

Supporting Information for

Lewis Acid catalytic Cores sandwiched by Inorganic Polyanion

Caps: Selective H₂O₂ based Oxidations with [Al^{III}₄(H₂O)₁₀(β-XW₉O₃₃H)₂]⁴⁻ (X= As^{III}, Sb^{III})

**Mauro Carraro, Bassem S. Bassil, Antonio Sorarù, Serena Berardi, Andreas Suchopar,
Ulrich Kortz, Marcella Bonchio**

Experimental Details

General: All reagents were purchased from commercial sources, and used as received, without further purification. Vacant POMs Na₉[B-α-XW₉O₃₃].19.5H₂O (X= As or Sb) were prepared as described in the literature.¹ FT-IR (KBr) spectra were collected on a Thermo Quest Nicolet 5700 instrument. UV-Vis spectra were recorded between 800 and 175 nm, with a VARIAN UV-Nir Cary 5000 instrument, using 1 cm path length quartz cells, and a scan rate of 200 nm/min. CD spectra (4-6 scans) were recorded with a Jasco J715 polarimeter, in the range 400-195 nm, using 1 cm or 1 mm path length quartz cells, with scan rate 50 nm/min. GC analyses have been performed with a Shimadzu 2010 instrument, equipped with EQUITY-TM-5 (15 m × 0.1mm) capillary column with 0.1μm film thickness and a Hewlett Packard 5890 Series II instrument equipped with STABILWAX® (60 m × 0.53 mm) capillary column with 0.1 μm film thickness. Elemental analyses were performed at Microanalysis Laboratory of Padova University (C, H, N) and at Analytische Laboratorien, Lindlar, Germany (Rb, Al, As, Sb, W, Na). Thermogravimetric analyses were performed on a TA instruments SDT Q600 thermobalance by heating up to 800° C at 5° C/min under N₂ or air.

Catalytic tests: Reactions were performed dissolving 0.8 μmol of catalyst in 0.6 ml of acetonitrile or in 1.2 ml of water under stirring at 70/50 °C (30 °C for sulfide), then 0.5 mmol of substrate and 0.1 mmol of H₂O₂ (11.19 M) were added. Reactions were carried for 1-2 hours, testing H₂O₂ consumption with iodinated paper. GC analysis were performed on 50-

100 μl of reaction mixture, diluted with 500 μl of CH_2Cl_2 containing dodecane as internal standard and supported Ph_3P as quencher. For the reactions in water, extraction with CH_2Cl_2 (1 ml x 3) was done before analysis.

Synthesis of the salts of $[\text{Al}_4(\text{H}_2\text{O})_{10}(\beta\text{-XW}_9\text{O}_{33}\text{H})_2]^{4-}$ (1 and 2):² To a 30 mL aqueous solution of AlCl_3 (0.29 g, 2.22 mmol) was added 1.0 mmol of $\text{Na}_9[\text{B-}\alpha\text{-XW}_9\text{O}_{33}] \cdot 19.5\text{H}_2\text{O}$ (X = As or Sb). The pH was then adjusted to 3 with 4 M HCl. The colorless solution was stirred at 70 °C for 1.5 h (a white precipitate may form in the presence of $[\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$). After cooling to room temperature the solution was filtered. Colorless crystals were obtained by evaporating the filtrate at room temperature for a few days in the presence of RbCl (1) or NH_4Cl (2), added as 0.5 mL of 1 M solutions.

$\text{Rb}_2\text{Na}_2[\text{Al}_4(\text{H}_2\text{O})_{10}(\beta\text{-AsW}_9\text{O}_{33}\text{H})_2] \cdot 20\text{H}_2\text{O}$ (NaRb-1): Yield 0.45 g (17%). Elemental analysis, calcd (%) for $\text{H}_{62}\text{Al}_4\text{As}_2\text{O}_{96}\text{Rb}_2\text{W}_{18}$, Al 2.00, As 2.78, Na 0.85, Rb 3.16, W 61.5. Found: Al 2.09, As 2.32, Na 0.86, Rb 3.09, W 62.0; FT-IR (KBr, cm^{-1}): 1624, 1402, 964, 826, 713, 470; **$(\text{NH}_4)_2\text{Na}_2[\text{Al}_4(\text{H}_2\text{O})_{10}(\beta\text{-SbW}_9\text{O}_{33}\text{H})_2] \cdot 20\text{H}_2\text{O}$ (NaNH₄-2):** Yield 0.58 g (22%). Elemental analysis, calcd (%) for $\text{H}_{70}\text{Al}_4\text{N}_2\text{Na}_2\text{O}_{96}\text{Sb}_2\text{W}_{18}$: H 1.32, N 0.52, Al 2.02, Na 0.86, Sb 4.52, W 62.0. Found: H 1.25, N 0.38, Al 1.98, Na 0.50, Sb 4.80, W 60.5. FT-IR (KBr, cm^{-1}): 1624, 1403, 960, 816, 704, 455. The salts **NaRb-1** and **NaNH₄-2** were not soluble enough to allow for ^{183}W NMR studies.

