Electronic Supplementary Material (ESI) for Chemical Science

A collection of robust methodologies for the preparation of asymmetric hybrid Mn-Anderson polyoxometalates for multifunctional materials

Supplementary Information

Carine Yvon,‡ Andrew Macdonell,‡ Saskia Buchwald, Andrew J. Surman, Noémie Follet, Jennifer Alex, De-Liang Long and Leroy Cronin*

‡ These authors contributed equally to this publication.

* School of Chemistry, University of Glasgow, Glasgow, UK.

Fax: + 44 (0)141 330 4888; Tel: + 44 (0)141 330 6650; E-mail: L.Cronin@chem.gla.ac.uk

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1 Instrumentation

RP-HPLC

RP-HPLC measurements were performed on an Agilent 1100 Series (Agilent Technologies) equipped with a vacuum degasser, a binary pump (G1312A), a thermostated column compartment (G1316A), a standard autosampler (G1313A), and a variable wavelength detector (VWD) (G1314A). 5 μL of the samples were injected on a Phenomenex Luna® 3 μm C18(2) 100 Å, 150 x 2 mm column and eluted at 0.5 mL/min with a gradient of 0.05 M ammonium acetate (pH = 6.7 - 6.9) (**A**)/Acetonitrile (**B**) (solvent gradient given in table 1). The oven temperature was set to 25 °C and elution was detected by UV (λ = 254 nm). The data recorded were processed using Bruker compass Hystar 3.2 (Bruker Daltonics) and Hyphenation Star PP software.

Time (min)	**A** (%)	**B** (%)
0.0	95	5
3.0	95	5
15.0	5	95
17.0	5	95

Table S1: Eluent composition for RP-HPLC measurements. Runlength 17.0 min.

Flash Chromatography:

Flash chromatography separations were performed on a Reveleris® iES Flash chromatography system using the Reveleris® *Navigator*^{TM} software. Before injection, columns were equilibrated for 4 min with 65:35 of A/B solvents at 18 mL/min. Samples were injected dry on Pre-packed Reveleris® C_{18} 4 g columns (two in series) by adsorption on celite (20wt%, maximum total weight 1.8 g (*i.e.* 300 mg of compound adsorbed on 1.5 g of celite® 535 coarse)). Columns were eluted at 18 mL/min with a gradient of solvent A and B (see table 2) and elution was detected by UV (at λ_{UV1} = 254 nm and λ_{UV2} = 350 nm) and an evaporative light scattering detector (ELSD; carrier solvent: isopropanol).

Time (min)	**A** (%)	**B** (%)
0.0	65.0	35.0
2.2	65.0	35.0
11.8	5.0	95.0
12.9	5.0	95.0

Table S2: Eluent composition for flash chromatography. Run length 12.9 min.

Microanalysis: Carbon, nitrogen, and hydrogen content were determined by the microanalysis services within the Department of Chemistry, University of Glasgow using an EA 1110 CHNS, CE-440 Elemental Analyser.

Single crystal X-ray diffraction

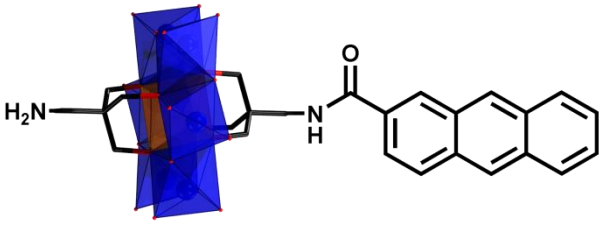
Single crystal structure determination were performed on a Bruker Apex II Quasar charge-coupled device (CCD) detector (λ ($Mo_{K\alpha}$) = 0.71073Å) at 150(2) K, where the data reduction was performed using the Apex2 software package and structure solution. Corrections for incident and diffracted beam absorption effects were applied using empirical absorption correction.[1] Refinement was carried out with SHELXS-97[2] and SHELXL-97[2] using WinGX[3] *via* a full matrix least-squares on F2 method. All non-hydrogen atoms were refined anisotropically unless otherwise stated.

NMR Microscopy: All NMR data was recorded on a Bruker Advanced 400 MHz, ^{1}H NMR at 400 MHz with deuterated dimethyl sulfoxide from Goss Scientific.

ESI-MS: Measurements were carried out at 180 °C in acetonitrile (MeCN) using a Bruker MaXis Impact instrument. The calibration solution used was Agilent ESI-L low concentration tuning mix solution, Part No. G1969-85000, enabling calibration between approximately 50 m/z and 2000 m/z. Samples were dissolved in MeCN and introduced into the MS at a dry gas temperature of 180 °C. The ion polarity for all MS scans recorded was negative, with the voltage of the capillary tip set at 4500 V, end plate offset at −500 V, funnel 1 RF at 400 Vpp and funnel 2 RF at 400 Vpp, hexapole RF at 400 Vpp, ion energy 5.0 eV, collision energy at 15 eV, collision cell RF at 2100 Vpp, transfer time at 120.0 μs, and the pre-pulse storage time at 20.0 μs. Each spectrum was collected for 2 min.

2 Compound Information

Compound 1 – Anthracene-TRIS/TRIS Mn-Anderson Compound $(C_{16}H_{36}N)_3[MnMo_6O_{24}(C_{19}H_{16}NO)(C_4H_8N)]$



STEP 1: Synthesis of the Anthracene-TRIS ligand

Adapted from a published procedure.[4]

To a solution of anthracene-2-carboxylic acid (407 mg, 1.83 mmol) and *N*-methylmorpholine (0.22 mL, 2.00 mmol) in tetrahydrofuran (10 mL) at 0 ˚C, ethylchloroformate (0.19 mL, 2.00 mmol) was added dropwise, causing a white precipitate to form. The reaction mixture was then stirred for 30 min at 0 ˚C, then filtered directly into a solution of tris(hydroxymethyl)aminomethane (TRIS, ($(HOCH_2)_3CNH_2$), 218 mg, 1.83 mmol) and triethylamine (TEA, 0.28 mL, 2.00 mmol) in *N*,*N*-dimethylformamide (DMF, 10 mL) which had been stirring for 10 min. The reaction mixture was then stirred overnight, after which solvents were removed under reduced pressure until only DMF remained. The product was crystallized by ether diffusion (Et_2O) into this DMF solution over 2 days, giving clear yellow needles. **Yield:** 428 mg, 1.32 mmol, 36%; **^{1}H NMR** (DMSO-d_6, 400 MHz): δ = 3.77 (s, 6H, $3CH_2$), 4.84 (s, 3H, 3OH), 7.57 (m, 3H, 2CH + NH), 7.86 (m, 1H, CH), 8.15 (m, 3H, 3CH), 8.62 (s, 2H, 2CH), 8.74 ppm (s, 1H, CH); **^{13}C DEPTQ NMR (DMSO-d_6, 100 MHz):** δ = 60.4 (CH_2), 62.8 (C), 123.8 (CH), 125.9 (CH), 125.9 (CH), 126.3 (CH), 127.7 (CH), 128.0 (CH), 128.0 (CH), 128.1 (CH), 128.2 (CH), 130.0 (C), 131.5 (C), 132.0 (C), 132.1 (C), 167.3 ppm (CO); **Elemental analysis:** Calc. for $C_{19}H_{19}NO_4$ (325.36 g.mol^{-1}): C, 70.14; H, 5.89; N, 4.31; Found C, 69.71; H, 5.97; N, 4.58.

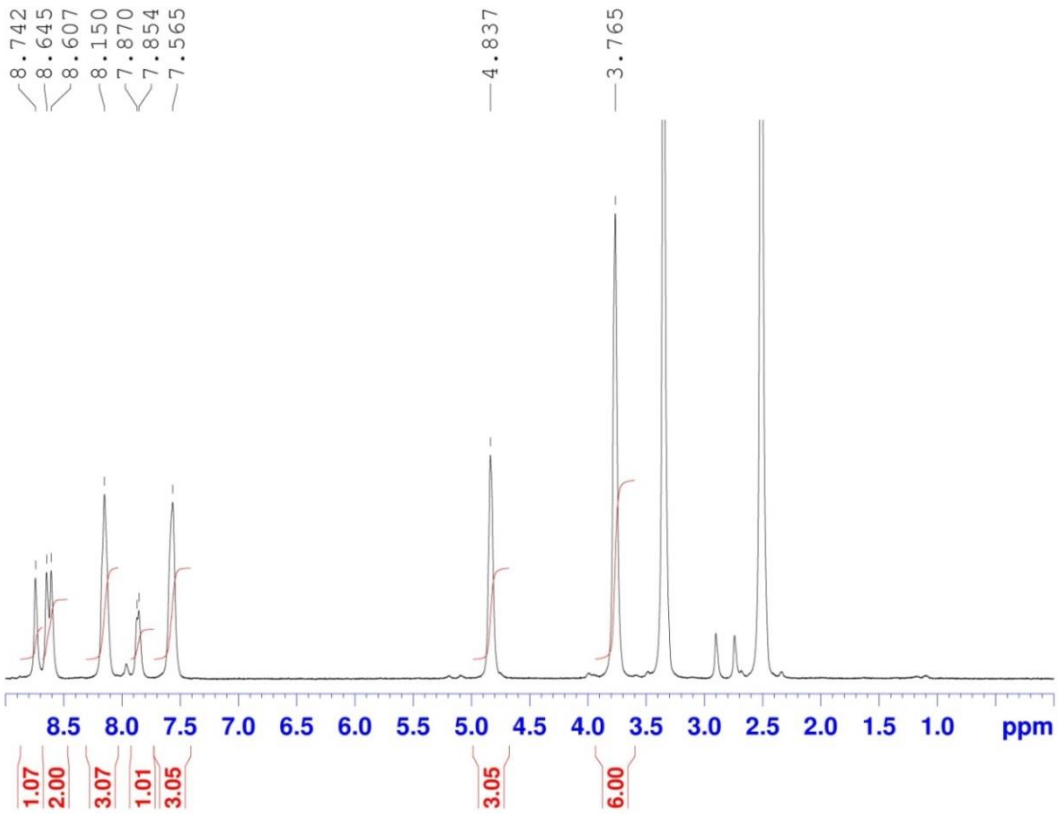


Fig. S1: ^{1}H NMR of the Anthracene-TRIS ligand in DMSO-d_6 at 400 MHz. Residual DMF from the crystallization is observed at 2.7, 2.9 and 7.9 ppm.

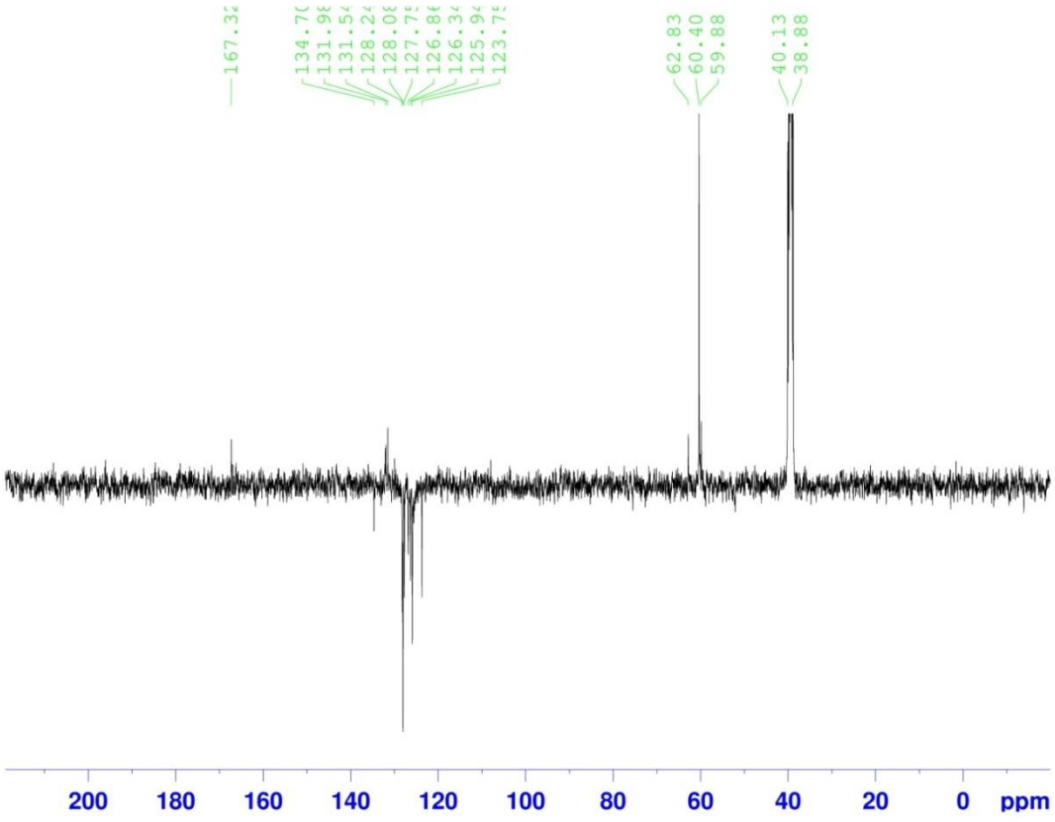


Fig. S2: ^{13}C DEPTQ NMR of the Anthracene-TRIS ligand in DMSO-d_6 at 100 MHz.

STEP 2: Synthesis of the Anthracene-TRIS/TRIS Mn-Anderson compound (1)

The crude mixture was synthesized according to an adapted literature procedure.[5]

A mixture of tetrabutylammonium octamolybdate[6] ($(TBA)_4[\alpha\text{-}Mo_8O_{26}]$, 765 mg, 0.36 mmol), manganese acetate dihydrate ($Mn(OAc)_3 \cdot 2H_2O$, 220 mg, 0.91 mmol), TRIS (139 mg, 0.94 mmol) and Anthracene-TRIS ligand (304 mg; 0.94 mmol) was refluxed in MeCN (15 mL) for 18 h. The resulting brown mixture was cooled down to room temperature and the precipitate removed by centrifugation to lead to a bright orange solution. The crude mixture was isolated by crystallization by Et_2O diffusion. After three days, orange crystals were formed and isolated (crude mixture yield: 557 mg). 100 mg of the crude mixture adsorbed on celite (500 mg) were purified *via* flash chromatography (see instrumentation for operation conditions). The purity of the fractions was established by RP-HPLC. The fractions composed exclusively of the asymmetric Anthracene-TRIS/TRIS Mn-Anderson cluster (retention time 10.4 min) were combined and a large excess of TBA bromide (500 mg; 1.55 mmol) was added to the resulting solution. MeCN was evaporated under vacuum leading to the formation of an orange precipitate in the remaining aqueous solution. This precipitate was isolated by centrifugation and then dissolved in MeCN. The solution was centrifuged to remove any insoluble material and set up for crystallization with Et_2O diffusion. Within 3 days crystals of compound **1** were formed, dried and analyzed. Single crystals suitable for X-ray diffraction were grown from DMF by slow Et_2O diffusion (needle crystal, 3 days). **Yield:** 167 mg, 0.08 mmol, 17% based on Mo (estimated form the purification of 100 mg of the crude material); **^{1}H NMR** (DMSO-d_6, 400 MHz): δ = 0.95 (m, 36H, CH_3 from TBA^+), 1.32 (m, 24H, CH_2 from TBA^+), 1.58 (m, 24H, CH_2 from TBA^+), 3.17 (m, 24H, CH_2 from TBA^+), 7.56 (m, 2H, 2CH), 7.84 (m, 2H, CH + NH), 8.15 (m, 3H, 3CH), 8.54 (s, 1H, CH), 8.63 (s, 1H, CH), 8.68 (s, 1H, CH), 60.0 - 66.0 ppm (s, br, $6CH_2$); **^{13}C DEPTQ NMR** (DMSO-d_6, 100 MHz): δ = 13.5 (CH_3), 19.2 (CH_2), 23.1 (CH_2), 57.5 (CH_2), 124.5 (CH), 125.7 (CH), 126.2 (CH), 127.5 (CH), 127.9 (CH), 128.0 (CH), 128.1 (CH), 128.3 (CH), 128.7 (C), 129.0 (CH), 129.7 (C), 131.3 (C), 131.8 (C), 132.1 ppm (C); **Elemental analysis:** Calc. for $C_{71}H_{132}MnMo_6N_5O_{25}$ (2086.35 g.mol^{-1}): C, 40.87; H, 6.38; N, 3.36; Found: C, 40.72; H, 6.30; N, 3.34.

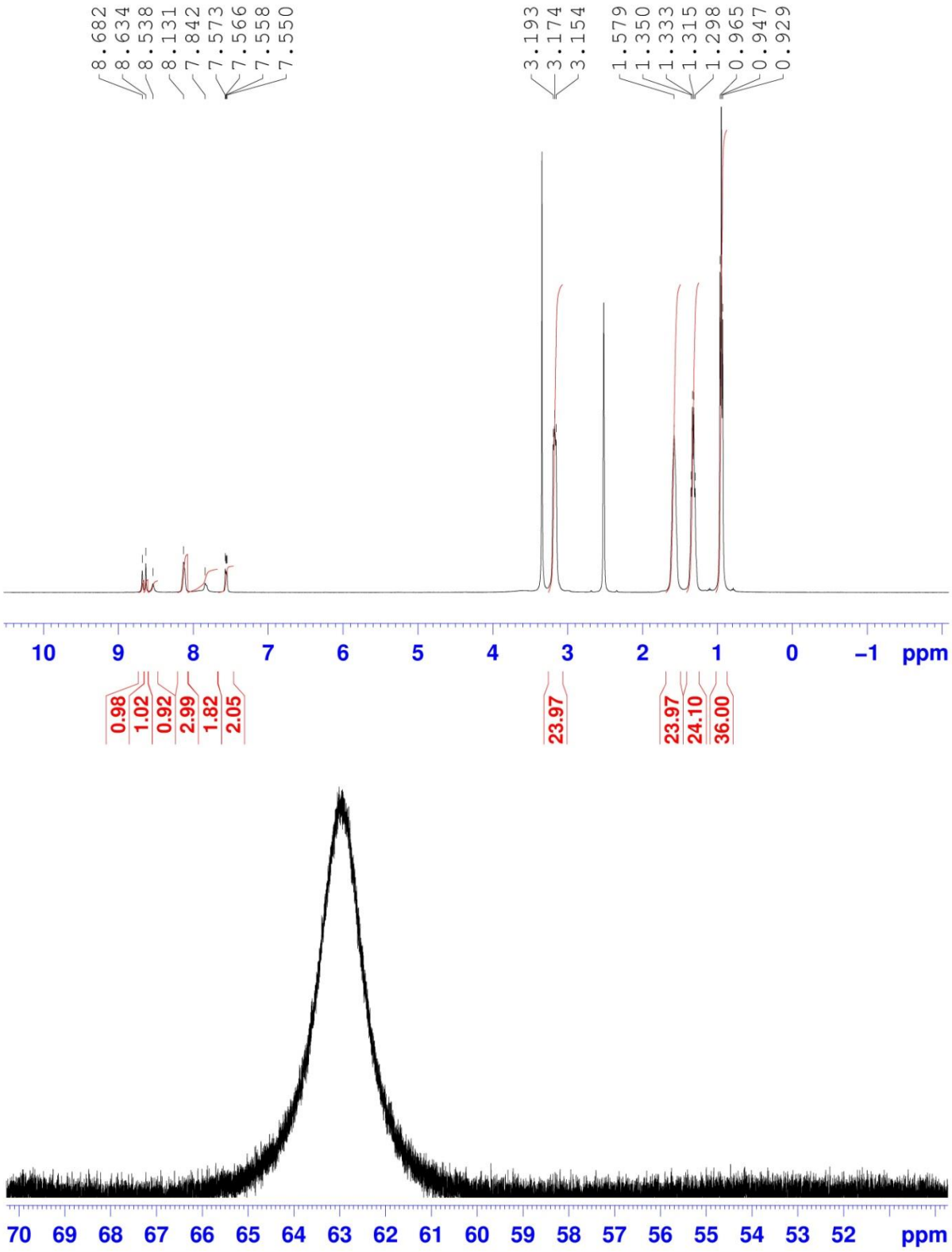


Fig. S3: ^{1}H NMR of the Anthracene-TRIS/TRIS Mn-Anderson (**1**) in DMSO-d_6 at 400 MHz and peak at 60 ppm.

