was very difficult after the first run, and gave a small amount of a solid, identified using ^{31}P NMR by two signals at 0.5 and −0.99 ppm. These ^{31}P NMR signals differed from those obtained for **46** at 3.12 ppm, indicating that the structure of these POM species had changed. In addition, attempts to recover the POM compound, [Arquad]$^+_3$[PO$_4$\{WO(O$_2$)$_2$\}$_4$]$^{3-}$ **47** (Arquad = didecyldimethylammonium) after the first run were unsuccessful. These results indicate that dendritic structures stabilized the POM species and facilitated the recovery and recycling of the POM catalysts.

Conclusion

In this paper, we are reporting the synthesis of two series of dendrimers with POM units at the periphery. In the first series, dendritic tripods were directly bonded to the arene core, whereas in the second series, spacer groups were introduced between the arene core and the dendritic wedges. These POM compounds were found to be effective in the catalytic oxidation of alkenes, sulfides and alcohols, with good to excellent conversion and selectivity. Among these dendritic POM catalysts, those with spacer groups were especially efficient in the oxidation of alcohols, displaying possibilities of recycling up to the second cycle. The dendritic structures dramatically increase the stability of the POM unit, allowing the recovery and eventually a re-use of the catalyst with variable success depending on the catalyst structure. Given the recycle capabilities, as well as the competitive efficiency in the oxidation of alcohols, dendritic POMs with spacer groups between the core and the peripheral POM units are more stable than their homologues without a spacer group in the presence of air (both series being stable in the absence of air). This stability feature is a key one in the oxidation of more challenging substrates as well as in catalyst recovery.

Experimental

General remarks

Reagent-grade tetrahydrofuran (THF), diethyl ether, and pentane were pre-dried over Na foil and distilled from sodium-benzophenone anion 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 ^1H, ^{13}C, ^{31}P NMR spectra were recorded at 25 °C with a Brucker AC 250 FT spectrometer (^1H: 250.13, ^{13}C: 62.91 MHz) and a Brucker AC 200 FT spectrometer (^1H: 200.16, ^{13}C: 50.33, ^{31}P: 81.02 MHz). All chemical shifts are reported in parts per million (δ, ppm) with reference to Me_4Si (TMS). Elemental analyses were carried out at the Vernaison CNRS center. The infrared spectra were recorded in KBr pellets on a FT-IR Paragon 1000 Perkin-Elmer spectrometer. The matrix-assisted laser-desorption (MALDI) mass spectra were recorded using a Perspective Biosystems Voyager Elite (Framingham, MA) time-of-flight (TOF) mass spectrometer. Organic oxidation products were identified by ^1H and ^{13}C NMR using comparison of these spectra with those of authentic samples.

Synthesis of dendritic polyoxometalate compounds 7, 10, 11 and 17 without spacer group between dendritic tripods and the arene core: [CpFe]$^+$ induced activation of polymethylarene procedure

Tris(POM) dendrimer 7. H_2O_2 (5.1 ml , 35% in water) was added to a water solution (5 mL) of commercial hetero-polyacid $H_3PW_{12}O_{40}$ (8.941 g, 3.11 mmol). The mixture was stirred at room temperature for 30 minutes. Then, a CH_2CH_2 solution of BF_4^- ammonium salt **6** (0.896 mmol) was added, and the mixture was stirred for an additional hour. The

