Supporting Information

Solution dynamics of hybrid Anderson-Evans polyoxometalates

David E. Salazar Marcano, Sarah Lentink, Mhamad A. Moussawi, and Tatjana N. Parac-Vogt*

Department of Chemistry, KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium

*E-mail: tatjana.vogt@kuleuven.be; Tel: +32 (0)16 327612

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Characterization Techniques

Electrospray Ionization Mass Spectrometry (ESI-MS)

ESI-MS spectra in the range m/z 50-2000 of the samples in acetonitrile (ACN) were obtained in negative ion mode on a Thermo Finnigan LCQ Advantage Mass Spectrometer with a quadrupole ion trap mass analyzer and were then processed with the Xcalibur Software.

Fourier Transform Infrared (FT-IR) Spectroscopy

FT-IR spectra of the solid samples were acquired with a Bruker Vertex 70 spectrometer by attenuated total reflection.

Nuclear Magnetic Resonance (NMR) Spectroscopy

^1H NMR spectra were acquired on Bruker Avance 300 (300 MHz), 400 (400 MHz) and 600 (600 MHz) spectrometers for 5 mg/mL solutions (unless stated otherwise in the text) in deuterated dimethyl sulfoxide (DMSO-d_6), acetonitrile (ACN-d_3), MeOD-d_4 , D_2O or buffered solutions made with D_2O . The buffers used for stability studies were: 100 mM acetate buffer at pD 4.4, phosphate buffer (10 mM Na_2HPO_4 , 1.8 mM KH_2PO_4) at pD 7.4, phosphate buffered saline 1X (PBS(1X), 1X = 10 mM Na_2HPO_4 , 1.8 mM KH_2PO_4 , 137 mM NaCl and 2.7 mM KCl) at pD 7.4, and 100 mM carbonate buffer at pD 10. For measurements at 25 °C, 37 °C and 50 °C, samples in deuterated PBS(1X) were left inside a Bruker Avance 600 (600 MHz) spectrometer for around 6 hours with the probe kept at the desired temperature and spectra were acquired at least every hour. For measurements in deuterated organic solvents tetramethylsilane (TMS) was used as an internal reference while for samples in D_2O the sodium salt of 3-(trimethylsilyl)propionic-2,2,3,3- d_4 acid (TMSP- d_4) was used as a reference ($\delta = 0$ ppm).

UV-Vis Spectroscopy

UV-Vis spectra between 600 nm and 200 nm were acquired with an Agilent Cary 6000i UV-VIS-NIR spectrometer at room temperature and with a scan rate of 600 nm/min for 0.02 mg/mL solutions of AE-R HPOMs in ACN, MeOH, Milli-Q ultrapure water or in PBS(1X). UV-Vis measurements in DMSO, acetate buffer and carbonate buffer were not performed as these absorb in the region of interest.

Synthesis of TBA-HPOMs

All reagents and solvents were used as obtained from commercial sources without further purification. Tetrabutylammonium α -octamolybdate ($\text{TBA}_4[\alpha\text{-Mo}_8\text{O}_{26}]$) was synthesized as a precursor for the synthesis of AE-R HPOMs following the procedure reported by Ikegami et al.¹

Synthesis of $((\text{C}_4\text{H}_9)_4\text{N})_3[\text{MnMo}_6\text{O}_{18}((\text{OCH}_2)_3\text{CNH}_2)_2]$ - TBA-AE-NH₂

TBA-AE-NH₂ was synthesized from α -octamolybdate based on a procedure reported by Marcoux et al.² 4 g of $\text{TBA}_4[\alpha\text{-Mo}_8\text{O}_{26}]$ (1.86 mmol, 1 eq), 0.75 g of $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ (2.79 mmol, 1.5 eq) and 0.79 g of tris(hydroxymethyl)aminomethane (9.8 mmol, 3.5 eq) were added to 75 mL of dry ACN under argon atmosphere. The mixture was stirred and refluxed at 80 °C for 56 hours. Once the orange solution was allowed to cool to room temperature, the solution was centrifuged to remove any residual black solid. The solid product was crystallized from the supernatant by slow vapor diffusion of diethyl ether over two days. The crystals were removed by filtration, washed with diethyl ether and then dried under vacuum at 30 °C overnight. ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) = 60.76 (br, 12H, CH₂O), 3.76 (br, 4H, NH₂), 3.16 (m, 24H, H_{TBA}), 1.57 (m, 24H, H_{TBA}), 1.31 (m, 24H, H_{TBA}), 0.94 (t, ³J = 7.3 Hz, 36H, H_{TBA}). IR: $\tilde{\nu}$ (cm⁻¹) = 3273 (ν NH, w), 2969 (ν CH, m), 2935 (ν CH, m), 2873 (ν CH, m), 1642 (δ NH, w), 1479 (δ CH, s), 1381 (δ CH, s), 1347 (ν CO, w), 1152 (ν CN, w), 1128 (ν CN, w), 1108 (ν CO, w), 1038 (ν CO, s), 937 (ν Mo=O, s), 918 (ν Mo=O, s), 900 (ν Mo=O, s), 826 (w), 793 (w), 755 (w), 651 (ν_{as} Mo-O-Mo, vs), 559 (ν_{s} Mo-O-Mo, s), 525 (w), 460 (m), 408 (m). ESI-MS (negative mode, ACN, M = 1882.2 gmol⁻¹): m/z = 1398.7 ([M-2TBA+H]⁻), 1640.6 ([M-TBA]⁻).

Synthesis of $((\text{C}_4\text{H}_9)_4\text{N})_3[\text{MnMo}_6\text{O}_{18}((\text{OCH}_2)_3\text{CCH}_3)_2]$ - TBA-AE-CH₃

TBA-AE-CH₃ was synthesized following a similar procedure to that used for **TBA-AE-NH₂** with tris(hydroxymethyl)ethane instead of tris(hydroxymethyl)aminomethane. ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) = 59.94 (br, 12H, CH₂O), 8.87 (s, 6H, CH₃), 3.16 (m, 24H, H_{TBA}), 1.57 (m, 24H, H_{TBA}), 1.31 (m, 24H, H_{TBA}), 0.94 (t, ³J = 7.3 Hz, 36H, H_{TBA}). IR: $\tilde{\nu}$ (cm⁻¹) = 2957 (ν CH, m), 2931 (ν CH, m), 2874 (ν CH, m), 1478 (δ CH, s), 1381 (δ CH, w), 1153 (ν CN, w), 1121 (ν CN, m), 1021 (ν CO, s), 937 (ν Mo=O, s), 918 (ν Mo=O, s), 899 (ν Mo=O, s), 816 (w), 793 (w), 740 (w), 650 (ν_{as} Mo-O-Mo, vs), 559 (ν_{s} Mo-O-Mo, s), 513 (w), 462 (s), 411 (s). ESI-MS (negative mode, ACN, M = 1880.2 gmol⁻¹): m/z = 1636.1 ([M-TBA]⁻).

