Supporting Information for:

Hydrogen peroxide activation by fluorophilic polyoxotungstates for fast and selective oxygen transfer catalysis

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General Remarks:

NMR spectroscopy: ^{1}H-NMR spectra were recorded with a Bruker AC 250 spectrometer operating at ν = 250.18 MHz. Chemical shifts were determined using $Si(CH_3)_4$ as reference (δ ^{1}H-NMR = 0 ppm). For protonic spectra, the following symbolism has been used: s: singlet; d: doublet; t: triplet; q: quartet; m: multiplet; s = sextet. *^{13}C-NMR* spectra were recorded with a Bruker Avance AX 330 spectrometer operating at ν = 75.47 MHz. Chemical shifts were determined using $Si(CH_3)_4$ as reference (δ ^{13}C-NMR = 0 ppm). *^{19}F-NMR* spectra were recorded with a Bruker Avance DRX 400 spectrometer operating at ν = 376.45 MHz with trifluorotoluene in benzene-d_6 as external reference (δ ^{19}F-NMR = 0 ppm). *^{29}Si-NMR* spectra were recorded with a Bruker Avance DRX 400 spectrometer operating at ν = 79.49 MHz, using a 10 mm tube. Chemical shifts were determined using $Si(CH_3)_4$ as external reference (δ ^{29}Si-NMR = 0 ppm). *^{183}W-NMR* spectra were recorded with a Bruker Avance DRX 400 spectrometer operating at ν = 16.67 MHz. using a 10 mm tube. Na_2WO_4 2M in D_2O was used as external reference (δ ^{183}W-NMR = 0 ppm).

FT-IR spectra were recorded with a Nicolet 5700-Thermo Electron Corporation instrument. For FT-IR spectra following symbolism has been used: w: weak signal; s: strong signal; b: broad band signal.

Scanning Electronic Microscopy (SEM) were obtained using a Zeiss SUPRA 40VP instrument, using an accelerating voltage of 1-20 kV. Samples were prepared by drop casting the sample solution onto a silicon plate.

Transmission Electronic Microscopy (TEM) were obtained in collaboration with Prof. Markus Antonietti at Max Planck Institute of Colloids and Interfaces, Potsdam (Germany), using a ZEISS EM 912 Omega, transmission electron microscope at an acceleration voltage of 120 kV. Samples grids were prepared by drop casting the sample solution onto a carbon-coated 400 - mesh copper grid and left to dry.

ESI-MS spectra were recorded on a Agilent 1100 series instrument with a LC/MSD Trap SL. (+3500 V capillary potential, -20 V skimmer potential and –100 V capillary exit potential).

GLC analysis were performed on a Hewlett Packard 6890 series instrument equipped with a flame ionisation detector (FID) using a 30 m (0.32 mm internal diameter, 0.25 μm film thickness) HP-5

capillary column; with a Hewlett Packard 5890 series II instrument equipped with FID using a 60 m (0,53 mm internal diameter, 1 μm film thickness) Alcohols Stabilwax® (Restek) capillary column or with a Shimadzu GC-2100 instrument for GLC-flash chromatography equipped with FID, using a 15 m (0.10 mm internal diameter, 0.10 μm film thickness) Equity™-5 capillary column whose composition is: 5% biphenyl and 95% dimethylsiloxane.

GC-MS spectra were recorded on a Agilent GC6850 series coupled with a Agilent 5973 Network Mass Selective Detector. GC system is equipped with a 30 m (0.32 mm internal diameter, 0.25 μm film thickness) HP-5 capillary column.

MW assisted reactions were performed with a MW-lab-station Discover (CEM instruments) upon constant irradiation power (100 W) and with simultaneous compressed air cooling.

Dynamic Light Scattering (DLS) measurements were performed with NICOMP 170 – Spectra Physics instrument, by using 1cm pathlength quartz cuvettes.

Elemental Analysis were performed at microanalysis laboratory of Chemical Science Department, University of Padova.

Materials. Acetonitrile, 1,1,1,3,3,3-hexafluoro-2-propanol ($CF_3CH(OH)CF_3$), hexafluoroacetone ($CF_3C(O)CF_3$), 35% and 70 % H_2O_2, $CF_3(CF_2)_7(CH_2)_2SiCl_3$, $(CF_3)_2CFO(CH_2)_3SiCl_3$ and olefins were commercial products and were used as received without further purification. Vacant POMs $K_8[\alpha\text{-}SiW_{11}O_{39}]\bullet 13H_2O$, $K_8[\gamma\text{-}SiW_{10}O_{36}]\bullet 12H_2O$ and $Na_{10}[\alpha\text{-A-}SiW_9O_{34}]\bullet 12H_2O$ were synthesized and characterized according to known literature procedures.[1]

$Na_4W_{10}O_{32}$[2] and $[CF_3(CF_2)_7CH_2CH_2CH_2]_3CH_3N^+$ $CH_3OSO_3^-$ salt were prepared following previously reported procedures.[3]

General oxidation procedure:

$CF_3CH(OH)CF_3$ (0.6 ml), POM (0.8 μmol) and the substrate (0.5 mmol) were mixed, and 0.1 mmol of hydrogen peroxide (35 or 70% aqueous solutions were used) was added, in a closed glass reactor. [*Caution: The uncontrolled heating of large amount of peroxides must be avoided. Care must be taken to avoid possible explosion*]. The reaction mixture was heated at 25-70°C. Sample aliquots were taken (20 μl), diluted with 500 μl of CH_2Cl_2 containing dodecane as internal standard and triphenyphosphine as quencher, and analysed by GC-FID. Hydrogen peroxide content was verified by iodinated paper, and the reactions were generally monitored until oxidant consumption. POM stabilities were assessed by comparison of their FT-IR spectra before and after the reaction upon precipitation and washing with methanol.

*A stoichiometric reaction, with H_2O_2: cis-cyclooctene 1:1 was also performed in the presence of **3**, at 25°C. In this case, the stepwise addition of H_2O_2 (5 portions of 0.1 mmol H_2O_2 each, added every 15 min) is convenient to obtain the epoxidation of cis-cyclooctene in 120 min total time (>98% substrate conversion with 92% epoxide selectivity).*

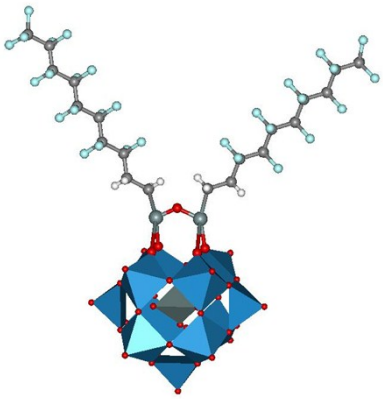
The epoxidation of 1-octene was finally explored by adding hexafluoroacetone, as a possible intermediated active species. However, a different product distribution was obtained, including diols and carboxylic acids.

General procedure for the synthesis of tetrabutylammonium salts of fluorinated hybrid vacant polyoxotungstates (1-4):

Vacant polyoxotungstates grafted with fluorinated alkyl silanes were prepared by adding 2 (products **1** and **2**) or 4 (product **3**) equivs of $CF_3(CF_2)_7(CH_2)_2SiCl_3$ to a suspension containing 4 equivs of n-Bu_4NBr and 0.2 mmol of polyoxotungstate in 10 ml of CH_3CN, and left overnight (t= 14 h) at room temperature (t= 20°C) under vigorous stirring. After removal of the insoluble material by paper filtration, the products were collected by evaporation of most of the solvent and washing with water on a fritted funnel. Yields: 65-75%. The identity of products **1-3** was demonstrated by FT-IR, ^{19}F NMR, ^{183}W NMR, ^{29}Si NMR, ESI-MS (-) and elemental analysis.

(*^1H NMR and ^{13}C NMR, being dominated by counterions signals, were included only for POM **1***)

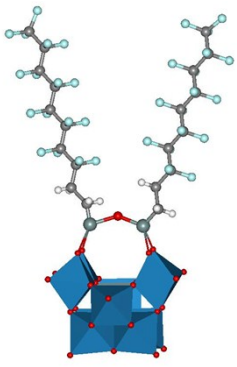
$((CH_3CH_2CH_2CH_2)_4N)_4[\alpha\text{-}SiW_{11}O_{39}\{CF_3(CF_2)_7(CH_2)_2Si\}_2O]$ **(1).**



*Structure of POM **1** (counterions not shown)*

FT-IR (KBr): 2964(s), 2876(s), 1630(w), 1484(m), 1473(w), 1457(w), 1382(w), 1242(s), 1206(s), 1152(s), 1134(m), 1112(w), 1051(s), 981(w), 965(m), 953(m), 905(s), 805(s), 761(w), 721(w), 668(m), 656(w), 534(m) cm^{-1}; ^1H NMR (200 MHz, CD_3CN, 301 K): 3.16 (32H, m), 1.66 (36H, m), 1.42 (32H, m), 1.0 (48H, t, *J*=7.2 Hz) ppm, 0.90 (4H, t, *J*=9Hz); $^{13}C\{H\}$ NMR (75.47 MHz, CD_3CN/CH_3CN, 301 K, only counterions signals can be distinguished): 59, 23, 21, 14 ppm; ^{29}Si NMR (79.49 MHz, CD_3CN/CH_3CN, 298 K): -53.8 (2Si, s); -80.3(1Si, s) ppm; ^{19}F NMR (376.45 MHz, CD_3CN/CH_3CN, 298 K): -86.3 (6F, s), -121.4 (4F, s), -127.2 (12F, m), 128.1 (4F, m), 128.8 (4F, m), 131.6 (4F, s) ppm; ^{183}W NMR (16.67 MHz, CD_3CN/CH_3CN, 298 K): -107.6 (4W, s), -113.8 (1W, s), -126.9 (2W, s), -170.8 (2W, s), -248.2 (2W, s) ppm; ESI-MS(-), (CH_3CN): m/z= 910.0 (calcd. for $[SiW_{11}O_{39}\{CF_3(CF_2)_7(CH_2)_2Si\}_2O]^{4-}$: 910.3); Elem. Anal. for $C_{84}H_{152}F_{34}N_4O_{40}Si_3W_{11}$ (%): found C 21.79, H 3.30, N 1.18; calcd. C 21.88, H 3.32, N 1.21.

