

Electronic Supporting Information

Polyoxomolybdate-Calix[4]arene Hybrid: a Catalyst for Sulfoxidation Reactions with Hydrogen Peroxide

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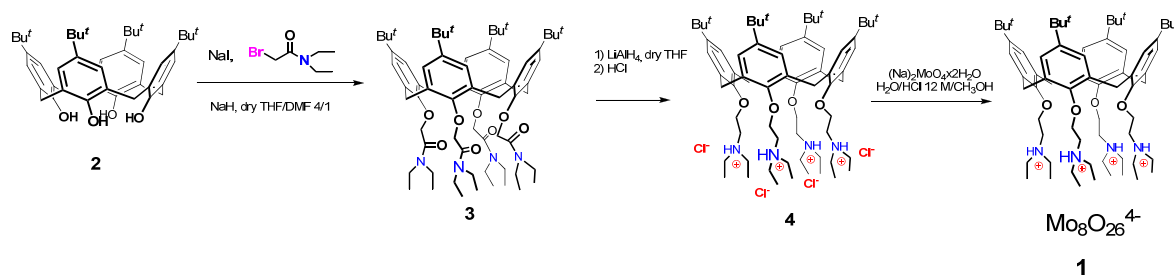
General methods

All reactions requiring dry or inert conditions were conducted in flame dried glassware under a positive pressure of nitrogen.

Reactions were monitored by thin layer chromatography (TLC) on Macherey-Nagel pre-coated silica gel plates (0.25 mm) and visualized by UV light or by potassium permanganate spray test. Flash chromatography was performed on Merck silica gel (60, particle size: 0.040–0.063 mm). ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avance-400 spectrometer, Bruker Avance-300 or Bruker Avance-250 spectrometer in CDCl_3 or DMSO-d_6 as solvent at room temperature. Chemical shifts for protons are reported using residual solvent protons (^1H NMR: $\delta = 7.26$ ppm for CDCl_3 , $\delta = 2.50$ ppm for DMSO-d_6) as internal standard. Carbon spectra were referenced to the shift of the ^{13}C signal of CDCl_3 ($\delta=77.0$ ppm), DMSO-d_6 ($\delta = 39.5$ ppm).

FTIR spectra were recorded as thin films on KBr plates using Bruker Tensor 27 spectrometer and absorption maxima are reported in wavenumber (cm^{-1}). Elemental analyses were carried out by using Flash EA 1112 (Thermo Electron Corporation) analyzer. Melting points were measured with a Stuart Model SMP 30 melting point apparatus and are uncorrected. Petrol ether (PE) refers to light petroleum ether (boiling point 40-60°C). Anhydrous THF, acetonitrile and all starting materials (unless otherwise noted) were purchased from Aldrich and used as received.

Experimental procedures and compounds characterization



Scheme S1

Synthesis of calix[4]arene derivative **3**

A suspension of *p*-*tert*-butylcalix[4]arene **2** (2.0 g, 3.0 mmol), α -bromo-*N,N*-diethylacetamide (3.6 mL, 28 mmol) and NaI (4.1 g, 28 mmol) in dry THF/DMF (60 mL, 4/1 v/v), under N_2 , was gently warmed for 30 min. After cooling, NaH (0.9 g, 37 mmol) was added and the reaction mixture was stirred under N_2 for 15 h. Then 150 mL of a 1N HCl solution was added (caution) and the solid was filtered and washed with H_2O and dried (24 h at 50 °C) on CaCl_2 to obtain **3** as a pale yellow solid (3.1 g, yield 94%). The ^1H and ^{13}C NMR spectra and melting point of **3** were in agreement with the literature.¹

Synthesis of calix[4]arene derivative **4**

To a mixture of **3** (2.3 g, 2.1 mmol) in dry THF (65 mL) at 0 °C was added LiAlH_4 (3.2 g, 84 mmol) and successively refluxed under N_2 for 8 h. Then 150 mL of a 1N HCl solution was added (caution) and the product was extracted with ethyl acetate (2x50 mL). The organic phase was dried on Na_2SO_4 filtered and the solvent was removed in vacuo to give **4** as a white solid (1.4 g, yield 56%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 298 K): δ 11.1 (br s, NH, 4H), 6.90 (s, ArH, 8H), 4.38 (br t, OCH_2 , 8H), 4.24 (d, ArCH_2Ar , $J=12.9$ Hz, 4H), 3.60 (broad, CH_2NH , 8H), 3.30-3.40 (overlapped, $\text{ArCH}_2\text{Ar} + \text{CH}_2\text{NH}$, 20H), 1.30 (t, CH_3 , $J=8.1$ Hz, 12H), 1.09 (s, $-\text{C}(\text{CH}_3)_3$, 36H); ^{13}C NMR (100 MHz, CDCl_3 , 298 K): δ 151.4, 146.0, 133.1, 125.5, 68.8, 50.7, 47.1, 33.8, 31.3, 31.1, 8.7. Anal. Calcd for $\text{C}_{68}\text{H}_{112}\text{Cl}_4\text{N}_4\text{O}_4$: C, 68.55; H, 9.47. Found: C, 68.64; H, 9.39.

¹ Arduini, A.; Ghidini, E.; Pochini, A.; Ungaro, R. *J. Incl. Phenom. Macrocycl. Chem.* **1988**, 119-134.

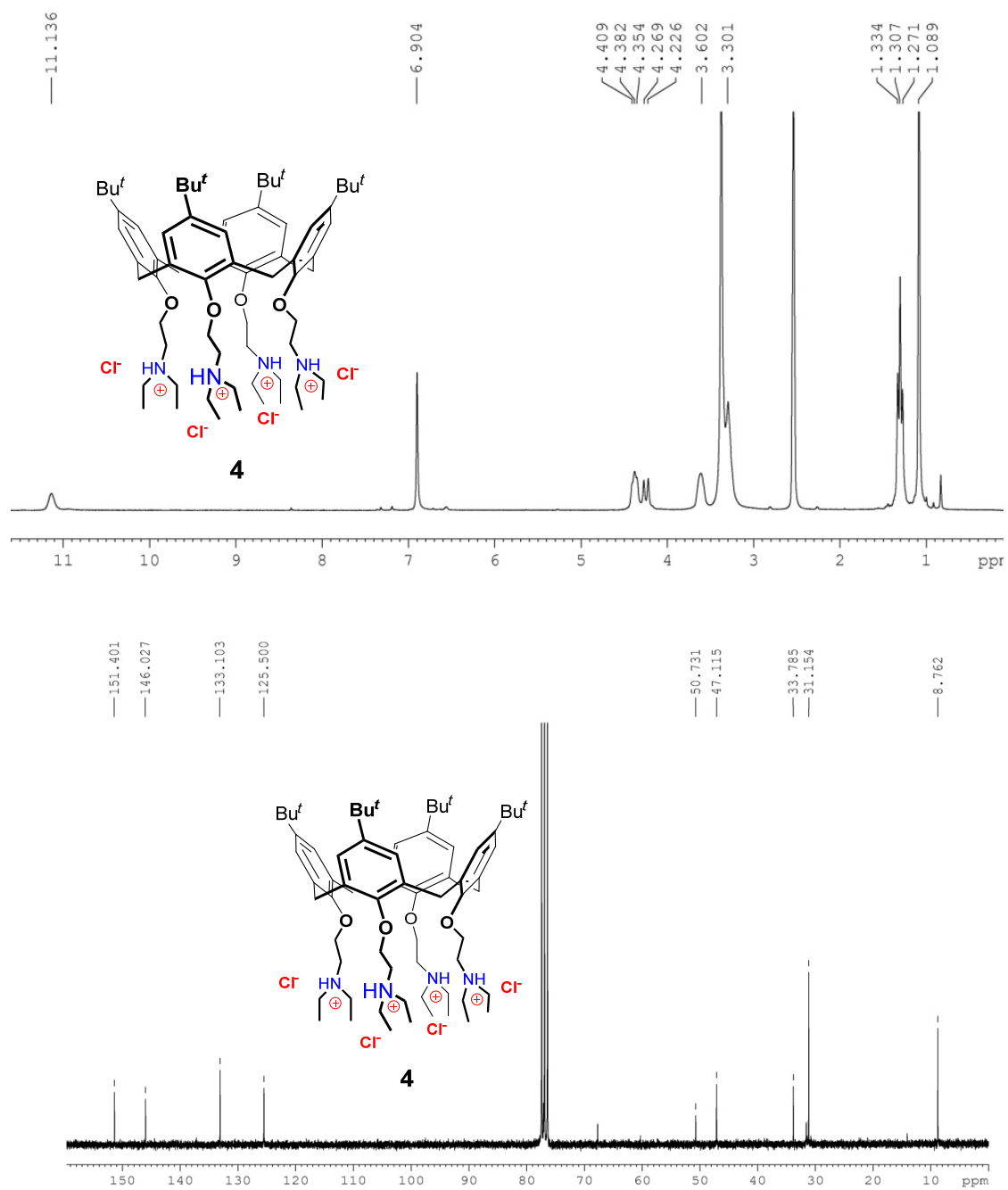


Figure S1. (top) ^1H NMR spectrum of **4** ($\text{DMSO}-d_6$, 300 MHz, 298 K). (bottom) ^{13}C NMR spectrum of **4** (CDCl_3 , 75 MHz, 298 K).