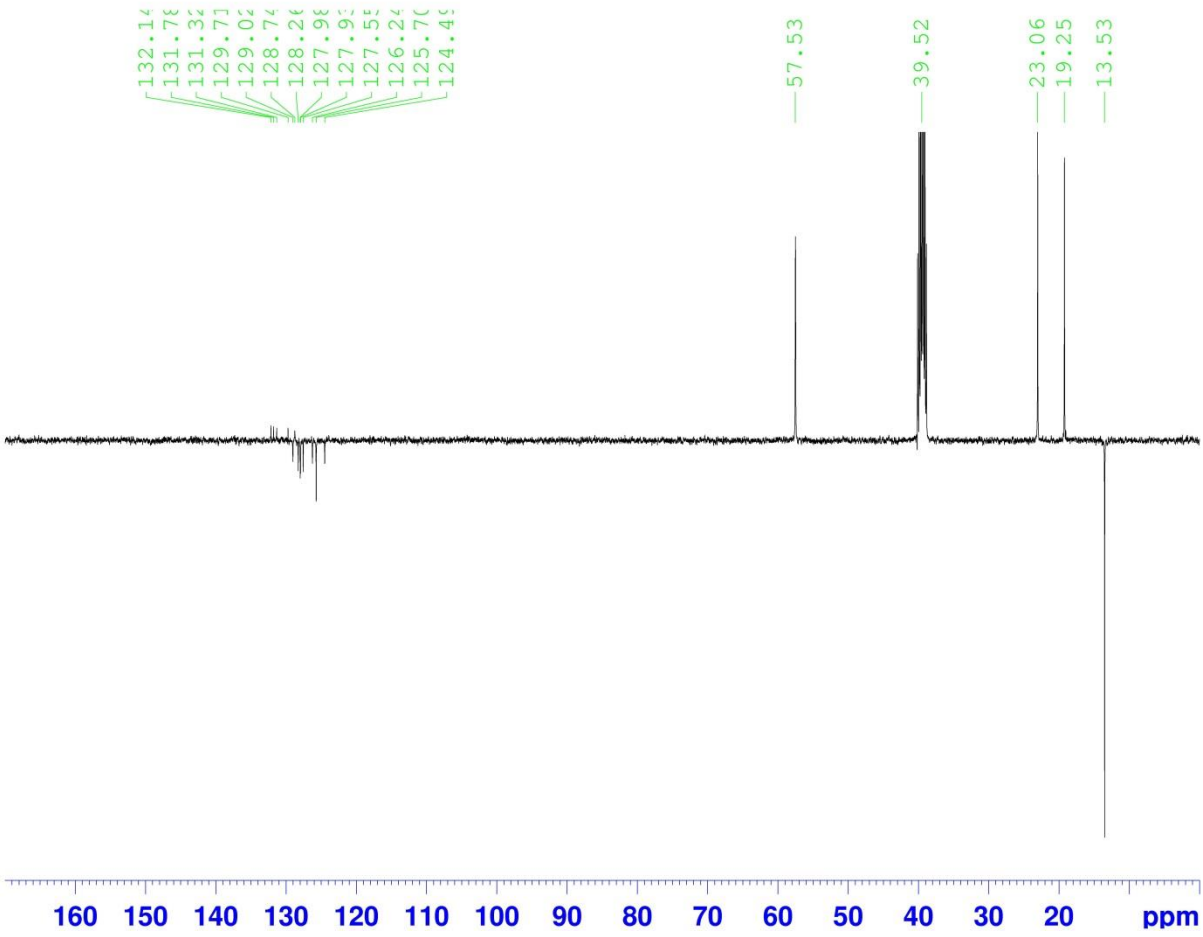


Fig. S4: ^{13}C DEPTQ NMR of the Anthracene-TRIS/TRIS Mn-Anderson (**1**) in DMSO-d_6 at 100 MHz.

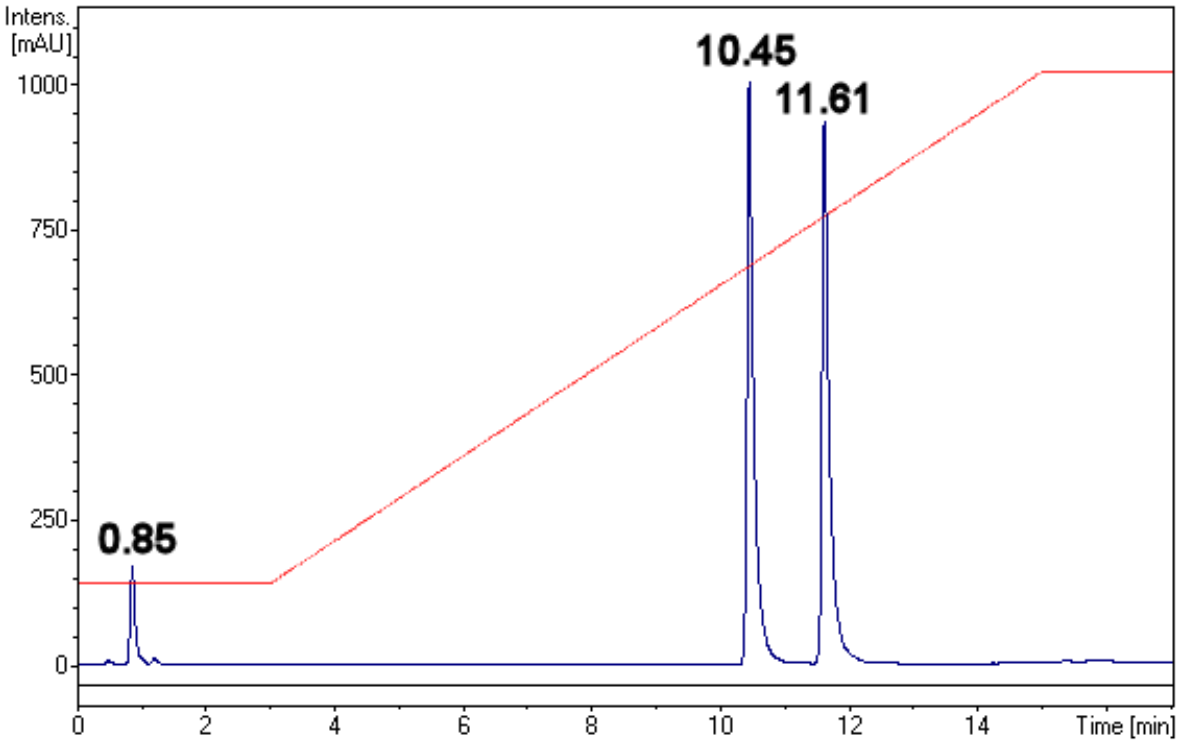


Fig. S5: RP-HPLC of the crude material (mixture of **1** with the two symmetric by-products: TRIS Mn-Anderson and Anthracene Mn-Anderson compounds).

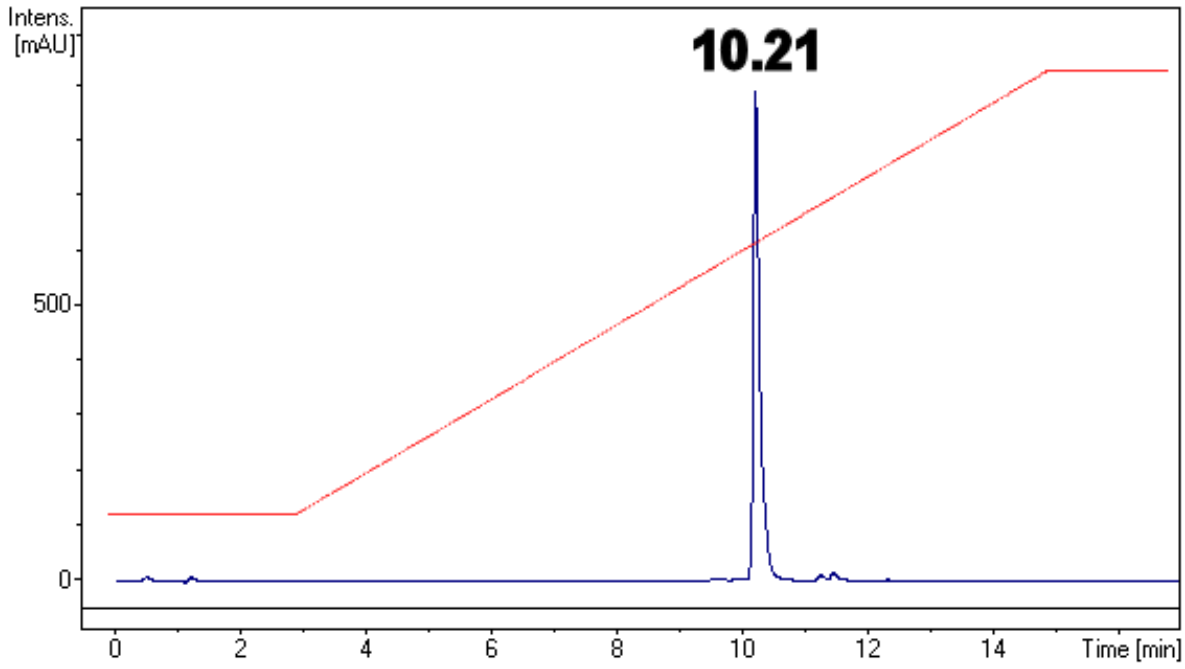


Fig. S6: RP-HPLC of pure compound **1**.

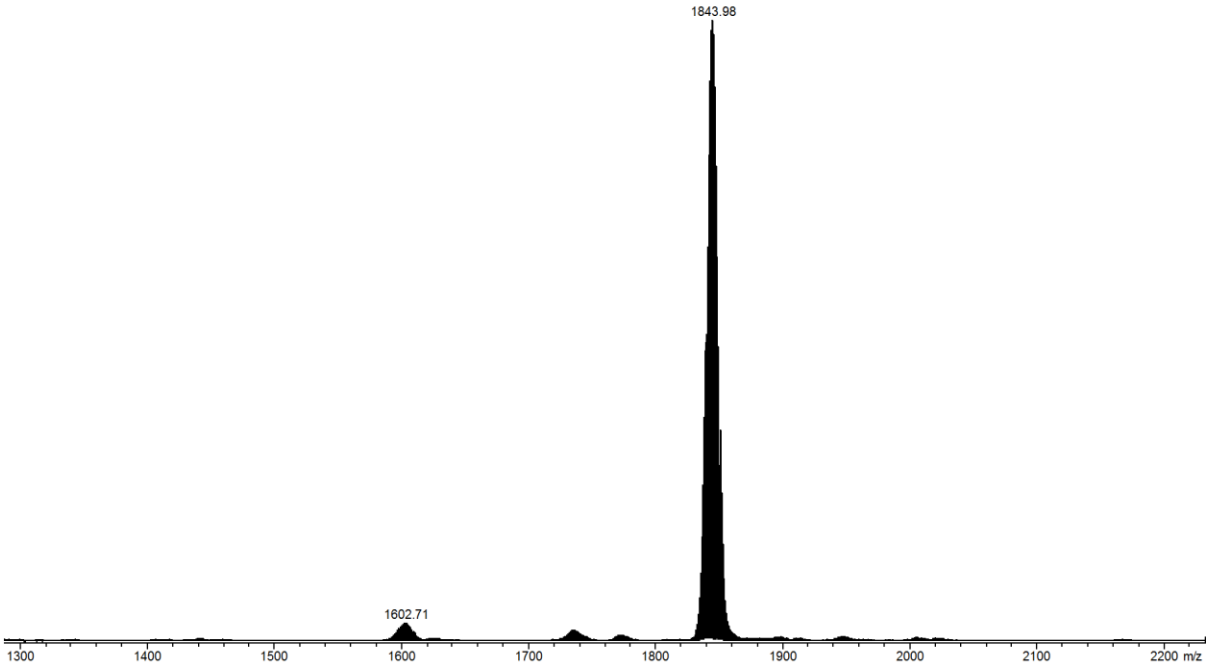


Fig. S7: ESI-MS spectra of compound **1**. See Table S3 for peak assignments.

Formula assigned	**z**	**m/z calculated**	**m/z observed**
$[MnMo_6O_{24}(C_{19}H_{16}NO)(C_4H_8N)](C_{16}H_{36}N)_1H$	-1	1602.73	1602.71
$[MnMo_6O_{24}(C_{19}H_{16}NO)(C_4H_8N)](C_{16}H_{36}N)_2$	-1	1844.01	1843.98
Potential by-products (not observed)	**z**	**m/z calculated**	
$[MnMo_6O_{24}(C_4H_8N)_2](C_{16}H_{36}N)_1H$	-1	1397.68	
$[MnMo_6O_{24}(C_4H_8N)_2](C_{16}H_{36}N)_2$	-1	1639.95	
$[MnMo_6O_{24}(C_{19}H_{16}NO)_2](C_{16}H_{36}N)_1H$	-1	1806.79	
$[MnMo_6O_{24}(C_{19}H_{16}NO)_2](C_{16}H_{36}N)_2$	-1	2048.07	

Table S3: Assignment of the peak envelopes found in the ESI-MS spectrum of compound **1**, shown in Fig. S7. Expected peak envelopes belonging to by-products (not observed) are indicated; their absence demonstrates the purity of the sample.

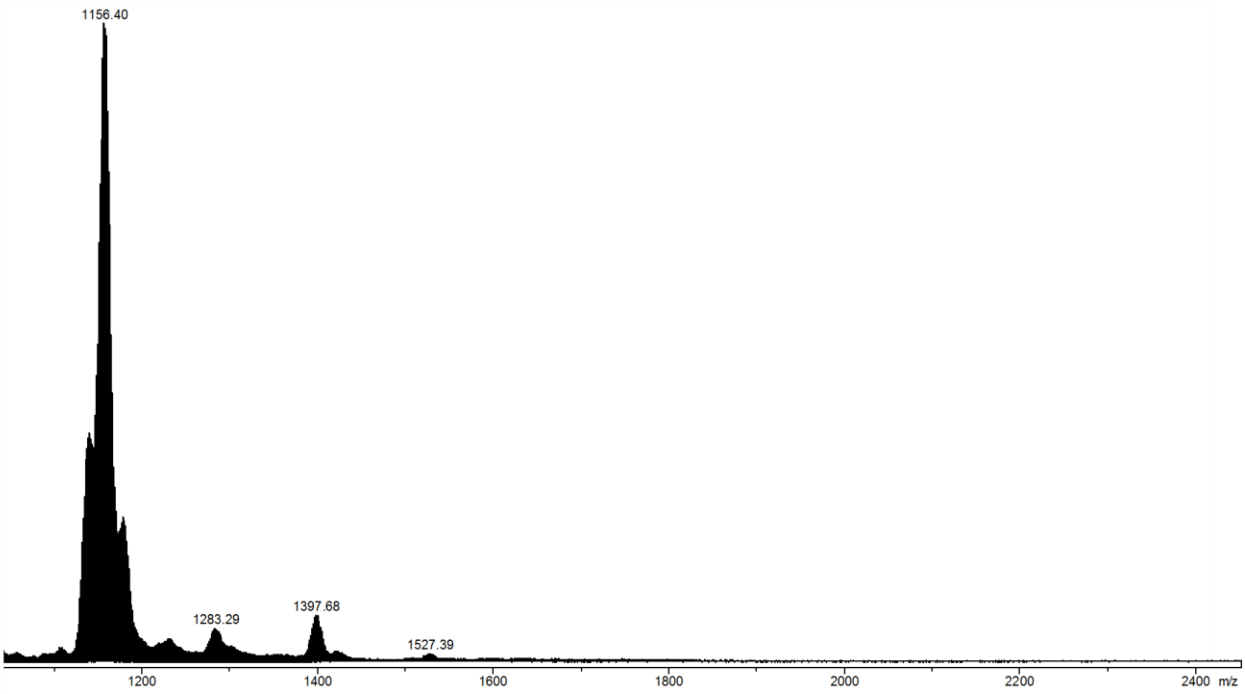


Fig. S8: ESI-MS spectra of region **I**. See Table S4 for peak assignments.

Formula assigned	**z**	**m/z calculated**	**m/z observed**
$[MnMo_6O_{24}(C_4H_8N)_2]H_2$	-1	1156.40	1156.40
$[MnMo_6O_{24}(C_4H_8N)_2](C_{16}H_{36}N)_1H$	-1	1397.68	1397.68
Potential by-products (not observed)	**z**	**m/z calculated**	
$[MnMo_6O_{24}(C_{19}H_{16}NO)(C_4H_8N)](C_{16}H_{36}N)_1H$	-1	1602.73	
$[MnMo_6O_{24}(C_{19}H_{16}NO)_2](C_{16}H_{36}N)_1H$	-1	1806.79	
$[MnMo_6O_{24}(C_{19}H_{16}NO)(C_4H_8N)](C_{16}H_{36}N)_2$	-1	1844.01	
$[MnMo_6O_{24}(C_{19}H_{16}NO)_2](C_{16}H_{36}N)_2$	-1	2048.07	

Table S4: Assignment of the peak envelopes found in the ESI-MS spectrum of region **I**, shown in Fig. S8. Expected peak envelopes belonging to by-products (not observed) are indicated; their absence demonstrates the purity of the sample.