Synthesis of $((\text{C}_4\text{H}_9)_4\text{N})_3[\text{MnMo}_6\text{O}_{18}((\text{OCH}_2)_3\text{CNHCOCH}_2\text{Cl})_2]$ - TBA-AE-Cl

TBA-AE-Cl was synthesized from previously synthesized α -octamolybdate based on a similar procedure to the one used for **TBA-AE-NH₂** with tris(hydroxymethyl)chloroacetamidomethane instead of tris(hydroxymethyl)aminomethane. The tris(hydroxymethyl)chloroacetamidomethane ligand was synthesized from tris(hydroxymethyl)aminomethane and ethyl chloroacetate based on the procedure reported by Vanhaecht et al.³ ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) = 64.33 (br, 12H, CH₂O), 8.08 (br, 2H, NH), 4.25 (s, 4H, CH₂Cl), 3.17 (m, 24H, H_{TBA}), 1.57 (m, 24H, H_{TBA}), 1.32 (m, 24H, H_{TBA}), 0.94 (t, ³J = 7.3 Hz, 36H, H_{TBA}). IR: $\tilde{\nu}$ (cm⁻¹) = 3300 (ν NH, w), 3076 (ν NH, w), 2960 (ν CH, m), 2934 (ν CH, m), 2873 (ν CH, m), 1694 (ν C=O, s), 1558 (δ NH, m), 1467 (δ CH, s), 1410 (δ CH, w), 1380 (δ CH, s), 1336 (ν CO, w), 1229 (ν CN, m), 1153 (ν CN, w), 1108 (ν CO, m), 1031 (ν CO, s), 939 (ν Mo=O, s), 915 (ν Mo=O, s), 899 (ν Mo=O, s), 824 (w), 789 (w), 738 (w), 655 (ν_{as} Mo-O-Mo, vs), 561 (ν_s Mo-O-Mo, s), 461 (m), 413 (m). ESI-MS (negative mode, ACN, M = 2035.1 g mol⁻¹): m/z = 1793.6 ([M-TBA]⁻).

Synthesis of $((\text{C}_4\text{H}_9)_4\text{N})_3[\text{MnMo}_6\text{O}_{18}((\text{OCH}_2)_3\text{CN}=\text{CH}(\text{2-C}_5\text{H}_4\text{N}))_2]$ - TBA-AE-Pyr

TBA-AE-Pyr was synthesized from the previously synthesized **TBA-AE-NH₂** based on a procedure previously reported by Marcoux et al.² ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) = 61.68 (br, 12H, CH₂O), 8.77 (d, ³J = 4.3 Hz, 2H, 6-H_{pyr}), 8.39 (s, 2H, N=CH), 8.01 (m, 2H, 3-H_{pyr}), 7.83 (m, 2H, 4-H_{pyr}), 7.30 (m, 2H, 5-H_{pyr}), 3.17 (m, 24H, H_{TBA}), 1.58 (m, 24H, H_{TBA}), 1.32 (m, 24H, H_{TBA}), 0.94 (t, ³J = 7.3 Hz, 36H, H_{TBA}). IR: $\tilde{\nu}$ (cm⁻¹) = 2959 (ν CH, m), 2933 (ν CH, m), 2873 (ν CH, m), 1643 (ν C=N, m), 1583 (ν Ar, w), 1566 (ν Ar, w), 1481 (δ CH, s), 1467 (δ CH, s), 1380 (δ CH, m), 1344 (δ CH, m), 1227 (ν CN, w), 1152 (ν CN, w), 1087 (ν CO, w), 1022 (ν CO, s), 991 (ν CO, m), 939 (ν Mo=O, s), 918 (ν Mo=O, s), 902 (ν Mo=O, s), 803 (w), 781 (m), 743 (w), 651 (ν_{as} Mo-O-Mo, vs), 591 (s), 561 (ν_s Mo-O-Mo, s), 461 (s), 408 (s). ESI-MS (negative mode, ACN, M = 2060.4 g mol⁻¹): m/z = 1575.7 ([M-2TBA+H]⁻), 1818.5 ([M-TBA]⁻).

Synthesis of $((C_4H_9)_4N)_3[MnMo_6O_{18}((OCH_2)_3CNHCOC_9H_{15}N_2OS)_2]$ - TBA-AE-Biot

TBA-AE-Biot was synthesized by post-functionalization of the previously synthesized **TBA-AE-NH₂**. 2.5 g of **TBA-AE-NH₂** (1.3 mmol, 1 eq) was dissolved in 60 mL of dry ACN under argon atmosphere. 1.48 g of N-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (5.86 mmol, 4.5 eq) and 1.30 g of biotin (5.2 mmol, 4 eq) were then added, and the reactant mixture was stirred while heated at 50 °C for 3 days under argon atmosphere. After 3 days, a light orange precipitate was observed in an orange solution. The solution was filtered through a glass frit and reduced to a minimum volume, before being added dropwise into an excess of diethyl ether. The mixture was then filtered through a glass frit, to obtain an orange precipitate. The precipitate was re-dissolved in a minimum volume of ACN and the residual off-white precipitate was removed. The yellow solution was added to an excess of diethyl ether, and an orange precipitate was obtained. The orange precipitate obtained was washed with cold dichloromethane and then dried under vacuum at 50 °C overnight. ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) = 64.03 (br, 12H, CH₂O), 7.34 (br, 2H, CNHCO), 6.40 (s, 2H, CNHCO), 6.29 (s, 2H, CNHCO), 4.29 (m, 2H, CHN), 4.14 (m, 2H, CHN), 3.16 (m, 26H, 24H_{TBA} & 2H CHS), 2.85 (dd, ²J = 4.9 Hz, ³J = 12.6 Hz, 2H, SCH₂), 2.55 (d, ³J = 12.6 Hz, 2H, SCH₂), 2.39 (m, 4H, COCH₂), 1.57 (m, 26H, 24H_{TBA} & 2H CH₂), 1.48 (m, 6H, CH₂), 1.31 (m, 28H, 24H_{TBA} & 4H CH₂), 0.93 (t, ³J = 7.3 Hz, 36H, H_{TBA}). IR: $\tilde{\nu}$ (cm⁻¹) = 3287 (ν NH, m), 3073 (ν NH, w), 2959 (ν CH, m), 2933 (ν CH, m), 2873 (ν CH, m), 1674 (ν C=O, s), 1553 (δ NH, m), 1481 (δ CH, m), 1456 (δ NH, m), 1381 (δ CH, w), 1332 (ν CO, w), 1262 (ν CO, w), 1153 (ν CN, w), 1128 (ν CO, w), 1113 (ν CO, w), 1059 (ν CO, m), 1022 (ν CO, s), 939 (ν Mo=O, s), 918 (ν Mo=O, s), 900 (ν Mo=O, s), 812 (w), 736 (w), 654 (ν_{as} Mo-O-Mo, vs), 563 (ν_s Mo-O-Mo, s), 461 (s), 410 (s). ESI-MS (negative mode, ACN, M = 2334.8 g mol⁻¹): m/z = 926.0 ([M-2TBA]²⁻).