Calix[4]arene tetraamonium-octamolybdate hydrid 1

To an aqueous solution of $(\text{Na})_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (0.16 g, 0.67 mmol in 0.4 mL) was added a solution 12.0 M of HCl (0.17 mL). Then a methanol solution (0.24 mL) of **4** (0.10 g, 0.084 mmol) was added and the precipitate was filtered and washed with water and methanol to give a pale green solid (0.14 g). **FTIR** λ_{max} max (KBr)/ cm^{-1} 3435, 2953, 2907, 2871, 1637, 1560, 1477, 1458, 1362, 1298, 1258, 1192, 1121, 1016, 943 $\nu(\text{M}=\text{O})$, 910, 842, 796, 708, 660, 636, 552, 518.^{2,3,4} **Mp**: > 217.5 °C dec. **^1H NMR** (300 MHz, $\text{DMSO}-d_6$, 298 K): δ 9.59 (s, NH, 4H), 6.87 (s, ArH, 8H), 4.26 (br t, OCH_2 , 8H), 4.15 (d, ArCH_2Ar , $J = 9.5$ Hz, 4H), 3.25 (broad, NCH_2 , 8H), 3.00 (broad, NCH_2 , 8H), 1.25 (br t, CH_3 , 12H), 1.06 [s, $\text{C}(\text{CH}_3)_3$, 36H]. **^{13}C NMR** (100 MHz, $\text{DMSO}-d_6$, 298 K): δ 152.4, 146.7, 133.6, 125.9, 68.2, 50.0, 47.4, 34.2, 31.6, 9.3.

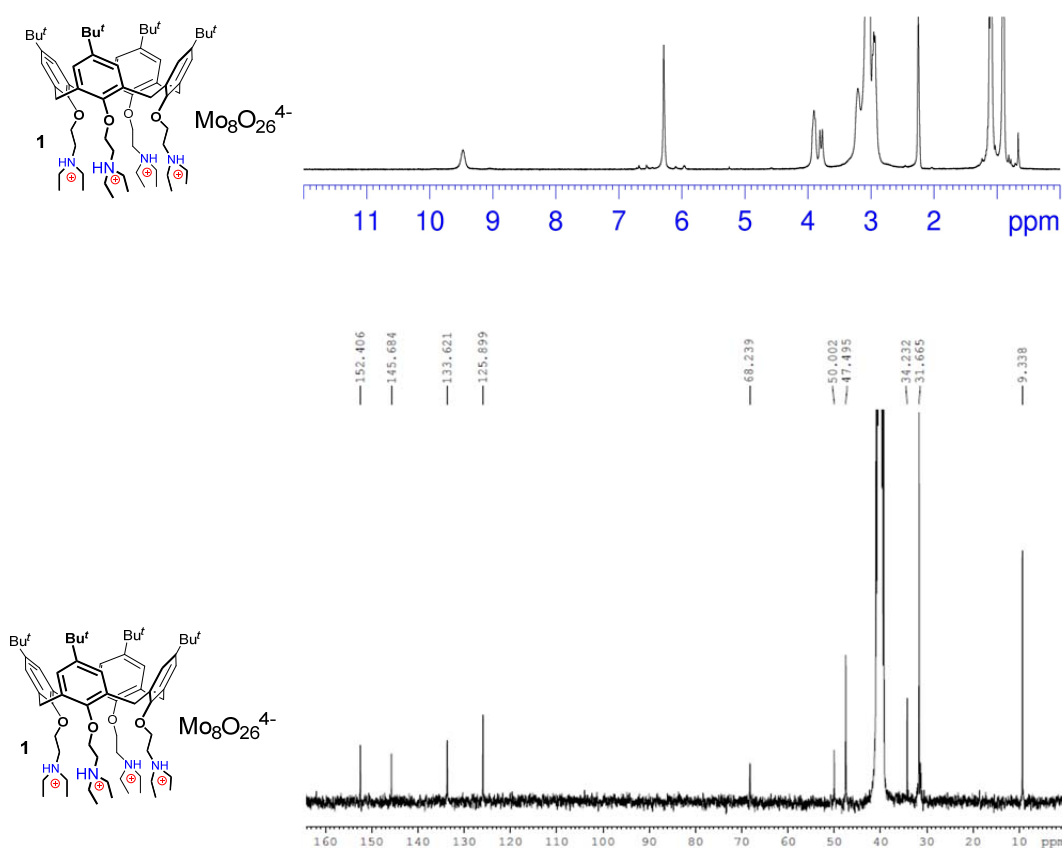


Figure S2. (top) ^1H NMR spectrum of **1** ($\text{DMSO}-d_6$, 300 MHz, 298 K). (bottom) ^{13}C NMR spectrum of **1** ($\text{DMSO}-d_6$, 75 MHz, 298 K)

² Veltman, T. R.; Stover A. K.; Sarjeant, A. N.; Ok K. M.; Halasyamani, P. S.; Norquist, A. J. *Inorg. Chem.* **2006**, *45*, 5529-5537.

³ Yang, C.; Jin, Q.; Zhang, H.; Liao, J.; Zhu, J.; Yu, B.; Deng, J. *Green Chem.* **2009**, *11*, 1401-1405.

⁴ Zhang, B.; Li, S.; Pöthig A.; Cokoja, M.; Zang S.-L.; Herrmann, W. A.; Kühn, F. E. *Z. Naturforsch.* **2013**, *68b*, 587-597.

Reaction progress profile for the oxidation of phenyl methyl sulfide monitored by ^1H NMR

Table S1. TON and TOF values for the oxidation of phenyl methyl sulfide at room temperature in CD_3CN and CD_3OD (Figure 2 of the main text)

<p>◆ Blue curve, Figure 2: in CD_3CN, at room temperature with H_2O_2 (1.0 equiv), 1 (0.1 mol %) at $[\text{sulfide}] = 0.5 \text{ M}$;</p>			<p>■ Red curve, Figure 2: in CD_3OD, at room temperature with H_2O_2 (1.0 equiv), 1 (0.1 mol %) at $[\text{sulfide}] = 0.5 \text{ M}$.</p>		
Time (min)	TON	TOF (h^{-1})	Time (min)	TON	TOF (h^{-1})
4.7	769	9889	4.6	211	2740
10.3	912	5331	10.6	464	2623
19.1	924	2907	19.6	674	2060
29.5	923	1880	31.6	815	1547

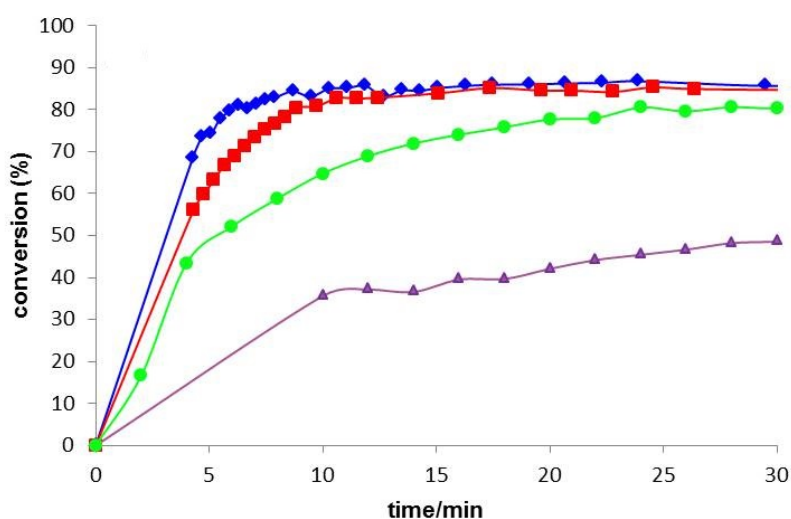


Figure S3. Reaction progress profile for the oxidation of phenyl methyl sulfide. The curves show the conversion to the sulfoxide. The reactions were performed in a NMR tube using 1,3,5-trimethoxybenzene as internal standard and monitored by ^1H NMR. Reaction conditions:

H_2O_2 (30 wt. % in H_2O , 1.0 equiv), **1** (0.1 mol %), at r.t. in CD_3CN . ◆: At $[\text{sulfide}] = 0.5 \text{ M}$. ■: Using **1** (0.05 mol %) at $[\text{sulfide}] = 0.5 \text{ M}$. ●: Using **1** (0.05 mol %) at $[\text{sulfide}] = 0.3 \text{ M}$. ▲ Using **1** (0.01 mol %) at $[\text{sulfide}] = 0.5 \text{ M}$.