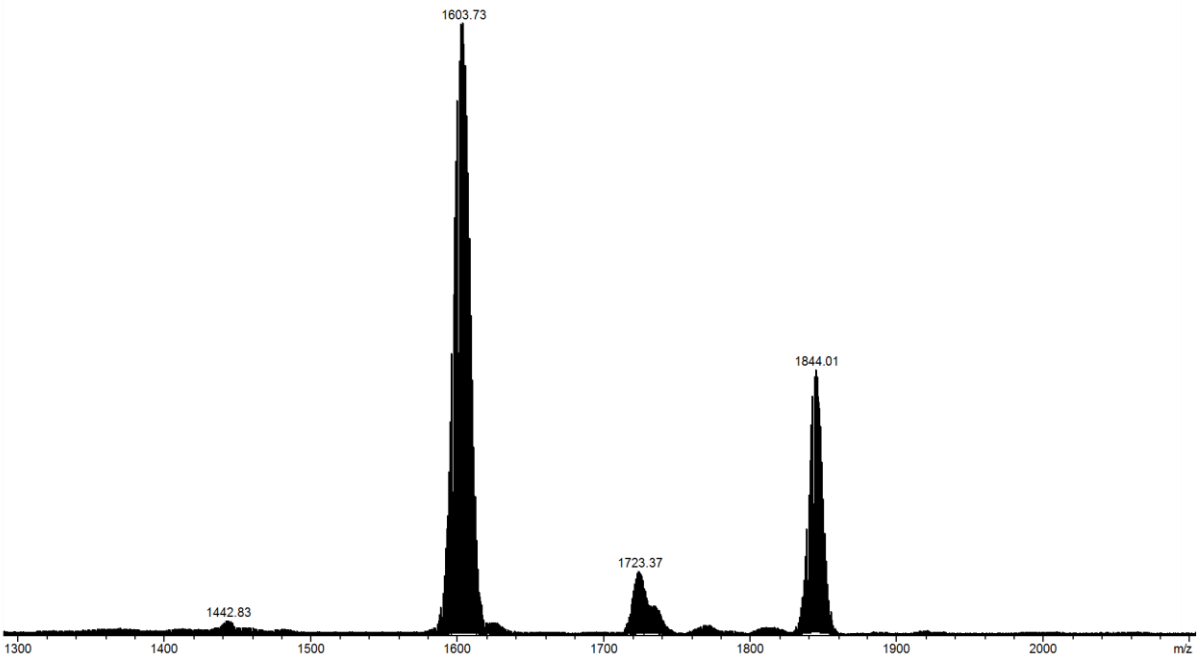


Fig. S9: ESI-MS spectra of region **II**. See Table S5 for peak assignments.

Formula assigned	**z**	**m/z calculated**	**m/z observed**
$[MnMo_6O_{24}(C_{19}H_{16}NO)(C_4H_8N)](C_{16}H_{36}N)_1H$	-1	1602.73	1603.73
$[MnMo_6O_{24}(C_{19}H_{16}NO)(C_4H_8N)]_2(C_{16}H_{36}N)_3H$	-2	1723.37	1723.37
$[MnMo_6O_{24}(C_{19}H_{16}NO)(C_4H_8N)](C_{16}H_{36}N)_2$	-1	1844.01	1844.01
Potential by-products (not observed)	**z**	**m/z calculated**	
$[MnMo_6O_{24}(C_4H_8N)_2](C_{16}H_{36}N)_1H$	-1	1397.68	
$[MnMo_6O_{24}(C_4H_8N)_2](C_{16}H_{36}N)_2$	-1	1639.95	
$[MnMo_6O_{24}(C_{19}H_{16}NO)_2](C_{16}H_{36}N)_1H$	-1	1806.79	
$[MnMo_6O_{24}(C_{19}H_{16}NO)_2](C_{16}H_{36}N)_2$	-1	2048.07	

Table S5: Assignment of the peak envelopes found in the ESI-MS spectrum of region **II**, shown in Fig. S9. Expected peak envelopes belonging to by-products (not observed) are indicated; their absence demonstrates the purity of the sample.

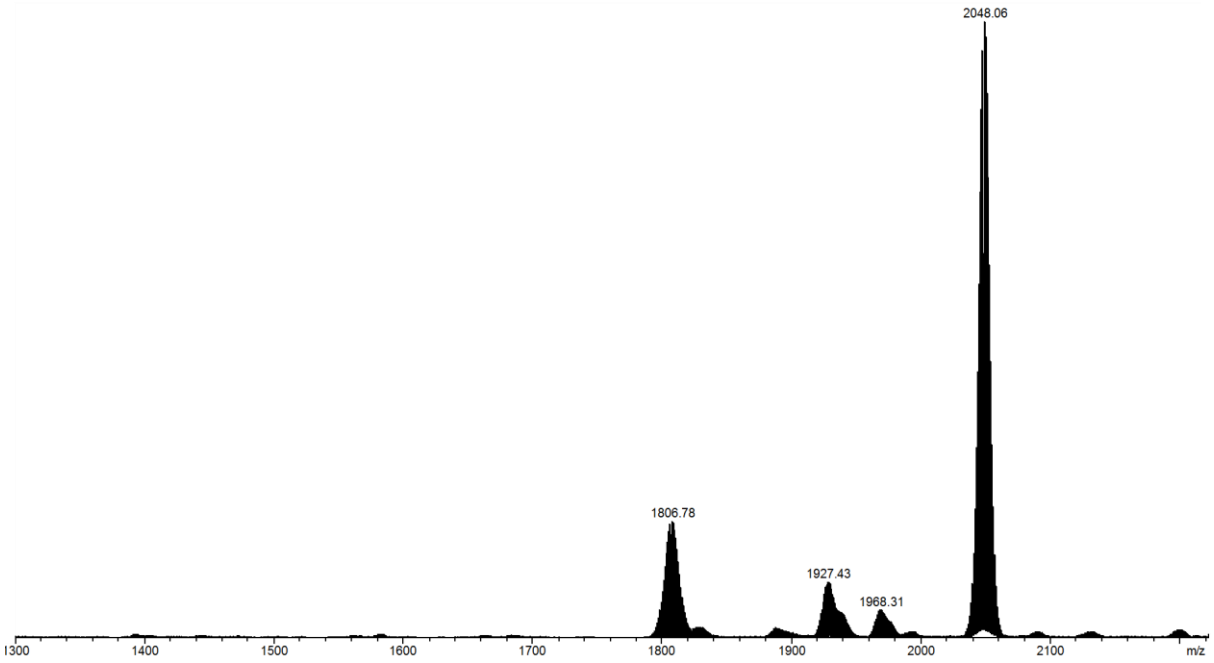


Fig. S10: ESI-MS spectra of region **III**. See Table S6 for peak assignments.

Formula assigned	**z**	**m/z calculated**	**m/z observed**
$[MnMo_6O_{24}(C_{19}H_{16}NO)_2](C_{16}H_{36}N)_1H$	-1	1806.79	1806.78
$[MnMo_6O_{24}(C_{19}H_{16}NO)_2]_2(C_{16}H_{36}N)_3H$	-2	1927.43	1927.43
$[MnMo_6O_{24}(C_{19}H_{16}NO)_2]_3(C_{16}H_{36}N)_5H$	-3	1967.64	1968.31
$[MnMo_6O_{24}(C_{19}H_{16}NO)_2](C_{16}H_{36}N)_2$	-1	2048.07	2048.06
Potential by-products (not observed)	**z**	**m/z calculated**	
$[MnMo_6O_{24}(C_4H_8N)_2](C_{16}H_{36}N)_1H$	-1	1397.68	
$[MnMo_6O_{24}(C_{19}H_{16}NO)(C_4H_8N)](C_{16}H_{36}N)_1H$	-1	1602.73	
$[MnMo_6O_{24}(C_4H_8N)_2](C_{16}H_{36}N)_2$	-1	1639.95	
$[MnMo_6O_{24}(C_{19}H_{16}NO)(C_4H_8N)](C_{16}H_{36}N)_2$	-1	1844.01	

Table S6: Assignment of the peak envelopes found in the ESI-MS spectrum of region **III**, shown in Fig. S10. Expected peak envelopes belonging to by-products (not observed) are indicated; their absence demonstrates the purity of the sample.

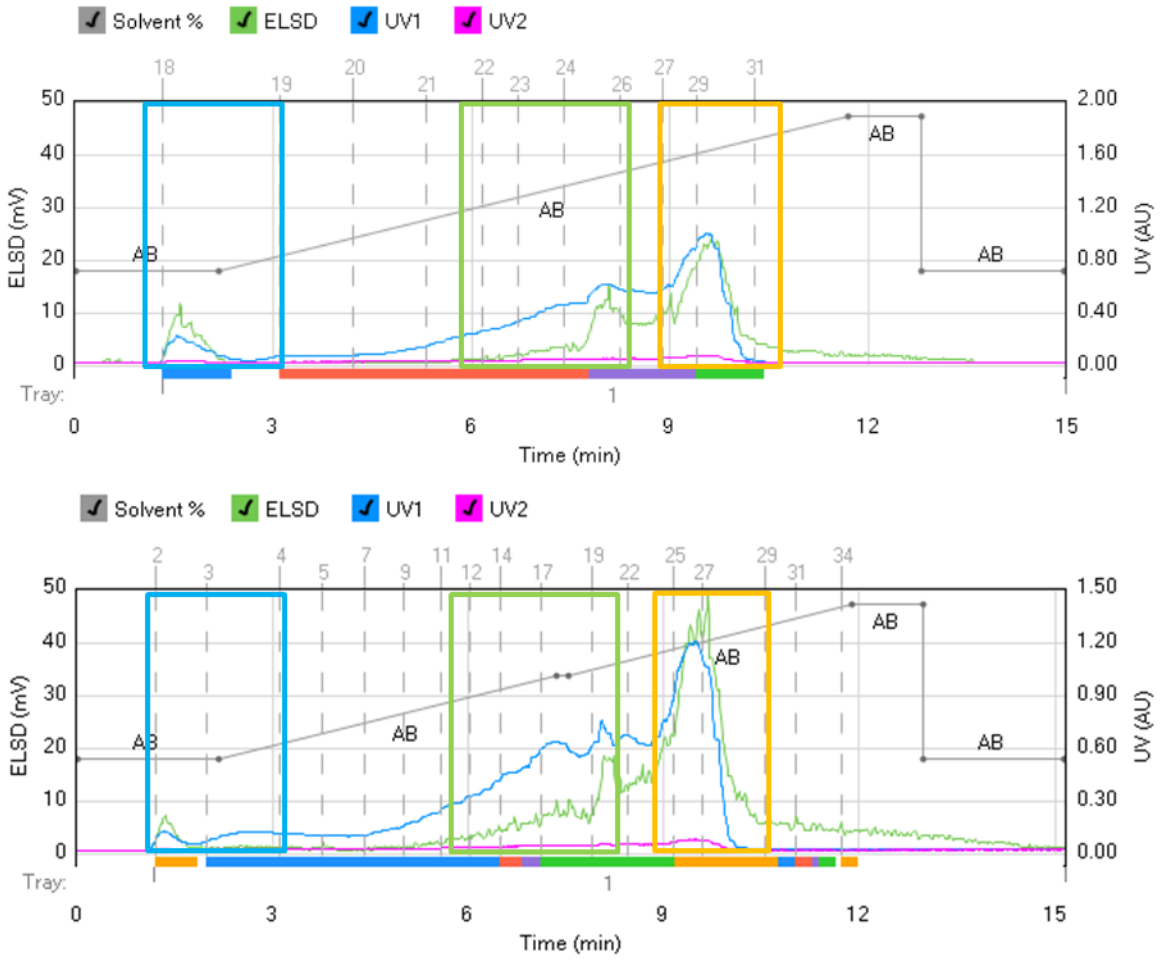


Fig. S11: Flash chromatography pattern and reproducibility. Color scheme: region **I** (blue box); region **II** (green box); region **III** (orange box); ELSD (green line); UV at λ = 254 nm (blue line); UV at λ = 350 nm (pink line).

Control compound (A): Anthracene Mn-Anderson $(C_{16}H_{36}N)_3[MnMo_6O_{24}(C_{19}H_{16}NO)_2]$:

A mixture of $(TBA)_4[\alpha\text{-}Mo_8O_{26}]$[6] (400 mg, 0.19 mmol), $Mn(OAc)_3{\cdot}2H_2O$ (74 mg, 0.28 mmol) and Anthracene-TRIS ligand (213 mg; 0.66 mmol) was refluxed in MeCN (20 mL) for 16 h. The resulting brown mixture was cooled down to room temperature and the precipitate removed by centrifugation to lead to a bright orange solution. The crude mixture was isolated by crystallization by Et_2O diffusion. After three days, orange crystals were formed, isolated and analyzed. Single crystals suitable for X-ray diffraction were grown from MeCN by slow Et_2O diffusion (square crystal, 3 days). **Yield:** 200 mg, 0.09 mmol, 36% based on Mo; **^{1}H NMR** (DMSO-d_6, 400 MHz): δ = 0.93 (m, 36H, CH_3 from TBA^+), 1.30 (m, 24H, CH_2 from TBA^+), 1.56 (m, 24H, CH_2 from TBA^+), 3.15 (m, 24H, CH_2 from TBA^+), 7.56 (m, 4H, 4CH), 7.84 (m, 4H, 2CH + 2NH), 8.12 (m, 6H, 6CH), 8.55 (s, 2H, 2CH), 8.63 (s, 2H, 2CH), 8.68 (s, 2H, 2CH), 62.0 - 67.0 ppm (s, br, $6CH_2$), **^{13}C DEPTQ NMR** (DMSO-d_6, 100 MHz): δ = 13.5 (CH_3), 19.3 (CH_2), 23.1 (CH_2), 57.5 (CH_2), 124.5 (CH), 125.7 (CH), 126.3 (CH), 127.6 (CH), 127.9 (CH), 128.0 (CH), 128.3 (CH), 128.7 (C), 129.1 (CH), 129.7 (C), 131.3 (C), 131.8 (C), 132.2 (C), 167.9 ppm (CO); **Elemental analysis:** Calc. for $C_{86}H_{140}MnMo_6N_5O_{26}{\cdot}CH_3CN$ (2331.68 g.mol^{-1}): C, 45.33; H, 6.18; N, 3.60; Found: C, 45.22; H, 6.17; N, 3.81.

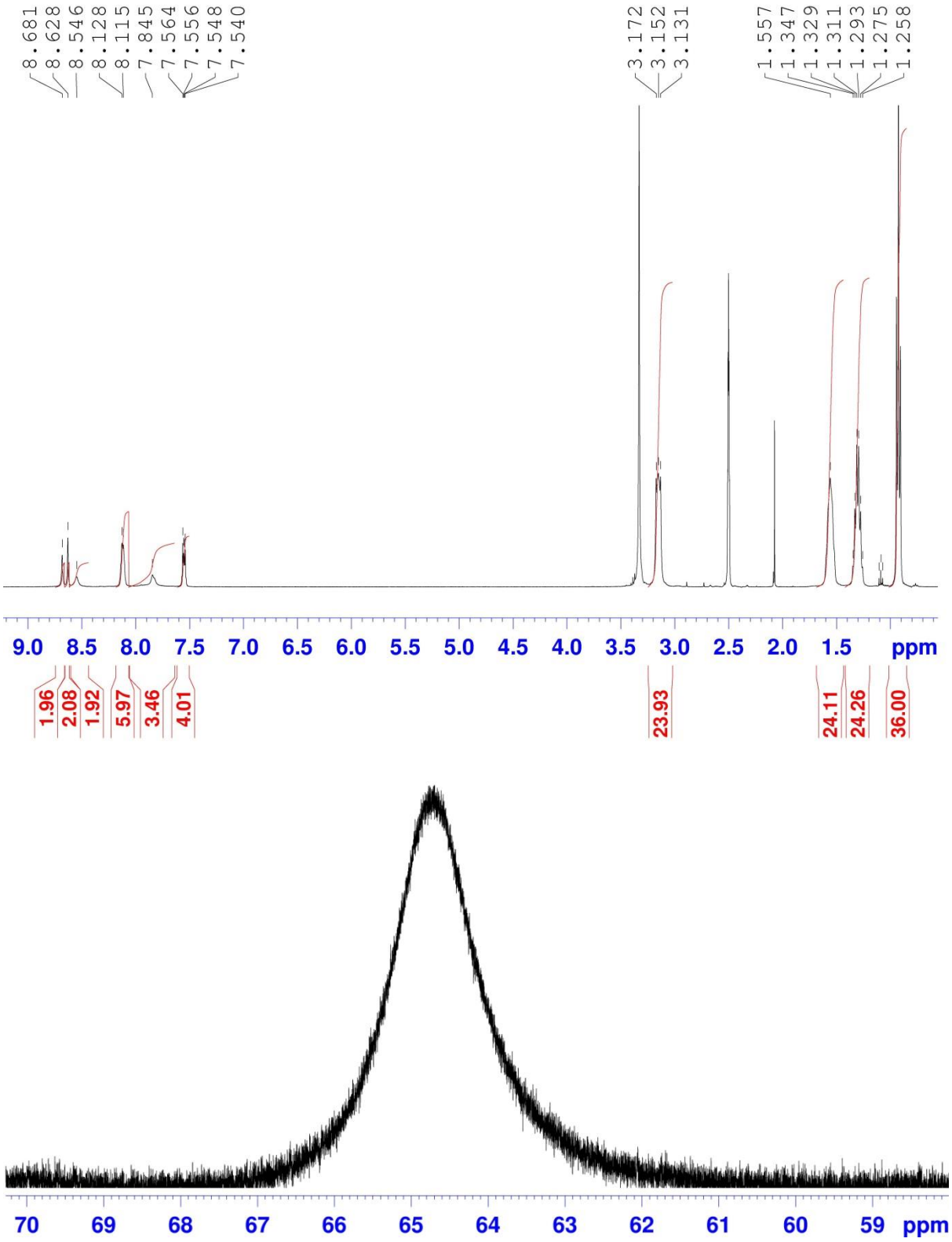


Fig. S12: ^{1}H NMR of the Anthracene Mn-Anderson (**A**) in DMSO-d_6 at 400 MHz and peak at 60 ppm