Cation metathesis

Li- & Na-HPOMs

The TBA-HPOM and 30 eq of the anhydrous metal perchlorate were dissolved separately in a minimum amount of ACN. The perchlorate solution was added to the HPOM solution and instant formation of a pale orange precipitate was observed while the solution became clear and colorless. The precipitate was separated from the supernatant by centrifugation (5000-14000 rpm for at least 5 min) and was then washed several times by mixing and sonication for a few minutes with slightly more ACN than was used for the precipitation. The washed precipitate was then separated from the colorless supernatant by centrifugation. The number of washes necessary to completely remove any traces of the TBA perchlorate or of excess metal perchlorate was determined by following the disappearance of the TBA and perchlorate peaks by ESI-MS (positive mode: $m/z = 242.3$ ($[TBA]^+$), $1124.4 + 121.9(n - 6)$ ($[Na(NaClO_4)_n]^+$ for $n = 6-16$); negative mode: $m/z = 524.9 + 106.4n$ ($[ClO_4(LiClO_4)_n]^-$ for $n = 1-14$) or $588.7 + 121.9(n-4)$ ($[ClO_4(NaClO_4)_n]^-$ for $n = 4-14$). Finally, the precipitate was dried at 50 °C under vacuum overnight and complete conversion to the metal salt was then confirmed by IR and NMR spectroscopy. The bands in the IR spectra due to C-H stretching and bending vibrations of TBA at 2800 – 3000 cm^{-1} and 1480 cm^{-1} decreased in intensity after the cation metathesis, while the fingerprint of the POM core with peaks due to vibrations of Mo=O and Mo-O-Mo bonds remained intact (**Figure S1-S5**). The typical ^1H NMR resonances of TBA were also absent in the spectra after the cation metathesis (**Figure S9-S13**): δ (ppm) = 3.16 (m, 24H), 1.57 (m, 24H), 1.31 (m, 24H), 0.94 (t, $^3J = 7.3$ Hz, 36H).

Li₃[MnMo₆O₁₈((OCH₂)₃CNH₂)₂] - Li-AE-NH₂

Yield: 85%. ^1H NMR (400 MHz, DMSO- d_6): δ (ppm) = 60.94 (br, 12H, CH₂O), 3.62 (br, 4H, NH₂). IR: $\tilde{\nu}$ (cm^{-1}) = 3412 (ν NH, w), 3311 (ν NH, w), 3261 (ν NH, w), 2934 (ν CH, w), 2909 (ν CH, w), 2863 (ν CH, w), 1622 (δ NH, m), 1594 (δ NH, m), 1449 (δ CH, m), 1442 (δ CH, m), 1380 (δ CH, w), 1313 (ν CO, w), 1245 (ν CN, w), 1106 (ν CO, m), 1086 (ν CO, w), 1018 (ν CO, s), 939 (ν Mo=O, s), 916 (ν Mo=O, s), 909 (ν Mo=O, s), 870 (s), 818 (w), 617 (ν_{as} Mo-O-Mo, s), 558 (ν_s Mo-O-Mo, m), 527 (m), 462 (s), 416 (s).

Na₃[MnMo₆O₁₈((OCH₂)₃CNH₂)₂] - Na-AE-NH₂

Yield: 96%. ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) = 60.80 (br, 12H, CH₂O), 3.60 (br, 4H, NH₂). IR: $\tilde{\nu}$ (cm⁻¹) = 3487 (ν NH, m), 3442 (ν NH, m), 3320 (ν NH, m), 3267 (ν NH, m), 2924 (ν CH, w), 2908 (ν CH, w), 2862 (ν CH, w), 1643 (δ NH, m), 1600 (δ NH, m), 1464 (δ CH, m), 1447 (δ CH, m), 1370 (δ CH, w), 1318 (ν CO, w), 1260 (ν CN, w), 1241 (ν CN, w), 1106 (ν CO, m), 1017 (ν CO, s), 982 (m), 965 (ν Mo=O, s), 941 (ν Mo=O, s), 930 (ν Mo=O, s), 920 (ν Mo=O, s), 900 (ν Mo=O, s), 634 (ν_{as} Mo-O-Mo, s), 559 (ν_s Mo-O-Mo, m), 520 (m), 462 (s), 416 (s).

Li₃[MnMo₆O₁₈((OCH₂)₃CCH₃)₂] - Li-AE-CH₃

Yield: 91%. ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) = 60.08 (br, 12H, CH₂O), 8.90 (s, 6H, CH₃). IR: $\tilde{\nu}$ (cm⁻¹) = 3435 (m), 2938 (ν CH, w), 2871 (ν CH, w), 1653 (w), 1623 (w), 1462 (δ CH, w), 1409 (δ CH, w), 1209 (w), 1109 (m), 992 (ν CO, s), 928 (ν Mo=O, s), 913 (ν Mo=O, s), 895 (ν Mo=O, s), 624 (ν_{as} Mo-O-Mo, s), 564 (ν_s Mo-O-Mo, s), 525 (w), 466 (s), 418 (s).

Na₃[MnMo₆O₁₈((OCH₂)₃CCH₃)₂] - Na-AE-CH₃

Yield: 92%. ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) = 60.05 (br, 12H, CH₂O), 8.89 (s, 6H, CH₃). IR: $\tilde{\nu}$ (cm⁻¹) = 3436 (m), 2927 (ν CH, w), 2866 (ν CH, w), 1645 (w), 1615 (w), 1461 (δ CH, w), 1409 (δ CH, w), 1366 (δ CH, w), 1209 (w), 1109 (m), 998 (ν CO, s), 959 (ν Mo=O, s), 943 (ν Mo=O, s), 931 (ν Mo=O, s), 916 (ν Mo=O, s), 897 (ν Mo=O, s), 651 (ν_{as} Mo-O-Mo, vs), 567 (ν_s Mo-O-Mo, s), 525 (w), 466 (s), 418 (s).