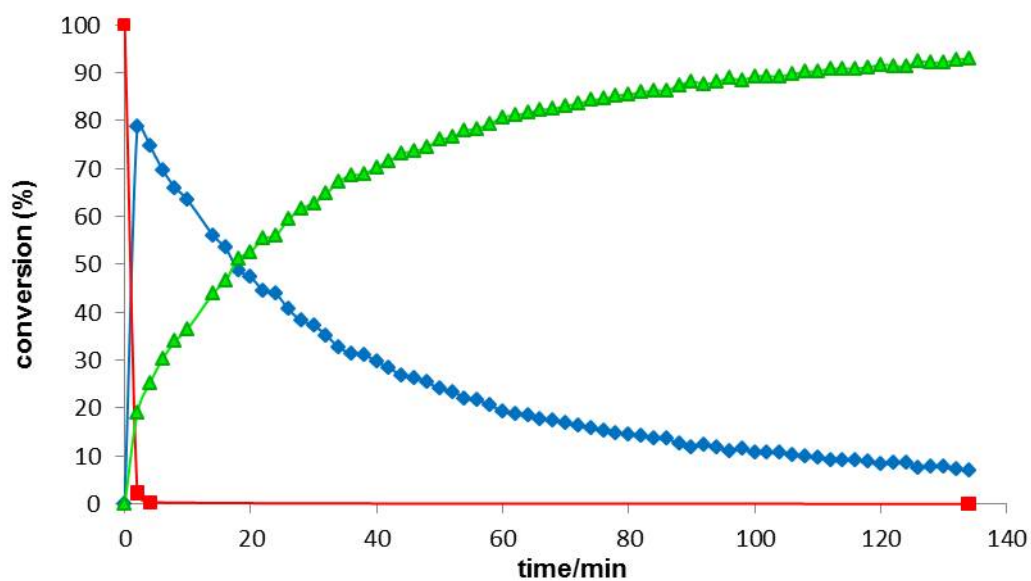


Figure S4. Reaction progress profile for the oxidation of phenyl methyl sulfide (■) to sulfoxide (◆) and sulfone (▲). The reaction was performed in a NMR tube using 1,3,5-trimethoxybenzene as internal standard and monitored by ^1H NMR. Reaction conditions: H_2O_2 (30 wt. % in H_2O , 2.0 equiv), **1** (0.05 mol%), at r.t. in CD_3CN at $[\text{sulfide}] = 0.5 \text{ M}$

General procedure for oxidation of sulfides

Oxidation of sulfides to sulfoxides

A sample vial was charged with sulfide (0.2 mmol), CH₃CN dry (400 µL), **1** (0.0001 mmol, 0.22 mg) and H₂O₂ (30 wt. % in H₂O, 0.2 mmol, 22 µL). When adding H₂O₂ a slight evolution of heat occurred. The reaction was stirred at room temperature for 40-105 minutes, monitored by TLC. For methyl octyl sulfoxide the TLC was visualized by potassium permanganate spray test. The products were isolated (72-92% yield) by silica gel flash chromatography. Methyl phenyl sulfoxide,^{5,6,7,8,9,10} 4-methylphenyl methyl sulfoxide,^{6,8,10,11} 4-methoxyphenyl methyl sulfoxide,^{7,10} 2-methoxyphenyl methyl sulfoxide,¹⁰ 4-chlorophenyl methyl sulfoxide,^{7,10} 2-bromoophenyl methyl sulfoxide,¹² 4-(methylsulfinyl)benzaldehyde,^{5,13} ethyl phenyl sulfoxide,^{7,9} cyclopropyl phenyl sulfoxide,¹¹ phenyl allyl sulfoxide,^{5,9,11} 2-(phenylsulfinyl)ethanol,^{6,8,9} methyl 2-(phenylsulfinyl) acetate,^{9,10} 2-methyl(sulfinyl)benzimidazole,^{14,15} benzyl methyl sulfoxide,^{7,11} methyl octyl sulfoxide,^{7,8} thian-4-one S-oxide,^{5,11} *trans*-2-phenyl-1λ⁴,3-dithian-1-one,^{16,17} and *trans*-2-phenyl-1λ⁴,3-dithiolan-1-one,^{16,17} are known compounds and their spectral data were consistent with those in the literature.

Oxidation of sulfides to sulfones

A sample vial was charged with sulfide (0.2 mmol), CH₃CN dry (400 µL), **1** (0.0001 mmol, 0.22 mg) and H₂O₂ (30 wt. % in H₂O, 0.4 mmol, 44 µL). The reaction mixture was stirred at 50 °C for 60-180 minutes, monitored by TLC. For methyl octyl sulfone the TLC was visualized by potassium permanganate spray test. The products were isolated (77-98% yield) by flash chromatography. Methyl phenyl sulfone,^{3,6} 4-nitrophenyl methyl sulfone,^{3,6} 4-methoxyphenyl methyl sulfone,^{3,6} cyclopropyl phenyl sulfone,¹⁸ diphenyl sulfone,^{6,7} allyl phenyl sulfone,⁶ 2-(phenylsulfonyl)ethanol,⁶ benzyl methyl sulfone,³ methyl octyl sulfone,⁷ and benzothiophene 1,1-dioxide⁶ are known compounds and their spectral data were consistent with those in the literature.

⁵ Gao, Y.; Lam, Y. *Adv. Synth. Catal.* **2008**, *350*, 2937-2946.

⁶ Postigo, L.; Ventura, M.; Cuenca, T.; Jiménez, G.; Royo, B. *Catal. Sci. Technol.* **2015**, *5*, 320-324.

⁷ Kamata, K.; Hirano, T.; Mizuno, N. *Chem. Commun.* **2009**, 3958-3960.

⁸ Zelenka, J.; Hartman, T.; Klímová, K.; Hampl, F.; Cibulka, R. *ChemCatChem* **2014**, *6*, 2843-2846.

⁹ Zhang, B.; Zhou, M.-D.; Cokoja, M.; Mink, J.; Zang, S.-L.; Kühn, F. E. *RSC Adv.* **2012**, *2*, 8416-8420.

¹⁰ Zhang, H.; Wang, G. *Tetrahedron Lett.* **2014**, *55*, 56-58.

¹¹ Secci, F.; Arca, M.; Frongia, A.; Piras, P. P. *Catal. Sci. Technol.* **2014**, *4*, 1407-1415.

¹² Kinen, C. O.; Rossi, L. I.; de Rossi, R. H. *Green Chem.* **2009**, *11*, 223-228.

¹³ Gamba, I.; Palavicini, S.; Monzani, E.; Casella, L. *Chem. Eur. J.* **2009**, *15*, 12932-12936.

¹⁴ Seenivasaperumal, M.; Federsel, H.-J.; Szabó, K. J. *Adv. Synth. Catal.* **2009**, *351*, 903-919.

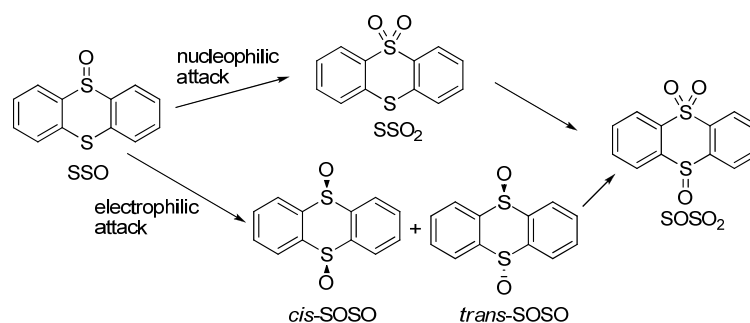
¹⁵ Shin, J. M.; Cho, Y. M.; Sachs, G. *J. Am. Chem. Soc.* **2004**, *126*, 7800-7811.

¹⁶ Di Furia, F.; Licini, G.; Modena, G. *Gazz. Chim. It.* **1990**, 165-170.

¹⁷ Della Sala, G.; Labano, S.; Lattanzi, A.; Tedesco, C.; Scettri, A. *Synthesis* **2002**, *4*, 505-510.

¹⁸ Holland, H. L.; Chernishenko, M. J.; Conn, M.; Munoz, A.; Manoharan, T. S.; Zawadzki, M. A. *Can. J. Chem.* **1990**, *68*, 696-700.

Oxidation of thianthrene 5-oxide by hybrid 1



Time (min)	Yield (%)	Selectivity				X_{SO}^b
		SSO ₂	<i>cis</i> -SOSO	<i>trans</i> -SOSO	SOSO ₂	
60	87	23	15	60	2	0.25

^aReaction conditions: SSO (0.2 mmol), H₂O₂ (0.05 mmol), **1** (0.02 mmol), in CH₃CN (5 mL) stirred at room temperature. Yield and selectivity were determined by ¹H-NMR analysis with an internal standard. ^bCalculated according to equation reported in ref. 19b.