TBA-salts were prepared by initial bulk precipitation of the polyanion as K-salts from the reaction mixture with excess KCl (0.5 g), followed by washing of the precipitate with 3M KCl, redissolution of the white solids (ca 1 g) and precipitation with 1.67 g of solid TBACl (6 mmol). The product was collected, after stirring overnight, by centrifugation and washing with water. Yield: 50-60%.

TBA and water content were determined by elemental analysis and TGA (Fig. S13 and S14).

$(\text{Bu}_4\text{N})_4[\text{Al}_4(\text{H}_2\text{O})_{10}(\beta\text{-AsW}_9\text{O}_{33}\text{H})_2] \cdot 4\text{H}_2\text{O}$ (TBA-1): Elemental analysis for $\text{C}_{64}\text{H}_{174}\text{N}_4\text{O}_{80}\text{Al}_4\text{As}_2\text{W}_{18}$, calcd (%) C 13.13; H 3.00; N 0.96. Found: C 13.04; H 3.09; N 0.99; FT-IR (KBr, cm^{-1}): 3440 (s,br), 2961 (m), 2873 (m), 1631 (m), 1484 (m), 1380 (w), 1153 (w), 1063 (w), 984 (s), 884 (s), 844 (s), 732 (m), 621 (w), 462 (m). **$(\text{Bu}_4\text{N})_4[\text{Al}_4(\text{H}_2\text{O})_{10}(\beta\text{-SbW}_9\text{O}_{33}\text{H})_2] \cdot 4\text{H}_2\text{O}$ (TBA-2):** Elemental analysis for $\text{C}_{64}\text{H}_{174}\text{N}_4\text{O}_{80}\text{Al}_4\text{Sb}_2\text{W}_{18}$, calcd (%) C 12.93; H 2.95; N 0.94. Found: C 13.68; H 2.93; N 0.94. FT-IR (KBr, cm^{-1}): 3440 (s,br), 2962 (m), 2874 (m), 1635 (m), 1484 (m), 1382 (w), 960 (s), 883 (s), 825 (s), 707 (m), 457 (m).

TBA-3 was prepared by an analogous procedure, upon precipitation of 100 mg of $\text{RbNa}_3[\text{In}_4(\text{H}_2\text{O})_{10}(\beta\text{-AsW}_9\text{O}_{32}\text{OH})_2] \cdot 36\text{H}_2\text{O}^3$ dissolved in 0.5 ml of water, with 12 equivalents

of TBACl. Then 40 mg of $(\text{Bu}_4\text{N})_6[\text{In}_4(\text{H}_2\text{O})_{10}(\beta\text{-AsW}_9\text{O}_{33})_2] \cdot 4\text{H}_2\text{O}$ were isolated. Elemental analysis for $\text{C}_{96}\text{H}_{244}\text{As}_2\text{In}_4\text{N}_6\text{O}_{80}\text{W}_{18}$, calcd (%) C 17.24; H 3.68; N 1.26. Found: C 17.64; H 3.50; N 1.03.

Crystal structure determination:

Single crystals of **NaRb-1** and **NaNH₄-2** were each mounted on a Hampton cryo-loop for indexing and intensity data collection at 173 K on a Bruker D8 APEX II CCD using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Lorentz and polarization corrections were applied, and an absorption correction was performed using the SADABS program.

Direct methods were used for structure solution of all structures (SHELXS-97). Structural refinement was obtained from successive Fourier maps (SHELXL-97). All heavy atoms (W, As, Sb, Al, Rb) were refined anisotropically, whereas disordered cations and oxygen atoms were refined isotropically. Ammonium ions could not be determined by XRD, as they cannot be distinguished from crystal waters. The crystallographic data for **NaRb-1** and **NaNH₄-2** are summarized in Table S1.

Further details of the crystal structure investigation(s) may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: [crysdta\(at\)fiz-karlsruhe.de](mailto:crysdta(at)fiz-karlsruhe.de), http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the CSD numbers 425246 for **NaRb-1** and 425247 for **NaNH₄-2**.