CH_2Cl_2 layer was dried over sodium sulfate and evaporated under reduced pressure, providing **7** (4.456 g, 70%) as a white solid. ^1H NMR (200 MHz, CDCl₃) δ_{ppm}: 3.6–3.3 (m$_{broad}$, N–CH_2), 1.83 (m$_{broad}$, N–CH_2–CH_2), 1.35 (m, CH_2), 0.88 (m, CH_3). ^{13}C NMR (63 MHz, CDCl₃) δ_{ppm} 58.5 (CH_2–N), 31.1 (CH_2–CH_2–N), 29.6 (CH_2), 26.2 (C_q–CH_2), 25.8 (CH_2), 23.2 (CH_2), 22.3 (CH_2), 21.6 (CH_2), 13.8 CH_3. ^{31}P (81 MHz, CDCl₃) δ_{ppm} 3.44 (PO_4). FTIR (KBr plates) $\nu_{cm^{-1}}$: 1088–1052 (P–O), 970 (W=O), 845 (O–O), 580 and 521 $W(O_2)_{s,as}$, other bands at 649.8, 574.6, 549.0. Elemental analysis calcd for $C_{198}H_{408}N_9P_3W_{12}O_{72}$: C, 37.35; H, 6.46; P, 1.46. Found: C, 37.48; H, 6.08; P, 1.56%.

Bis(POM) dendrimer 10. Dendrimer **10** was obtained from the hexa-allyl **8** as a colorless solid in 52% yield using the procedure described above for **7**. ^1H NMR (200 MHz, CDCl₃) δ_{ppm}: 3.18 (m$_{broad}$, N–CH_2), 1.78 (m, N–CH_2–CH_2), 1.34 (m, CH_2), 0.91 (m, CH_3). ^{13}C NMR (63 MHz, CDCl₃) δ_{ppm}: 58.5 (CH_2–N), 31.8 (CH_2–CH_2–N), 29.6 (CH_2), 26.3 (C_q–CH_2), 25.8 (CH_2), 23.2 (CH_2), 22.7 (CH_2), 21.6 (CH_2), 14.3 (CH_3). ^{31}P (81 MHz, CDCl₃) δ_{ppm}: 3.54 (PO_4). FTIR (KBr plates) $\nu_{cm^{-1}}$: 1086 and 1057 (P–O), 974 (W=O), 845 (O–O), 590 and 522 $W(O_2)_{s,as}$, other bands at 651, 575, 548.8. Elemental analysis calcd for $C_{134}H_{274}N_6P_2W_8O_{48}$: C, 38.67; H, 6.49. Found: C, 39.01; H, 6.49%.

Mono(POM)dendrimer 11. Dendrimer **11** was obtained as a colorless solid in 73% yield from the tri-allyl **9** using the procedure described above for **7**. ^1H NMR (CDCl₃, 200 MHz) δ_{ppm}: 7.4 (m, 4H, H_{arom}), 3.3 (m$_{broad}$, CH_2–N), 1.7 (m, CH_2), 1.3 (m, CH_2), 0.9 (s, 27H, CH_3). ^{13}C NMR (CDCl₃, 63 MHz) δ_{ppm}: 58.5 (CH_2–N), 31.3 (CH_2–CH_2–N), 26.5 (CH_2–C_q), 22.5 (CH_2), 14.0 (CH_3). ^{31}P NMR (CDCl₃, 81 MHz) δ_{ppm}: 3.37 (PO_4). FTIR (KBr plates) $\nu_{cm^{-1}}$: 1083 and 1057 (P–O), 974 (W=O), 845 (O–O), 590 and 517 $W(O_2)_{s,as}$, other bands at 652, 574, 548. Elemental analysis calcd for $C_{70}H_{140}N_3P_1W_4O_{24}$: C, 37.69; H, 6.47. Found: C, 38.67; H, 6.49%.