The oxidation of thianthrene 5-oxide was carried out in order to assess the electrophilic or nucleophilic character of hybrid **1**/H₂O₂. This compound has been introduced by Adam and coauthors as a probe to determine the electrophilic or nucleophilic character of several classes of oxidants.¹⁹ The calculated low X_{SO} value in the above Table supported the electrophilic nature of this system, with a preferential oxidation of the sulfide moiety in thianthrene 5-oxide SSO.

The thianthrene 5-oxide was synthesized according to the literature.²⁰

Thianthrene 5-oxide (SSO), thianthrene 5,5-dioxide (SSO₂), *cis*-thianthrene 5,10-dioxide (*cis*-SOSO), *trans*-thianthrene 5,10-dioxide (*trans*-SOSO), thianthrene 5,5,10-trioxide (SOSO₂) were synthesized according to literature procedures²¹ and their spectral data were consistent with those in the literature.^{21,22}

In a sample vial, thianthrene 5-oxide SSO (0.20 mmol, 46.6 mg), **1** (0.02 mmol, 44.6 mg) and H₂O₂ (30 wt. % in H₂O, 0.050 mmol, 6 μ L) were dissolved in CH₃CN (5 mL). After stirring for 1 hour at room temperature the solvent was removed under reduced pressure. The crude reaction mixture was

¹⁹ (a) Adam, W.; Haas, W.; Sieker, G. *J. Am. Chem. Soc.* **1984**, *106*, 5020-5022. (b) Adam, W.; Golsch, D. *J. Org. Chem.* **1997**, *62*, 115-119.

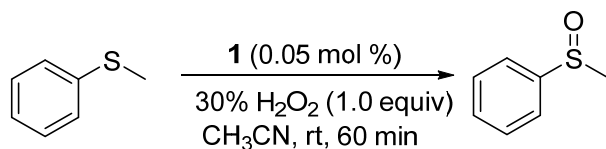
²⁰ Fujita, T.; Kamiyama, H.; Osawa, Y.; Kawaguchi, H.; Kim, B. J.; Tatami, A.; Kawashima, W.; Maeda, T.; Nakanishi, A.; Morita, H. *Tetrahedron* **2007**, *63*, 7708-7716.

²¹ Bonchio, M.; Conte, V.; De Conciliis, M. A.; Di Furia, F.; Ballistreri, F. P.; Tomaselli, G. A.; Toscano, R. M. *J. Org. Chem.* **1995**, *60*, 4475-4480.

²² Kamata, K.; Hirano, T.; Ishimoto, R.; Mizuno, N. *Dalton Trans.* **2010**, *39*, 5509-5518.

taken up in CDCl₃ and 1,2-dichloroethane was added as internal standard in order to evaluate the yields of the products and selectivity by ¹H NMR analysis.

Reusability of **1** in the oxidation of phenyl methyl sulfide



Catalyst **1** (0.002 mmol, 4.47 mg) was suspended in acetonitrile (8 mL) in a centrifuge tube and phenyl methyl sulfide (4 mmol, 470 μ L) and H₂O₂ (30 wt. % in H₂O, 4 mmol, 408 μ L) were added in sequence. The reaction was stirred at room temperature for 1 h, then concentrated under reduced pressure and the crude was washed and centrifuged three times with hexane/CHCl₃ solvent mixtures, separating and combining the supernatant solutions. The solutions were concentrated under reduced pressure and the sulfoxide isolated by silica gel flash chromatography. Residual catalyst was then dried at room temperature and used for the next run (Scheme 2 in the manuscript). Sulfoxide yields: 87-91%.

FTIR spectra of catalyst 1

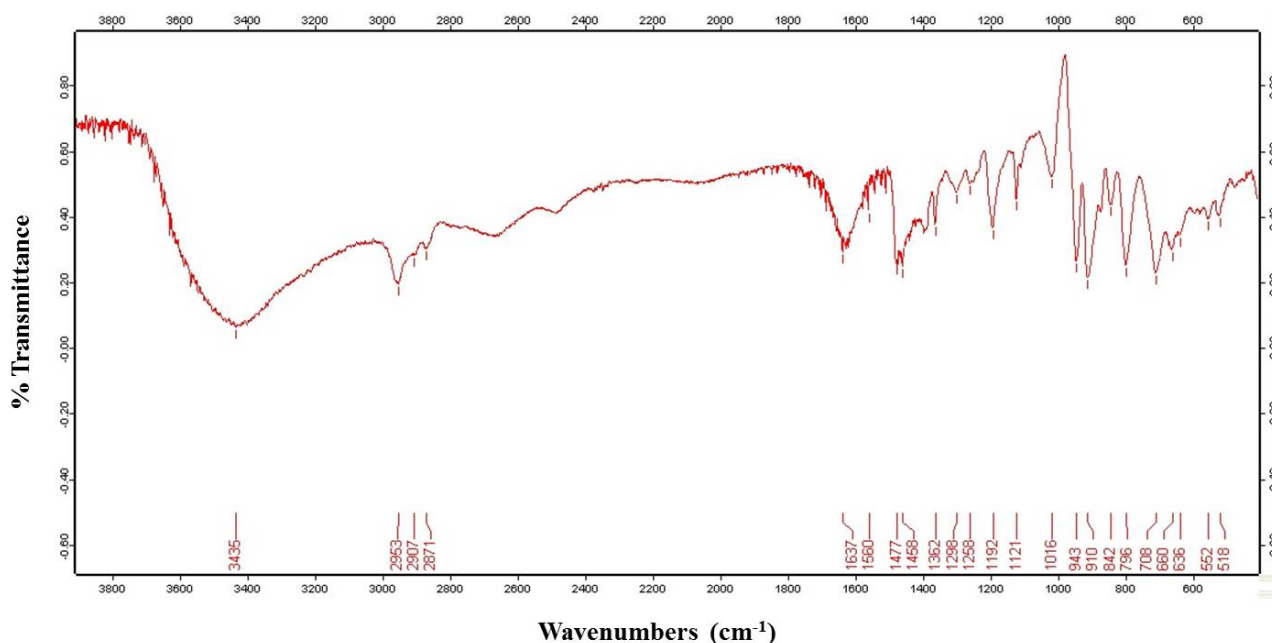


Figure S5. FTIR of the catalyst **1**, recorded by forming a thin layer on a KBr plate.

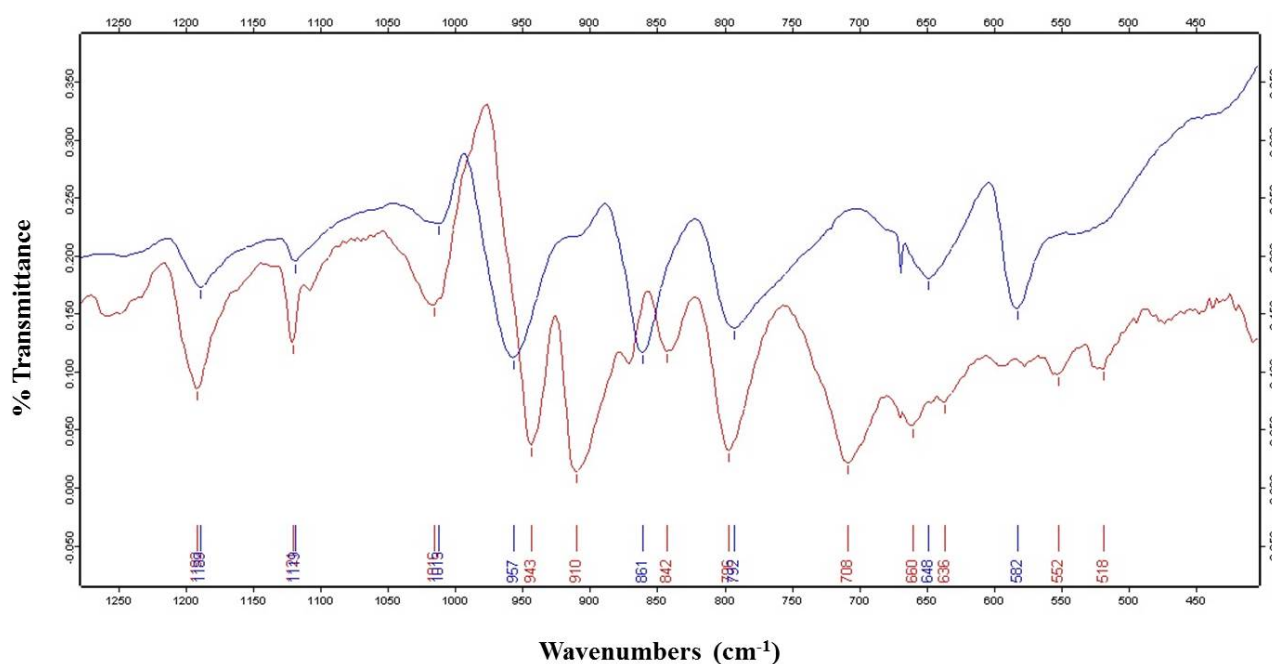
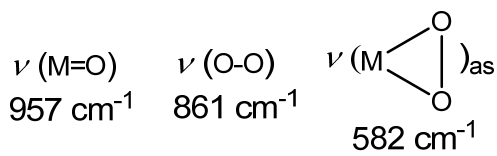


Figure S6. Comparison of FTIR spectra of catalyst **1** before and after treatment with H₂O₂.