Table S1. Crystal data for **NaRb-1** and **NaNH₄-2**.

Compound	NaRb-1	NaNH₄-2
Formula Unit	Rb ₂ Na ₂ [Al ₄ (H ₂ O) ₁₀ (β-AsW ₉ O ₃₃ H ₂) ₂]·20H ₂ O	(NH ₄) ₂ Na ₂ [Al ₄ (H ₂ O) ₁₀ (β-SbW ₉ O ₃₃ H ₂) ₂]·20H ₂ O
Formula weight, g/mol	5336.50	5341.28
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> , Å	12.5177(3)	12.5011(5)
<i>b</i> , Å	12.6671(4)	12.5288(5)
<i>c</i> , Å	15.7160(5)	15.9248(7)
<i>α</i> , °	86.132(2)	73.995(2)
<i>β</i> , °	82.6840(10)	88.077(2)
<i>γ</i> , °	83.438(2)	77.976(2)
Volume, Å ³	2451.95(12)	2344.16(17)
<i>Z</i>	1	1
<i>D</i> _{calc} , g/cm ³	3.645	3.784
Absorption coefficient	22.829	22.711
F(000)	2376	2360
Crystal size, mm	0.4 x 0.16 x 0.09	0.14 x 0.11 x 0.04
Theta range for data collection, °	2.43 – 27.56	2.64 – 27.57
Reflections collected	155955	126545
Independent reflections	11290	10749
R(int)	0.0748	0.0662
Observed (<i>I</i> > 2σ(<i>I</i>))	9469	10749
Goodness-of-fit on F ²	1.007	1.012
R ₁ [<i>I</i> > 2σ(<i>I</i>)] ^[a]	0.0464	0.0532
wR ₂ (all data) ^[b]	0.1267	0.1244

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

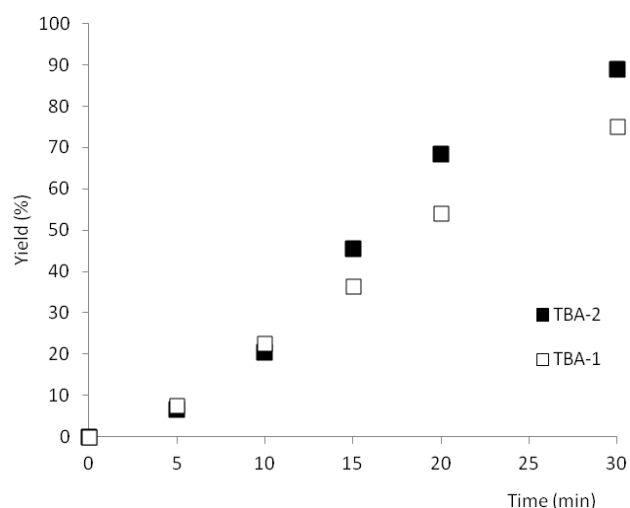


Fig. S1: Conversion of cyclohexanol to cyclohexanone in the presence of H_2O_2 and **TBA-1** or **TBA-2**, in CH_3CN . Calculations are based on the limiting reagent H_2O_2 .

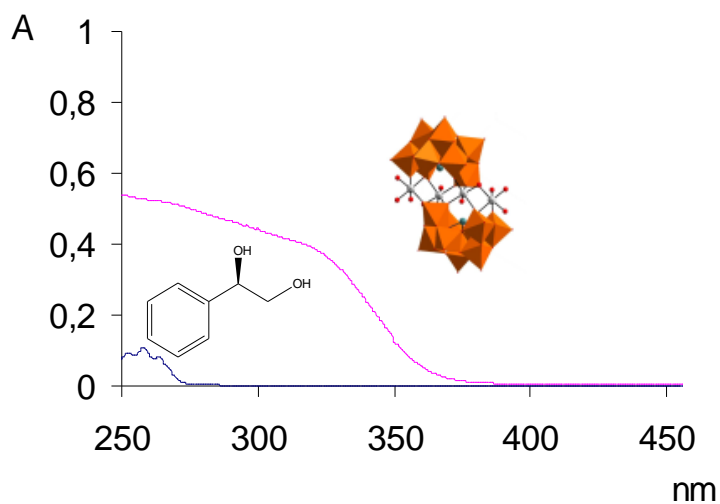


Fig. S2. UV-Vis spectra of 1-Phenyl-1,2-ethandiol (dark blue) and of **TBA-2** (purple), in CH_3CN .