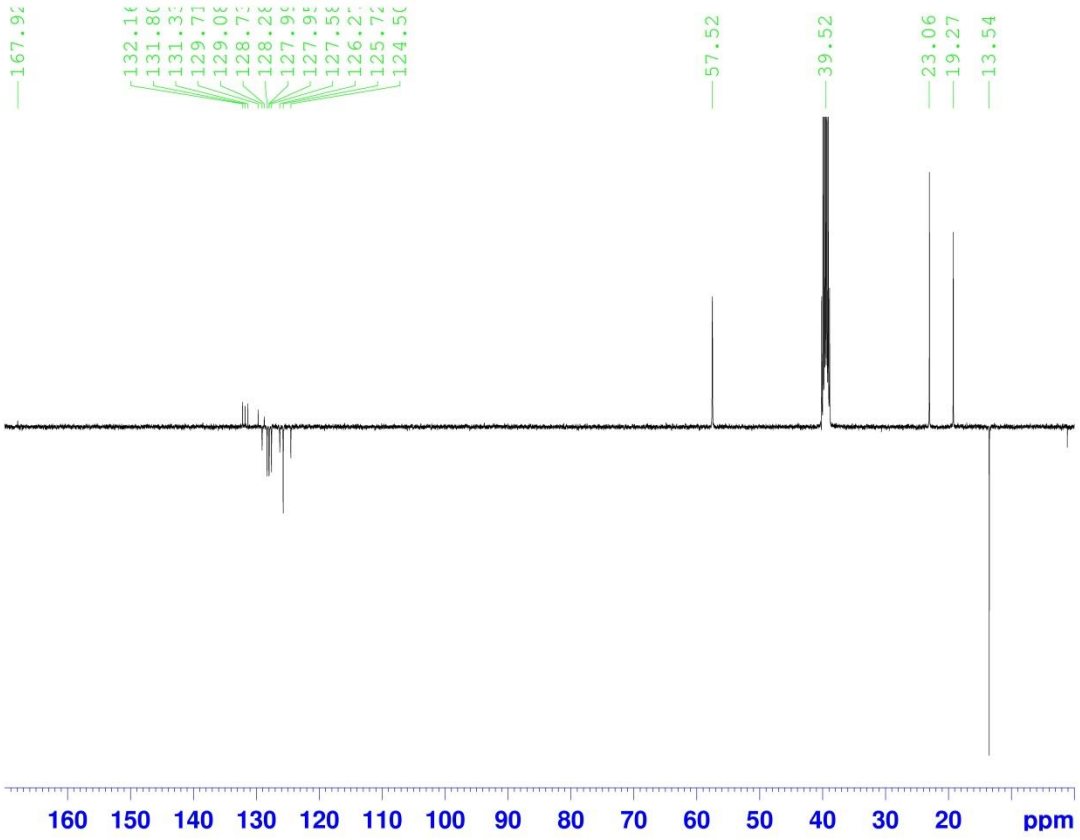


Fig. S13: ^{13}C DEPTQ NMR of the Anthracene Mn-Anderson (**A**) in DMSO-d_6 at 100 MHz

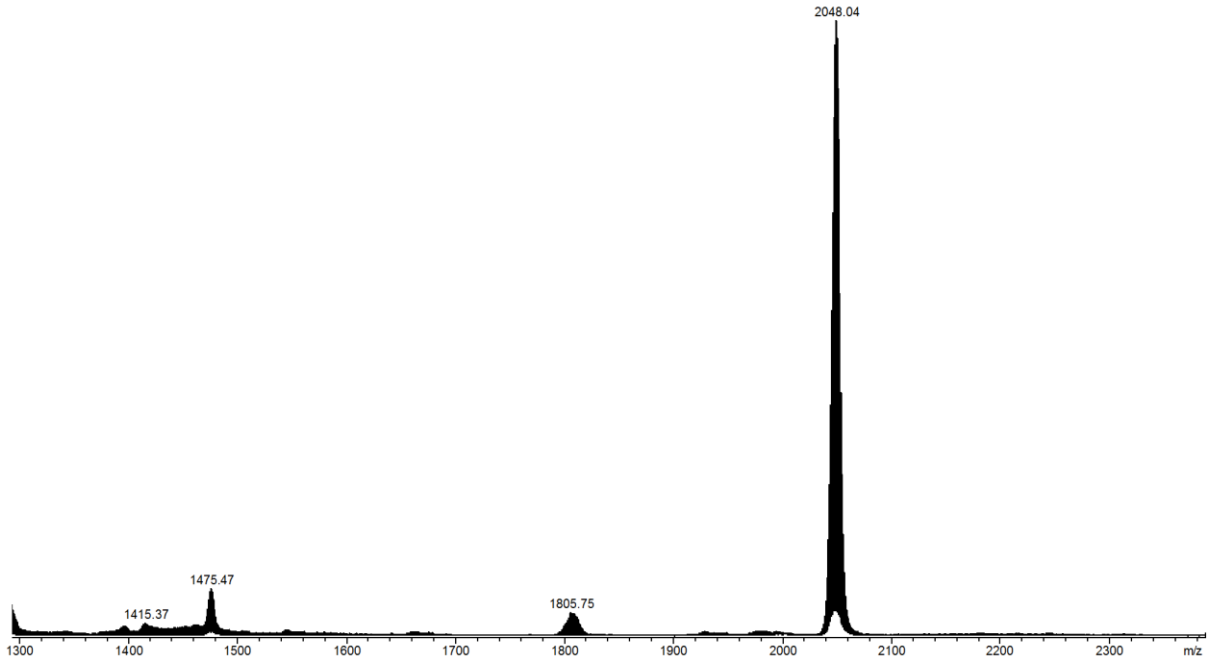
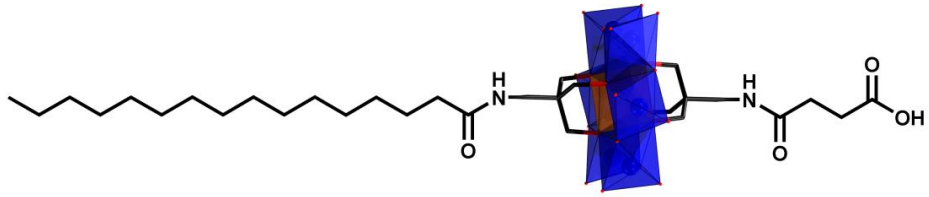


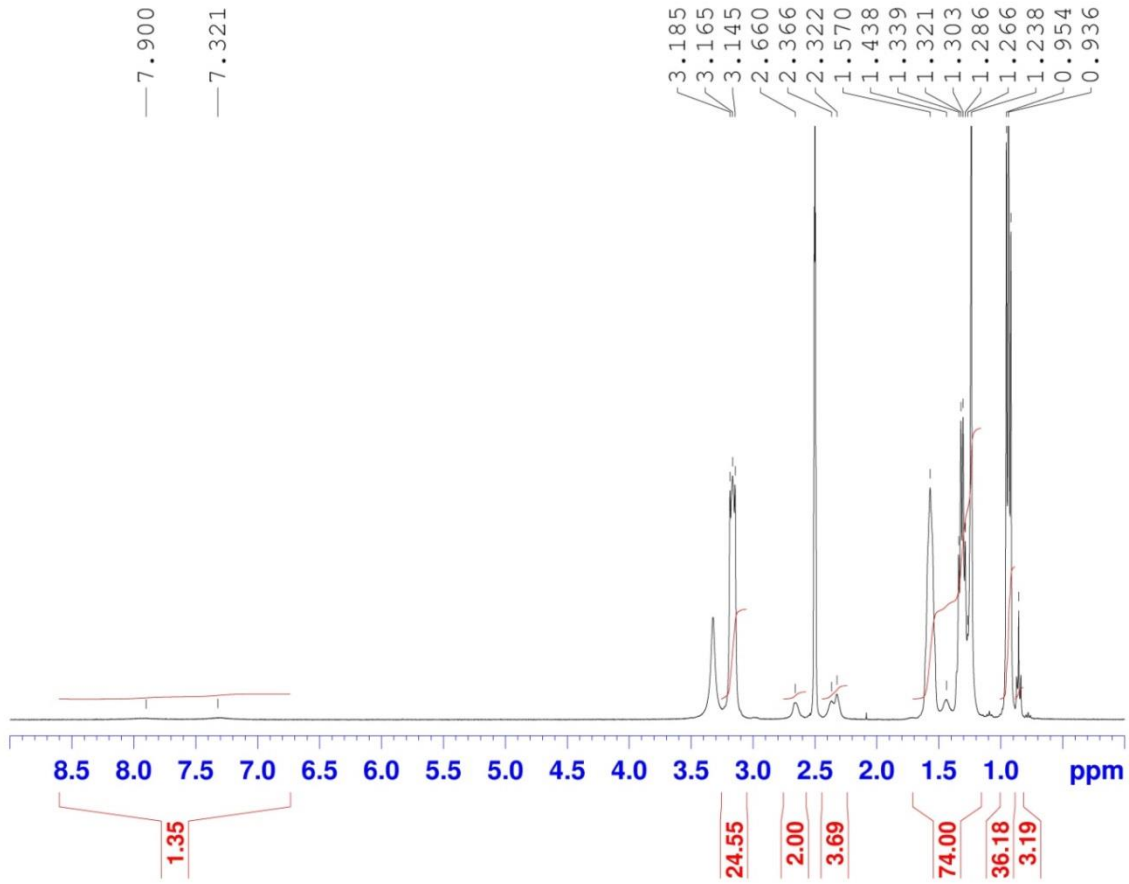
Fig. S14: ESI-MS spectra of pure Anthracene Mn-Anderson (**A**). See Table S7 for peak assignments.

Formula assigned	z	m/z calculated	m/z observed
$[MnMo_6O_{24}(C_{19}H_{16}NO)_2](C_{16}H_{36}N)_1H$	-1	1806.79	1805.75
$[MnMo_6O_{24}(C_{19}H_{16}NO)_2](C_{16}H_{36}N)_2$	-1	2048.07	2048.04

Table S7: Assignment of the peak envelopes found in the ESI-MS spectrum of the Anthracene Mn-Anderson (**A**), shown in Fig. S14.

Compound 2 – Palmitic-TRIS/Succinic-Acid-TRIS Mn-Anderson Compound $(C_{16}H_{36}N)_3[MnMo_6O_{24}(C_{20}H_{38}NO)(C_8H_{12}NO_3)]$





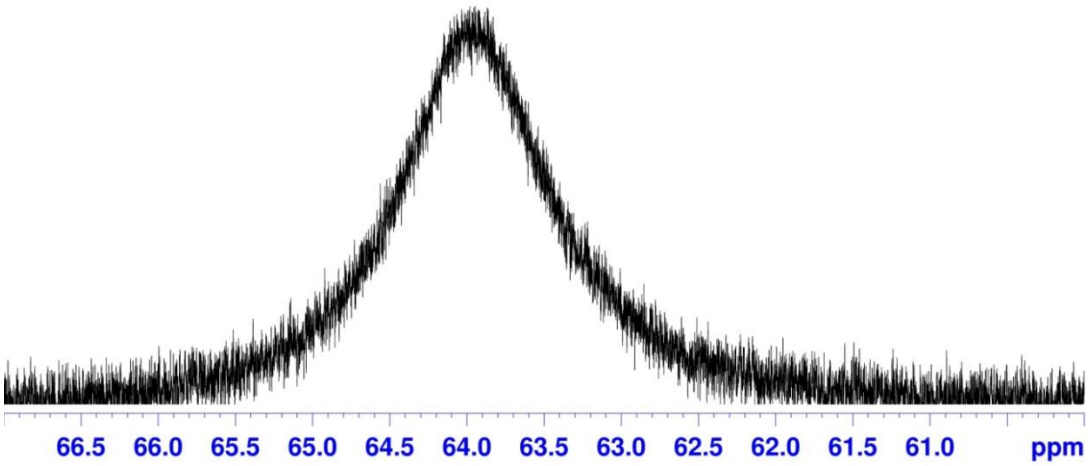


Fig. S15: ^{1}H NMR of the Palmitic-TRIS/Succinic-Acid-TRIS Mn-Anderson (**2**) in DMSO-d_6 at 400 MHz and peak at 60 ppm

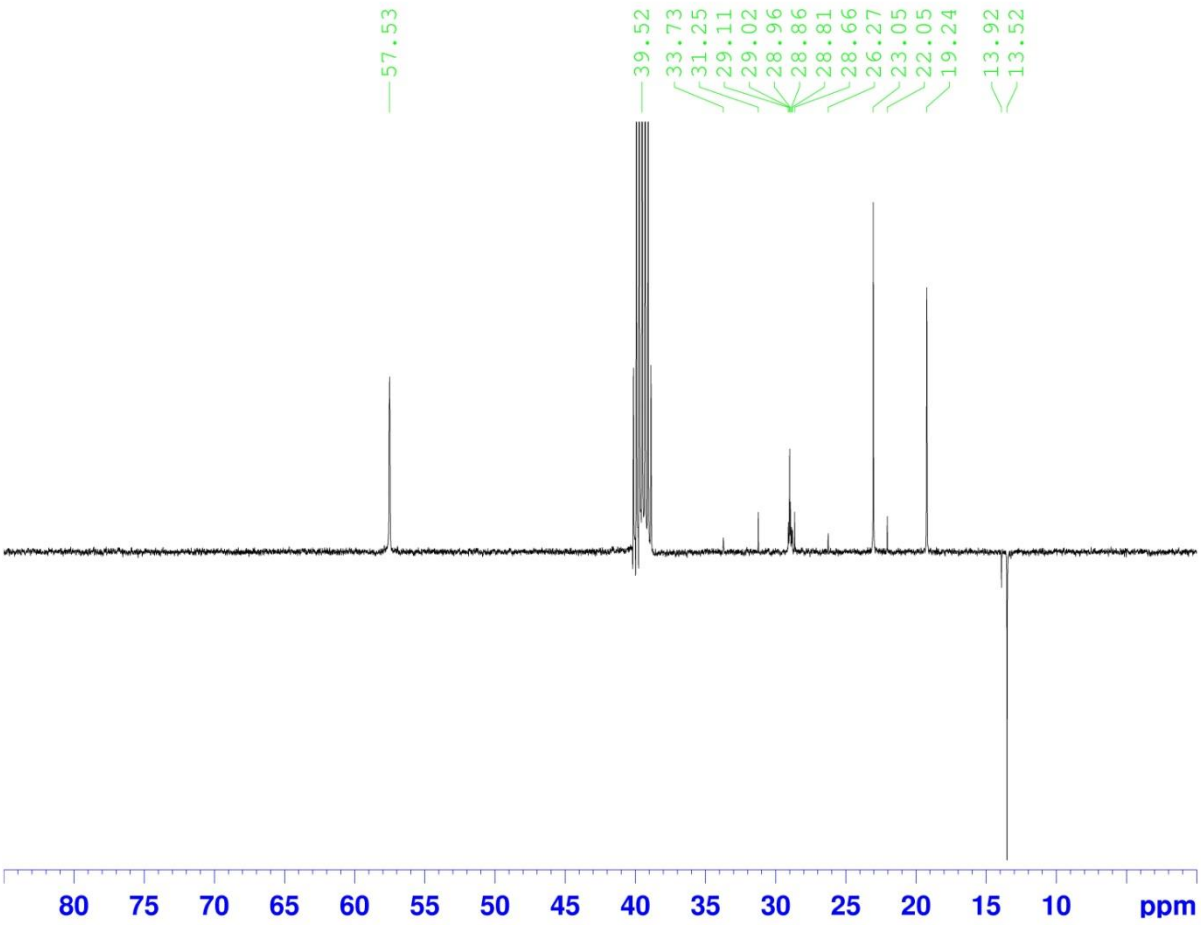


Fig. S16: ^{13}C DEPTQ NMR of the Palmitic-TRIS/Succinic-Acid-TRIS Mn-Anderson (**2**) in DMSO-d_6 at 100 MHz

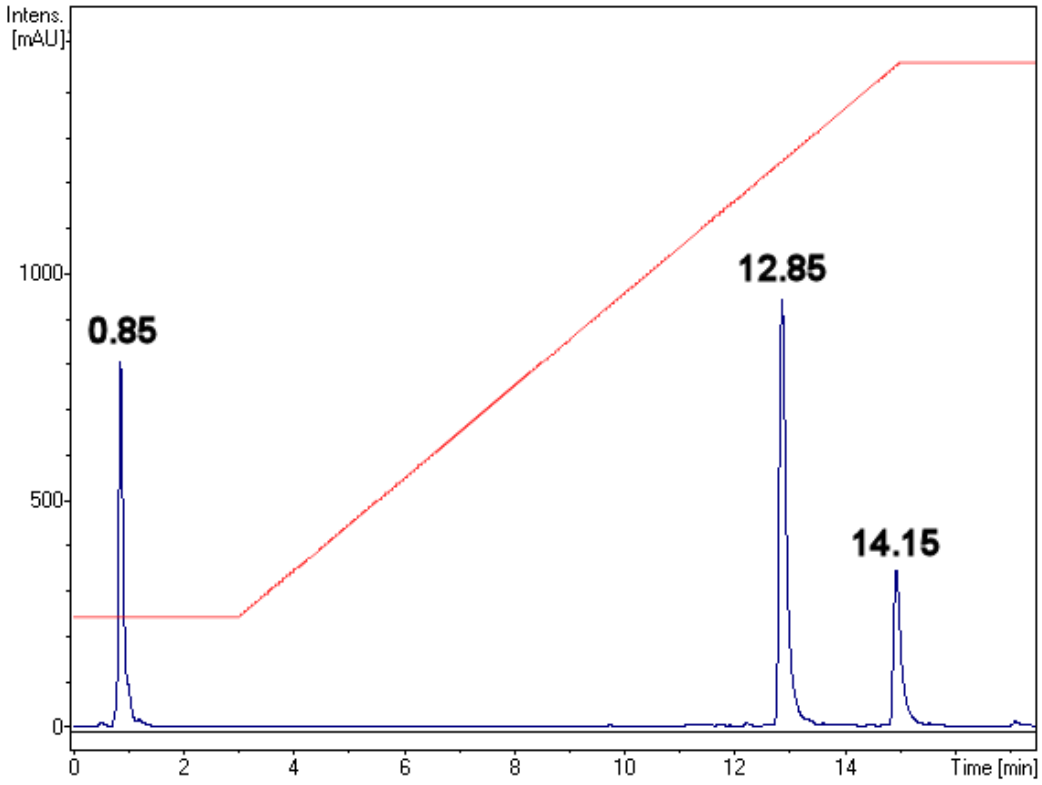


Fig. S17: RP-HPLC of the crude material (mixture of **2** with the two symmetric by-products: Succinic-Acid Mn-Anderson and Palmitic Mn-Anderson compounds)