The red line refers to FTIR spectrum of the catalyst **1**. The blue line refers to FTIR spectrum of the catalyst **1** after the following treatment: in a sample vial, **1** (0.002 mmol, 4 mg) and H₂O₂ (30 wt. % in H₂O, 0.1 mmol, 10 μ L) were dissolved in CH₃CN (1 mL). After stirring for 20 minutes at room temperature the solvent was removed under reduced pressure and the IR spectrum of the solid was recorded forming a thin layer on a KBr plate.

The IR spectrum of the precipitate showed that a peroxo-molybdenum species is formed. Comparing the red spectrum of the catalyst without hydrogen peroxide (red line, Figure S6) with that one of the catalyst recorded after the treatment with hydrogen peroxide (blue line, Figure S6) the following strong bands were observed:



The absorption bands at 582 and 861 cm^{-1} , which are absent in the red spectrum, are consistent with characteristic absorption bands of the peroxo-molibdenum complexes reported in the literature.^{23,24}

²³ Ishii, Y.; Yamawaki, K.; Yoshida T.; Ura, T.; Ogawa, M. *J. Org. Chem.* **1987**, 52, 1868-1870.

²⁴ Jacobson, S. E.; Tang, R.; Mares, F. *Inorg. Chem.* **1978**, 17, 3055-3063.

Crystal structure determination of compound **1**

Very small and thin crystals (0.110 x 0.070 x 0.030 mm³) were obtained by slow diffusion of diethyl ether into a DMF solution of compound **1**. Data collection was carried out at the Macromolecular crystallography XRD1 beamline of Elettra synchrotron (Trieste, Italy), by employing the rotating-crystal method and cryo-cooling techniques. Routinely the crystals were dipped in the cryoprotectant agent and then mounted on a loop and immediately flash frozen to 100 K with liquid nitrogen. Diffraction data were indexed and integrated by the XDS package²⁵ and scaled by XSCALE²⁶ software. The structure was solved in the triclinic centro-symmetric space group *P*-1 by using the SIR2011²⁷ software and refined by full-matrix least-squares methods on *F*² using SHELXL-13.²⁸ In the asymmetric unit a tetracationic calixarene molecule was found together with two halves of the anionic POM (Mo₈O₂₆⁴⁻), one water molecules and three DMF solvent molecules one at full occupancy and two refined at 0.85 and 0.75 of partial occupancy (Figure S7 or S8). In the crystallographic model a *t*-butyl group at the upper rim of the calixarene molecule was found disordered over two positions refined at equal occupancy and two orientations were distinguished for a diethylammonium substituent at the lower rim and refined at 0.6 and 0.4 of partial occupancy. Furthermore in the asymmetric unit some DMF solvent molecules were highly disordered and were not modelled. Thus their contribute to the overall scattering was removed through the SQUEEZE function of PLATON²⁹ software. The residual electron density of 330 electrons/cell found in the voids of **1** (corresponding to about 22% of the cell volume) was attributed to about 8 DMF molecules. A refinement using reflections modified by the SQUEEZE procedure behaved well and the *R*-factor was reduced from 13.2 to 10.5%. Non-hydrogen atoms at full occupancy, or with population higher than 0.5 were anisotropically refined (H atoms at the calculated positions). Details on the crystallographic model and on the refinement are reported in **Table S2**.

²⁵ Kabsch, W. *Acta Crystallogr.* **2010**, *D66*, 125–132.

²⁶ Kabsch, W. *Acta Crystallogr.* **2010**, *D66*, 133–144.

²⁷ Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Siliqi, D.; Spagna, R. *J. Appl. Crystallogr.* **2007**, *40*, 609–613.

²⁸ Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

²⁹ Sluis, P. v.d.; Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, 194–201.

Table S2. Crystal data and structure refinement for 1

Formula	C ₆₈ H ₁₁₂ N ₄ O ₄ , Mo ₈ O ₂₆ , H ₂ O, 2.6(C ₃ H ₇ NO)
Formula weight	2439.18
<i>T</i> (K)	100(2)
λ (Å)	1.000
Crystal system	Triclinic
Space group	<i>P</i> -1
Unit cell dimensions (Å, °)	<i>a</i> = 12.23(1), α = 100.01(3) <i>b</i> = 22.27(2), β = 90.72(2) <i>c</i> = 22.92(1), γ = 104.62(2)
<i>V</i> (Å ³)	5938(8) Å ³
<i>Z</i>	2
ρ_{calc} (g/mm ³)	1.364
μ (mm ⁻¹)	2.194
F(000)	2472
Crystal size (mm ³)	0.110 x 0.070 x 0.030
Reflections collected	11939
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	11939 / 182 / 1157
GooF	1.084
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ (<i>I</i>)]	0.0823, 0.2279
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0911, 0.2357

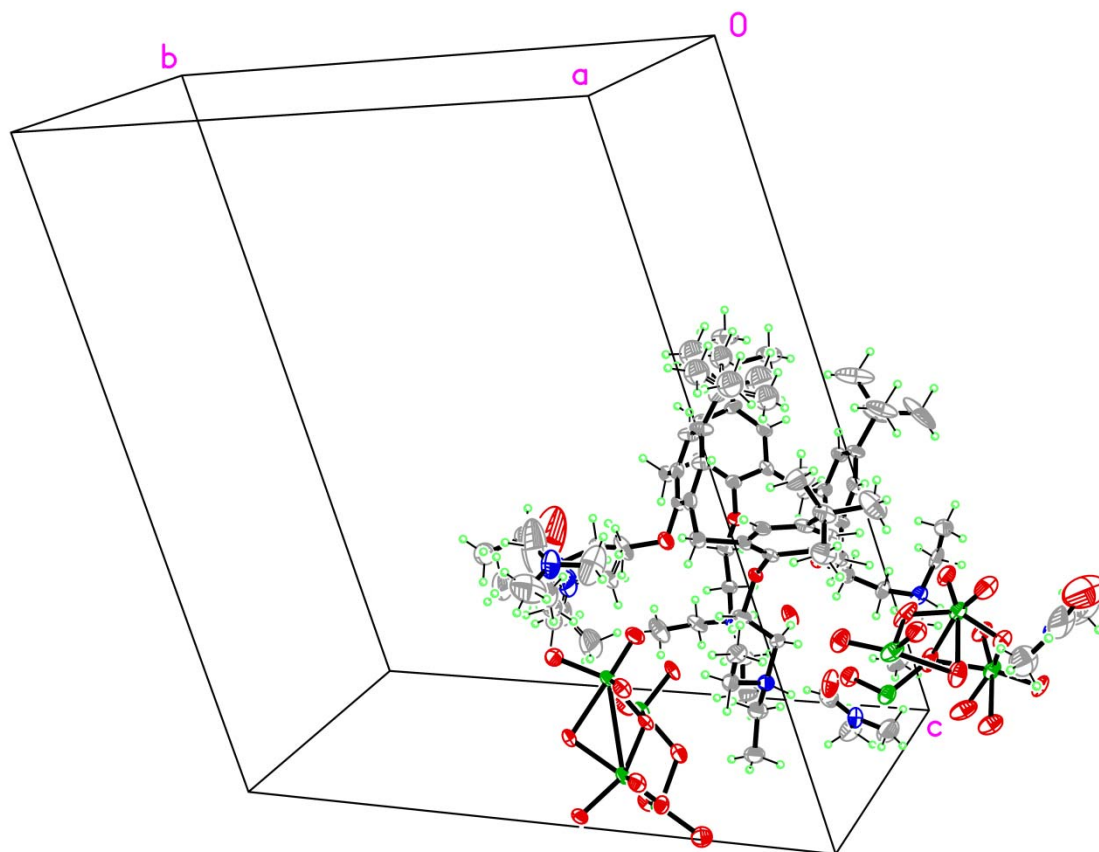


Figure S7. Asymmetric unit content of compound **1**. The asymmetric unit consists of the tetracationic calixarene molecule, two halves of the anionic $\text{Mo}_8\text{O}_{26}^{4-}$ POM, and three DMF solvent molecules at partial occupancy. One *t*-butyl group and one diethylammonium fragment of the calixarene molecule are disordered over two positions refined respectively at 0.5/0.5 and 0.6/0.4 of partial occupancy. Thermal parameters are displayed at the 30% of probability.