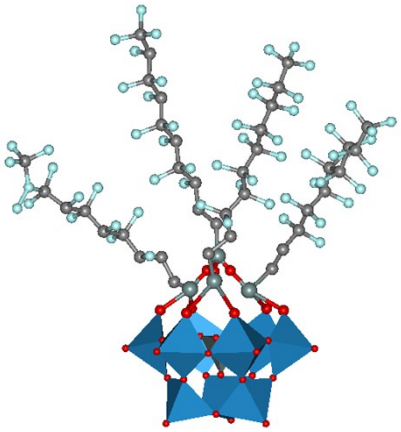
$((CH_3CH_2CH_2CH_2)_4N)_4$ $[\gamma\text{-}SiW_{10}O_{36}\{CF_3(CF_2)_7(CH_2)_2Si\}_2O]$ **(2).**



Structure of POM 2 (counterions not shown)

FT-IR (KBr): 2965(s), 2876(s) 1630(w), 1483(m), 1383(w), 1243(s), 1207(s), 1152(s), 1134(m), 1109(m), 968(m), 904(s), 823(m), 736(m), 555(w), 511(w) cm^{-1}; ^{19}F NMR (376.45 MHz, CD_3CN/CH_3CN, 298 K): -86.2 (6F, s), -120.8 (4F, s), -127.0 (12F, m), -127.8 (8F, m), -131,3 (4F, s) ppm; ^{29}Si NMR (79.49 MHz, CD_3CN/CH_3CN, 298 K): -64.4 (2Si, s), -88.1 (1Si, s) ppm; ^{183}W NMR (16.67 MHz, CD_3CN/CH_3CN, 298 K): -106.7 (4W, s), -133.2 (2W, s), -140.5 (4W, s) ppm; ESI-MS(-),(CH_3CN): m/z= 851.5 (calcd. for $[SiW_{10}O_{36}\{CF_3(CF_2)_7(CH_2)_2Si\}_2O]^{4-}$ 850.6); Elem. Anal. for $C_{84}H_{152}F_{34}N_4O_{37}Si_3W_{10}$ (%): found C 21.99, H 3.17, N 2.07; calcd. C 23.04, H 3.50, N 1.28.

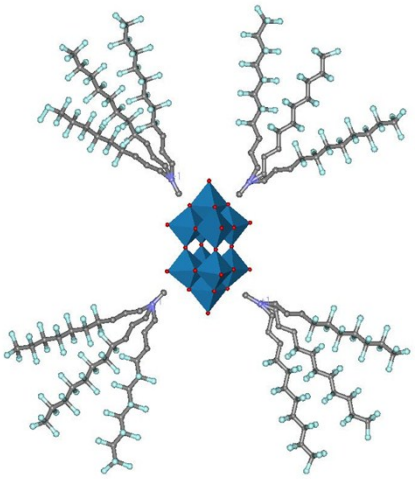
$((CH_3CH_2CH_2CH_2)_4N)_4[\alpha\text{-}SiW_9O_{34}\{CF_3(CF_2)_7(CH_2)_2Si\}_4O_3]$ **(3).**



*Structure of POM **3** (counterions not shown)*

FT-IR (KBr) 2965(s), 2876(s) 1630(w), 1485(m), 1473(w), 1457(w), 1382(w), 1240(s), 1206(s), 1152(s), 1134(m), 1115(m), 1062(m), 963(w), 950(w), 893(s), 824(m), 736(m), 668(w), 657(w) cm^{-1}; ^{19}F NMR (376.45 MHz, CD_3CN/CH_3CN, 298 K): -87.4 (12F, m), -121.8 (8F, m), -127.7 (24F, m), -128.7 (16F, m), -132.2 (8F, m) ppm; ^{29}Si NMR (79.49 MHz, CD_3CN/CH_3CN, 298 K): -62.2 (3Si, s), -83.7 (1Si, s), -88.4 (1Si, s) ppm; ^{183}W NMR (16.67 MHz, CD_3CN/CH_3CN, 298 K): - 80.1 (3W, s), -154.3 (6W, s) ppm; ESI-MS(-), (CH_3CN): m/z= 1043.6 (calcd. for $[SiW_9O_{34}\{CF_3(CF_2)_7(CH_2)_2Si\}_4O_3^{4-}$ 1043.3); Elem. Anal. for $C_{104}H_{160}F_{68}N_4O_{37}Si_5W_9$ (%): found C 23.05, H 2.88, N 1.12; calcd. C 24.28, H 3.13, N 1.09.

Procedure for the synthesis of tetra fluoroalkylammonium salts of decatungstate $\{CF_3(CF_2)_7CH_2CH_2CH_2\}_3NCH_3[W_{10}O_{32}]$ (4):



Structure of POM ***4***

The fluorophilic salt of decatungstate **(4)** has been isolated by introducing 4.3 equivalents of $[CF_3(CF_2)_7CH_2CH_2CH_2]_3CH_3N^+$ $CH_3OSO_3^-$ (0.882 mmol) in a solution of 2,2,2-trifluoroethanol and water (3:1) containing $Na_4W_{10}O_{32}$ (0.205 mmol). The resulting complex has been recovered by filtration, then it was dried under vacuum and reprecipitated from hexafluoro *iso*-propanol/water. Yield= 70%. FT-IR (KBr): 2361(m), 1653(w), 1237(s), 1202(s), 1149(s), 1134(w), 1117(w), 961(m), 895(w), 810(m), 705(w), 659(w) cm^{-1}; ^{19}F NMR (376.45 MHz, $CF_3CH(OH)CF_3/CF_3CD(OD)CF_3$, solvent suppression, 298K) : -90.6 (48F, s), -122.3 (32F, s), -130.3 (32F, s), -130.7 (64F, m), -131.6 (32F, s), -132.1 (32F, s), -135.3 (32F, s) ppm; ^{183}W NMR (16.67 MHz, $CF_3CH(OH)CF_3$, 298K) -45.1 (8W, s), -186.5 (2W, s) ppm; Elem. Anal. for $C_{136}H_{84}F_{204}N_4O_{32}W_{10}$ (%): found C 20.10, N 1.00, H: 0.66 calcd. C 20.42, N 0.70, H: 1.06.

Spectra of POMs 1-4

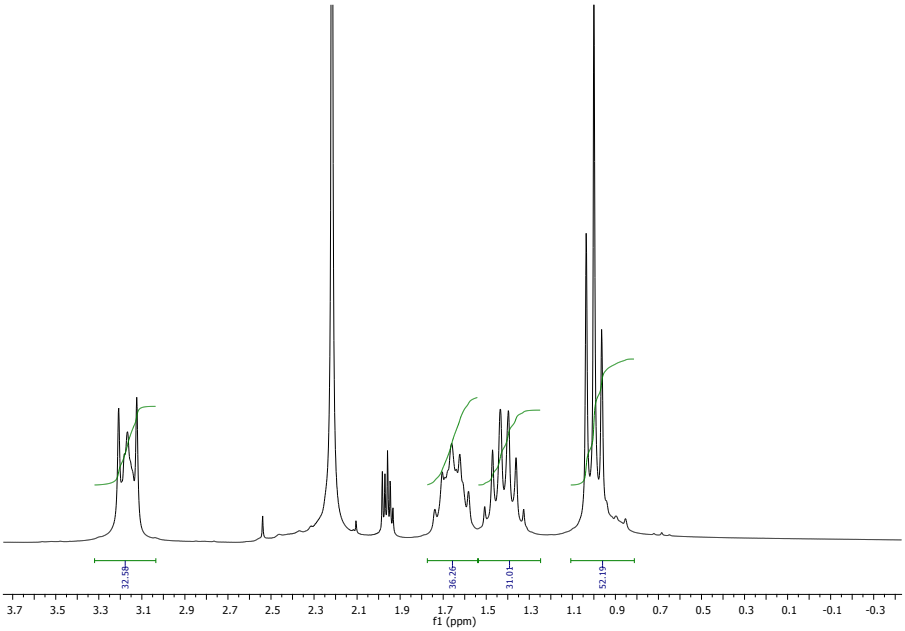


Figure S1. ^{1}H NMR (CD_3CN, 301 K) of **1.** The peak at 2.2 ppm is due to residual water.