Li₃[MnMo₆O₁₈((OCH₂)₃CNHCOCH₂Cl)₂] - Li-AE-Cl

Yield: 60%. ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) = 64.49 (br, 12H, CH₂O), 8.09 (br, 2H, NH), 4.25 (s, 4H, CH₂Cl). IR: $\tilde{\nu}$ (cm⁻¹) = 3324 (ν NH, m), 3096 (ν NH, m), 2947 (ν CH, w), 2880 (ν CH, w), 1703 (ν C=O, m), 1634 (w), 1565 (δ NH, m), 1451 (δ CH, w), 1404 (δ CH, w), 1350 (δ CH, w), 1306 (ν CO, w), 1242 (ν CN, m), 1182 (ν CN, w), 1113 (ν CO, m), 1035 (ν CO, s), 1020 (ν CO, s), 959 (ν Mo=O, s), 932 (ν Mo=O, s), 905 (ν Mo=O, s), 830 (w), 789 (w), 792 (w), 648 (ν_{as} Mo-O-Mo, s), 566 (ν_s Mo-O-Mo, m), 513 (w), 456 (m), 411 (m).

Na₃[MnMo₆O₁₈((OCH₂)₃CNHCOCH₂Cl)₂] - Na-AE-Cl

Yield: 87%. ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) = 64.46 (br, 12H, CH₂O), 8.09 (br, 2H, NH), 4.25 (s, 4H, CH₂Cl). IR: $\tilde{\nu}$ (cm⁻¹) = 3386 (ν NH, w), 3007 (ν CH, w), 1695 (ν C=O, m), 1645 (w), 1520 (δ NH, m), 1468 (δ CH, w), 1454 (δ CH, w), 1401 (δ CH, w), 1337 (ν CO, w), 1307 (ν CO, w), 1226 (ν CN, m), 1105 (ν CO, m), 1036 (ν CO, s), 1013 (ν CO, s), 940 (ν Mo=O, s), 914 (ν Mo=O, s), 900 (ν Mo=O, s), 827 (w), 792 (w), 738 (w), 644 (ν_{as} Mo-O-Mo, s), 564 (ν_s Mo-O-Mo, m), 525 (m), 457 (s), 410 (m).

Li₃[MnMo₆O₁₈((OCH₂)₃CN=CH(2-C₅H₄N))₂] – Li-AE-Pyr

Yield: 88%. ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) = 63.08 (br, 12H, CH₂O), 8.76 (m, 2H, 6-H_{pyr}), 8.41 (s, 2H, N=CH), 8.00 (m, 2H, 3-H_{pyr}), 7.83 (m, 2H, 4-H_{pyr}), 7.29 (m, 2H, 5-H_{pyr}). IR: $\tilde{\nu}$ (cm⁻¹) = 3412 (m), 1652 (v C=N, m), 1622 (m), 1594 (v Ar, w), 1445 (δ CH, w), 1380 (δ CH, w), 1086 (v CO, w), 1018 (v CO, s), 950 (v Mo=O, s), 927 (v Mo=O, s), 915 (v Mo=O, s), 800 (w), 783 (m), 743 (w), 647 (v_{as} Mo-O-Mo, s), 597 (m), 564 (v_s Mo-O-Mo, m), 506 (m), 463 (s), 409 (s).

Na₃[MnMo₆O₁₈((OCH₂)₃CN=CH(2-C₅H₄N))₂] – Na-AE-Pyr

Yield: 65%. ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) = 61.66 (br, 12H, CH₂O), 8.76 (d, ³J = 4.2 Hz, 2H, 6-H_{pyr}), 8.38 (s, 2H, N=CH), 8.00 (m, 2H, 3-H_{pyr}), 7.83 (m, 2H, 4-H_{pyr}), 7.29 (m, 2H, 5-H_{pyr}). IR: $\tilde{\nu}$ (cm⁻¹) = 3402 (m), 2935 (v CH, w), 2911 (v CH, w), 2864 (v CH, w), 1711 (w), 1651 (v C=N, m), 1588 (v Ar, m), 1569 (v Ar, m), 1477 (δ CH, w), 1461 (δ CH, w), 1438 (δ CH, w), 1392 (δ CH, w), 1354 (δ CH, w), 1306 (v CO, w), 1257 (v CO, w), 1222 (v CN, w), 1176 (v CN, w), 1148 (v CN, w), 1083 (v CO, m), 1013 (v CO, s), 940 (v Mo=O, s), 908 (v Mo=O, s), 799 (w), 783 (m), 642 (v_{as} Mo-O-Mo, s), 597 (s), 565 (v_s Mo-O-Mo, m), 509 (m), 461 (s), 408 (s).

Li₃[MnMo₆O₁₈((OCH₂)₃CNHCOC₉H₁₅N₂OS)₂] – Li-AE-Biot

Yield: 85%. ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) = 64.12 (br, 12H, CH₂O), 7.34 (br, 2H, CNHCO), 6.41 (s, 2H, CNHCO), 6.30 (s, 2H, CNHCO), 4.29 (m, 2H, CHN), 4.14 (m, 2H, CHN), 3.13 (m, 2H, CHS), 2.85 (dd, ²J = 4.9 Hz, ³J = 12.4 Hz, 2H, SCH₂), 2.56 (d, ³J = 12.5 Hz, 2H, SCH₂), 2.39 (m, 4H, COCH₂), 1.64 (m, 2H, CH₂), 1.49 (m, 6H, CH₂), 1.32 (m, 4H, CH₂). IR: $\tilde{\nu}$ (cm⁻¹) = 3347 (v NH, m), 3081 (v NH, w), 2923 (v CH, w), 2873 (v CH, w), 1659 (v C=O, m), 1596 (δ NH, m), 1462 (δ CH, w), 1408 (δ CH, w), 1354 (v CO, w), 1206 (v CN, w), 1106 (v CO, m), 990 (v CO, s), 941 (v Mo=O, s), 917 (v Mo=O, s), 902 (v Mo=O, s), 811 (w), 628 (v_{as} Mo-O-Mo, s), 562 (v_s Mo-O-Mo, s), 528 (w), 463 (s), 414 (s).