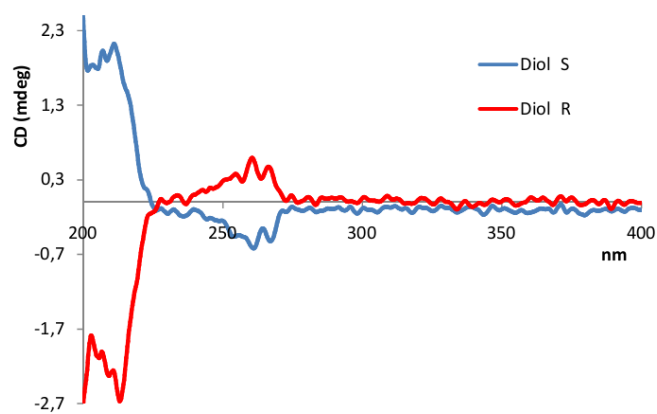


Fig. S3. CD spectra of R and S 1-Phenyl-1,2-ethandiol, in CH_3CN .

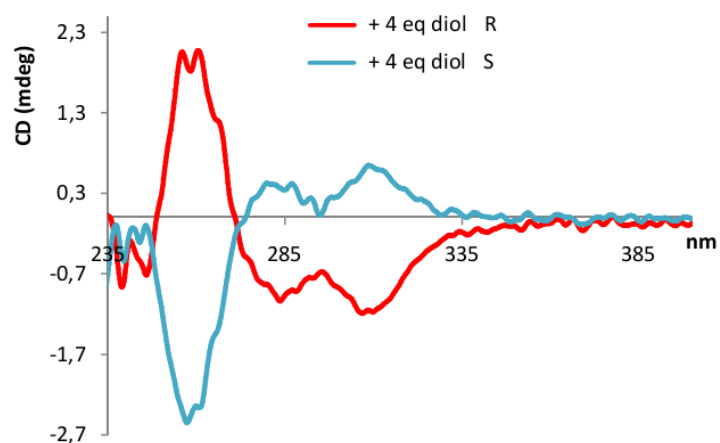


Fig. S4. CD spectra of 0.25 mM **TBA-1** in the presence of 4 eqs of 1-phenyl-1,2-ethandiol, in CH₃CN. Path length 1 mm.

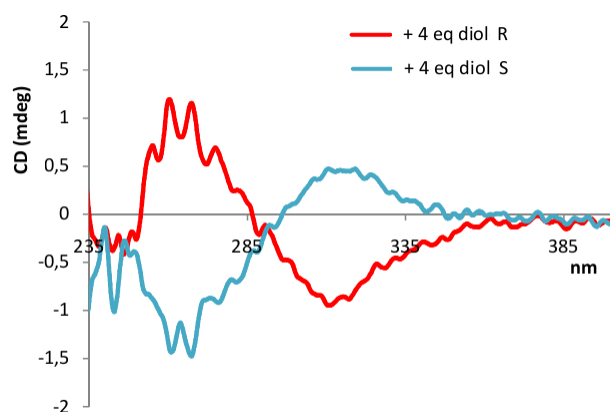


Fig. S5. CD spectra of 0.25 mM **TBA-2** in the presence of 4 eqs of 1-phenyl-1,2-ethandiol, in CH₃CN. Path length 1 mm.

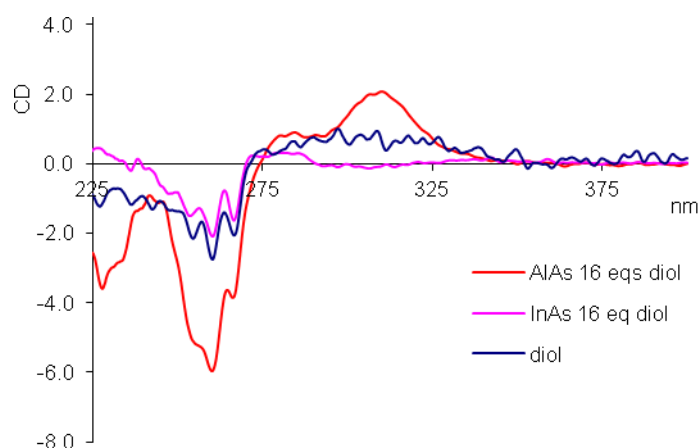


Fig. S6. CD spectra of S 1-Phenyl-1,2-ethandiol alone (blue) and in the presence of **TBA-2** (red line) or **TBA-3** (magenta line).