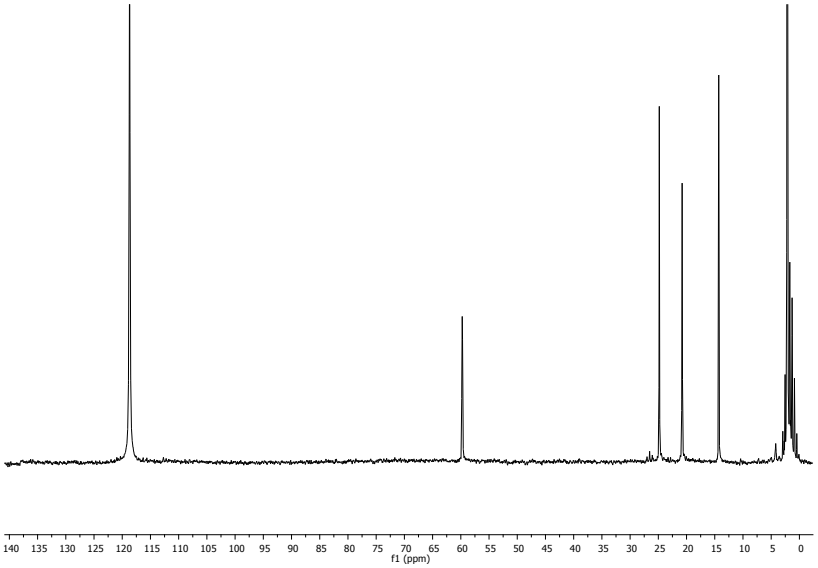


Figure S2. ^{13}C NMR (CD_3CN/CH_3CN, 301 K) of **1**

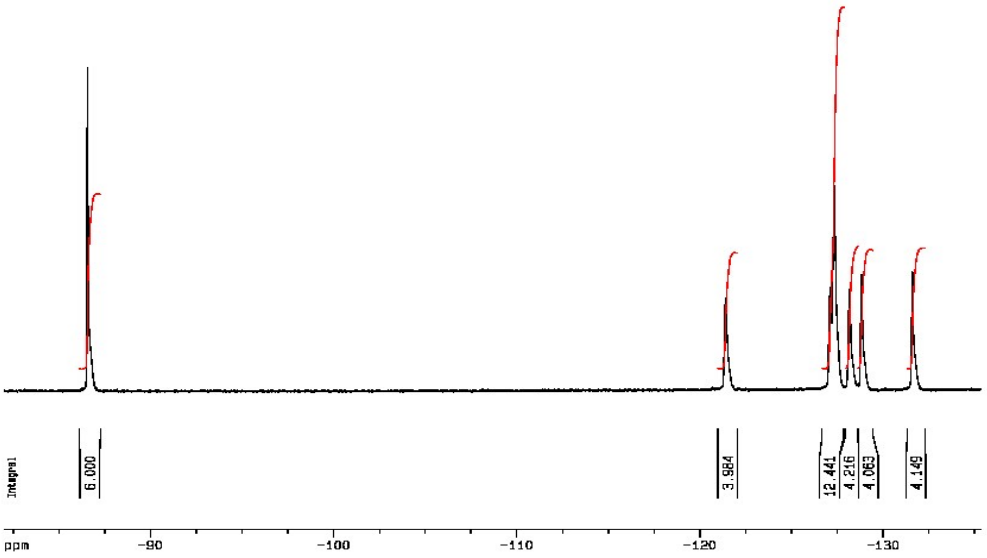


Figure S3. ^{19}F NMR (CD_3CN/CH_3CN, 301 K) of **1**

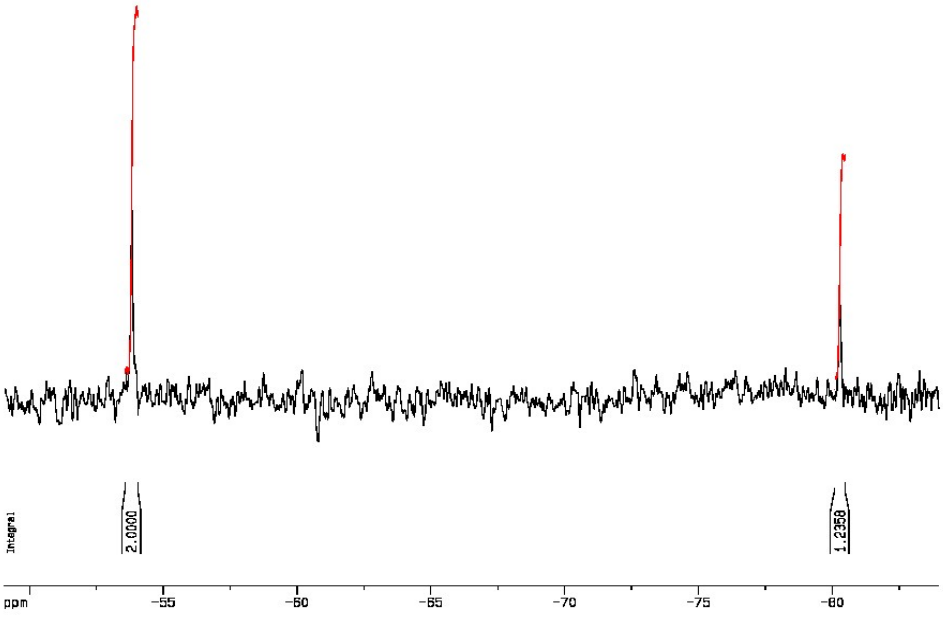


Figure S4. ^{29}Si NMR (CD_3CN/CH_3CN, 301 K) of **1**

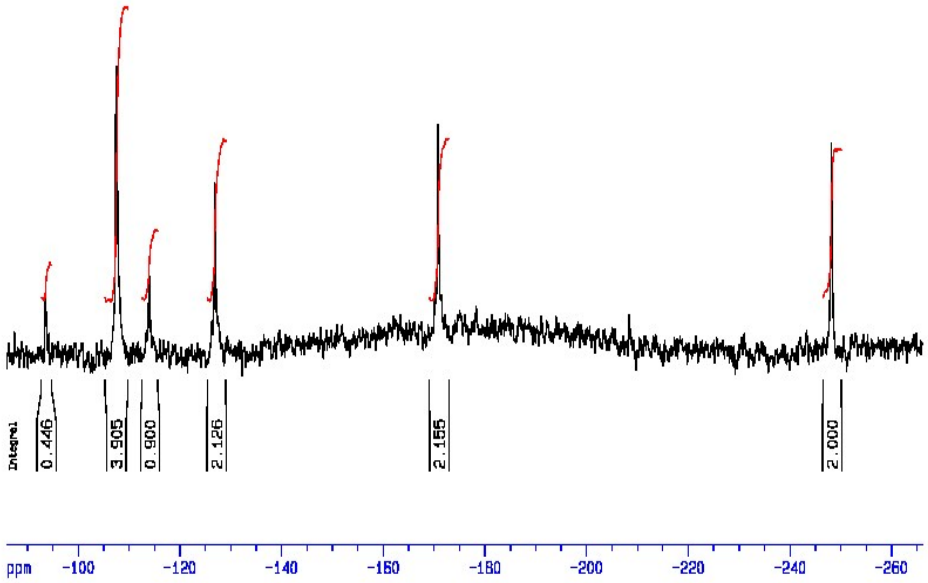


Figure S5. ^{183}W NMR (CD_3CN/CH_3CN, 301 K) of **1.**
The signal at 94 ppm is likely ascribed to residual $[SiW_{12}O_{40}]^{4-}$.

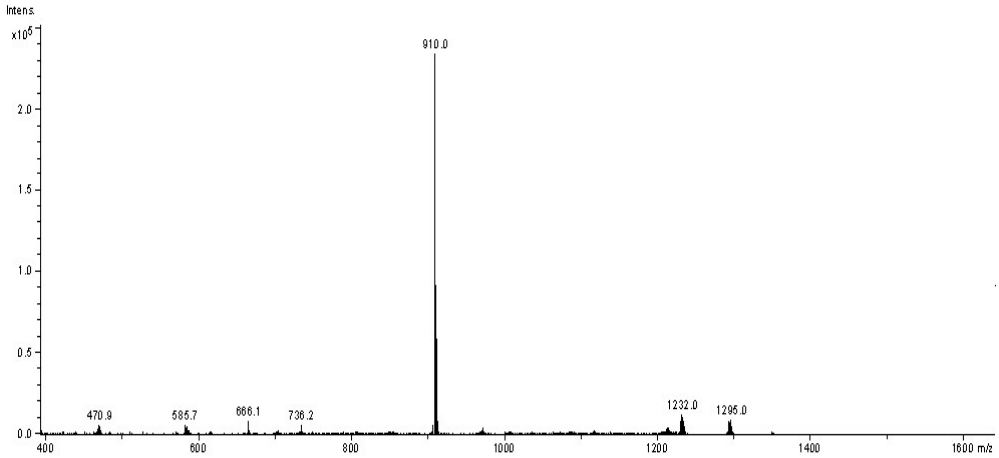


Figure S6. ESI-MS (-) of **1** (CH_3CN solution)