Tetra(POM)dendrimer 17. Dendrimer **17** was obtained as a colorless solid in 54% yield from the dodeca-allyl **12** using the procedure described above for **7**. ^1H NMR (200 MHz, CDCl₃) δ_{ppm}: 3.18 (m$_{broad}$, N–CH_2), 1.74 (m, N–CH_2–CH_2), 1.35 (m, CH_2), 0.91 (m, CH_3). ^{13}C NMR (63 MHz, CDCl₃) δ_{ppm}: 58.5 (CH_2–N), 31.1 (CH_2–CH_2–N), 29.6 (CH_2), 26.2 (C_q–CH_2), 25.8 (CH_2), 23.2 (CH_2), 22.3 (CH_2), 21.6 (CH_2), 13.8 (CH_3). ^{31}P (81 MHz, CDCl₃) δ_{ppm}: 3.15 (PO_4). FTIR (KBr plates) $\nu_{cm^{-1}}$: 1087 and 1057 (P–O), 972 (W=O), 846 (O–O), 580 and 521 $W(O_2)_{s,as}$, other bands at 658, 575, 549. Elemental analysis calcd for $C_{268}H_{546}N_{12}P_4W_{16}O_{96}$: C, 37.70; H, 6.45. Found: C, 38.00; H, 6.56%.

Synthesis of dendritic polyoxometalate complexes containing spacer groups between the arene core and dendritic tripod units: dendrimers 25 and 32

Nona-allyl dendrimer 19. A mixture of phenol-tri-allyl dendron **18** (1.000 g, 4.386 mmol), K_2CO_3 (0.817 g 5.839 mmol), and 2,4,6-tri(bromomethyl)mesitylene (0.387 g, 0.970 mmol) in DMF, was stirred for 2 days at 60 °C. The product was extracted with 3 × 30 ml of ether and the ether solution

washed with 5×20 ml of water. The organic phase was dried over sodium sulfate, then filtered and evaporated under vacuum. The product was purified by chromatography on a silica-gel column with a pentane–diethyl ether mixture (8 : 2) to provide **19** (2.767 g, 75%) as a colorless solid. ^{1}H NMR (CDCl$_3$, 200.16 MHz) δ_{ppm}: δ 7.24 (d, 6H, Ar), 6.93 (d, 2H, Ar), 6.98 (d, 6H, Ar), 5.57 (m, 9H, CH=CH$_2$), 5.03 (m, 24H, CH=CH$_2$, and CH$_2$O), 2.46 (s, 9H, CH$_3$), 2.44 (d, 18H, CH$_2$CH=CH$_2$). ^{13}C NMR (CDCl$_3$, 62.91 MHz) δ_{ppm}ù 157.07 (C$_q$, ArO), 139.35 (C$_q$, $_{arom}$), 138.04 (C$_q$, $_{arom}$), 134.72 (CH=CH$_2$), 131.92 (C$_q$, $_{arom}$), 127.73 (CH$_{arom}$), 117.57 (CH=CH$_2$), 114.08 (CH$_{arom}$), 64.88 (CH$_2$O), 42.71 (C$_q$–CH$_2$), 42.03 (CH$_2$), 16.01 (CH$_3$). MALDI TOF mass spectrum, m/z: 863.43 [M + Na]$^+$ (calcd 864.21). Elemental analysis calcd for C$_{60}$H$_{72}$O$_3$: C, 85.67; H, 8.63. Found: C, 85.31; H, 8.47%.

Nona-ol dendrimer 20. Dendrimer **20** was obtained as a colorless solid in 95% yield from the nona-allyl **19**, using the procedure described in ref. 14. ^{1}H NMR (CD$_3$OD, 200.16 MHz) δ_{ppm}: 7.12 (d, 6H, Ar), 6.80 (d, 2H, Ar), 4.90 (s, 6H, CH$_2$O), 3.28 (t, 18H, CH$_2$O), 1.55 (m, 18H, CH$_2$), 1.12 (m, 18H, CH$_2$). ^{13}C NMR (CD$_3$OD, 62.91 MHz) δ_{ppm}: 156.79 (C$_q$, ArO), 139.31 (C$_q$, $_{arom}$), 138.68 (C$_q$, $_{arom}$), 131.76 (C$_q$, $_{arom}$), 127.23 (CH$_{arom}$), 113.76 (CH$_{arom}$), 62.14 (CH$_2$O), 41.41 (C$_q$–CH$_2$), 33.28 (CH$_2$), 26.40 (CH$_2$), 14.57 (CH$_3$). MALDI TOF mass spectrum, m/z: 1025.88 [M + Na]$^+$ (calcd 1026.35). Elemental analysis calcd for C$_{60}$H$_{90}$O$_{12}$: C, 71.81; H, 9.04. Found: C, 71.09; H, 9.22%.