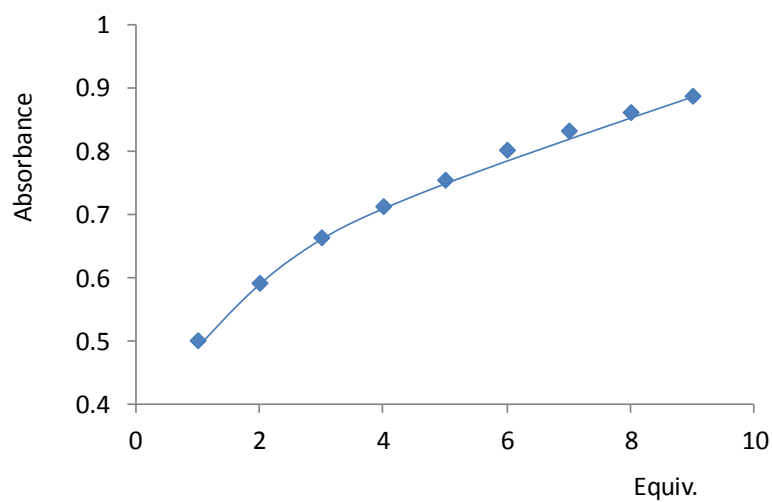
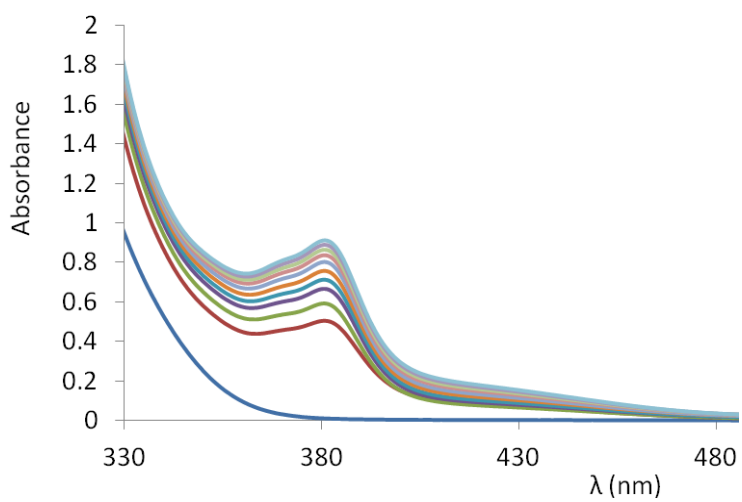


Fig. S7. Plots of the UV-vis absorbance recorded during the titration of 0,25mM **TBA-1**, in CH₃CN, with DTBC ($\lambda = 385$ nm).

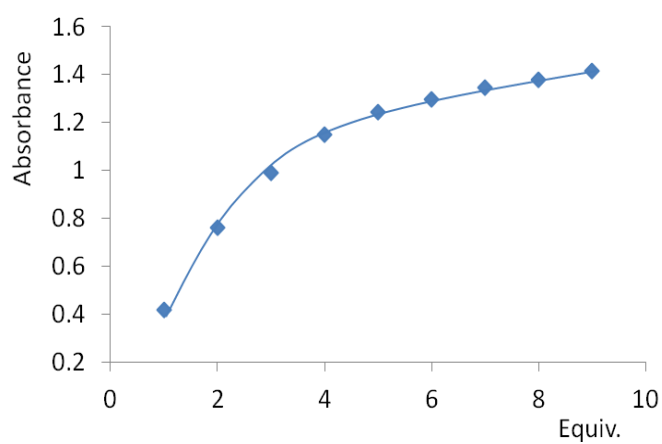
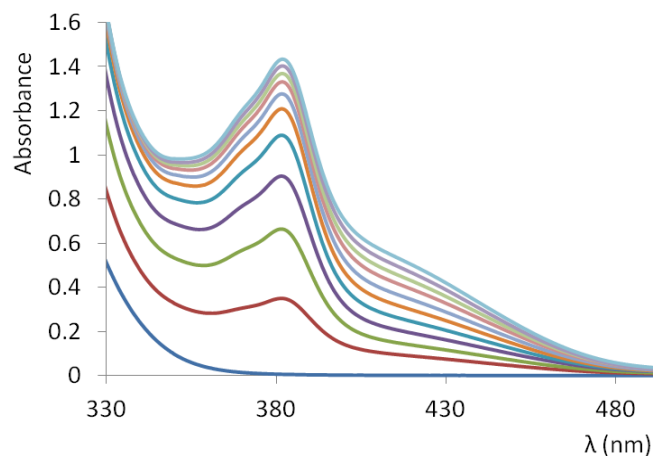


Fig. S8. Plots of the UV-vis absorbance recorded during the titration of 0,25mM **TBA-2**, in CH_3CN , with DTBC ($\lambda = 385 \text{ nm}$).