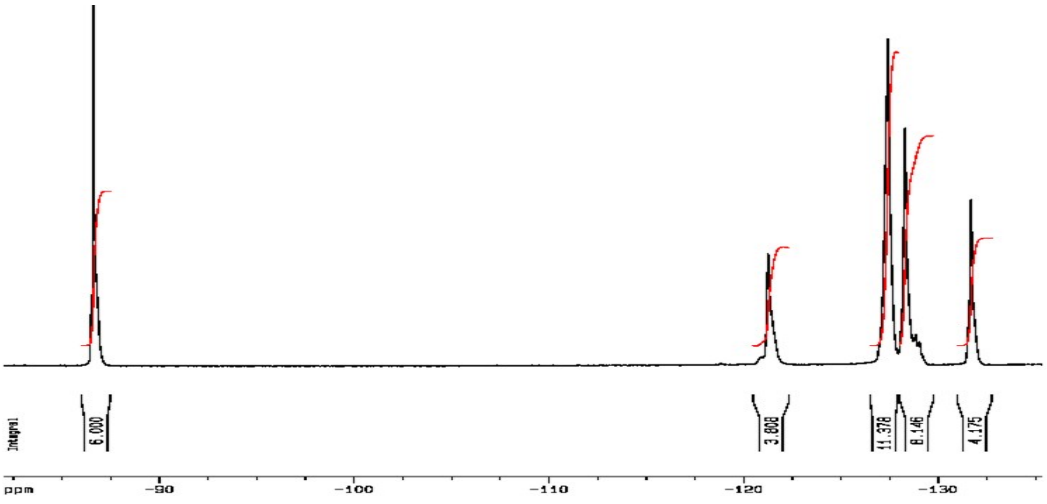


Figure S7. ^{19}F NMR (CD_3CN/CH_3CN, 301 K) of **2**

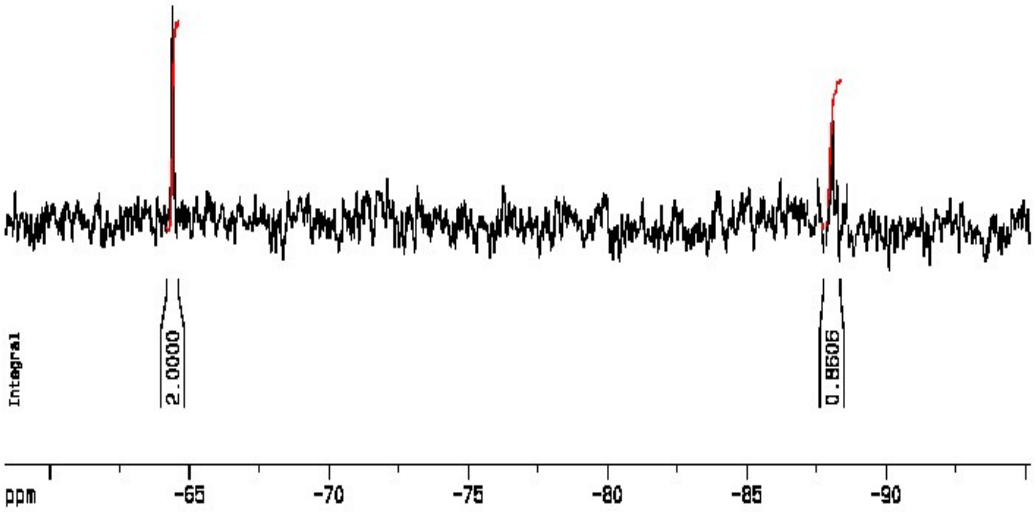


Figure S8. ^{29}Si NMR (CD_3CN/CH_3CN, 301 K) of **2**

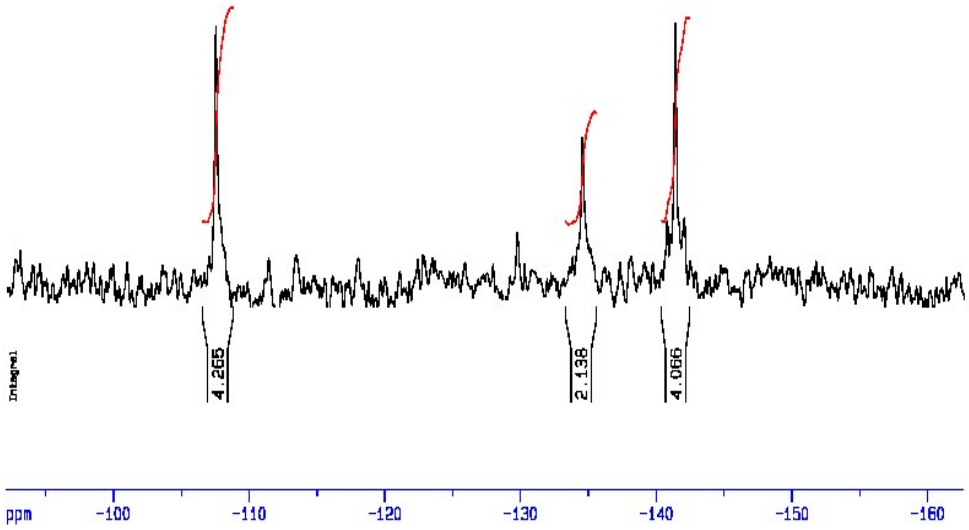


Figure S9. ^{183}W NMR (CD_3CN/CH_3CN, 301 K) of **2**

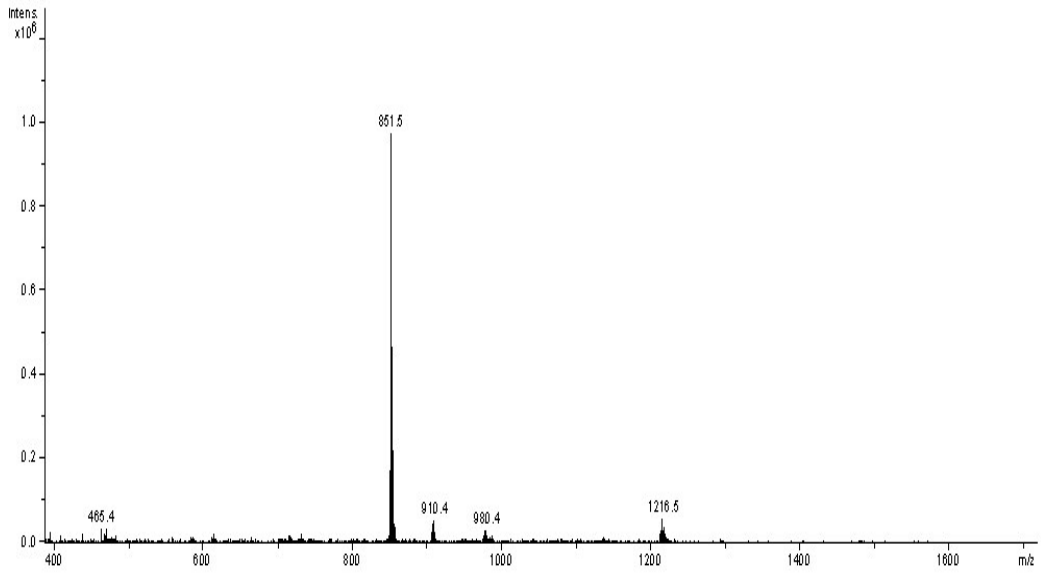


Figure S10. ESI-MS (-) of **2** (CH_3CN solution).