Nona-mesylate dendrimer 21. Dendrimer **21** was obtained as a yellow oil in 98% yield from the nona-ol **20**, using the procedure described in ref. 14. ^{1}H NMR (CDCl$_3$, 200.16 MHz) δ_{ppm}: 7.20 (d, 6H, Ar), 6.96 (d, 2H, Ar), 5.08 (s, 6H, CH$_2$O), 4.15 (t, 18H, CH$_2$O), 2.97 (s, 27H, CH$_3$SO$_2$), 1.75 (m$_{broad}$, 18H, CH$_2$), 1.53 (m$_{broad}$, 18H, CH$_2$). ^{13}C NMR (CDCl$_3$, 62.91 MHz) δ_{ppm}: 157.27 (C$_q$, ArO), 139.25 (C$_q$, $_{arom}$), 138.68 (C$_q$, $_{arom}$), 134.91 (C$_q$, $_{arom}$), 127.23 (CH$_{arom}$), 114.48 (CH$_{arom}$), 70.47 (CH$_2$OSO$_2$), 62.59 (CH$_2$O), 41.67 (C$_q$–CH$_2$), 37.37 (SO$_2$CH$_3$), 23.59 (CH$_2$), 15.98 (CH$_3$). Elemental analysis calcd for C$_{69}$H$_{108}$O$_{30}$S$_9$: C, 48.57; H, 6.38. Found: C, 48.78; H, 6.40%.

Nona-iodo dendrimer 22. This dendrimer was obtained as a yellow oil in 95% yield from the nona-mesylate **21** using the procedure described in ref. 14. ^{1}H NMR (CDCl$_3$, 200.16 MHz) δ_{ppm}: 7.28 (d, 6H, Ar), 7.02 (d, 2H, Ar), 5.13 (s, 6H, CH$_2$O), 3.18 (t, 18H, CH$_2$I), 2.51 (s, 9H, CH$_3$), 1.78 (m$_{broad}$, 18H, CH$_2$), 1.65 (m$_{broad}$, 18H, CH$_2$). ^{13}C NMR (CDCl$_3$, 62.91 MHz) δ_{ppm}: 157.16 (C$_q$, ArO), 139.30 (C$_q$, $_{arom}$), 137.94 (C$_q$, $_{arom}$), 131.75 (C$_q$, $_{arom}$), 127.15 (CH$_{arom}$), 114.35 (CH$_{arom}$), 64.86 (CH$_2$O), 41.71 (C$_q$–CH$_2$), 38.52 (CH$_2$), 27.55 (CH$_2$), 16.03 (CH$_3$), 7.89 (CH$_2$I). Elemental analysis calcd for C$_{60}$H$_{81}$O$_3$I$_9$: C, 36.17; H, 4.10. Found: C, 36.75; H, 4.56%.

Nona-ammonium nona-iodide dendritic salt 23. This dendritic salt was obtained from the nona-iodo derivative **22**, in 93% yield using the procedure described for **5**. ^{1}H NMR (CDCl$_3$, 200.16 MHz) δ_{ppm}: 7.28 (d, 6H, Ar), 7.01 (d, 6H, Ar), 5.13 (s, 6H, CH$_2$O), 3.3 (m$_{broad}$, CH$_2$–N), 1.85-1.66 (m$_{broad}$, N–CH$_2$–CH$_2$), 1.36 (m$_{broad}$, CH$_2$), 0.91 (m, CH$_3$). ^{13}C NMR