Na₃[MnMo₆O₁₈((OCH₂)₃CNHCOC₉H₁₅N₂OS)₂] – Na-AE-Biot

Yield: 98%. ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) = 64.11 (br, 12H, CH₂O), 7.36 (br, 2H, CNHCO), 6.41 (s, 2H, CNHCO), 6.30 (s, 2H, CNHCO), 4.29 (m, 2H, CHN), 4.14 (m, 2H, CHN), 3.12 (m, 2H, CHS), 2.85 (dd, ²J = 4.8 Hz, ³J = 12.5 Hz, 2H, SCH₂), 2.56 (d, ³J = 12.3 Hz, 2H, SCH₂), 2.39 (m, 4H, COCH₂), 1.64 (m, 2H, CH₂), 1.49 (m, 6H, CH₂), 1.32 (m, 4H, CH₂). IR: $\tilde{\nu}$ (cm⁻¹) = 3347 (v NH, w), 3081 (v NH, w), 2923 (v CH, w), 2873 (v CH, w), 1682 (v C=O, s), 1550 (δ NH, m), 1469 (δ CH, m), 1371 (δ CH, w), 1312 (v CO, w), 1267 (v CO, w), 1184 (v CN, w), 1162 (v CN, w), 1096 (v CO, w), 1043 (v CO, m), 1016 (v CO, s), 942 (v Mo=O, s), 917 (v Mo=O, s), 902 (v Mo=O, s), 811 (w), 645 (v_{as} Mo-O-Mo, vs), 565 (v_s Mo-O-Mo, s), 523 (w), 459 (s), 413 (s).

K-HPOMs

Potassium perchlorate is significantly less soluble in ACN than lithium or sodium perchlorate, but it is highly soluble in DMSO. So, for the exchange of the counterion a solution of potassium perchlorate in DMSO was used instead. However, since the K-HPOMs are also soluble in DMSO, but to a lesser extent than KClO₄, the volumes of solvents used to dissolve the potassium perchlorate (15 eq) and the TBA-HPOMs were chosen so that, when combined, the final solution consisted of 25% v/v DMSO and the final concentration of potassium perchlorate was 52.5 mg/mL or less. As with the Li- and Na-salts, a pale orange precipitate was observed upon combining the HPOM solution with the potassium perchlorate solution. The precipitate formed upon mixing these solutions was then separated and washed once with 25% v/v DMSO in ACN, to ensure all excess metal perchlorate was removed, and at least twice with ACN to remove residual TBA and perchlorate as well as wash away the DMSO. Finally, the precipitate was dried at 50 °C under vacuum overnight. Complete conversion to the metal salt and removal of all TBA was then confirmed by IR and NMR spectroscopy, like for the Li- and Na- HPOMs.

K₃[MnMo₆O₁₈((OCH₂)₃CNH₂)₂] – K-AE-NH₂

Yield: 84%. ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) = 59.70 (br, 12H, CH₂O), 3.60 (br, 4H, NH₂). IR: $\tilde{\nu}$ (cm⁻¹) = 3519 (ν NH, m), 3391 (ν NH, m), 3328 (ν NH, m), 3267 (ν NH, m), 2931 (ν CH, w), 2908 (ν CH, w), 2863 (ν CH, w), 1638 (δ NH, m), 1598 (δ NH, m), 1459 (δ CH, m), 1442 (δ CH, m), 1352 (δ CH, w), 1309 (ν CO, w), 1256 (ν CN, w), 1106 (ν CO, w), 1081 (ν CO, m), 1023 (ν CO, s), 934 (ν Mo=O, m), 906 (ν Mo=O, s), 623 (ν_{as} Mo-O-Mo, s), 562 (ν_s Mo-O-Mo, m), 520 (m), 464 (s), 413 (s).

K₃[MnMo₆O₁₈((OCH₂)₃CCH₃)₂] – K-AE-CH₃

Yield: 65 %. ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) = 58.80 (br, 12H, CH₂O), 8.72 (s, 6H, CH₃). IR: $\tilde{\nu}$ (cm⁻¹) = 3385 (m), 2905 (ν CH, w), 2854 (ν CH, w), 1634 (w), 1537 (w), 1459 (δ CH, w), 1365 (δ CH, w), 1332 (ν CO, w), 1206 (w), 1115 (m), 1012 (ν CO, m), 990 (ν CO, m), 942 (ν Mo=O, s), 911 (ν Mo=O, s), 897 (ν Mo=O, s), 876 (ν Mo=O, s), 629 (ν_{as} Mo-O-Mo, vs), 566 (ν_s Mo-O-Mo, s), 521 (w), 470 (s), 421 (s).

K₃[MnMo₆O₁₈((OCH₂)₃CNHCOCH₂Cl)₂] – K-AE-Cl

Yield: 48 %. ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) = 63.19 (br, 12H, CH₂O), 8.08 (br, 2H, NH), 4.24 (s, 4H, CH₂Cl). IR: $\tilde{\nu}$ (cm⁻¹) = 3506 (ν NH, w), 3318 (ν NH, w), 3080 (ν CH, w), 1673 (ν C=O, m), 1618 (w), 1530 (δ NH, m), 1466 (δ CH, w), 1448 (δ CH, w), 1420 (δ CH, w), 1336 (ν CO, w), 1234 (ν CN, w), 1182 (ν CN, w), 1112 (ν CO, m), 1039 (ν CO, s), 943 (ν Mo=O, s), 903 (ν Mo=O, s), 644 (ν_{as} Mo-O-Mo, vs), 561 (ν_s Mo-O-Mo, s), 524 (m), 450 (s), 415 (m).

K₃[MnMo₆O₁₈((OCH₂)₃CNHCOC₉H₁₅N₂OS)₂] – K-AE-Biot

Yield: 65 %. ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) = 62.90 (br, 12H, CH₂O), 7.36 (br, 2H, CNHCO), 6.38 (s, 2H, CNHCO), 6.28 (s, 2H, CNHCO), 4.30 (m, 2H, CHN), 4.15 (m, 2H, CHN), 3.13 (m, 2H, CHS), 2.85 (dd, ²J = 4.7 Hz, ³J = 12.6 Hz, 2H, SCH₂), 2.58 (br, 2H, SCH₂), 2.39 (m, 4H, COCH₂), 1.65 (m, 2H, CH₂), 1.49 (m, 6H, CH₂), 1.33 (m, 4H, CH₂). IR: $\tilde{\nu}$ (cm⁻¹) = 3545 (ν NH, w), 3343 (ν NH, w), 2919 (ν CH, w), 2869 (ν CH, w), 1675 (ν C=O, m), 1541 (δ NH, m), 1458 (δ CH, m), 1312 (ν CO, w), 1264 (ν CO, w), 1106 (ν CO, w), 1080 (ν CO, m), 1020 (ν CO, m), 941 (ν Mo=O, s), 916 (ν Mo=O, s), 905 (ν Mo=O, s), 649 (ν_{as} Mo-O-Mo, vs), 565 (ν_s Mo-O-Mo, s), 522 (w), 463 (m), 413 (m).