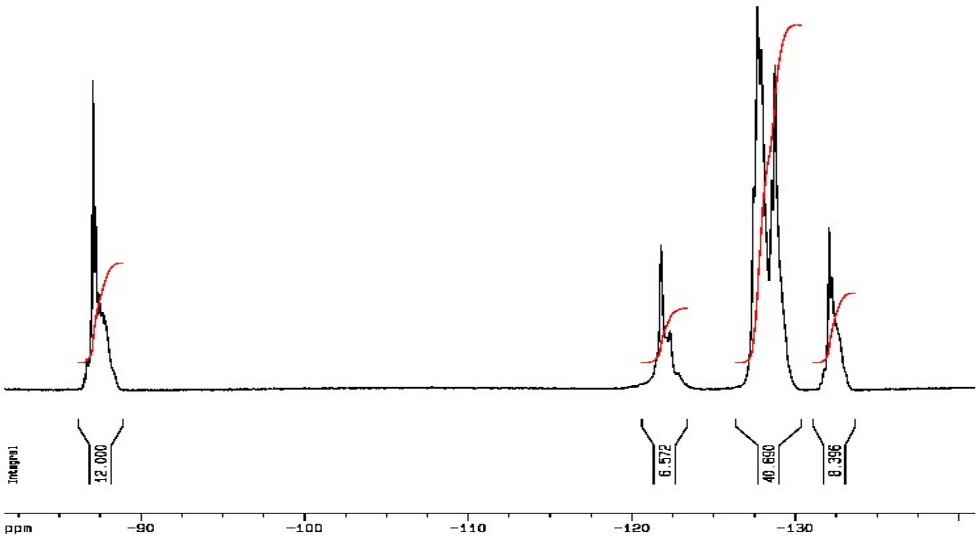


Figure S11. ^{29}Si NMR (CD_3CN/CH_3CN , 301 K) of **3**

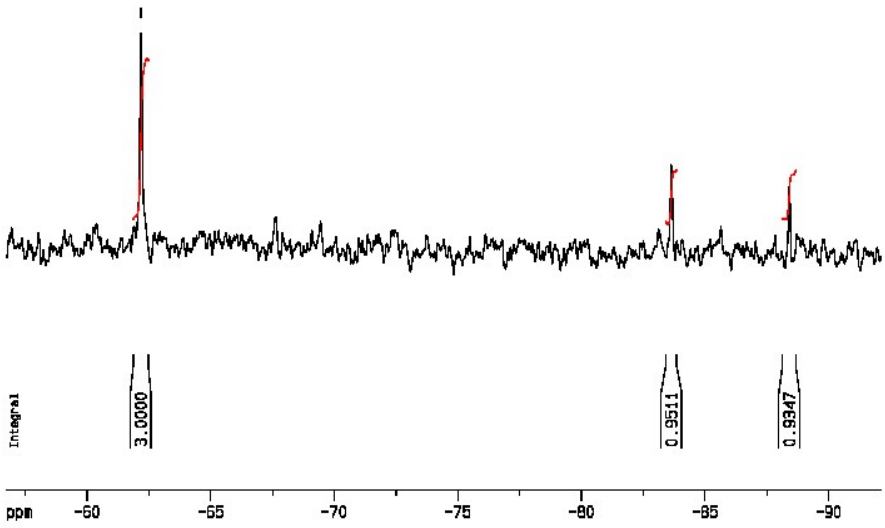


Figure S12. ^{19}F NMR (CD_3CN/CH_3CN, 301 K) of **3.**

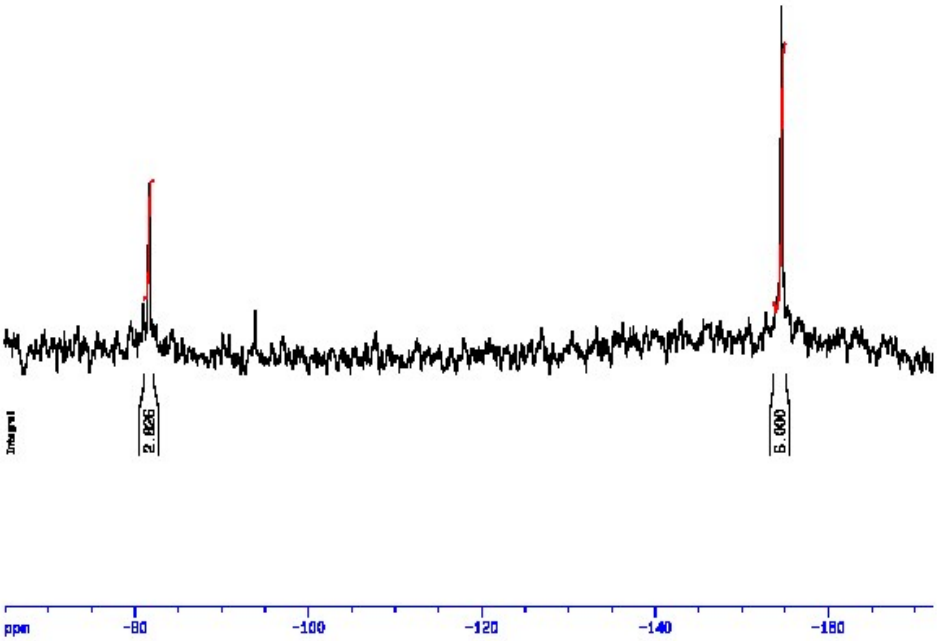


Figure S13. ^{183}W NMR (CD_3CN/CH_3CN, 301 K) of **3**

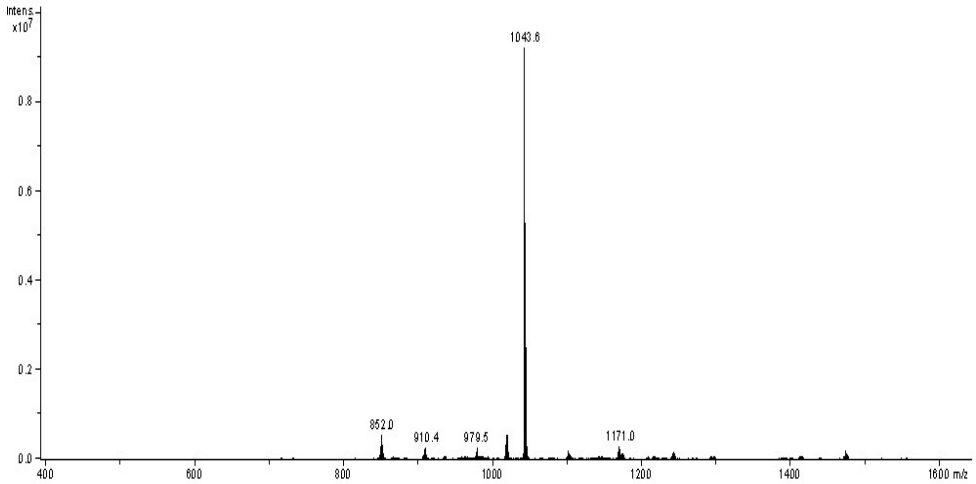


Figure S14. ESI-MS (-) of **3** (CH_3CN solution).