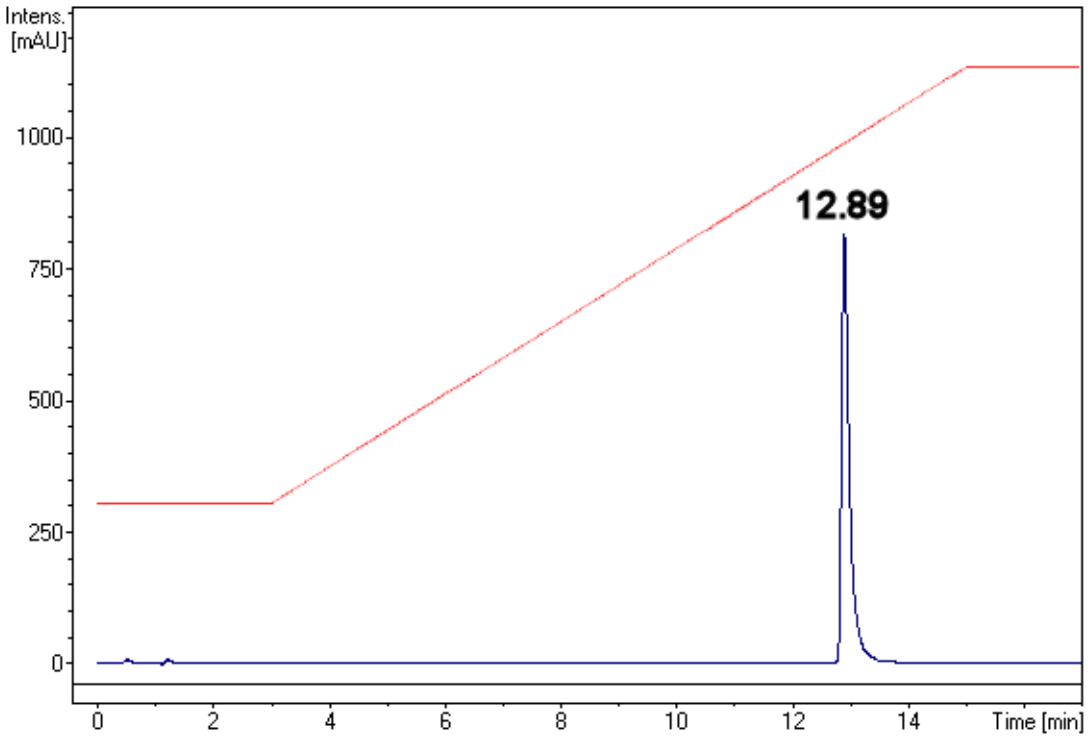


Fig. S18: RP-HPLC of pure compound **2**

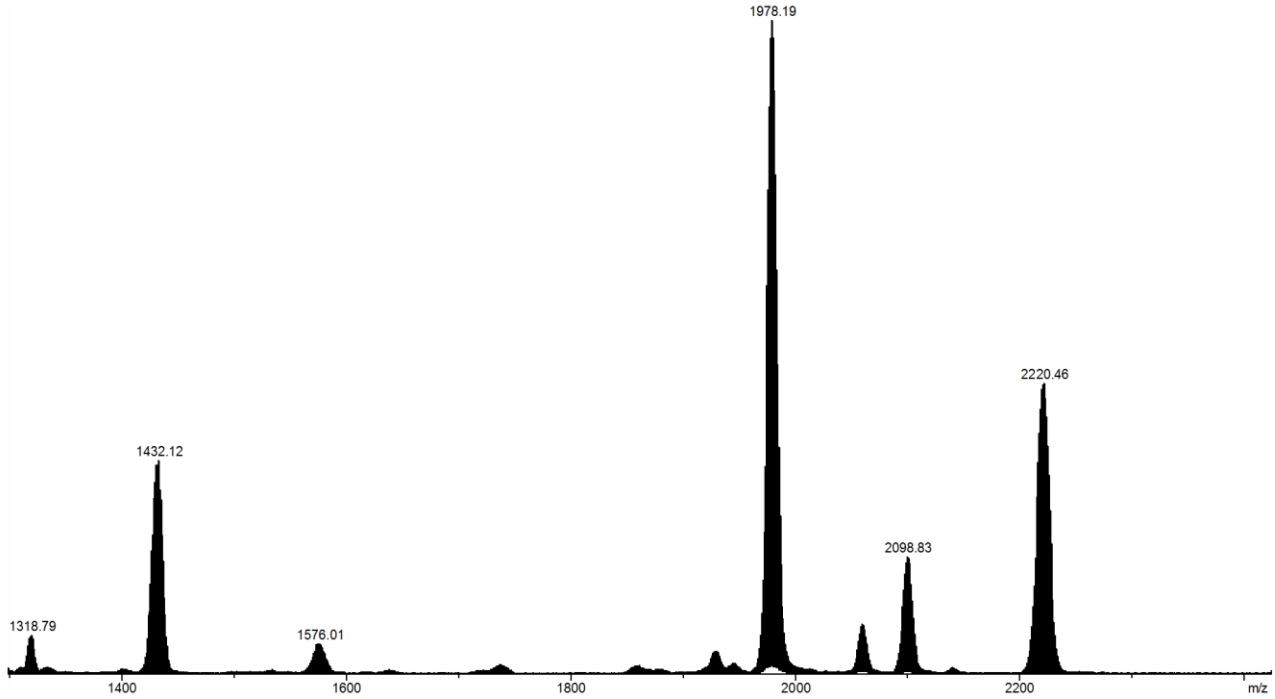


Fig. S19: ESI-MS spectra of pure compound **2**. See Table S8 for peak assignments.

Formula assigned	**z**	**m/z calculated**	**m/z observed**
$[MnMo_6O_{24}(C_{20}H_{38}NO)(C_8H_{12}NO_3)](C_{16}H_{36}N)_2$	-1	1978.20	1978.19
$[MnMo_6O_{24}(C_{20}H_{38}NO)(C_8H_{12}NO_3)MnMo_6O_{24}(C_{20}H_{38}NO)(C_8H_{11}NO_3)](C_{16}H_{36}N)_5$	-2	2098.84	2098.83
$[MnMo_6O_{24}(C_{20}H_{38}NO)(C_8H_{11}NO_3)](C_{16}H_{36}N)_3$	-1	2220.48	2220.46
Potential by-products (not observed)	**z**	**m/z calculated**	
$[MnMo_6O_{24}(C_4H_8N)_2](C_{16}H_{36}N)_1H$	-1	1397.68	
$[MnMo_6O_{24}(C_8H_{12}NO_3)_2](C_{16}H_{36}N)_1H$	-1	1598.71	
$[MnMo_6O_{24}(C_4H_8N)_2](C_{16}H_{36}N)_2$	-1	1639.95	
$[MnMo_6O_{24}(C_8H_{12}NO_3)_2](C_{16}H_{36}N)_2$	-1	1839.99	
$[MnMo_6O_{24}(C_{20}H_{38}NO)_2](C_{16}H_{36}N)_1H$	-1	1875.14	
$[MnMo_6O_{24}(C_{20}H_{38}NO)_2](C_{16}H_{36}N)_2$	-1	2117.41	

Table S8: Assignment of the peak envelopes found in the ESI-MS spectrum of compound **2**, shown in Fig. S19. A deprotonation of the acid carboxylic function on the ligand is observed

in some fragments (highlighted in red). Expected peak envelopes belonging to by-products (not observed) are indicated; their absence demonstrates the purity of the sample.

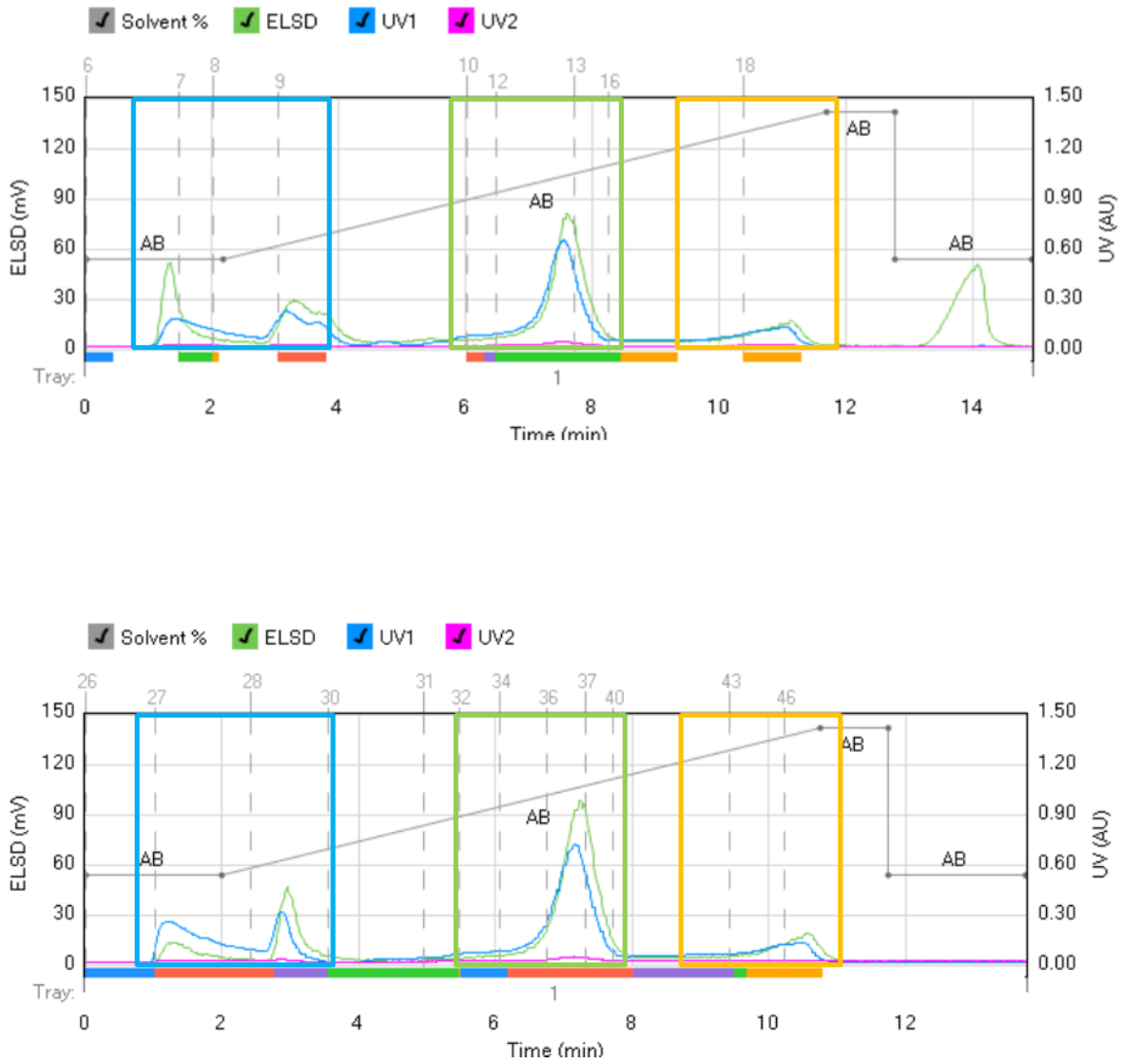


Fig. S20: Flash chromatography pattern and reproducibility. Color scheme: region **I** (blue box); region **II** (green box); region **III** (orange box); ELSD (green line); UV at λ = 254 nm (blue line); UV at λ = 350 nm (pink line).

To study the number of equivalents needed to form **2** as the major product, the reaction was investigated briefly on a small scale (TRIS Mn-Anderson (100 mg, 0.05 mmol)) using several different ratios of the anhydrides. The concentrations of the reagents were also studied by increasing or decreasing the solvent volume (DMF).

The resulting reaction mixtures were analysed *via* ESI-MS (examples of the resulting spectra are given in fig. S21). The m/z fragment observed at 1737.00 was assigned to a minus one charged fragment of the asymmetric compound ($[MnMo_6O_{24}(C_{20}H_{38}NO)(C_8H_{12}O_3N)](C_{16}H_{36}N)H$; calculated: 1736.92) while the peak envelope observed at 1875.22 was assigned as a fragment of one of the symmetric products ($[MnMo_6O_{24}(C_{20}H_{38}NO)_2](C_{16}H_{36}N)H$; calculated 1875.13). While not a formally quantitative technique, the relative intensity of the fragments observed closely mirrores the relative proportion of the compounds in solution.

A more indepth study of the reaction conditions may have allowed for better yields; but this was beyond the scope of the work presented herein.

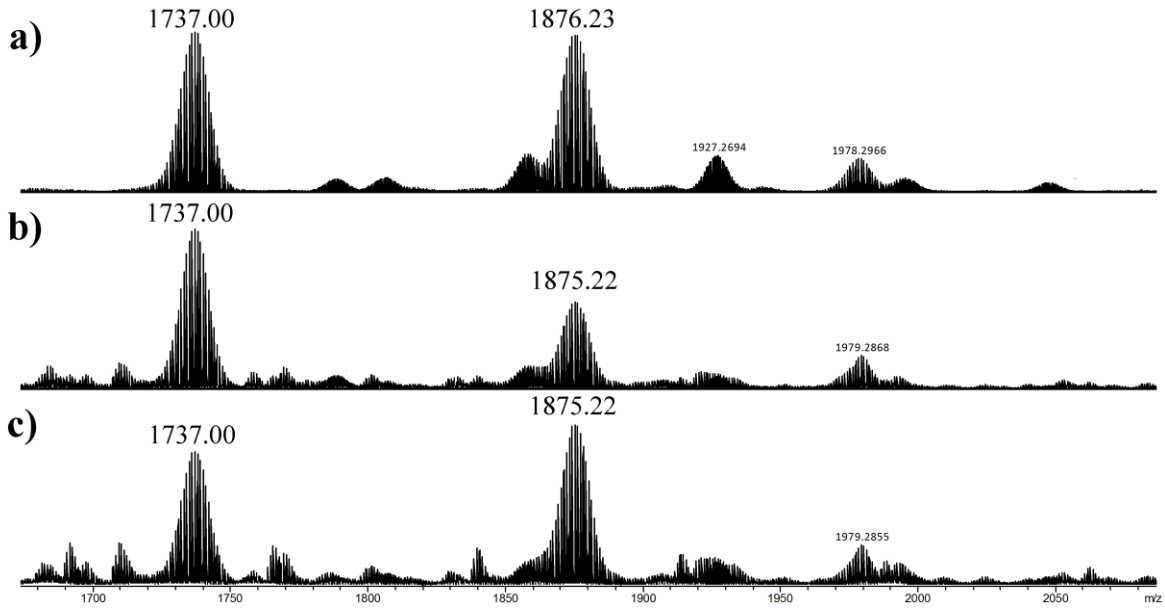
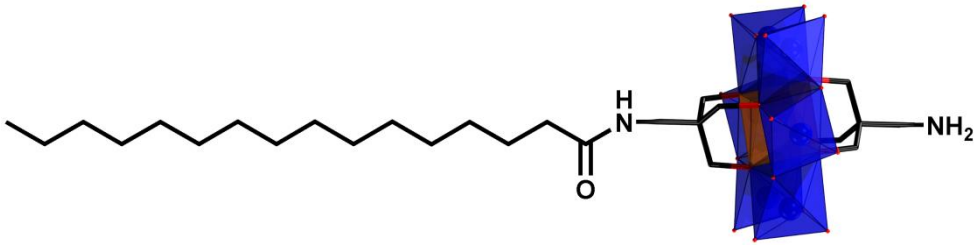


Fig. S21: Examples of ESI-MS spectra obtained during the study. Reaction conditions: (a) 2 equiv. of succinic anhydride and 2 equiv. of palmitic anhydride in 1.6 mL of DMF; (b) 4 equiv. of succinic anhydride and 2 equiv. of palmitic anhydride in 1.6 mL of DMF; (c) 4 equiv. of succinic anhydride and 2 equiv. of palmitic anhydride in 3.2 mL of DMF.

Compound 3 – Palmitic-TRIS/TRIS Mn-Anderson Compound $(C_{16}H_{36}N)_3[MnMo_6O_{24}(C_{20}H_{38}NO)(C_4H_8N)]$



Synthesis of compound **3** was adapted from a reported synthesis.[7]

Palmitoyl chloride (63 μL, 0.21 mmol, 1.3 equiv.) was slowly added to a solution of TRIS Mn-Anderson (300 mg, 0.16 mmol)[8] and TEA (90 μL; 0.64 mmol) in dry MeCN (5 mL) and the resulting solution refluxed overnight. The bright orange solution was then cooled to room temperature and, without any purification, celite (1.5 g) was added and the solvent evaporated under vacuum to obtain a powder ('dry loading'). The crude material adsorbed on celite was purified by flash chromatography (see instrumentation for further details). The pure fractions (purity checked by RP-HPLC, retention time of interest: 12.84 min) were combined and a large excess of TBA bromide (0.5 g; 1.55 mmol) was added to the resulting solution. The MeCN was evaporated under vacuum leading to the formation of an orange precipitate. This precipitate was isolated from the remaining acetate buffer solution by centrifugation and then dissolved in MeCN. The resulting orange solution was centrifuged to remove any insoluble material and left for crystallization with Et_2O diffusion. Within 3 days crystal of compound **3** were formed, dried and analyzed. **Yield:** 100 mg, 0.05 mmol, 32%; **^{1}H NMR** (DMSO-d_6, 400 MHz): δ = 0.85 (m, 3H, CH_3), 0.93 (m, 36H, CH_3 from TBA^+), 1.15 - 1.70 (m, 74H, 13 CH_2 + 2 x CH_2 from TBA^+), 2.36 (m, 2H, CH_2), 3.16 (m, 24H, CH_2 from TBA^+), 3.45 - 3.80 (s, br, 2H, NH_2), 7.00 - 7.80 (s, br, 1H, NH), 61.0 - 66.0 ppm (s, br, 6CH_2); **^{13}C DEPTQ NMR** (DMSO-d_6, 100 MHz): δ = 13.6 (CH_3), 14.0 (CH_3), 19.3 (CH_2), 22.1 (CH_2), 23.1 (CH_2), 26.3 (CH_2), 28.7 (CH_2), 28.9 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 31.3 (CH_2), 57.5 (CH_2); **Elemental analysis:** Calc. for $C_{72}H_{154}MnMo_6N_5O_{25}$ (2120.59 g.mol^{-1}): C, 40.78; H, 7.32; N, 3.30; Found: C, 40.61; H, 7.40; N, 3.37.