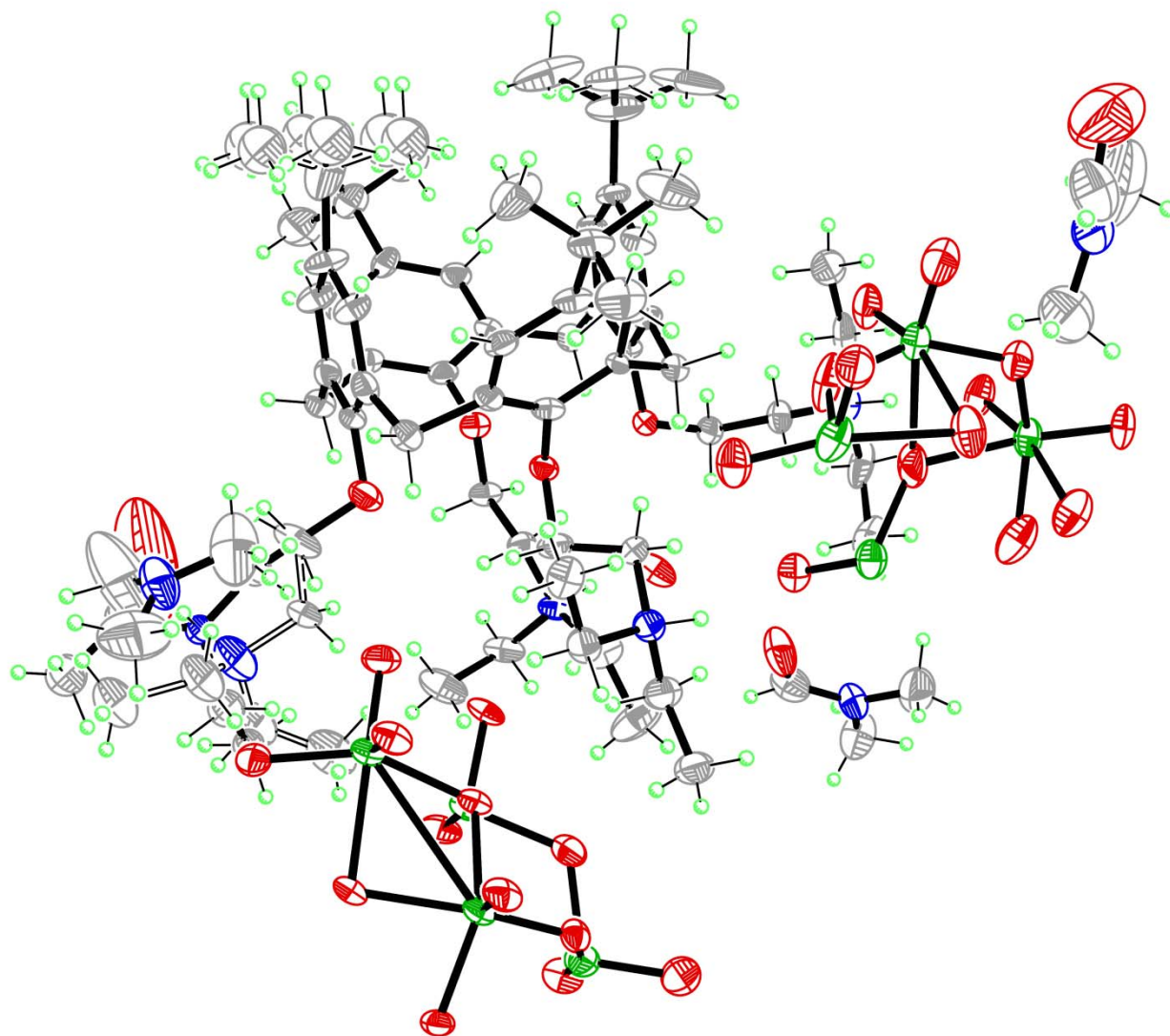


Figure S8. Asymmetric unit content of compound **1**. The asymmetric unit consists of the tetracationic calixarene molecule, two halves of the anionic $\text{Mo}_8\text{O}_{26}^{4-}$ POM, and three DMF solvent molecules at partial occupancy. One *t*-butyl group and one diethylammonium fragment of the calixarene molecule are disordered over two positions refined respectively at 0.5/0.5 and 0.6/0.4 of partial occupancy. Thermal parameters are displayed at the 30% of probability.

The X-ray structure of POM-calixarene **1** showed the presence of both α and β isomers of the octamolybdate $\text{Mo}_8\text{O}_{26}^{4-}$ cluster (Figure S9a). Regarding the α isomer, one $[\text{Mo}_8\text{O}_{26}]^{4-}$ cluster was sandwiched between two tetracationic calixarenes in antiparallel orientation (Figure S9b). In this assembly, each macrocycle forms two $^+\text{N}-\text{H}\cdots\text{O}-\text{Mo}$ hydrogen bonds ($^+\text{N}\cdots\text{O}$ distances 2.70(1) and 2.81(1) Å) between two ammonium groups at the lower rim and terminal oxygen atoms of the cluster. Concerning the β isomer, one tetra-anionic cluster was also sandwiched between two antiparallel calixarenes (Figure S9c), but differently from the α one, it forms hydrogen bonds with two H_2O molecules ($\text{O}\cdots\text{Mo}$ distances 2.88(1) and 2.99(1) Å). These latter act as H-bond acceptors for the $^+\text{N}-\text{H}$ ammonium groups ($^+\text{N}\cdots\text{O}$ distance 2.83(1) Å) of the calixarene macrocycles.

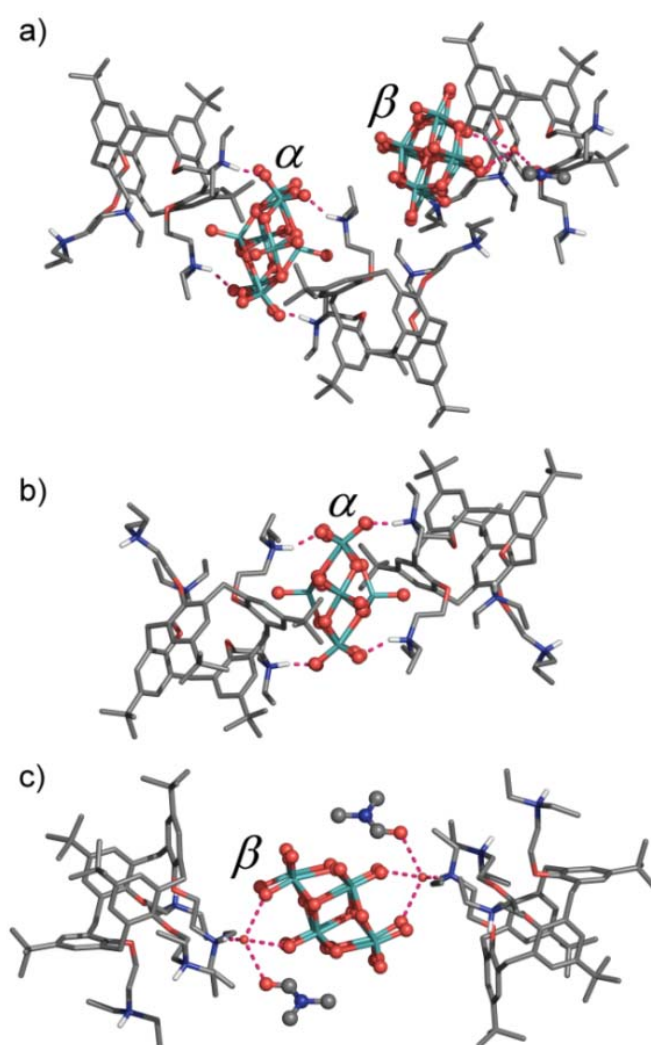


Figure S9. (a) Solid state assembly of POM/calix[4]arene **1**. Detailed views of the fundamental interactions of the α - $[\text{Mo}_8\text{O}_{26}]^{4-}$ (b) and β - $[\text{Mo}_8\text{O}_{26}]^{4-}$ (c) isomeric clusters.