Solubility Measurements

(a)		Solvent			
		ACN	DMSO	MeOH	H ₂ O
Cation	TBA	200	> 200	110	2
	Li	< 1	> 200	47	> 100
	Na	< 1	66	< 1	> 200
	K	< 1	1	< 1	14

(b)		Solvent			
		ACN	DMSO	MeOH	H ₂ O
Cation	TBA	83	> 200	21	1
	Li	< 1	> 200	180	> 200
	Na	< 1	1	< 1	> 200
	K	< 1	< 1	< 1	9

(c)		Solvent			
		ACN	DMSO	MeOH	H ₂ O
Cation	TBA	43	> 200	< 1	< 1
	Li	< 1	> 200	38	> 200
	Na	< 1	66	< 1	> 200
	K	< 1	4	< 1	10

(d)		Solvent			
		ACN	DMSO	MeOH	H ₂ O
Cation	TBA	9	131	< 1	< 1
	Li	< 1	> 200	N/A	N/A
	Na	< 1	63	N/A	N/A

(e)		Solvent			
		ACN	DMSO	MeOH	H ₂ O
Cation	TBA	27	> 200	< 1	< 1
	Li	< 1	> 200	20	> 200
	Na	< 1	64	< 1	> 200
	K	< 1	7	< 1	8

> 200
151-200
101-150
51-100
1-50
< 1

Table S1 Solubility in mg/mL in ACN, DMSO, MeOH and H₂O of (a) AE-NH₂, (b) AE-CH₃, (c) AE-Cl, (d) AE-Pyr, and (e) AE-Biot with different counter ions: TBA, Li, Na, K.

IR spectra

Figure S1 FT-IR spectra of (a) TBA-AE-NH₂, (b) Li-AE-NH₂, (c) Na-AE-NH₂, and (d) K-AE-NH₂.

Figure S2 FT-IR spectra of (a) TBA-AE-CH₃, (b) Li-AE-CH₃, (c) Na-AE-CH₃, and (d) K-AE-CH₃.

Figure S3 FT-IR spectra of (a) TBA-AE-Cl, (b) Li-AE-Cl, (c) Na-AE-Cl, and (d) K-AE-Cl.

Figure S4 FT-IR spectra of (a) TBA-AE-Pyr, (b) Li-AE-Pyr, and (c) Na-AE-Pyr.

Figure S5 FT-IR spectra of (a) TBA-AE-Biot, (b) Li-AE-Biot, (c) Na-AE-Biot and (d) K-AE-Biot.

Figure S6 FT-IR spectra of (a) Na-AE-NH₂, (b) the dark brown precipitate formed from a solution of Na-AE-NH₂ in carbonate buffer after several days, (c) the black precipitate formed from mixing manganese (III) acetate in carbonate buffer for a few minutes, and (d) manganese (III) acetate.

Figure S7 FT-IR spectra of (a) Na-AE-NH₂, (b) the pale orange precipitate formed from a solution of Na-AE-NH₂ in acetate buffer at pH 4.4 after several days, (c) the pale orange precipitate formed by adding 25 μ L of 1 M HCl to a solution of Na-AE-NH₂ lowering the pH from 6.3 to 4.3, and (d) manganese (III) acetate.

Figure S8 FT-IR spectra of (a) Na-AE-NH₂, (b) the dark brown precipitate formed from a solution of Na-AE-NH₂ in PBS(1X) at pH 7.4 after several days, (c) the black precipitate formed from mixing manganese (III) acetate in PBS(1X) for a few minutes, and (d) manganese (III) acetate.

¹H NMR spectra

Cation metathesis

Figure S9 ¹H NMR spectra of (a) TBA-AE-NH₂, (b) Li-AE-NH₂, (c) Na-AE-NH₂ and (d) K-AE-NH₂ in DMSO-d₆ showing the disappearance of the TBA peaks after cation metathesis.

Figure S10 ¹H NMR spectra of (a) TBA-AE-CH₃, (b) Li-AE-CH₃, (c) Na-AE-CH₃, and (d) K-AE-CH₃ in DMSO-d₆ showing the disappearance of the TBA peaks after cation metathesis.

Figure S11 ^1H NMR spectra of (a) TBA-AE-Cl, (b) Li-AE-Cl, (c) Na-AE-Cl and (d) K-AE-Cl in DMSO-d_6 showing the disappearance of the TBA peaks after cation metathesis.

Figure S12 ^1H NMR spectra of (a) TBA-AE-Pyr, (b) Li-AE-Pyr, and (c) Na-AE-Pyr in DMSO-d_6 showing the disappearance of the TBA peaks after cation metathesis.

Figure S13 ^1H NMR spectra of (a) TBA-AE-Biot, (b) Li-AE-Biot, (c) Na-AE-Biot, and (d) K-AE-Biot in DMSO-d_6 showing the disappearance of the TBA peaks after cation metathesis.

Stability in D₂O

Figure S14 ¹H NMR spectra of (a) 5 mg/mL, (b) 10 mg/mL and (c) 20 mg/mL Na-AE-NH₂ in D₂O at pD around 7.0 acquired over 7 days, displaying a decrease in the peak due to the POM-bound -OCH₂- protons and a matching increase in the peak due to the -OCH₂- protons of the free ligand resulting from the decomposition reaction shown above. Plots of the relative integration in proton equivalents over time of (d) the peak due to the bound -OCH₂- protons and (e) the -OCH₂- protons of the free ligand for the solutions of Na-AE-NH₂ in D₂O in different concentrations as well as the corresponding exponential curves for a pseudo first order reaction based on the average of the observed rate constants (k_{obs}): $8.0 \pm 0.4 \times 10^{-6} \text{ s}^{-1}$ for 5 mg/mL, $8.5 \pm 0.6 \times 10^{-6} \text{ s}^{-1}$ for 10 mg/mL and $11.8 \pm 0.7 \times 10^{-6} \text{ s}^{-1}$ for 20 mg/mL.

Figure S15 (a) ^1H NMR spectra of Na-AE-CH₃ in D₂O (5 mg/mL) at pD 6.9 acquired over 336 h, displaying a decrease in the peak due to the POM-bound -OCH₂- protons and a matching increase in the peak due to the -OCH₂- protons of the free ligand resulting from the decomposition reaction shown above. Plots of the relative integration in proton equivalents over time of (b) the peak due to the bound -OCH₂- protons and (c) the -OCH₂- protons of the free ligand for in Li-, Na- and K-AE-CH₃ in D₂O as well as the corresponding best fit lines.