(CDCl$_3$, 62.91 MHz): δ = 157.27 (C$_q$, ArO), 139.25 (C$_q$, $_{arom}$), 138.68 (C$_q$, $_{arom}$), 134.91 (C$_q$, $_{arom}$), 127.23 (CH$_{arom}$), 114.48 (CH$_{arom}$), 62.59 (CH$_2$O), 59.45 (CH$_2$–N), 31.48 (CH$_2$–CH$_2$–N), 26.93 (CH$_2$–C$_q$), 25.95 (CH$_2$), 22.53, (CH$_2$), 22.21 (CH$_2$), 13.93 (CH$_3$). Elemental analysis calcd for C$_{164}$H$_{305}$O$_3$I$_9$N$_9$: C, 54.79; H, 8.55. Found: C, 55.04; H, 8.74%.

Nona-ammonium nona-tetrafluoroborate dendrimer 24. Dendrimer **24** was obtained from the salt **23**, in 90% yield using the procedure described for **6**. ^{1}H NMR (200 MHz, CDCl$_3$) δ_{ppm}: 7.26 (s$_{broad}$, 6H, H$_{arom}$), 6.95 (s$_{broad}$, 6H, H$_{arom}$), 5.05 (s$_{broad}$, 6H, CH$_2$O), 3.34 (m$_{broad}$, N–CH$_2$), 1.75–1.53 (m$_{broad}$, N–CH$_2$–CH$_2$), 1.27 (m$_{broad}$, CH$_2$), 0.85 (m$_{broad}$, CH$_3$). ^{13}C NMR (CDCl$_3$, 62.91 MHz) δ_{ppm}: 157.27 (C$_q$, ArO), 139.25 (C$_q$, $_{arom}$), 138.68 (C$_q$, $_{arom}$), 134.91 (C$_q$, $_{arom}$), 127.23 (CH$_{arom}$), 114.48 (CH$_{arom}$), 62.59 (CH$_2$O), 58.81 (CH$_2$–N), 31.08 (CH$_2$–CH$_2$–N). Elemental analysis calcd for C$_{164}$H$_{305}$O$_3$I$_9$N$_9$ B$_9$F$_{36}$: C, 60.94; H, 9.51. Found: C, 60.32, H, 9.15%.

Tris(POM) dendrimer 25. This dendrimer was obtained as a colorless solid in 75% yield from the nona-ammonium salt **24** using the procedure described above for **7**. ^{1}H NMR (CDCl$_3$, 200.16 MHz) δ_{ppm}: 7.2 (d, 6H, Ar), 7.01 (d, 6H, Ar), 5.13 (s, 6H, CH$_2$O), 3.3 (m$_{broad}$, CH$_2$–N), 1.85–1.66 (m$_{broad}$, N–CH$_2$–CH$_2$), 1.36 (m$_{broad}$, CH$_2$), 0.91 (m, CH$_3$). ^{13}C NMR (CDCl$_3$, 62.91 MHz) δ_{ppm}: 157.27 (C$_q$, ArO), 139.25 (C$_q$, $_{arom}$), 138.68 (C$_q$, $_{arom}$), 134.91 (C$_q$, $_{arom}$), 127.23 (CH$_{arom}$), 114.48 (CH$_{arom}$), 62.59 (CH$_2$O), 59.45 (CH$_2$–N), 31.48 (CH$_2$–CH$_2$–N), 31.02 (CH$_3$), 26.93 (CH$_2$–C$_q$), 25.95 (CH$_2$), 22.53, (CH$_2$), 22.21 (CH$_2$), 13.93 (CH$_3$). ^{31}P NMR (CDCl$_3$, 81 MHz) δ_{ppm}: 3.12 (PO$_4$). FTIR (KBr plates) $\nu_{cm^{-1}}$: 1076 and 1058 (P–O), 963 (W=O), 830 (O–O), 580 and 521 W(O$_2$)$_{s,as}$. Elemental analysis calcd for C$_{219}$H$_{436}$O$_{75}$N$_9$ P$_3$W$_{12}$: C, 39.29; H, 6.56; P, 1.39. Found: C, 39.90; H, 6.58; P, 1.35%.