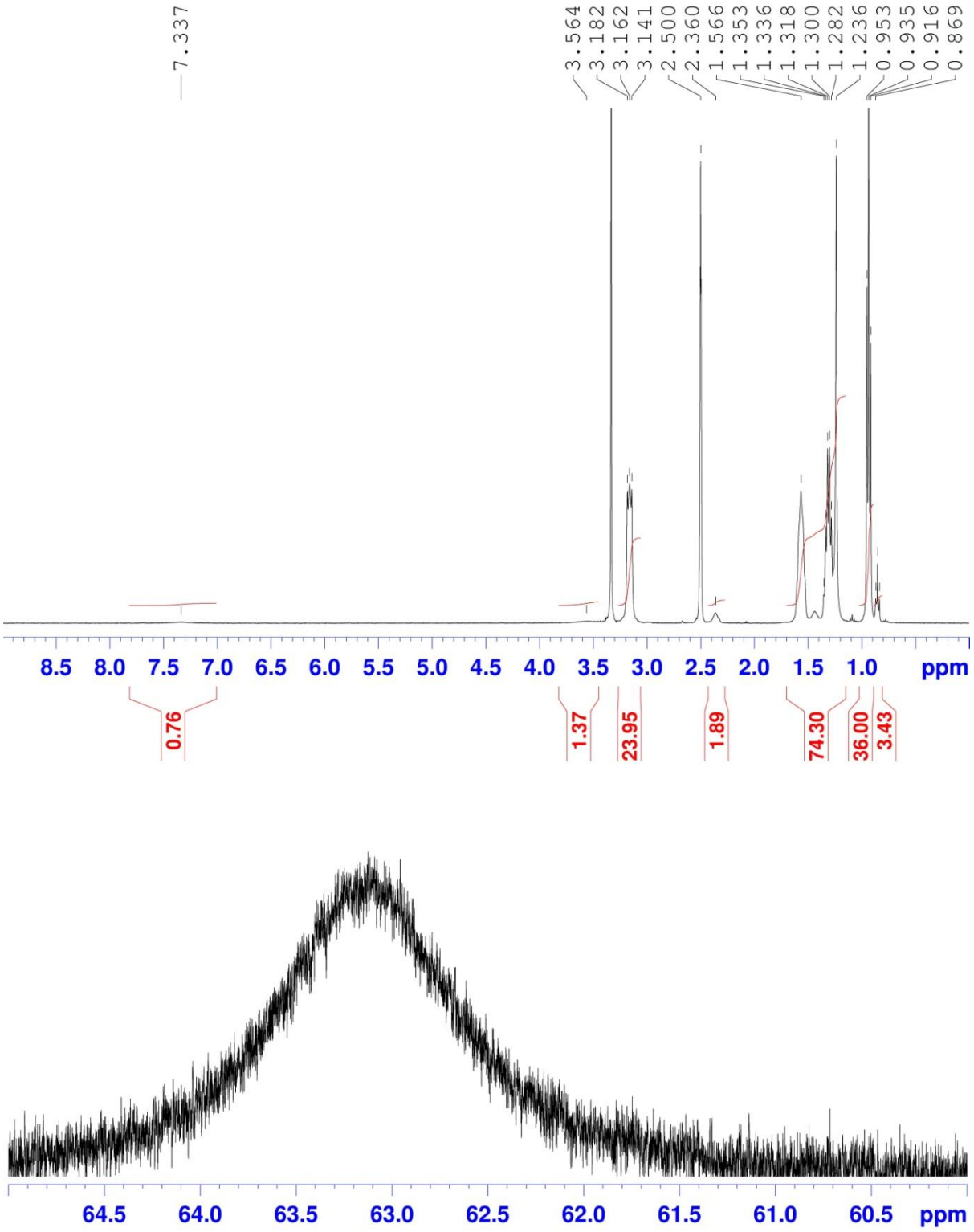


Fig. S22: ^{1}H NMR of the Palmitic-TRIS/ TRIS Mn-Anderson (**3**) in DMSO-d_6 at 400 MHz

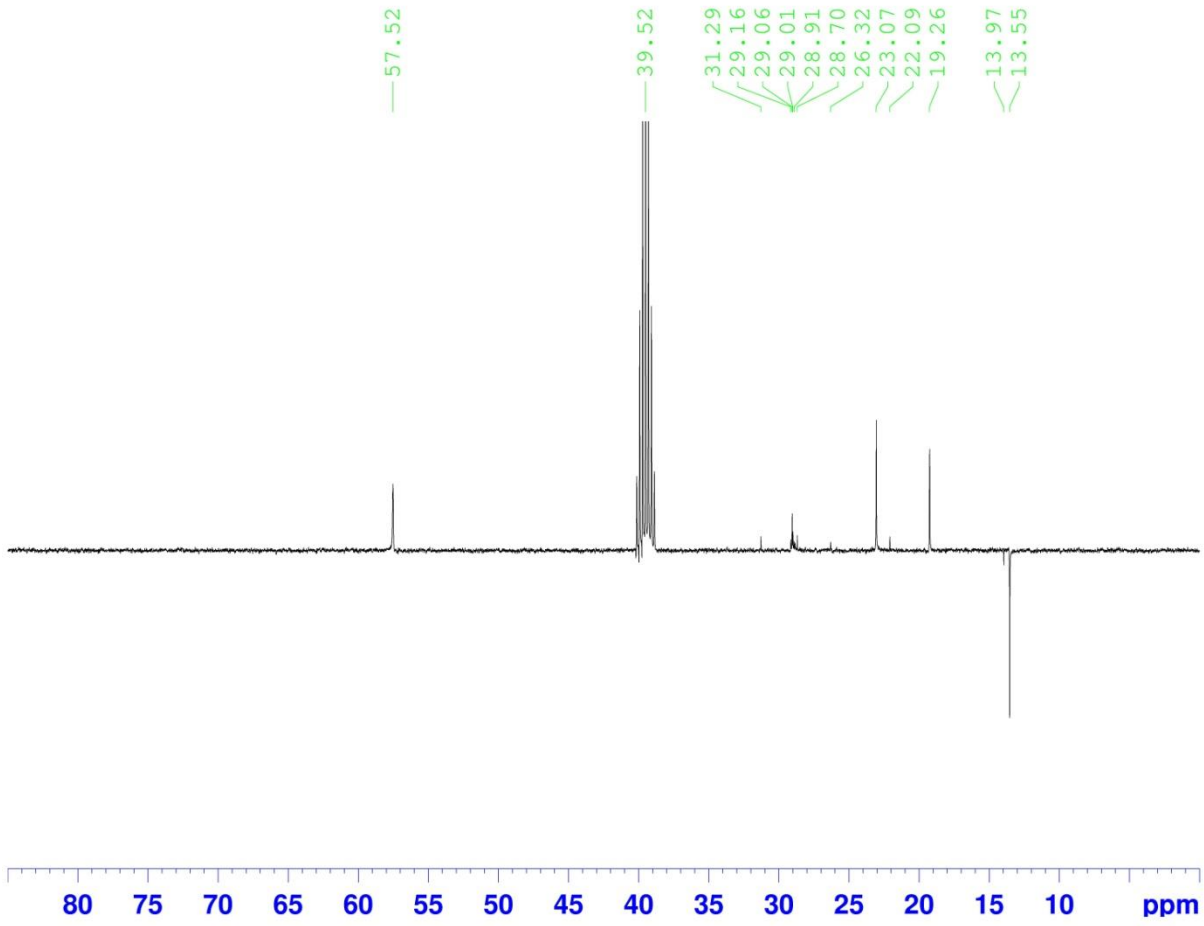


Fig. S23: ^{13}C DEPTQ NMR of the Palmitic-TRIS/ TRIS Mn-Anderson (**3**) in DMSO-d_6 at 100 MHz

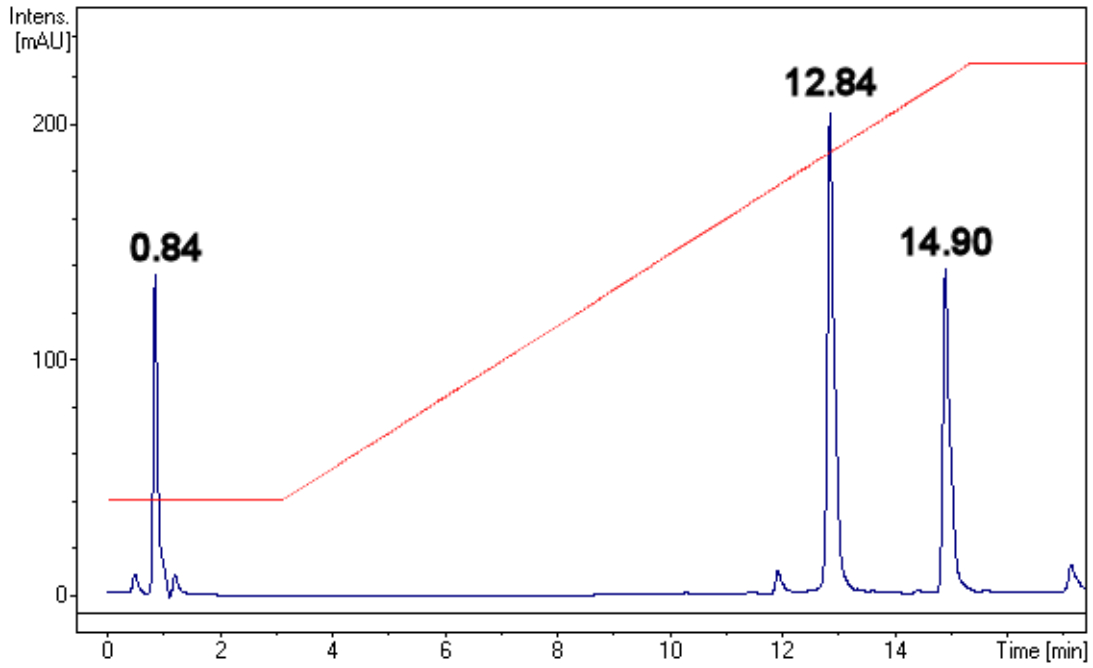


Fig. S24: RP-HPLC of the crude material (mixture of **3** with the two symmetric by-products: TRIS Mn-Anderson and palmitic Mn-Anderson compounds)

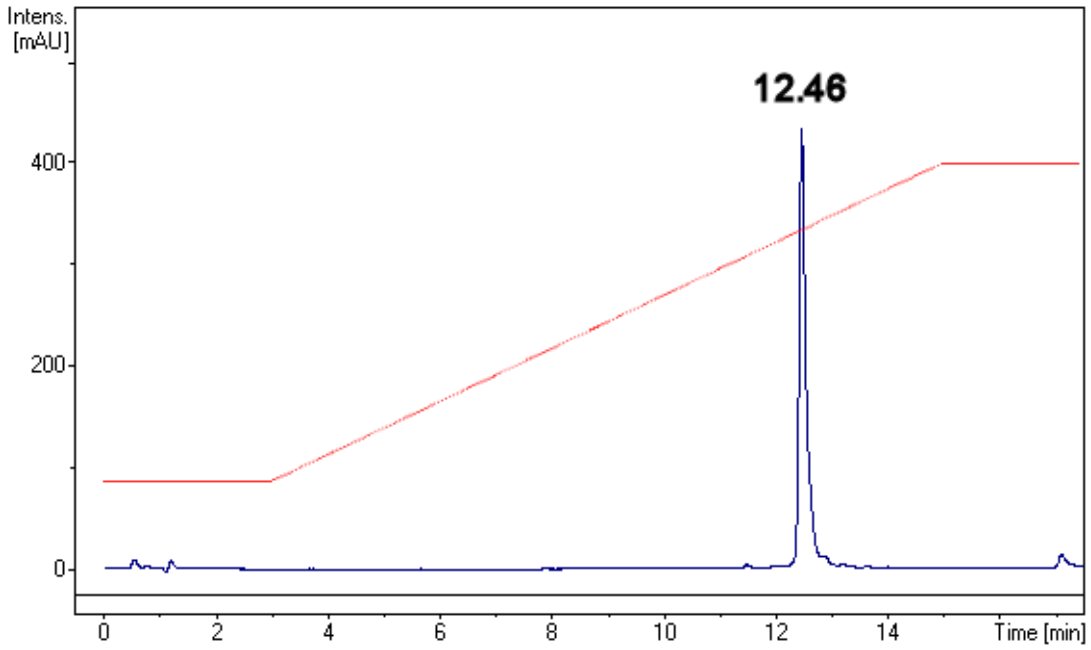


Fig. S25: RP-HPLC of pure compound **3**

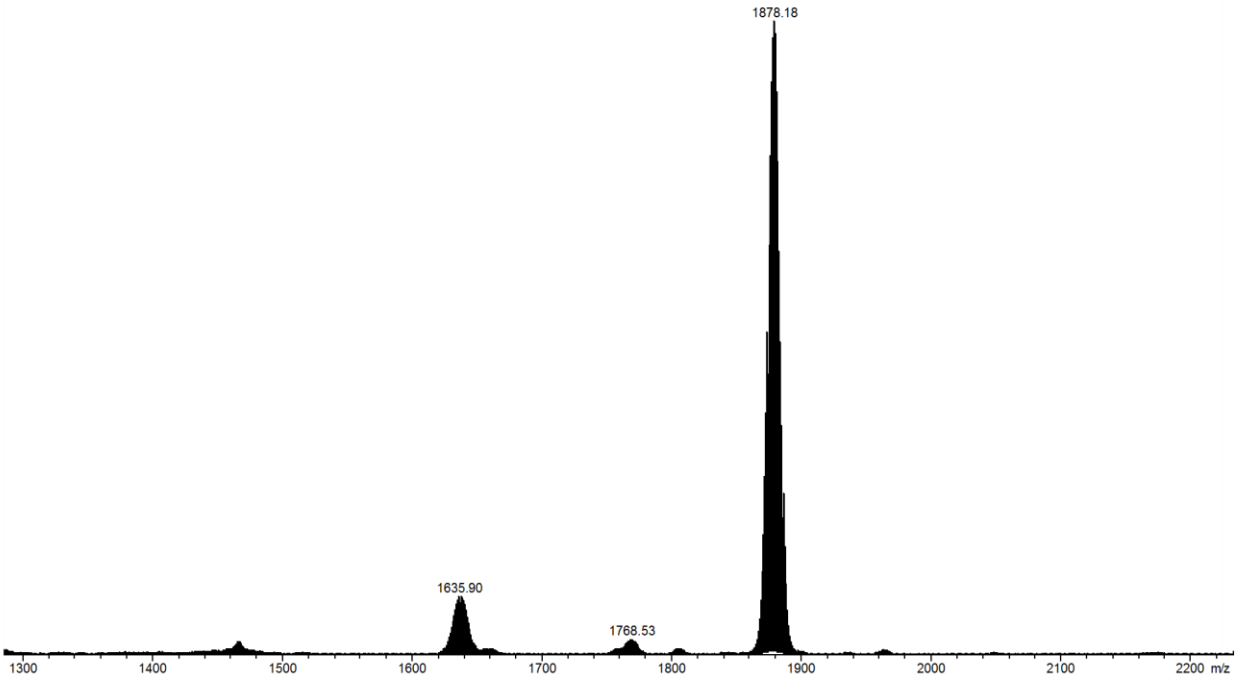


Fig. S26: ESI-MS spectra of pure compound **3**. See Table S9 for peak assignments.

Formula assigned	**z**	**m/z calculated**	**m/z observed**
$[MnMo_6O_{24}(C_{20}H_{38}NO)(C_4H_8N)](C_{16}H_{36}N)_1H$	-1	1636.90	1635.90
$[MnMo_6O_{24}(C_{20}H_{38}NO)(C_4H_8N)]_2(C_{16}H_{36}N)_3Na$	-2	1768.54	1768.53
$[MnMo_6O_{24}(C_{20}H_{38}NO)(C_4H_8N)](C_{16}H_{36}N)_2$	-1	1878.18	1878.18
Potential by-products (not observed)	**z**	**m/z calculated**	
$[MnMo_6O_{24}(C_4H_8N)_2](C_{16}H_{36}N)_1H$	-1	1397.68	
$[MnMo_6O_{24}(C_4H_8N)_2](C_{16}H_{36}N)_2$	-1	1639.95	
$[MnMo_6O_{24}(C_{20}H_{38}NO)_2](C_{16}H_{36}N)_1H$	-1	1875.14	
$[MnMo_6O_{24}(C_{20}H_{38}NO)_2](C_{16}H_{36}N)_2$	-1	2117.41	

Table S9: Assignment of the peak envelopes found in the ESI-MS spectrum of compound **3**, shown in Fig. S25. Expected peak envelopes belonging to by-products (not observed) are indicated; their absence demonstrates the purity of the sample.