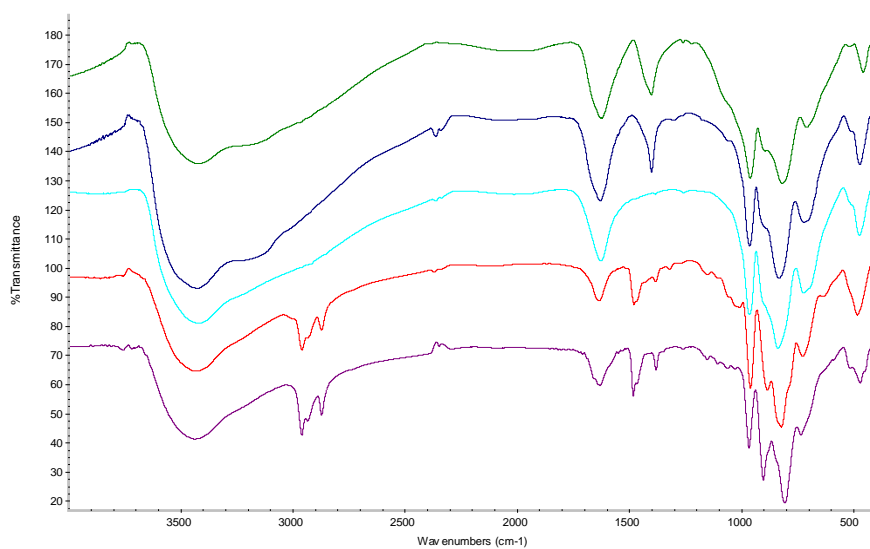


Fig. S9. FT-IR spectra of different salts of polyanions **1** and **2**. From top to bottom: crystals of $\text{NaNH}_4\text{-2}$ (dark green) and NaRb-1 (blue), amorphous **K-1** salt (light blue), **TBA-1** salt (red) before and (violet) after catalysis.

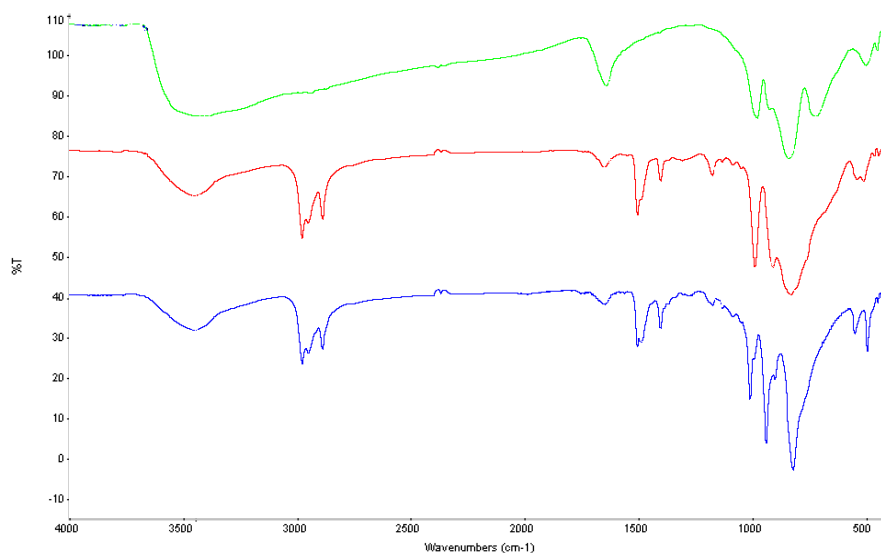


Fig. S10. FT-IR spectra of polyanion **3**. From top to bottom: **Na-3** (light green), **TBA-3** (red), **TBA-3** after catalysis (blue).