Hexa-allyl dendrimer 26. This dendrimer was obtained as a white solid in 90% yield using the procedure described above for the nona-allyl **19**. ^{1}H NMR (CDCl$_3$, 200.16 MHz) δ_{ppm}: 7.47 (s, 4H, Ar), 7.23 (d, 4H, Ar), 6.94 (d, 4H, Ar), 5.57 (m, 6H, CH=CH$_2$), 5.03 (m, 16H, CH=CH$_2$, and CH$_2$O), 2.43 (d, 9H, CH$_2$CH=CH$_2$). ^{13}C NMR (CDCl$_3$, 62.91 MHz) δ_{ppm}: 156.69 (C$_q$, ArO), 138.10 (C$_q$, $_{arom}$), 136.95 (C$_q$, $_{arom}$), 134.68 (CH=CH$_2$), 127.81 (C$_q$, $_{arom}$), 127.75 (CH$_{arom}$), 117.57 (CH=CH$_2$), 114.08 (CH$_{arom}$), 69.72 (CH$_2$O), 42.74 (C$_q$–CH$_2$), 41.99 (CH$_2$). MALDI TOF mass spectrum, m/z: 581.13 [M + Na]$^+$ (calcd 581.79). Elemental analysis calcd for C$_{40}$H$_{46}$O$_2$: C, 85.98; H, 8.30. Found: C, 85.86; H, 8.34%.

Hexa-ol dendrimer 27. The hexa-ol **27** was obtained as a colorless solid in 90% yield from **26** using the procedure described in ref. 14. ^{1}H NMR (CD$_3$OD, 200.16 MHz) δ_{ppm}: 7.43 (s, 4H, Ar), 7.20 (d, 4H, Ar), 7.95 (d, 4H, Ar), 5.03 (s, 4H, CH$_2$O), 3.46 (t, 12H, CH$_2$O), 1.65 (m, 12H, CH$_2$), 1.30 (m, 12H, CH$_2$). ^{13}C NMR (CD$_3$OD, 62.91 MHz) δ_{ppm}: 156.50 (C$_q$, ArO), 139.19 (C$_q$, $_{arom}$), 137.03 (C$_q$, $_{arom}$), 127.13 (CH$_{arom}$), 113.90 (CH$_{arom}$), 69.17 (CH$_2$O), 62.10 (CH$_2$O), 41.34 (C$_q$–CH$_2$), 33.25 (CH$_2$), 26.37 (CH$_2$). MALDI TOF mass spectrum, m/z: 689.65 [M + Na]$^+$ (calcd 689.88). Elemental

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analysis calcd for $C_{60}H_{90}O_{12}$: C, 72.04; H, 8.77. Found: C, 71.34; H, 8.67%.

Hexa-mesylate dendrimer 28. This dendrimer was obtained as yellow oil in 95% yield from the hexa-ol dendrimer **27** using the procedure described in ref. 14. ^{1}H NMR (CDCl$_3$, 200.16 MHz) δ_{ppm}: 7.50 (s, 4H, Ar), 7.25 (d, 4H, Ar), 6.98 (d, 4H, Ar), 5.09 (s, 6H, CH$_2$O), 4.19 (t, 18H, CH$_2$O), 3.01 (s, 18H, CH$_3$SO$_2$), 1.75 (m$_{broad}$, 12H, CH$_2$), 1.53 (m$_{broad}$, 12H, CH$_2$). ^{13}C NMR (CDCl$_3$, 62.91 MHz) δ_{ppm}: 156.92 (C$_q$, ArO), 137.13 (C$_{q, arom}$), 136.74 (C$_{q, arom}$), 127.78 (C$_{q, arom}$), 127.20 (CH$_{arom}$), 122.88 (CH$_{arom}$), 114.69 (CH$_{arom}$), 70.33 (CH$_2$O-SO$_2$), 69.63 (CH$_2$O), 41.67 (C$_q$–CH$_2$), 37.34 (SO$_2$CH$_3$), 32.87 (CH$_2$), 21.98 (CH$_2$). Elemental analysis calcd for $C_{46}H_{70}O_{20}S_6$: C, 48.66; H, 6.21. Found: C, 48.59; H, 6.75%.