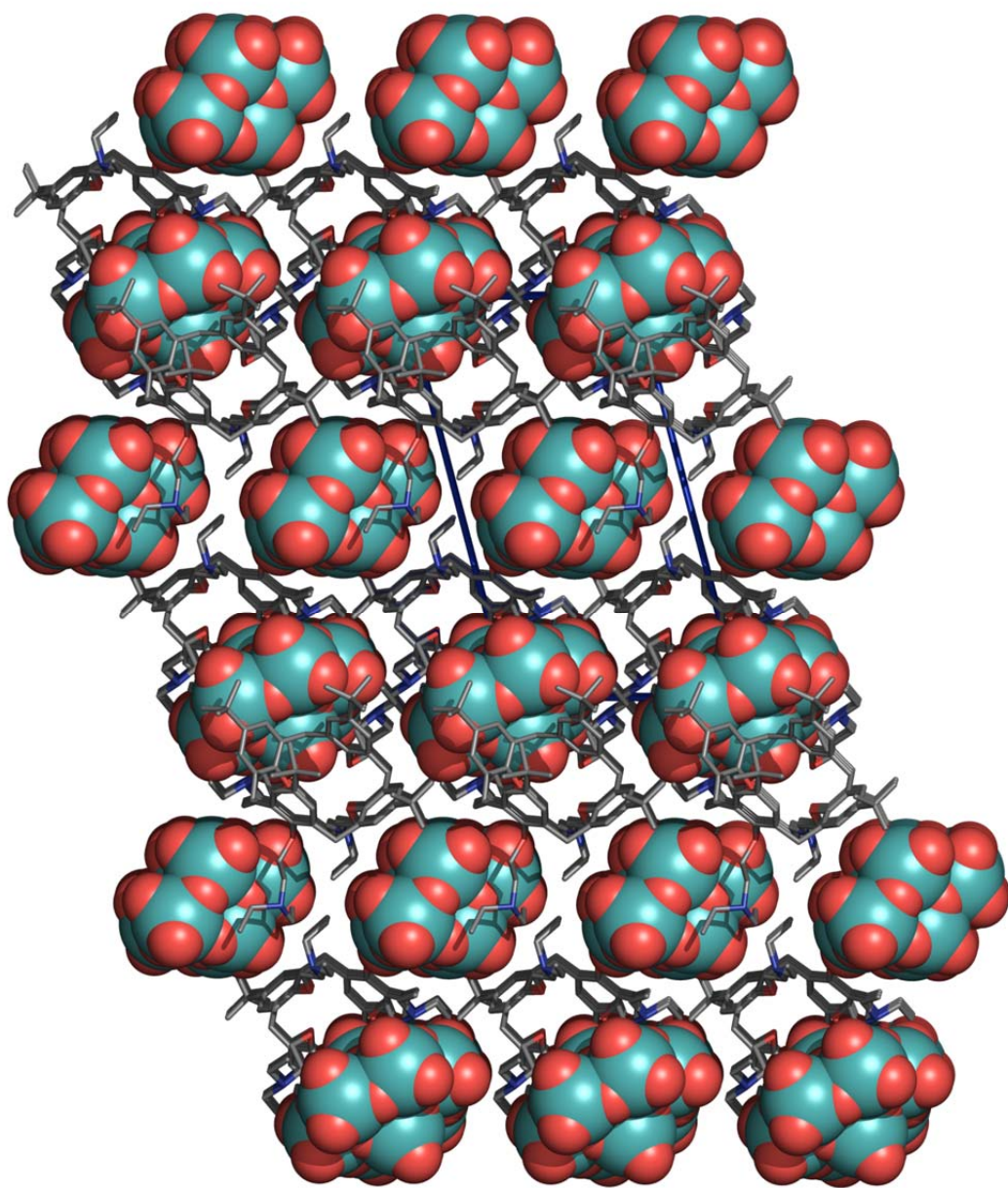


Figure S10. Bidimensional array of POM anions overlaid by tetracationic calix[4]arenes.

Bond lengths (Å) for α -[Mo₈O₂₆]⁴⁻ cluster

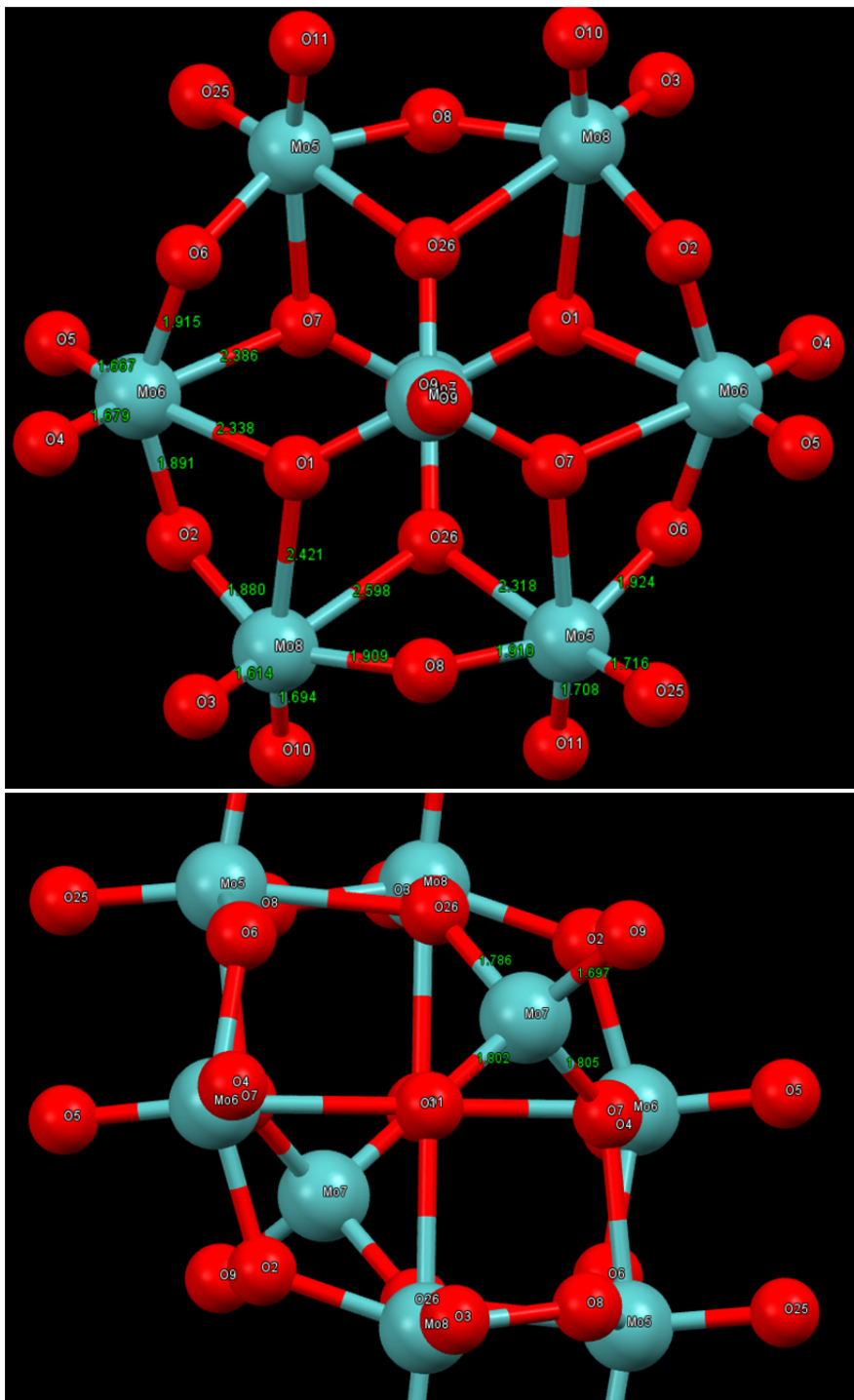


Figure S11.

Mo–O–Mo angles (°) in α -[Mo₈O₂₆]⁴⁻ cluster

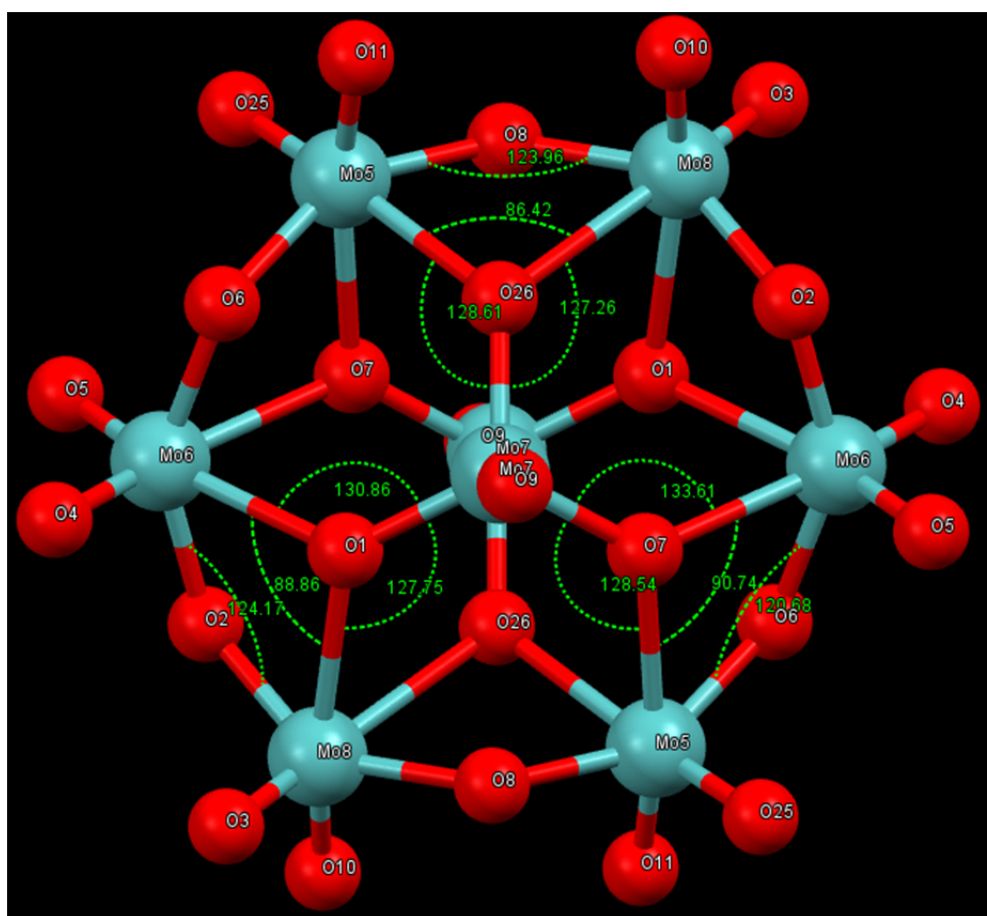


Figure S12.