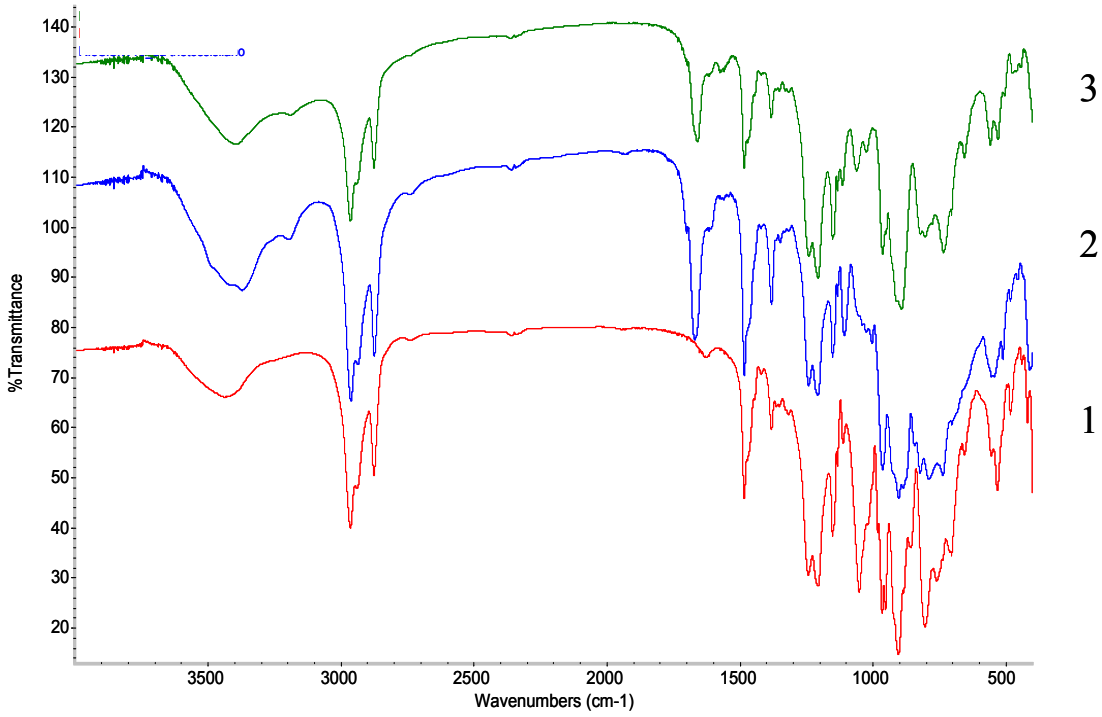


Figure S15. FT-IR (KBr pellet) of **1-3**

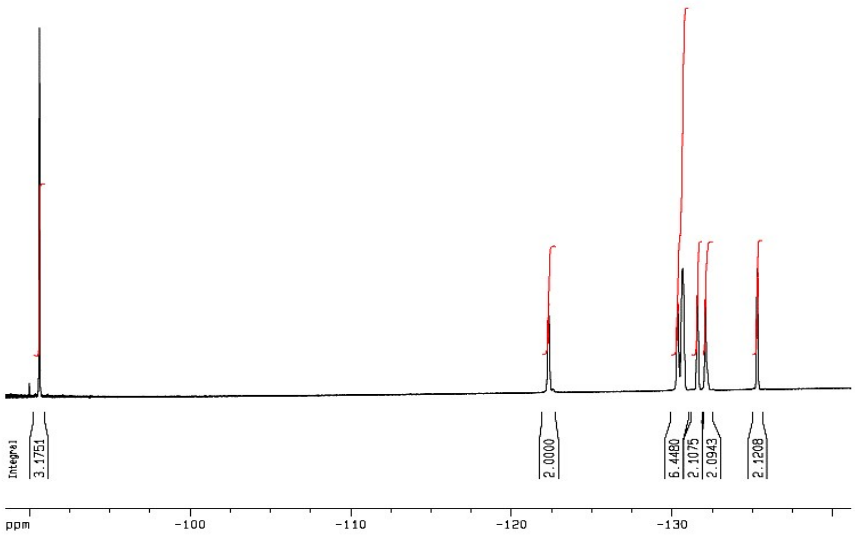


Figure S16. ^{19}F NMR (d_2-HFIP, with solvent suppression, 298 K) of **4**

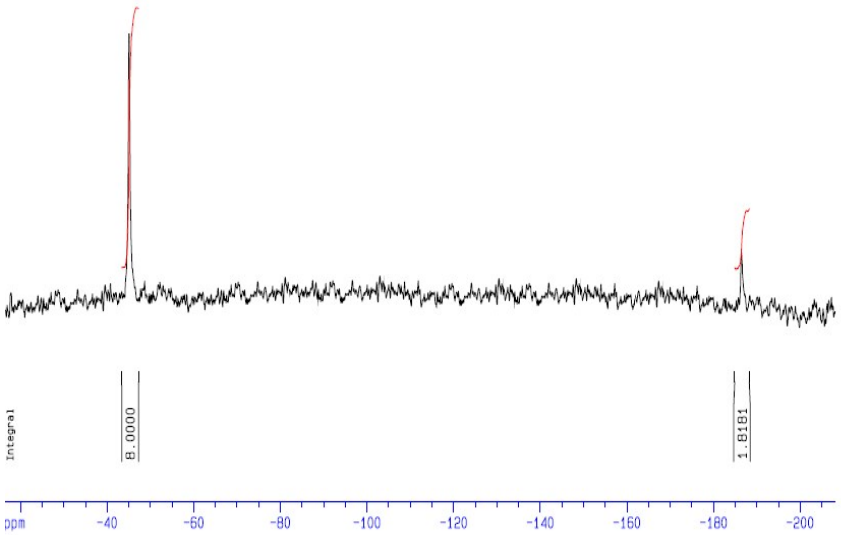


Figure S17. ^{183}W NMR (d_2-HFIP/HFIP, 298 K) of **4**

Characterization of the aggregates

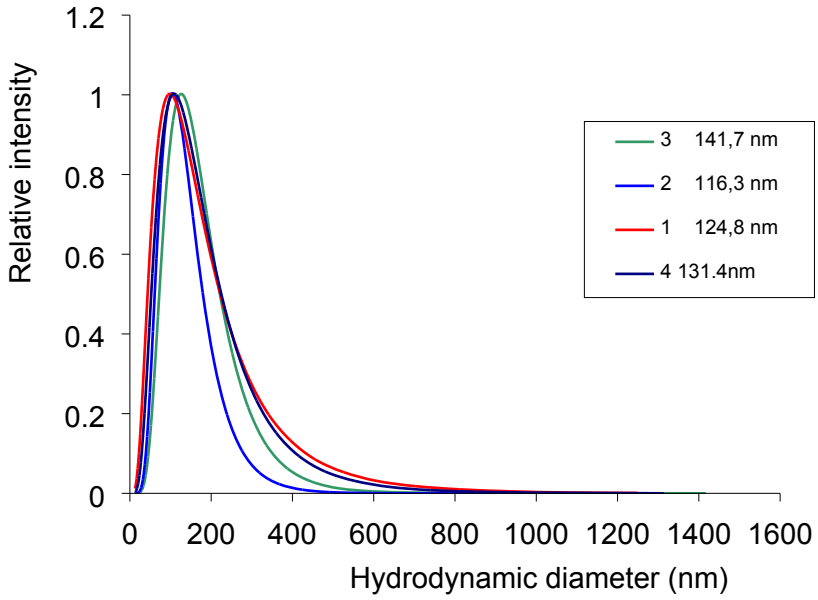


Figure S18. Dynamic Light scattering of POMs **1-4,** 1.33 mM in HFIP.

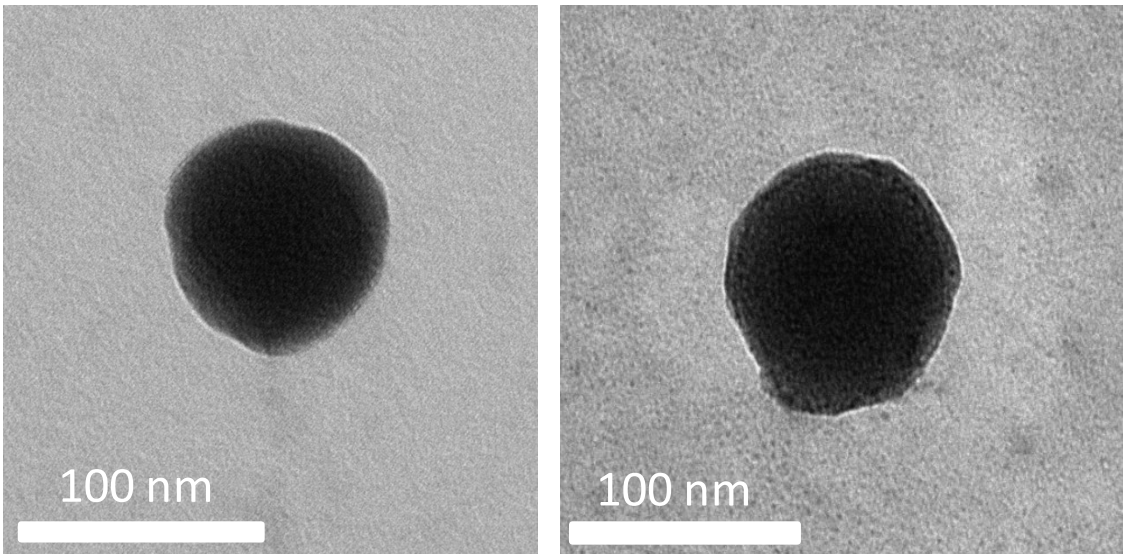


Figure S19. TEM images of POM **1** (left) and POM **2** (right) drop casted from 1.33 mM HFIP solutions.

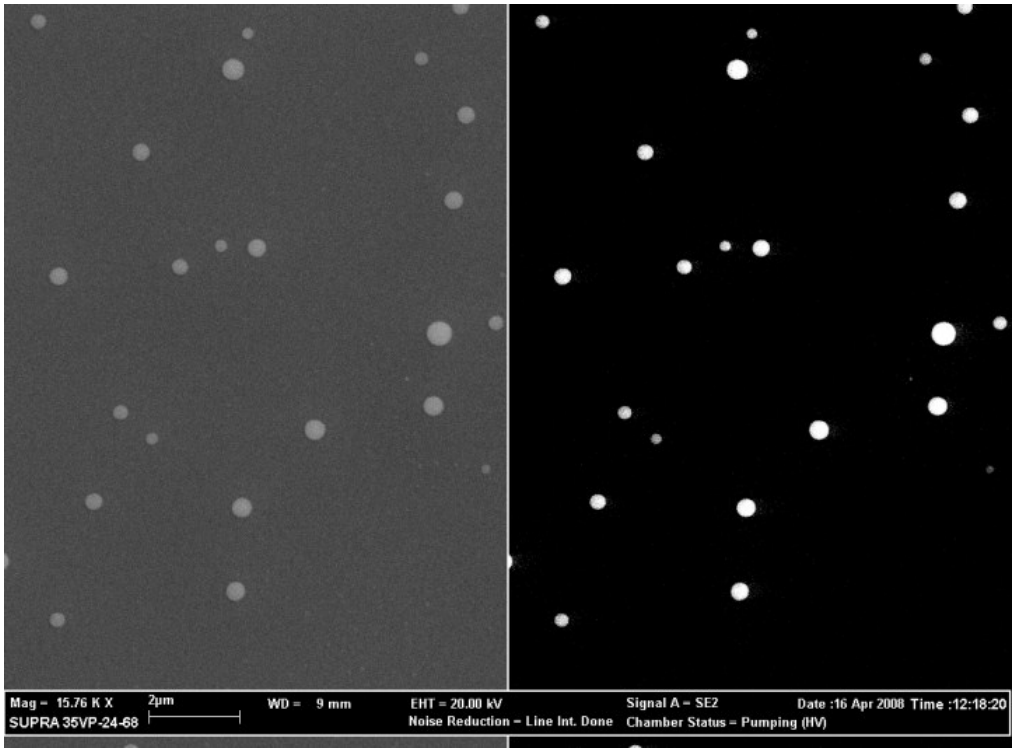
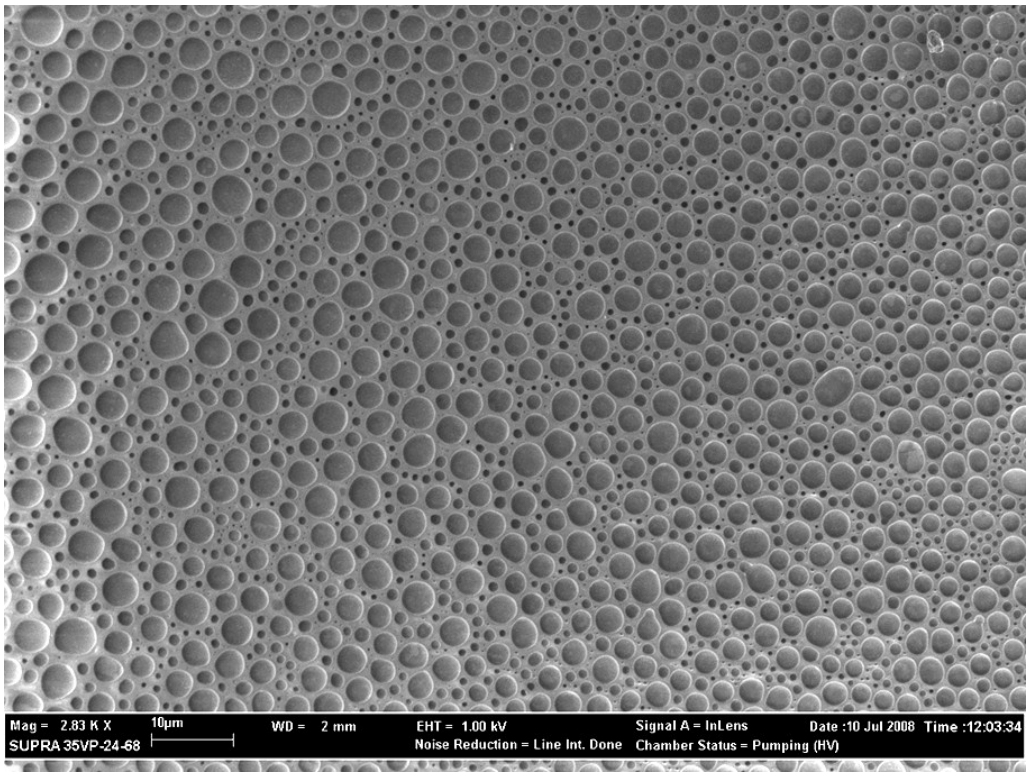
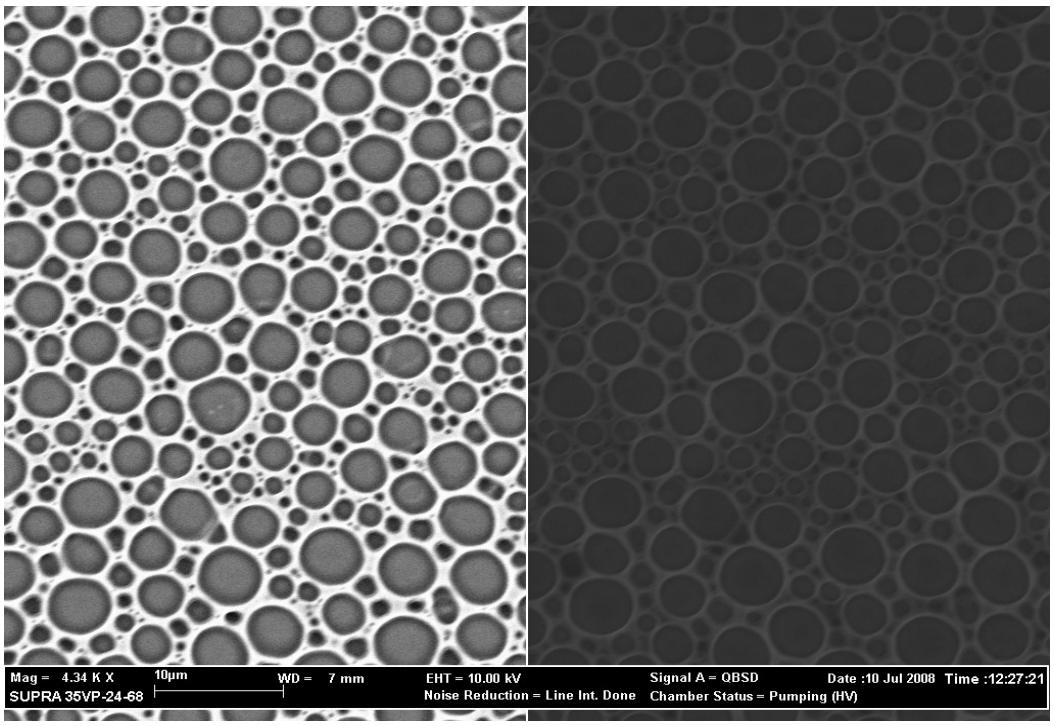