Hexa-iodo dendrimer 29. Dendrimer **29** was obtained as a yellow oil in 90% yield from the hexa-mesylate **28** using the procedure described in ref. 14. ^{1}H NMR (CDCl$_3$, 200.16 MHz) δ_{ppm}: 7.47 (s, 4H, Ar), 7.20 (d, 4H, Ar), 6.94 (d, 4H, Ar), 5.06 (s, 4H, CH$_2$O), 3.12 (t, 12H, CH$_2$I), 2.51 (s, 9H, CH$_3$), 1.75 (m$_{broad}$, 12H, CH$_2$), 1.65 (m$_{broad}$, 12H, CH$_2$). ^{13}C NMR (CDCl$_3$, 62.91 MHz) δ_{ppm}: 156.80 (C$_q$, ArO), 138.01 (C$_{q, arom}$), 136.78 (C$_{q, arom}$), 127.79 (C$_{q, arom}$), 127.16 (CH$_{arom}$), 114.51 (CH$_{arom}$), 69.67 (CH$_2$O), 41.70 (C$_q$–CH$_2$), 38.48 (CH$_2$), 27.52 (CH$_2$), 7.77 (CH$_2$I). Elemental analysis calcd for $C_{40}H_{52}O_2I_6$: C, 36.23; H, 3.95. Found: C, 36.75; H, 4.45%.

Hexa-ammonium hexa-iodide salt dendrimer 30. The hexa-iodo salt **30** was obtained from **29** in 85% yield using the procedure described for **5**. ^{1}H NMR (CDCl$_3$, 200.16 MHz) δ_{ppm}: 7.46 (s, 4H, Ar), 7.22 (d, 4H, Ar), 6.97 (d, 4H, Ar), 5.09 (s, 4H, CH$_2$O), 3.27 (m$_{broad}$, CH$_2$–N), 1.90–1.53 (m$_{broad}$, N–CH$_2$–CH$_2$), 1.25 (m$_{broad}$, CH$_2$), 0.84 (m, CH$_3$). ^{13}C NMR (CDCl$_3$, 62.91 MHz) δ_{ppm}: 157.27 (C$_q$, ArO), (C$_{q, arom}$), 138.68 (C$_{q, arom}$), 134.91 (C$_{q, arom}$), 127.23 (CH$_{arom}$), 114.56 (CH$_{arom}$), 69.72 (CH$_2$O), 59.45 (CH$_2$–N), 31.48 (CH$_2$–CH$_2$–N), 26.91 (CH$_2$–C$_q$), 25.04 (CH$_2$), 22.52, (CH$_2$), 22.39 (CH$_2$), 13.94 (CH$_3$). Elemental analysis calcd for $C_{148}H_{286}O_2I_6N_6$: C, 60.37; H, 9.79. Found: C, 60.32; H, 9.15%.