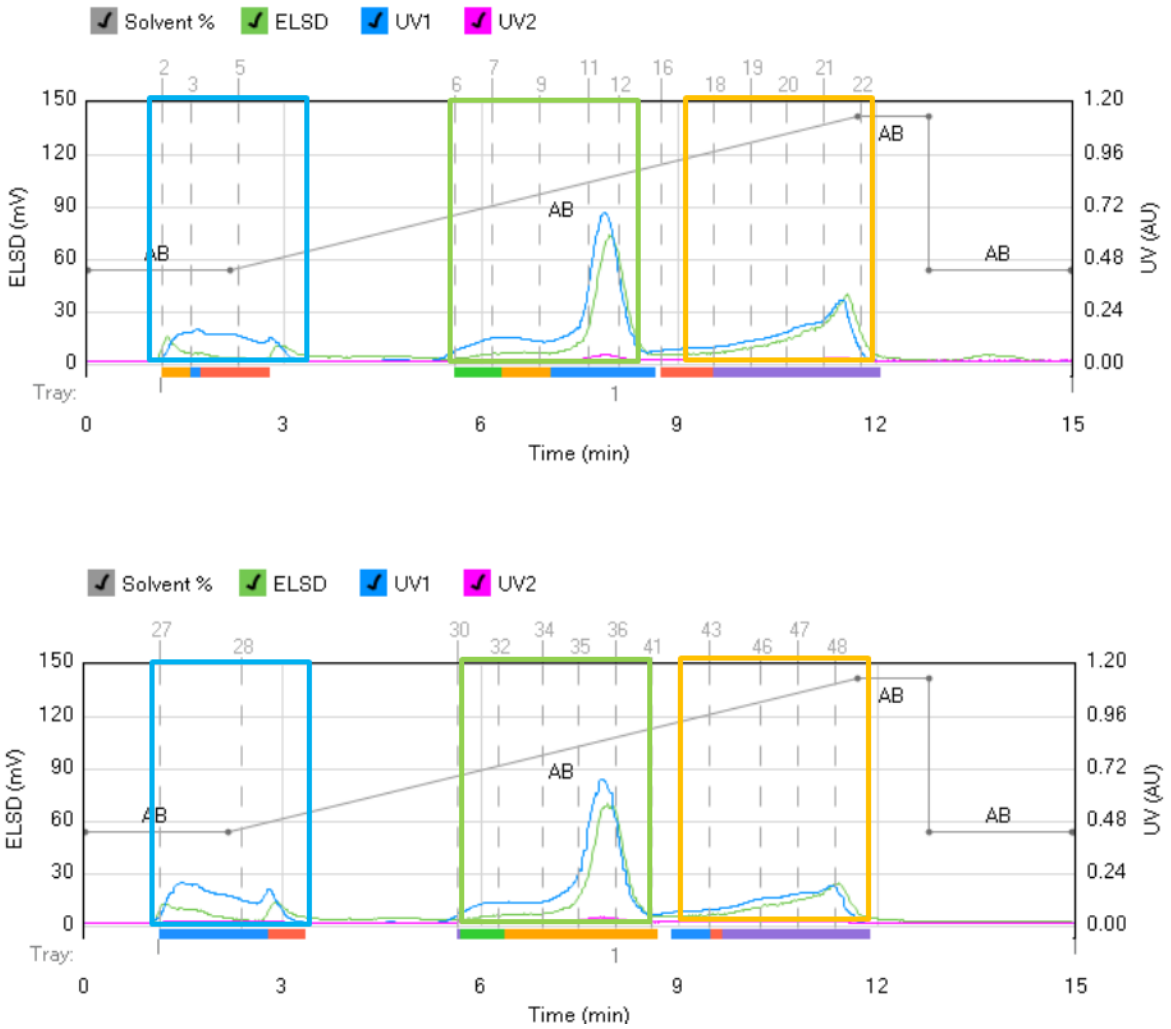
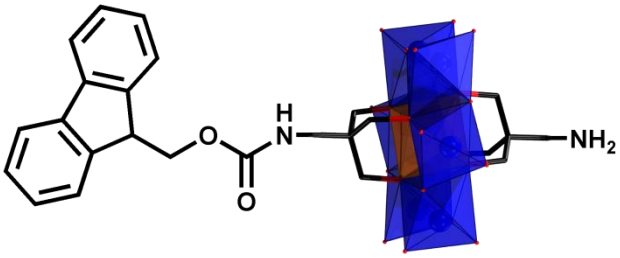
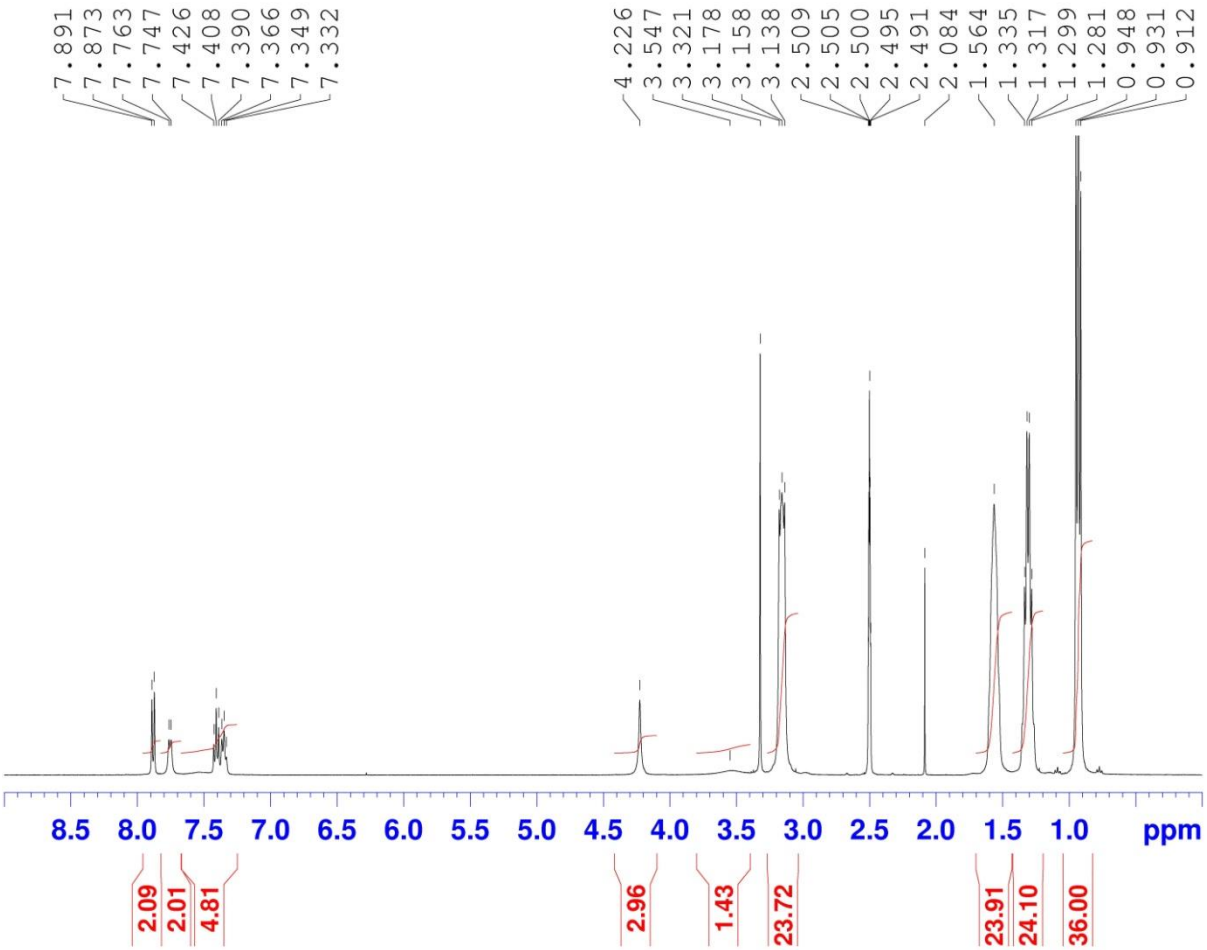


Fig. S27: Flash chromatography pattern and reproducibility. Color scheme: region **I** (blue box); region **II** (green box); region **III** (orange box); ELSD (green line); UV at λ = 254 nm (blue line); UV at λ = 350 nm (pink line).

Compound 4 – Fmoc-TRIS/TRIS Mn-Anderson Compound

$(C_{16}H_{36}N)_3[MnMo_6O_{24}(C_{19}H_{18}NO_2)(C_4H_8N)]$





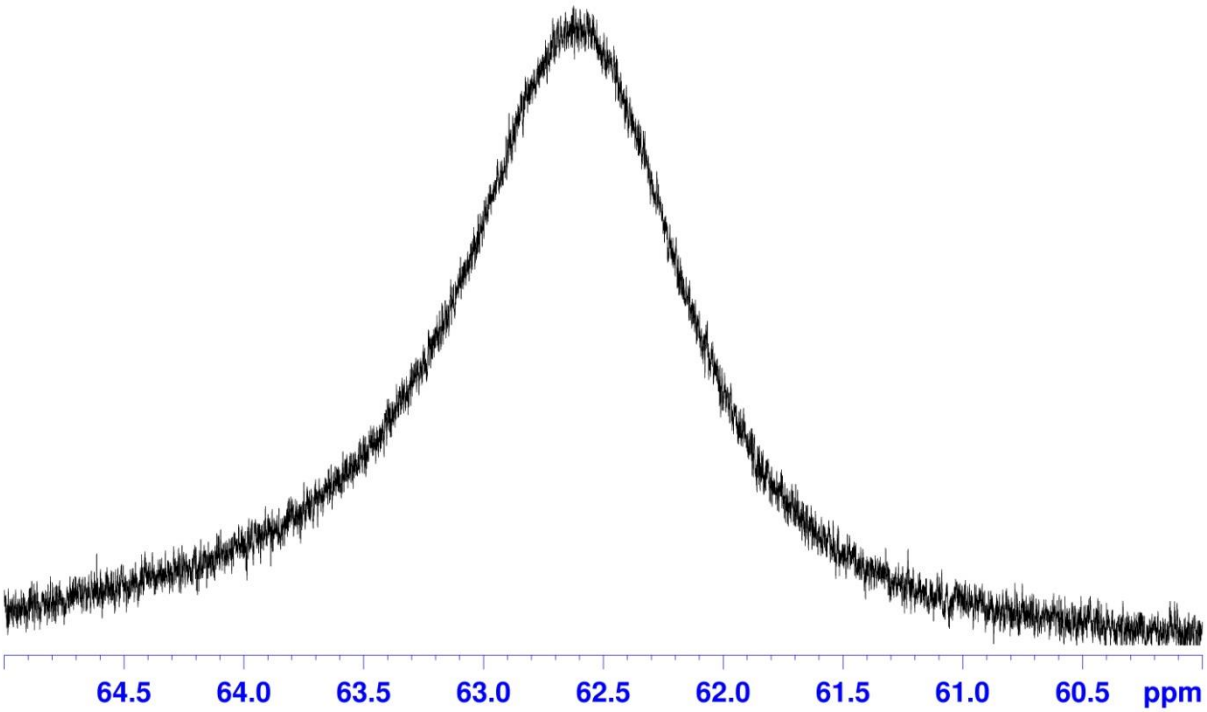


Fig. S28: ^{1}H NMR of the Fmoc-TRIS/TRIS Mn-Anderson (**4**) in DMSO-d_6 at 400 MHz

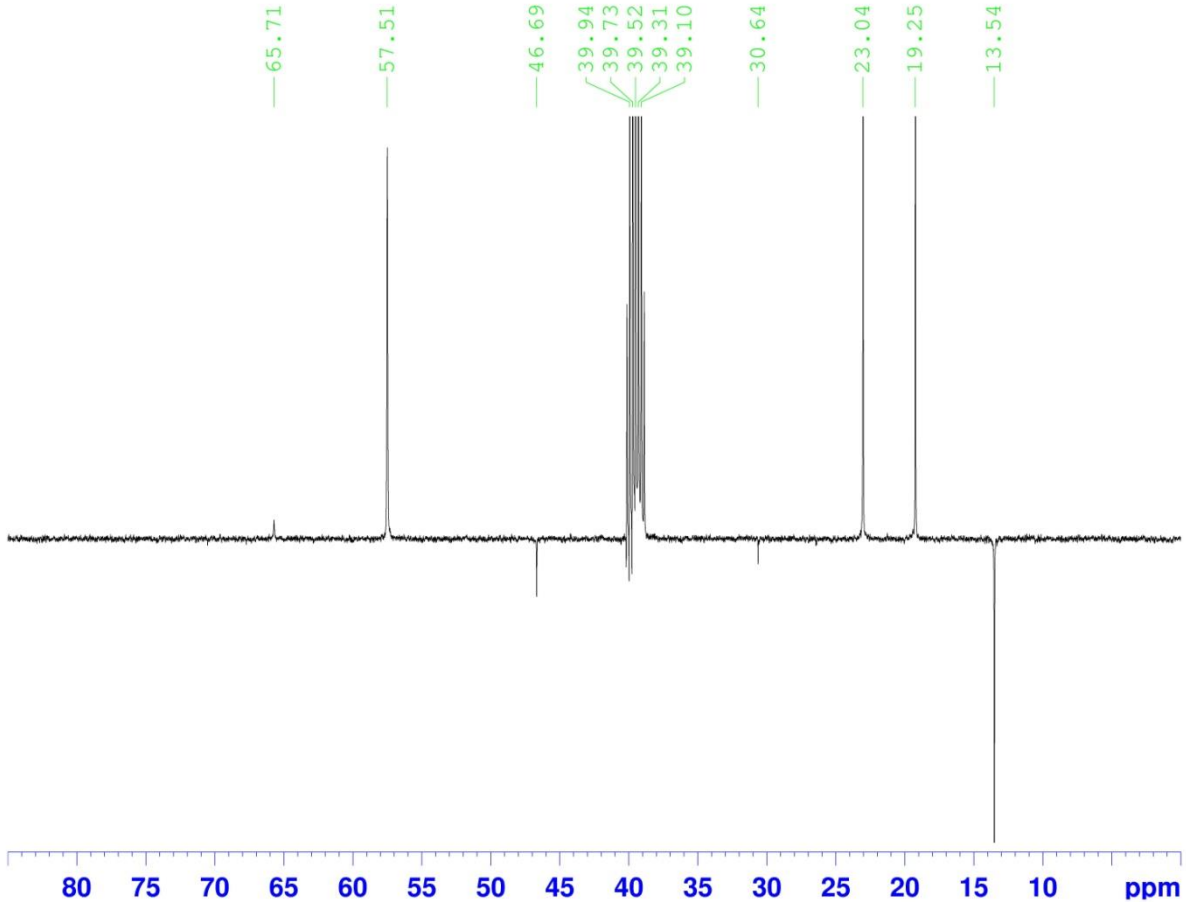


Fig. S29: ^{13}C DEPTQ NMR of the Fmoc-TRIS/TRIS Mn-Anderson (**4**) in DMSO-d_6 at 100 MHz

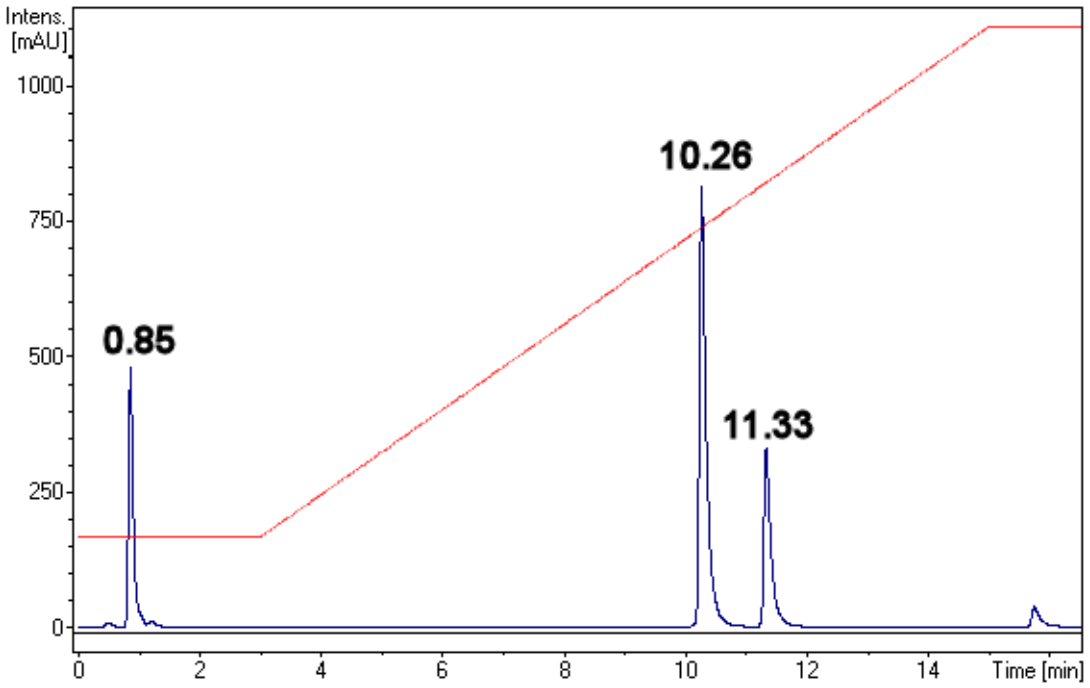


Fig. S30: RP-HPLC of the crude material (mixture of **4** with the two symmetric by-products: TRIS Mn-Anderson and Fmoc-TRIS Mn-Anderson compounds)

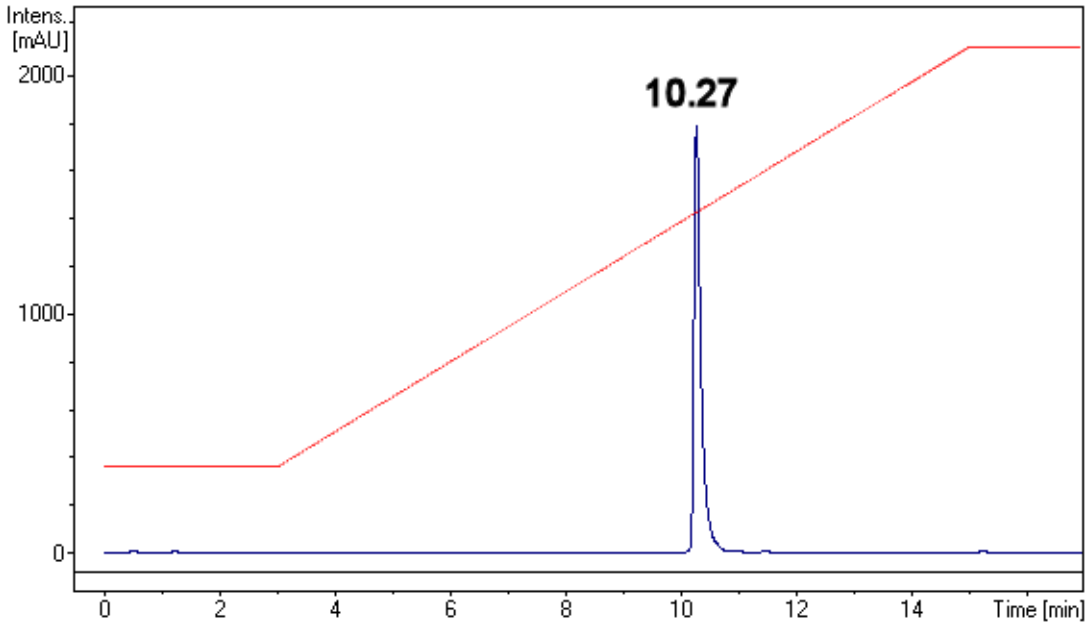


Fig. S31: RP-HPLC of pure compound **4**

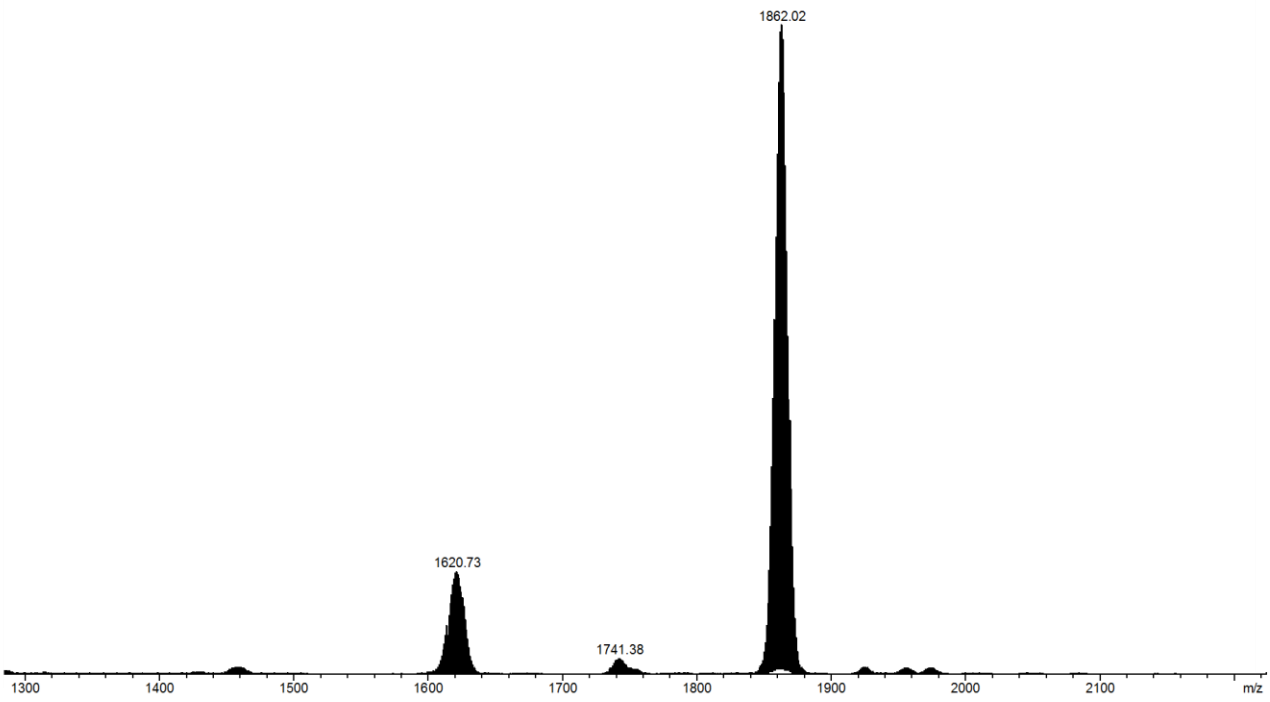


Fig. S32: ESI-MS spectra of pure compound **4**. See Table S10 for peak assignments.