Different views of the β -[Mo₈O₂₆]⁴⁺ cluster

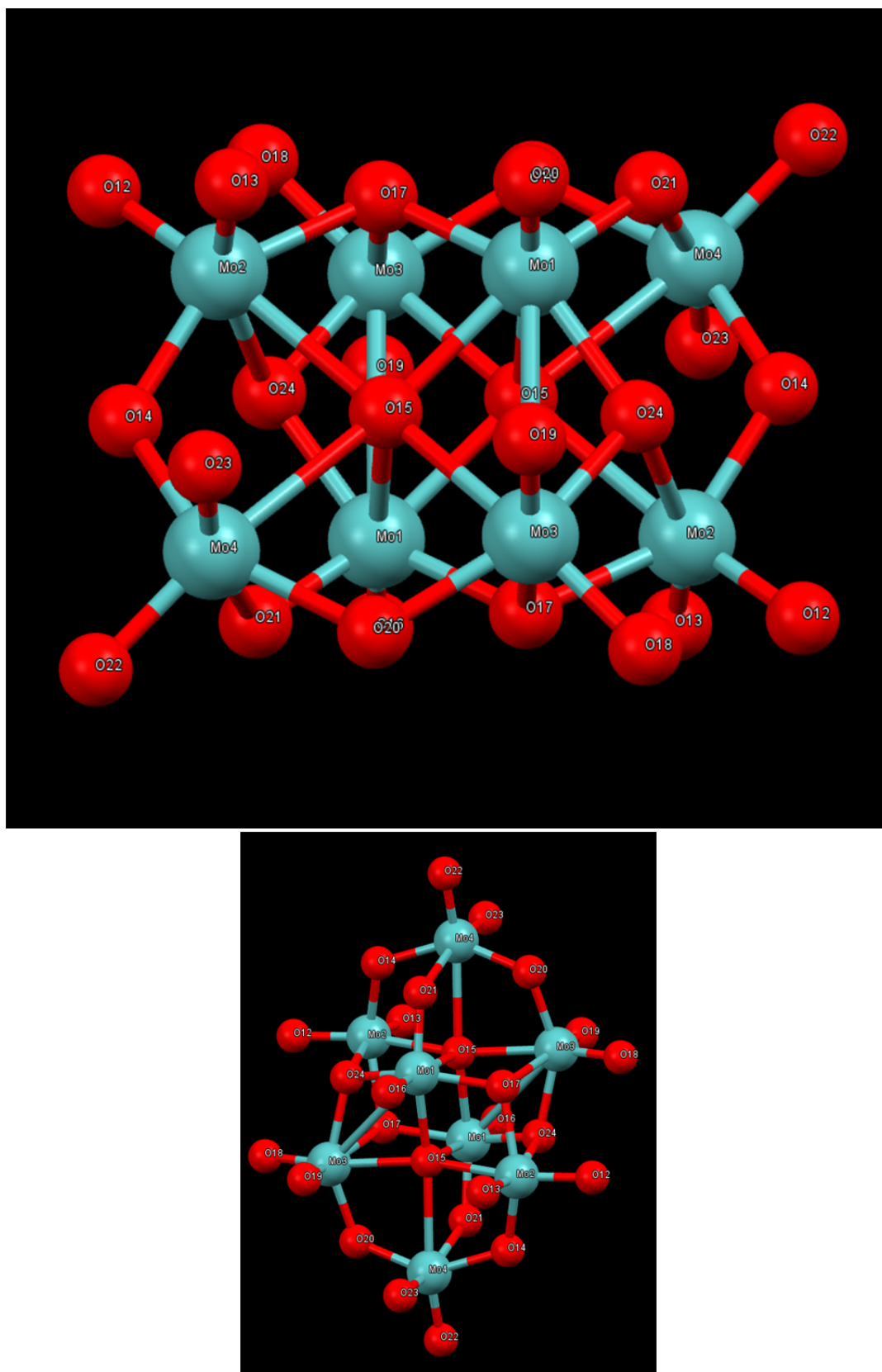


Figure S13.

Detailed views and geometric parameters [bond lengths (Å) and Mo–O–Mo angles (°)] of the six-coordinate molybdenums in β -[Mo₈O₂₆]⁴⁻ cluster

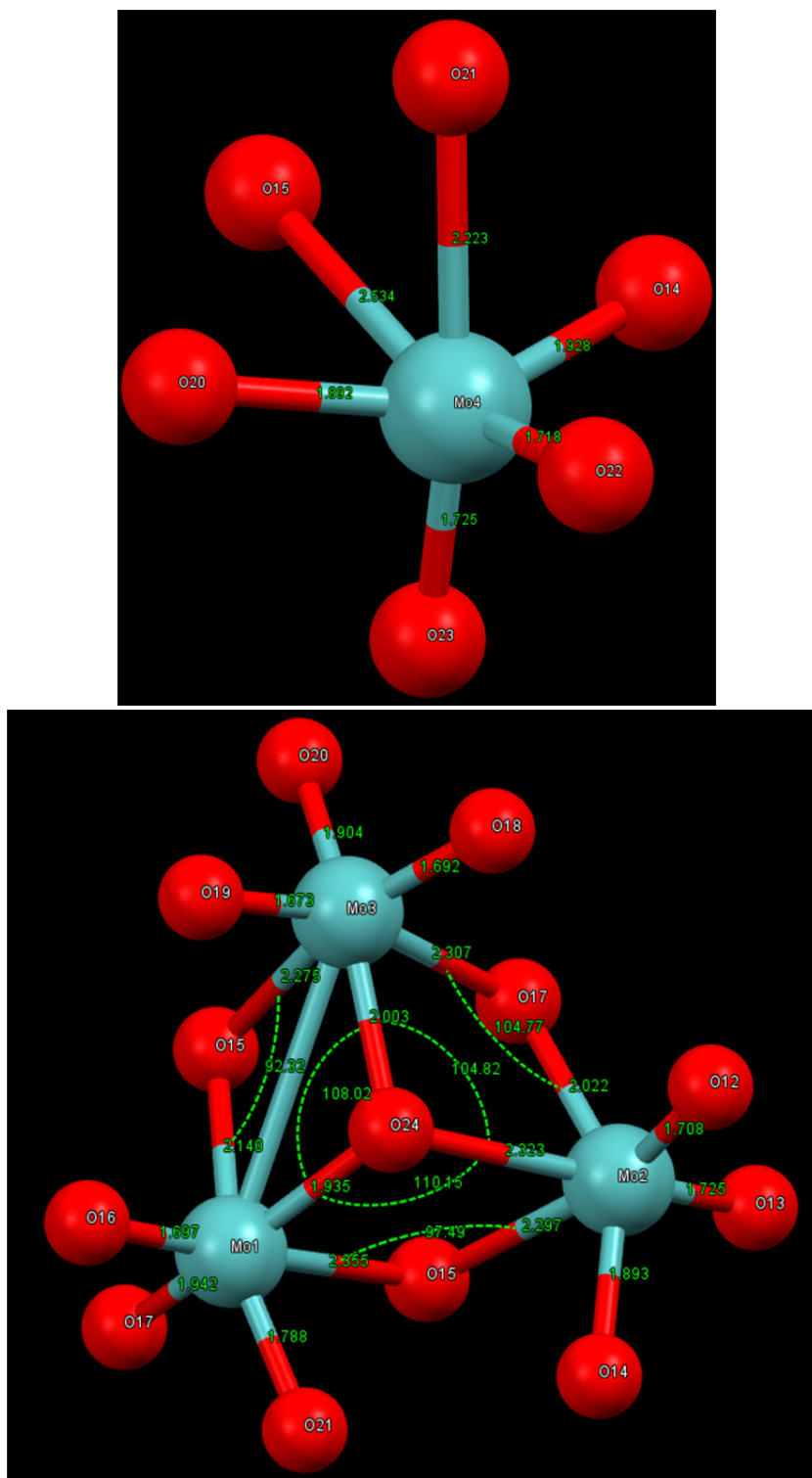


Figure S14.