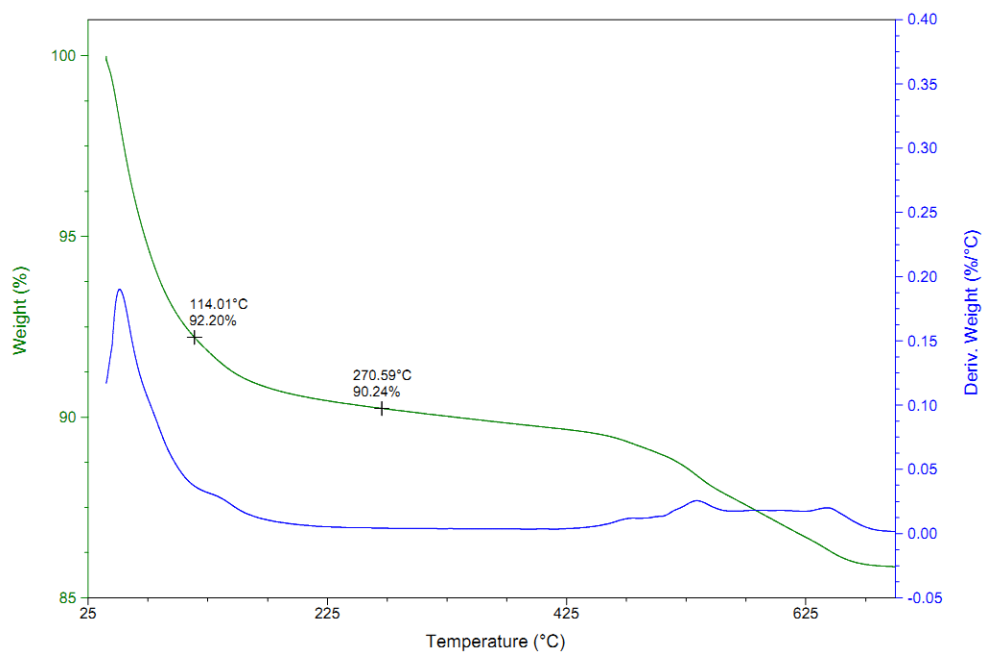


Fig. S11. Thermogram of **NaRb-1**.

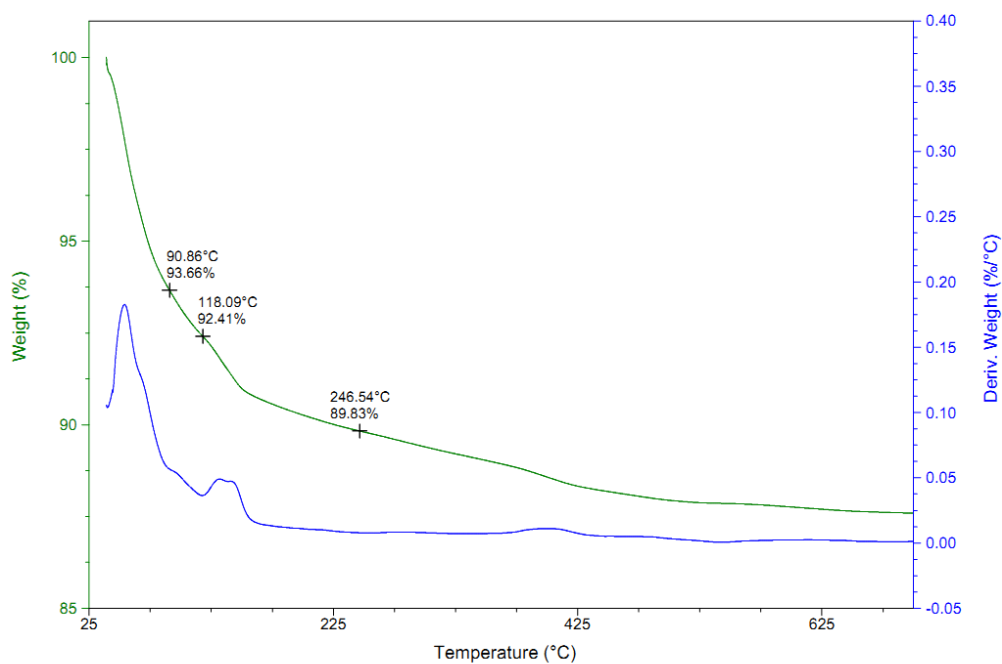


Fig. S12. Thermogram of $\text{NaNH}_4\text{-2}$.