Figure S16 (a) ^1H NMR spectra of Na-AE-Cl in D_2O (5 mg/mL) at pD 7.1 acquired over 338 h, displaying a decrease in the peak due to the POM-bound $-\text{OCH}_2-$ protons and a matching increase in the peaks due to the $-\text{OCH}_2-$ protons of the free ligand (Tris-Cl), resulting from the decomposition reaction shown above, as well as tris(hydroxymethyl)aminomethane (Tris-NH₂) from hydrolysis of the ligand. (b) Plot of the relative integration in proton equivalents of the $-\text{OCH}_2-$ peaks over time and corresponding best fit lines. (c) Plot of $\ln(\text{integration})$ against time from which the observed pseudo first order rate constants (k_{obs}) were determined: $0.35 \pm 0.03 \times 10^{-6} \text{ s}^{-1}$ ($R^2 = 0.977$), $0.23 \pm 0.04 \times 10^{-6} \text{ s}^{-1}$ ($R^2 = 0.942$) and $0.08 \pm 0.01 \times 10^{-6} \text{ s}^{-1}$ ($R^2 = 0.991$).

Figure S17 ^1H NMR spectra of the ligand $(\text{HOCH}_2)_3\text{CNHCOCH}_2\text{Cl}$ alone in D_2O (1.4 mg/mL) (a) 0.1 h and (b) 330.7 h after dissolution showing slow hydrolysis over time, compared with the much faster hydrolysis in the presence of $[\text{MoO}_4]^{2-}$ as can be seen from the spectra of the ligand with 3 eq of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (5.2 mg/mL) in D_2O (c) 0.1 h and (d) 330.7 h after dissolution. The samples were prepared so that the concentrations of the ligand and $[\text{MoO}_4]^{2-}$ are comparable to those obtained after full decomposition of AE-Cl in D_2O (5 mg/mL).

Figure S18 ^1H NMR spectra of Na-AE-Biot in D_2O (5 mg/mL) at pD 6.8 acquired over 338 h, displaying a decrease in the peak due to the POM-bound $-\text{OCH}_2-$ protons and a matching increase in the peak due to the $-\text{OCH}_2-$ protons of the free ligand resulting from the decomposition reaction shown above. (b) Plot of the relative integration in proton equivalents of the $-\text{OCH}_2-$ peaks over time and corresponding best fit lines. (c) Plot of $\ln(\text{integration})$ against time from which the observed pseudo first order rate constants (k_{obs}) were determined: $0.24 \pm 0.04 \times 10^{-6} \text{ s}^{-1}$ ($R^2 = 0.941$) and $0.22 \pm 0.03 \times 10^{-6} \text{ s}^{-1}$ ($R^2 = 0.964$).

Stability in PBS(1X) at pD 7.4

Figure S19 (a) ^1H NMR spectra of Na-AE-NH₂ in PBS(1X) (5 mg/mL) at pD 7.4 acquired over 337 h, displaying a decrease in the peak due to the POM-bound -OCH₂- protons and a matching increase in the peak due to the -OCH₂- protons of the free ligand resulting from the decomposition reaction shown above. (b) Plot of the relative integration in proton equivalents of the -OCH₂- peaks over time and corresponding exponential curves for a pseudo first order reaction based on the average of the observed rate constants (k_{obs}) determined from plot (c): $5.9 \pm 0.7 \times 10^{-6} \text{ s}^{-1}$ ($R^2 = 0.982$) and $7.1 \pm 1.0 \times 10^{-6} \text{ s}^{-1}$ ($R^2 = 0.972$).

Figure S20 (a) ^1H NMR spectra of Na-AE-CH₃ in PBS(1X) (5 mg/mL) at pH 7.4 acquired over 337 h, displaying a decrease in the peak due to the POM-bound -OCH₂- protons and a matching increase in the peak due to the -OCH₂- protons of the free ligand resulting from the decomposition reaction shown above. (b) Plot of the relative integration in proton equivalents of the -OCH₂- peaks over time and the corresponding best fit lines. (c) Plot of $\ln(\text{integration})$ against time from which the observed pseudo first order rate constants (k_{obs}) were determined to be more or less the same from both -OCH₂- peaks: $0.2 \pm 0.03 \times 10^{-6} \text{ s}^{-1}$ ($R^2 = 0.933$).

Stability in phosphate buffer at pD 7.4

(a)

(b)

(c)

Figure S21 (a) ^1H NMR spectra of Na-AE-NH₂ in phosphate buffer (5 mg/mL) at pD 7.4 acquired over 340 h, displaying a decrease in the peak due to the POM-bound -OCH₂- protons and a matching increase in the peak due to the -OCH₂- protons of the free ligand resulting from the decomposition reaction shown above. (b) Plot of the relative integration in proton equivalents of the -OCH₂- peaks over time and corresponding exponential curves for a pseudo first order reaction based on the average of the observed rate constants (k_{obs}) determined from plot (c): $5.6 \pm 1.0 \times 10^{-6} \text{ s}^{-1}$ ($R^2 = 0.965$) and $5.3 \pm 0.6 \times 10^{-6} \text{ s}^{-1}$ ($R^2 = 0.985$).

Figure S22 (a) ^1H NMR spectra of Na-AE-CH₃ in phosphate buffer (5 mg/mL) at pD 7.4 acquired over 341 h, displaying a decrease in the peak due to the POM-bound -OCH₂- protons and a matching increase in the peak due to the -OCH₂- protons of the free ligand resulting from the decomposition reaction shown above. (b) Plot of the relative integration in proton equivalents of the -OCH₂- peaks over time and the corresponding best fit lines. (c) Plot of $\ln(\text{integration})$ against time from which the observed pseudo first order rate constants (k_{obs}) were determined: $0.32 \pm 0.07 \times 10^{-6} \text{ s}^{-1}$ ($R^2 = 0.903$) and $0.23 \pm 0.02 \times 10^{-6} \text{ s}^{-1}$ ($R^2 = 0.984$).

Stability in acetate buffer at pD 4.4

Figure S23 ^1H NMR spectra of Na-AE-NH₂ in acetate buffer (5 mg/mL) at pD 4.4 acquired over 336 h, displaying a decrease in the peak due to the POM-bound -OCH₂- protons as AE-NH₂ becomes protonated and precipitates out of solution, but does not noticeably decompose since only a very slight increase in the peak due to the -OCH₂- protons of the free ligand can be seen.

Figure S24 ^1H NMR of Na-AE-CH₃ in acetate buffer (5 mg/mL) at pD 4.4 acquired over 336 h, displaying very little change in the integration of the peak due to the POM-bound -OCH₂- protons and only a slight increase in the peak due to the -OCH₂- protons of the free ligand resulting from the decomposition reaction shown above.

Stability in carbonate buffer at pD 10

Figure S25 ^1H NMR spectra of Na-AE-NH₂ in carbonate buffer (5 mg/mL) at pD 10 acquired over 336.5 h, displaying a decrease in the peak due to the POM-bound -OCH₂- protons and a matching increase in the peak due to the -OCH₂- protons of the free ligand resulting from the decomposition reaction shown above.