Hexa-ammonium hexa-tetrafluoroborate dendrimer 31. The hexa-tetrafluoroborate salt **31** was obtained from the corresponding hexa-iodo salt **30** in 95% yield, using the procedure described above for **6**. ^{1}H NMR (200 MHz, CDCl$_3$) δ_{ppm}: 7.42 (s, 4H, Ar), 7.22 (d, 4H, Ar), 6.92 (d, 4H, Ar), 5.06 (s, 4H, CH$_2$O), 3.32–3.10 (m$_{broad}$, CH$_2$–N), 1.90–1.55 (m$_{broad}$, N–CH$_2$–CH$_2$), 1.35 (m$_{broad}$, CH$_2$), 0.85 (m, CH$_3$). ^{13}C NMR (CDCl$_3$, 62.91 MHz) δ_{ppm}: 157.00 (C$_q$, ArO), 137.25 (C$_{q, arom}$), 138.68 (C$_{q, arom}$), 134.91 (C$_{q, arom}$), 127.38 (CH$_{arom}$), 114.56 (CH$_{arom}$), 69.60 (CH$_2$O), 59.72 (CH$_2$–N), 31.02 (CH$_2$–CH$_2$–N), 26.11 (CH$_2$–C$_q$), 25.84 (CH$_2$), 22.32, (CH$_2$), 22.04 (CH$_2$), 13.82 (CH$_3$).

Bis(POM) dendrimer 32. The Bis(POM) **32** was obtained as a colorless solid in 70% yield from the hexa-ammonium hexa-tetrafluoroborate dendrimer **31**, using the procedure described above for **7**. ^{1}H NMR (200 MHz, CDCl$_3$) δ_{ppm}: 7.44 (s, 4H, Ar), 7.31 (d, 4H, Ar), 6.98 (d, 4H, Ar), 5.09 (s, 4H, CH$_2$O),

3.56–3.18 (m$_{broad}$, CH$_2$–N), 1.90–1.57 (m$_{broad}$, N–CH$_2$–CH$_2$), 1.32 (m$_{broad}$, CH$_2$), 0.91 (m, CH$_3$). ^{13}C NMR (CDCl$_3$, 62.91 MHz) δ_{ppm}: 157.50 (C$_q$, ArO), 138.88 (C$_{q, arom}$), 134.18 (C$_{q, arom}$), 133.03 (C$_{q, arom}$), 127.62 (CH$_{arom}$), 114.62 (CH$_{arom}$), 69.36 (CH$_2$O), 58.43 (CH$_2$–N), 31.18 (CH$_2$–CH$_2$–N), 25.85 (CH$_2$), 22.41, (CH$_2$), 22.13 (CH$_2$), 13.98 (CH$_3$); ^{31}P NMR (CDCl$_3$, 81 MHz) δ_{ppm}: 3.21 (PO$_4$). FTIR (KBr plates) $\nu_{cm^{-1}}$: 1083 and 1056 (P–O), 960 (W=O), 840 (O–O), 580 and 521 W(O$_2$)$_{s,as}$. Elemental analysis calcd for $C_{148}H_{286}O_{50}N_6 P_2W_8$: C, 39.66; H, 6.43; P, 1.38. Found: C, 40.14; H, 7.06; P, 1.25%.

General procedure for catalytic reactions and recycling of the dendritic POM catalyst

The POM catalyst **7–32** (0.003 mmol) and cyclooctene (284 equiv. per POM unit) were dissolved in 3 ml CDCl$_3$ then H$_2$O$_2$ (35% in water, 800 equiv. per POM unit) was added. The mixture was stirred at 30 °C, and the reaction was followed by ^{1}H NMR. Upon completion, the CDCl$_3$ layer was separated and concentrated under a vacuum to about 1 ml. The catalyst was precipitated by addition of pentane or diethyl ether (10 ml). The solid was filtered and washed with diethyl ether (3 × 5 ml) which gave the POM catalyst in a good to excellent yield (see Table 2, main text). The catalyst was recovered following the typical procedure and conditions described above for the first cycle, CDCl$_3$ and reactants were adjusted to the amount of catalyst used. The reaction was performed with cyclooctene **36**, and cyclohexanol **42** using dried, recovered catalyst. The catalyst was completely dissolved in CDCl$_3$, and the reactants were added to the solution. After completion, the catalyst was recovered and checked by ^{1}H and ^{31}P NMR, with a yield between 20 and 85% (Table 2).

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