Figure S20. SEM image of POM **3**, drop casted on a silicon plate from a 1.33 mM in HFIP (0.4% H_2O). Images acquired with 20KV inlens potential (left) and with quadrant back scattering detector (QBSD, right). Scale bar 2 μm. POM-rich regions appear brighter with the QBSD.



(1)



(2)

Figure S21. SEM images of POM **2** drop casted on a silicon plate from a 1.33 mM solution in HFIP (0.4% H_2O). 1) Image acquired with 1KV inlens potential. Scale bar 10 µm; 2) image acquired with 1KV inlens potential, by using a quadrant back scattering detector (QBSD, left) and with secondary electrons (SE, right) detector. Scale bar 10 µm. Pores diameter: 1-4.5 µm. POM-rich regions appear brighter with the QBSD.

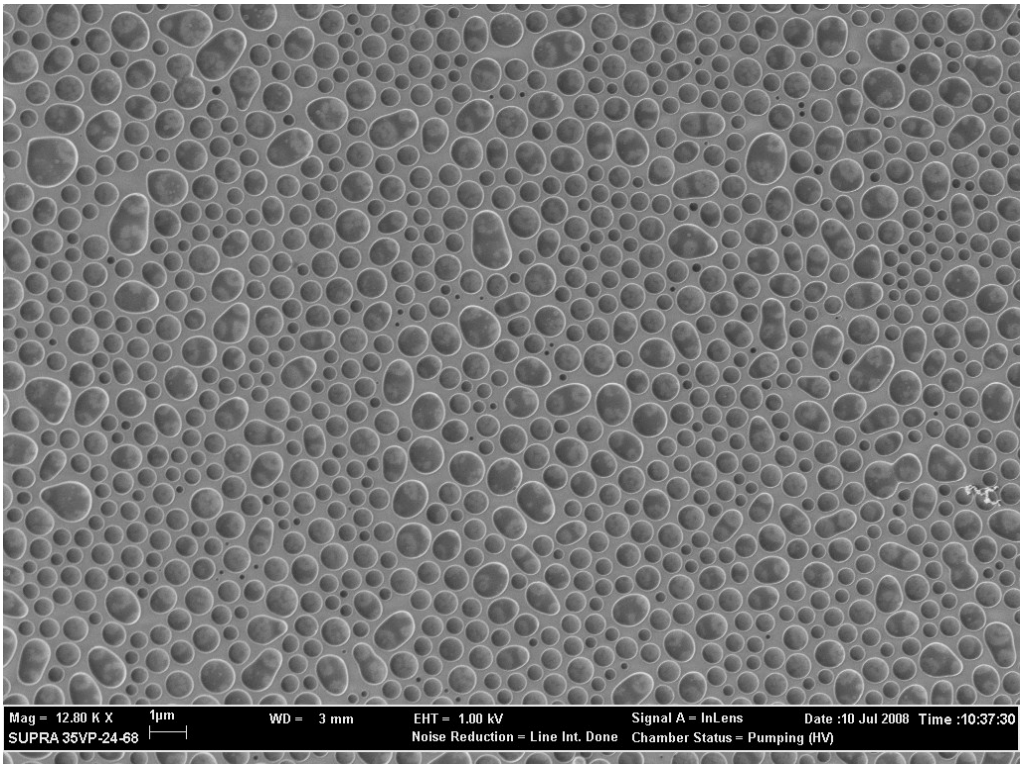


Figure S22. SEM image of POM **2** 2.66 mM in HFIP (0.4% H_2O). 1) SEM image acquired with 1KV inlens potential. Scale bar 1 µm. Pores diameter: 0.1-1.2 µm.

Additional reactivity data

Table S1. Reactivity data obtained for the epoxidation of olefins by H_2O_2 with POM **1** and with POMs **2** and **3** in acetonitrile

#	Substrate	yield % HFIP (min)	Yield % **1**/HFIP (min)	yield % **2**/CH_3CN (min)	yield % **3**/CH_3CN (min)
1	*cis*-cyclooctene	84 (15)	80 (15)	6 (15)	6 (15)
2	cyclohexene	59 (15)	56 (15)	18 (15)	<5 (15)
3	*trans*-2-octene	86 (15)	75 (15)	38 (15)	<5 (15)
4	1-octene	6 (25)	5 (25)	<5 (25)	<5 (25)
5	1-hexene	<5 (25)	<5 (25)	<5 (25)	<5 (25)
6	1-decene	<5 (25)	<5 (25)	9 (25)	< 5 (25)
7	1-dodecene	<5 (25)	<5 (25)	<5 (25)	< 5 (25)

Reaction conditions: POM 0.8 µmol; substrate 0.5 mmol; H_2O_2 0.1 mmol (from a 70% aqueous solution); 0.6 ml of CH_3CN, T=70°C. Yields calculated with respect to H_2O_2.

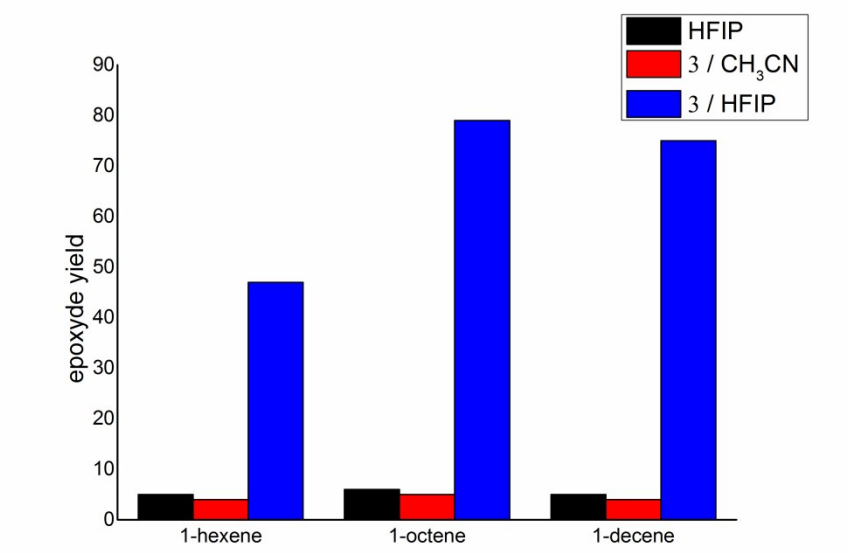


Figure S23. Reaction yields (calculated with respect to H_2O_2) observed during the oxidation of terminal olefins (0.5 mmol) by H_2O_2 (0.1 mmol) in the presence of POM **3** (0.8 µmol) in HFIP (0.6 mL) (blue bars), compared with analogue reactions without POM (black bars) or with POM **3** in acetonitrile (red bars). T=25°C.