Figure S26 ^1H NMR spectra of Na-AE-CH₃ in carbonate buffer (5 mg/mL) at pD 10 acquired over 336.5 h, displaying a decrease in the peak due to the POM-bound -OCH₂- protons and a matching increase in the peak due to the -OCH₂- protons of the free ligand resulting from the decomposition reaction shown above.

Stability at different temperatures

Figure S27 ^1H NMR spectra of Li-AE-NH₂ in PBS(1X) (5 mg/mL) at pD 7.4 and 25 °C acquired over 6 h, displaying a decrease in the peak due to the POM-bound -OCH₂- protons and a matching increase in the peak due to the -OCH₂- protons of the free ligand resulting from the decomposition reaction shown above.

Figure S28 ^1H NMR spectra of Li-AE-NH₂ in PBS(1X) (5 mg/mL) at pD 7.4 and 37 °C acquired over 5.5 h, displaying a decrease in the peak due to the POM-bound -OCH₂- protons and a matching increase in the peak due to the -OCH₂- protons of the free ligand resulting from the decomposition reaction shown above.

Figure S29 ^1H NMR spectra of Li-AE-NH₂ in PBS(1X) (5 mg/mL) at pD 7.4 and 50 °C, displaying a decrease over 6 h in the peak due to the POM-bound -OCH₂- protons and a matching increase in the peak due to the -OCH₂- protons of the free ligand resulting from the decomposition reaction shown above.

Figure S30 Plots displaying changes in the integration over time of (a) the peak at due to the POM-bound -OCH₂- protons and (b) the peak at due to the -OCH₂- protons in the free ligand for solutions of Na-AE-NH₂ in deuterated PBS(1X) (5 mg/mL) at pD 7.4 and temperatures of 25 °C, 37 °C and 50 °C.

Stability in MeOD-d₄

Figure S31 ¹H NMR spectra of Li-AE-NH₂ in MeOD-d₄ (5 mg/mL) displaying changes over 504 h.

Figure S32 ¹H NMR spectra of Li-AE-CH₃ in MeOD-d₄ (5 mg/mL) displaying changes over 504 h.

Stability in DMSO-d₆

Figure S33 ^1H NMR spectra of TBA-AE-NH₂ in DMSO-d₆ (5 mg/mL) (a) 0 h and (b) 14 days after dissolution, which show that no decomposition occurred in 2 weeks.

Figure S34 ^1H NMR spectra of TBA-AE-CH₃ in DMSO-d₆ (5 mg/mL) (a) 0 h and (b) 14 days after dissolution, which show that no decomposition occurred in 2 weeks.

Figure S35 ^1H NMR spectra of TBA-AE-Cl in DMSO-d_6 (5 mg/mL) (a) 0 h and (b) 14 days after dissolution, which show that no decomposition occurred in 2 weeks.

Figure S36 ^1H NMR spectra of TBA-AE-Pyr in DMSO-d_6 (5 mg/mL) acquired over 345 h, displaying changes in the peaks due to the POM-bound $-\text{OCH}_2-$ protons and the peaks due to the pyridine protons resulting from the decomposition reaction shown above involving the hydrolysis of the imine bond to form AE-Pyr- NH_2 and pyridinecarbaldehyde.

Figure S37 ^1H NMR spectra of TBA-AE-Biot in DMSO-d_6 (5 mg/mL) (a) 0 h and (b) 14 days after dissolution, which show that no decomposition occurred in 2 weeks.

Stability in ACN-d_3

Figure S38 ^1H NMR spectra of TBA-AE-NH₂ in ACN-d_3 (5 mg/mL) (a) 0 h and (b) 14 days after dissolution, which show that no decomposition occurred in 2 weeks.

Figure S39 ^1H NMR spectra of TBA-AE-CH₃ in ACN-d₃ (5 mg/mL) (a) 0 h and (b) 14 days after dissolution, which show that no decomposition occurred in 2 weeks.

Figure S40 ^1H NMR spectra of TBA-AE-Cl in ACN-d₃ (5 mg/mL) (a) 0 h and (b) 14 days after dissolution, which show that no decomposition occurred in 2 weeks.

Figure S41 ^1H NMR spectra of TBA-AE-Pyr in ACN-d_3 (5 mg/mL) acquired over 480 h, displaying changes in the peaks due to the POM-bound $-\text{OCH}_2-$ protons and the peaks due to the pyridine protons resulting from the decomposition reaction shown above involving the hydrolysis of the imine bond to form AE-Pyr-NH₂, AE-NH₂, and pyridinecarbaldehyde.

Figure S42 ^1H NMR spectra of TBA-AE-Pyr in a mixture of 95% ACN-d_3 and 5% D_2O (5 mg/mL) acquired over 28 h, displaying changes in the peaks due to the POM-bound $-\text{OCH}_2-$ protons and the peaks due to the pyridine protons resulting from the decomposition reaction shown above involving the hydrolysis of the imine bond to form AE-Pyr-NH₂, AE-NH₂, and pyridinecarbaldehyde.

Figure S43 ^1H NMR spectra of TBA-AE-Biot in ACN-d_3 (5 mg/mL) (a) 0 h and (b) 14 days after dissolution, which show that no decomposition occurred in 2 weeks.

UV-Vis spectra

Figure S44 UV-Vis spectra of 0.02 mg/mL Li-AE-NH₂ in a buffered solution of PBS(1X) pH 7.4 acquired over 90 h at 5 h intervals at room temperature. λ_{max} blue shifted from 212 nm to 208 nm and the maximum absorbance increased over 90 h indicating the HPOM decomposed into $[\text{MoO}_4]^{2-}$. The insert shows the weaker peak at 300-400 nm due to the d-d transition of Mn^{3+} in more detail, which also increased at first over time as the HPOM decomposed and then decreased as Mn^{3+} precipitated out of solution.

Figure S45 UV-Vis spectra of 0.02 mg/mL Li-AE-NH₂ in MeOH acquired over 89 h at 5 h intervals at room temperature. Only a slight decrease in the absorbance was observed over 89 h indicating very slow decomposition of the HPOM. The insert shows the weaker peak at 300-400 nm due to the d-d transition of Mn³⁺ in more detail, which also decreased slightly over 89 h.

Figure S46 UV-Vis spectra of 0.02 mg/mL TBA-AE-NH₂ in ACN acquired over 90 h at 5 h intervals at room temperature. λ_{max} remained at 215 nm and the absorbance did not change over 90 h indicating the HPOM was stable under these conditions. The insert shows the weaker peak at 300-400 nm due to the d-d transition of Mn³⁺ in more detail, which also remained unchanged over 90 h.

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