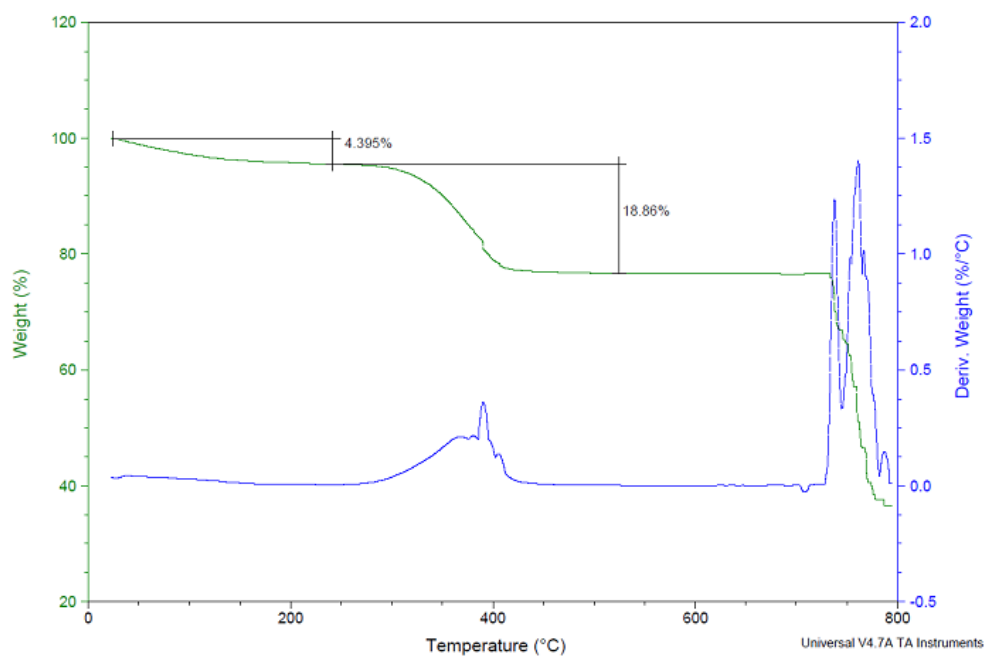


Fig. S13: Thermogram of TBA-1 .

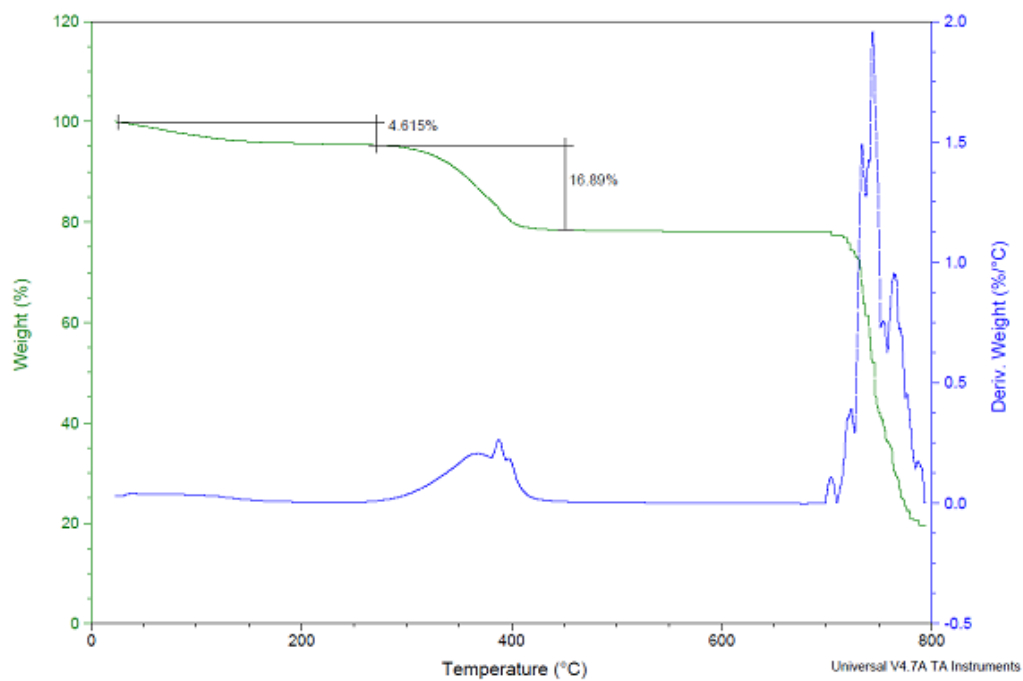


Fig. S14. Thermogram of **TBA-2**.

¹ M. Bösing, I. Loose, H. Pohlmann, B. Krebs *Chem. Eur. J.* **1997**, 1232-1237.

² M. Carraro synthesized polyanions **1** and **2** during a ESF COST D40 short term scientific mission at Jacobs University.

³ F. Hussain, M. Reicke, V. Janowski, S. de Silva, J. Futuwi, U. Kortz *C. R. Chimie* 2005, **8**, 1045-1056.