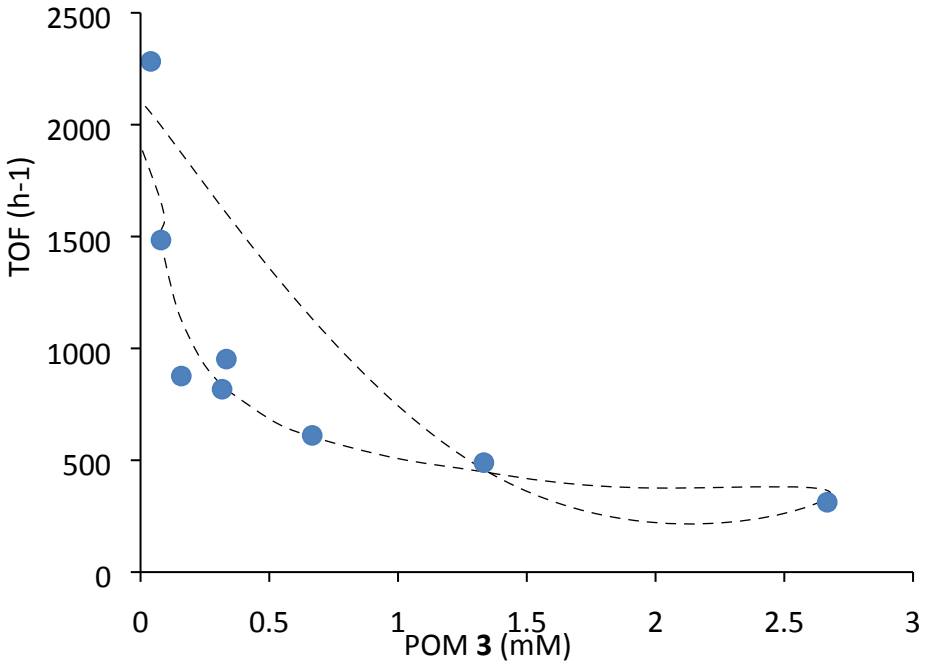


Figure S24. Maximum turnover frequencies (TON per min) calculated for the epoxidation of cyclooctene (0.5 mmol) with H_2O_2 (0.1 mmol), in the presence of **3,** in HFIP (0.6 mL) at T=25°C.

Stability data

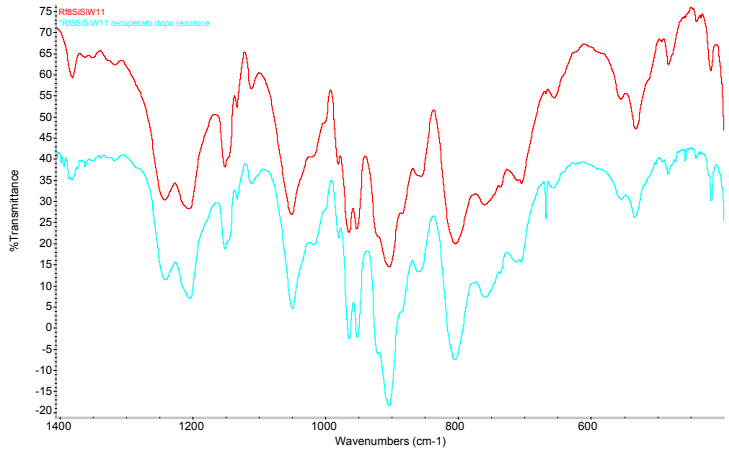


Figure S25. FT-IR (KBr) of **1** before (bottom) and after reaction (top)**.**

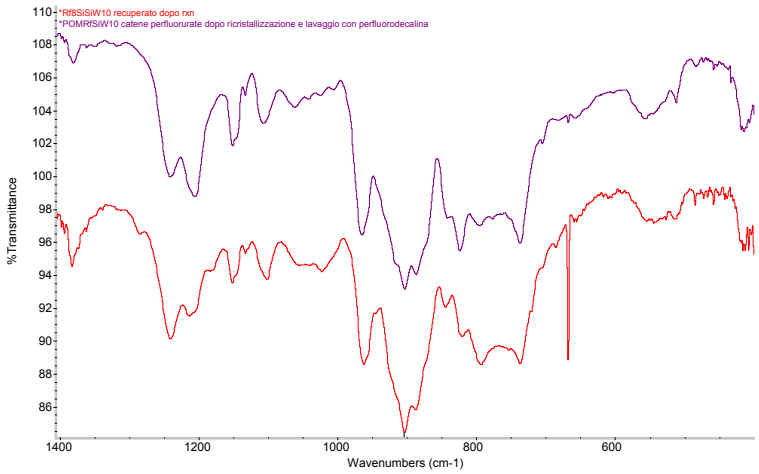


Figure S26. FT-IR (KBr) of **2** before (bottom) and after reaction (top)**.**

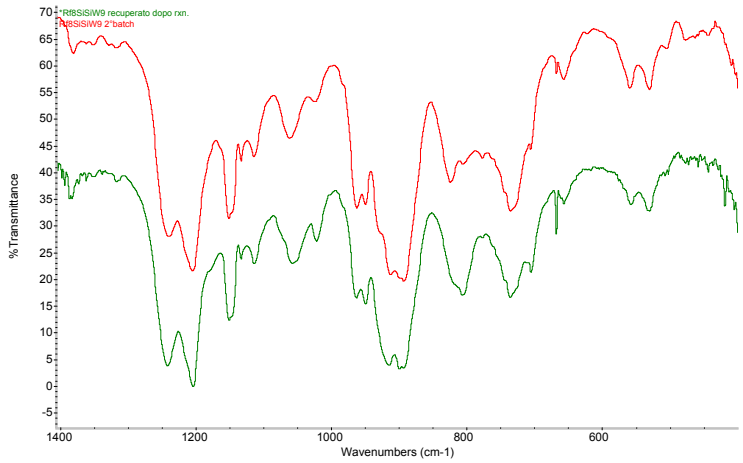


Figure S27. FT-IR (KBr) of **3** before (bottom) and after reaction (top)**.**

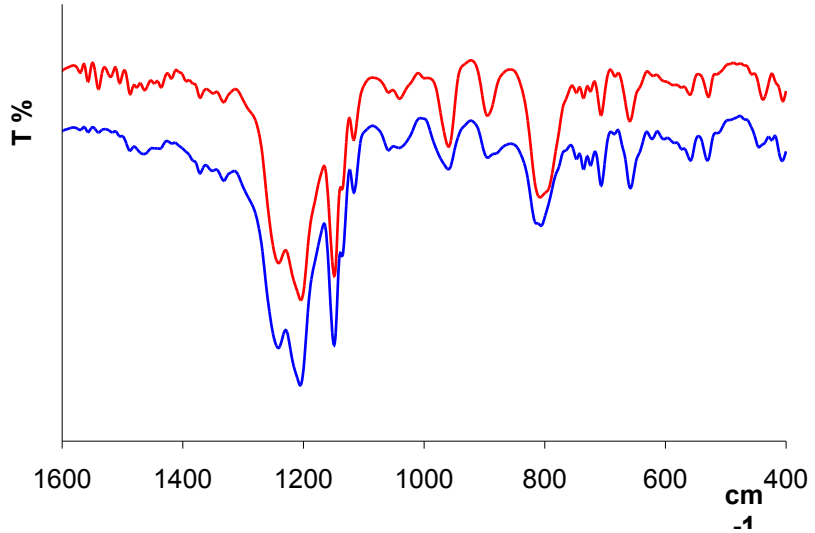


Figure S28. FT-IR (KBr) of **4** before (top) and after the reactions (bottom).

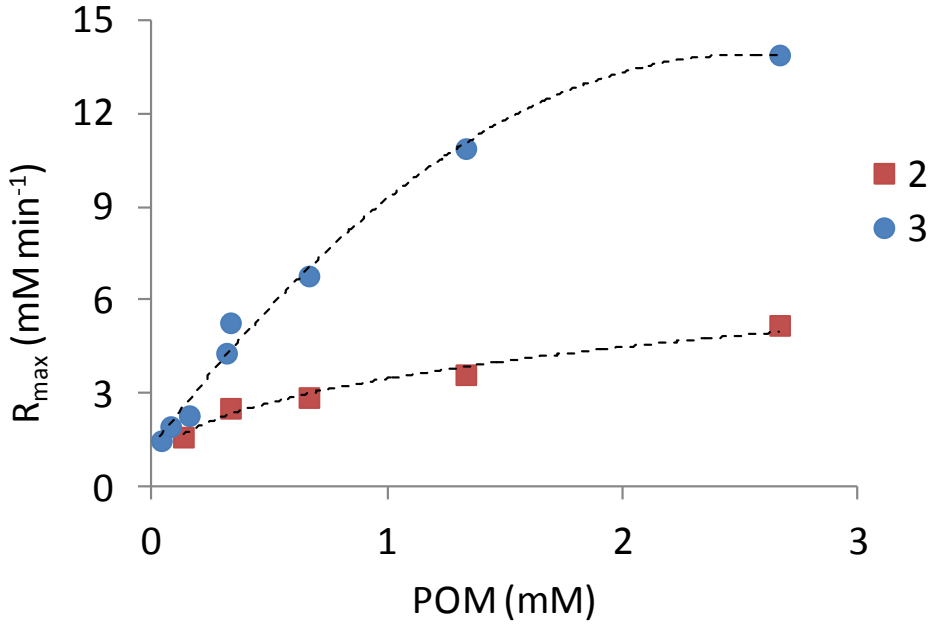


Figure S29. Maximum reaction rates measured during the epoxidation of *cis*-cyclooctene (0.5 mmol) by H_2O_2 (0.1 mmol) in the presence of POM **2** or **3** in HFIP (0.6 mL), at T=25°C.

[1] a) A. Tézé, G. Hervé, *J. Inorg. Nucl. Chem.*, **1977**, *39*, 999-1002; b) A. Tézé, G. Hervé, R. G. Finke, D. K. Lyon, in *Inorganic Syntheses*, ed. A. P. Ginsburg, John Wiley & Sons, New York, 1990, pp. 85-96.

[2] D.C. Duncan, T. L. Netzel, C. L. Hill, *Inorg. Chem.,* 1995, **34**, 4640-4646.

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