Formula assigned	**z**	**m/z calculated**	**m/z observed**
$[MnMo_6O_{24}(C_{19}H_{18}NO_2)(C_4H_8N)](C_{16}H_{36}N)_1H$	-1	1620.74	1620.73
$[MnMo_6O_{24}(C_{19}H_{18}NO_2)(C_4H_8N)]_2(C_{16}H_{36}N)_3H$	-2	1741.38	1741.38
$[MnMo_6O_{24}(C_{19}H_{18}NO_2)(C_4H_8N)](C_{16}H_{36}N)_2$	-1	1862.02	1862.02
Potential by-products (not observed)	**z**	**m/z calculated**	
$[MnMo_6O_{24}(C_4H_8N)_2](C_{16}H_{36}N)_1H$	-1	1397.68	
$[MnMo_6O_{24}(C_4H_8N)_2](C_{16}H_{36}N)_2$	-1	1639.95	
$[MnMo_6O_{24}(C_{19}H_{18}NO_2)_2](C_{16}H_{36}N)_1H$	-1	1842.81	
$[MnMo_6O_{24}(C_{19}H_{18}NO_2)_2](C_{16}H_{36}N)_2$	-1	2085.09	

Table S10: Assignment of the peak envelopes found in the ESI-MS spectrum of compound **4**, shown in Fig. S31. Expected peak envelopes belonging to by-products (not observed) are indicated; their absence demonstrates the purity of the sample.

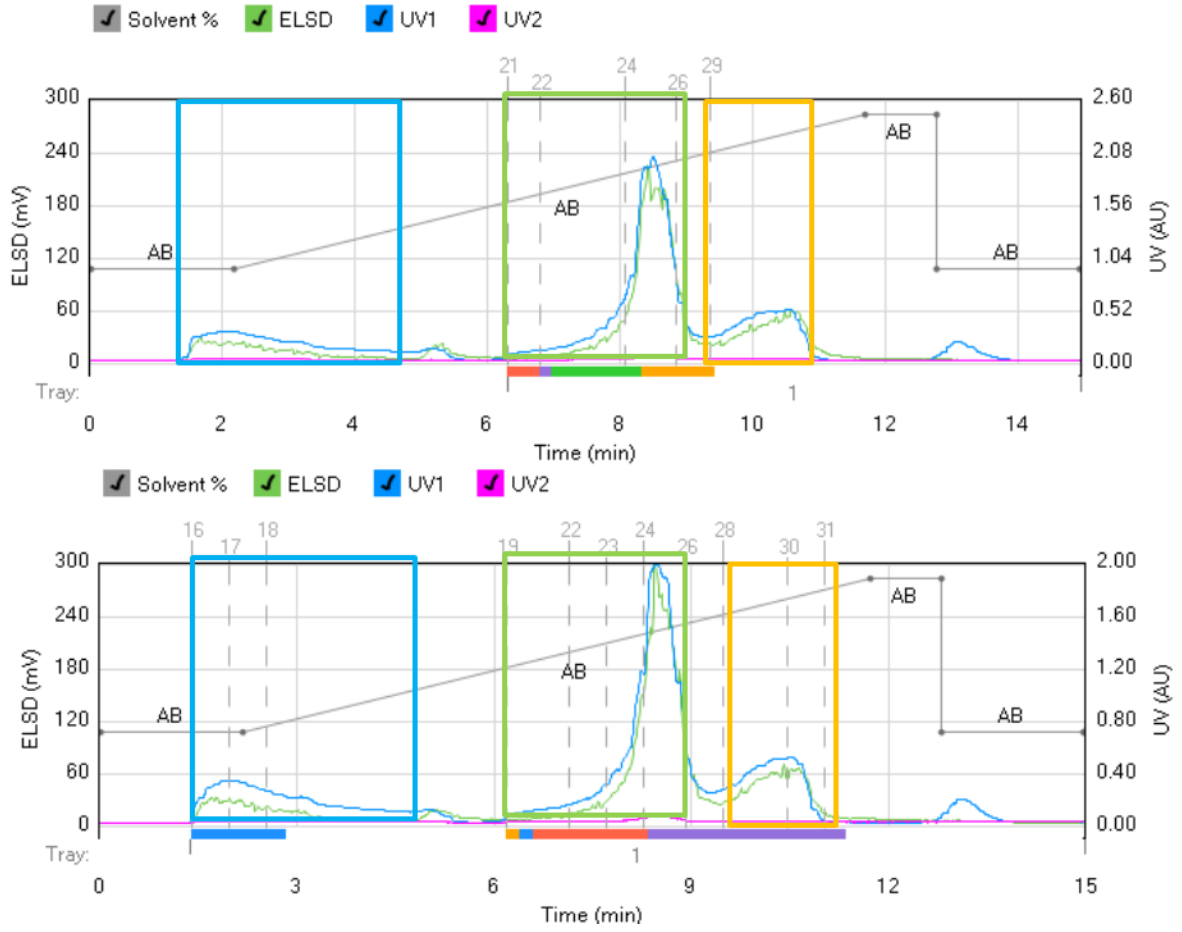
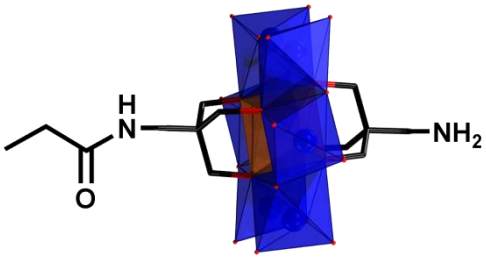
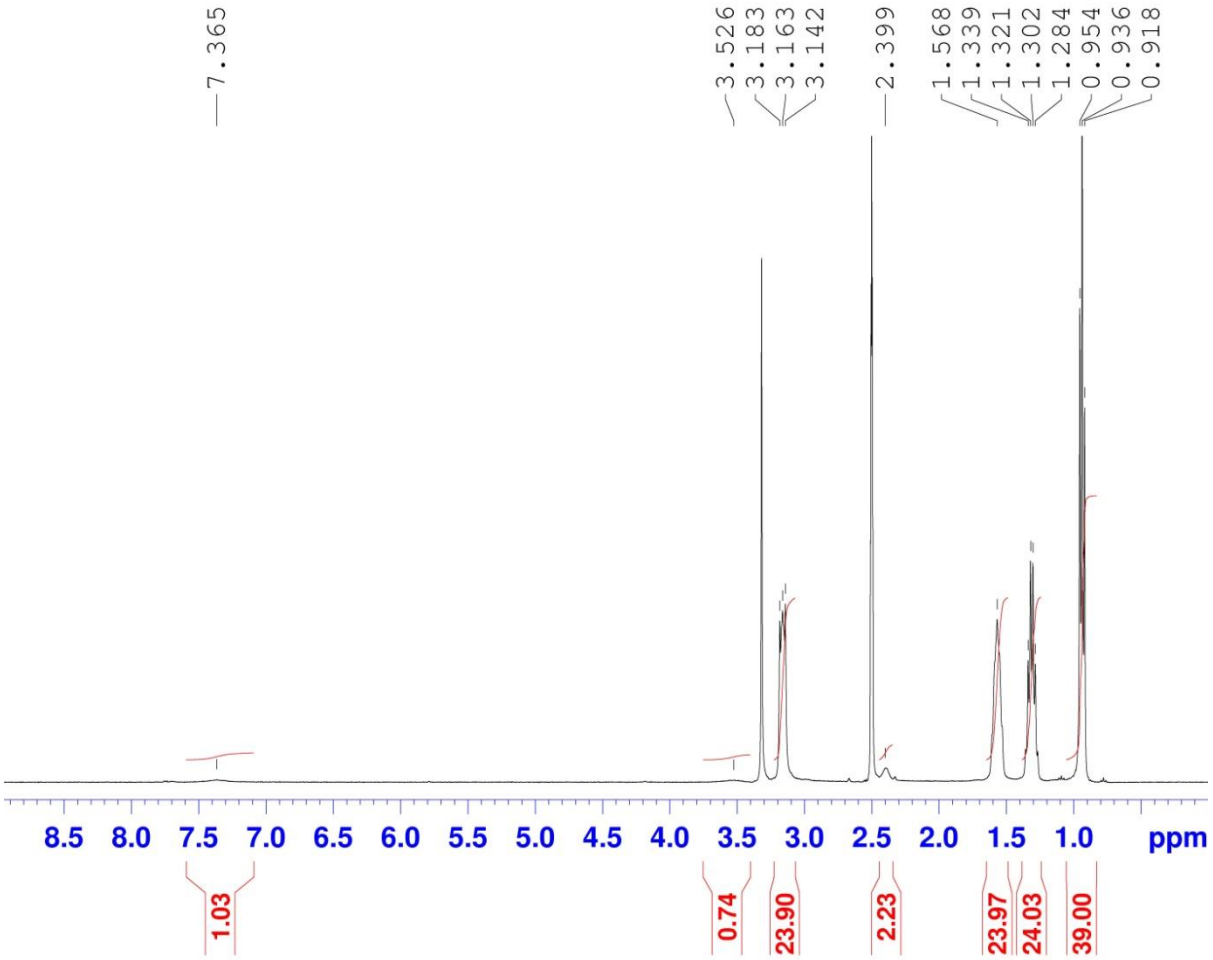


Fig. S33: Flash chromatography pattern and reproducibility. Color scheme: region **I** (blue box); region **II** (green box); region **III** (orange box); ELSD (green line); UV at λ = 254 nm (blue line); UV at λ = 350 nm (pink line).

Compound 5 – Propylamide-TRIS/TRIS Mn-Anderson Compound

$(C_{16}H_{36}N)_3[MnMo_6O_{24}(C_7H_{12}NO)(C_4H_8N)]$





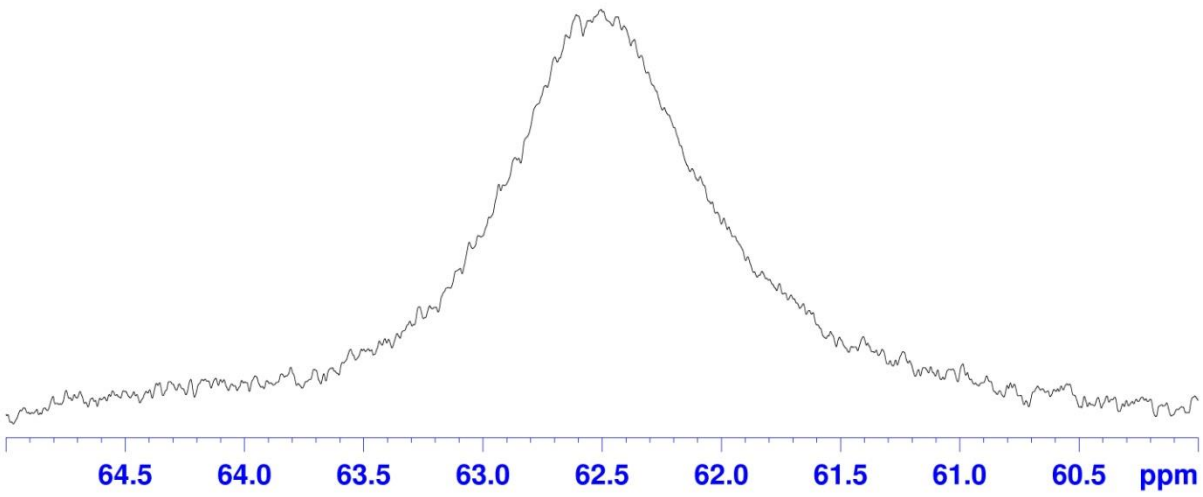


Fig. S34: ^{1}H NMR of the Propylamide-TRIS/TRIS Mn-Anderson (**5**) in DMSO-d_6 at 400 MHz

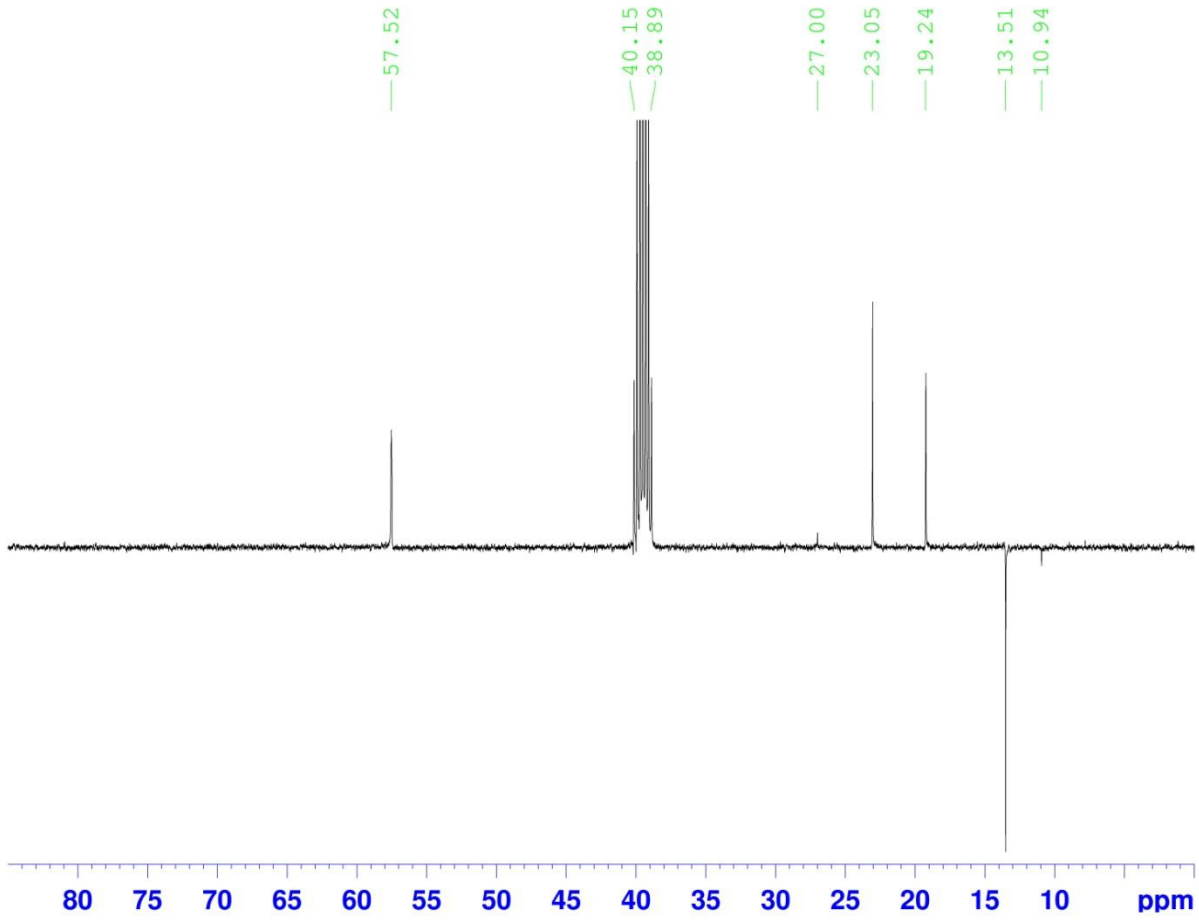


Fig. S35: ^{13}C DEPTQ NMR of the Propylamide-TRIS/TRIS Mn-Anderson (**5**) in DMSO-d_6 at 100 MHz

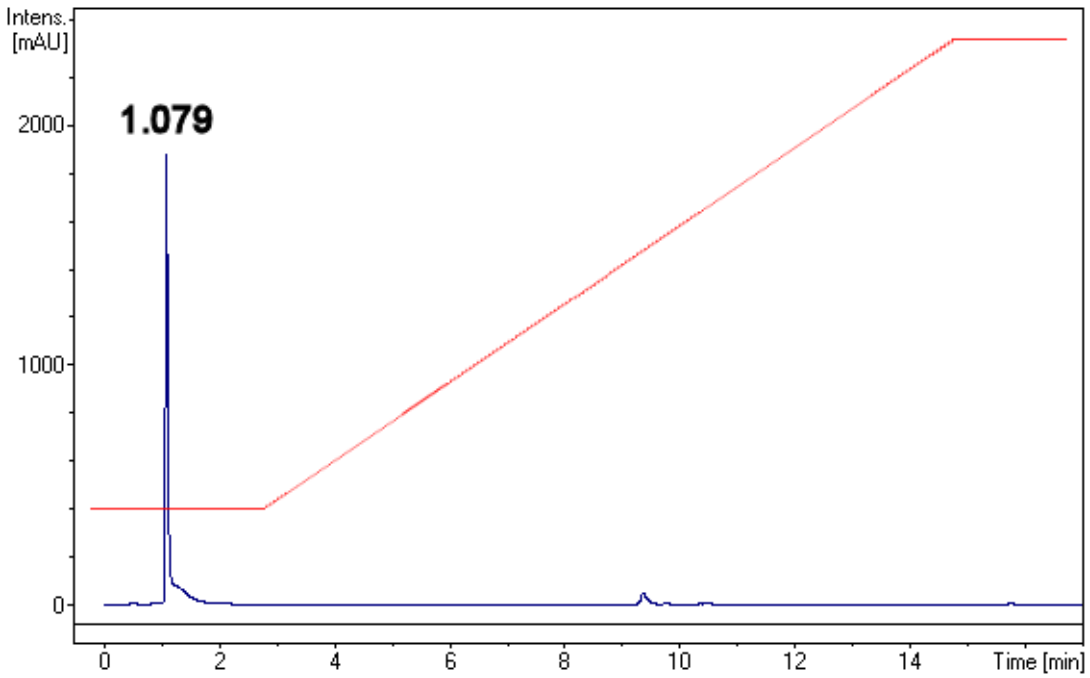


Fig. S36: RP-HPLC of pure compound **5**

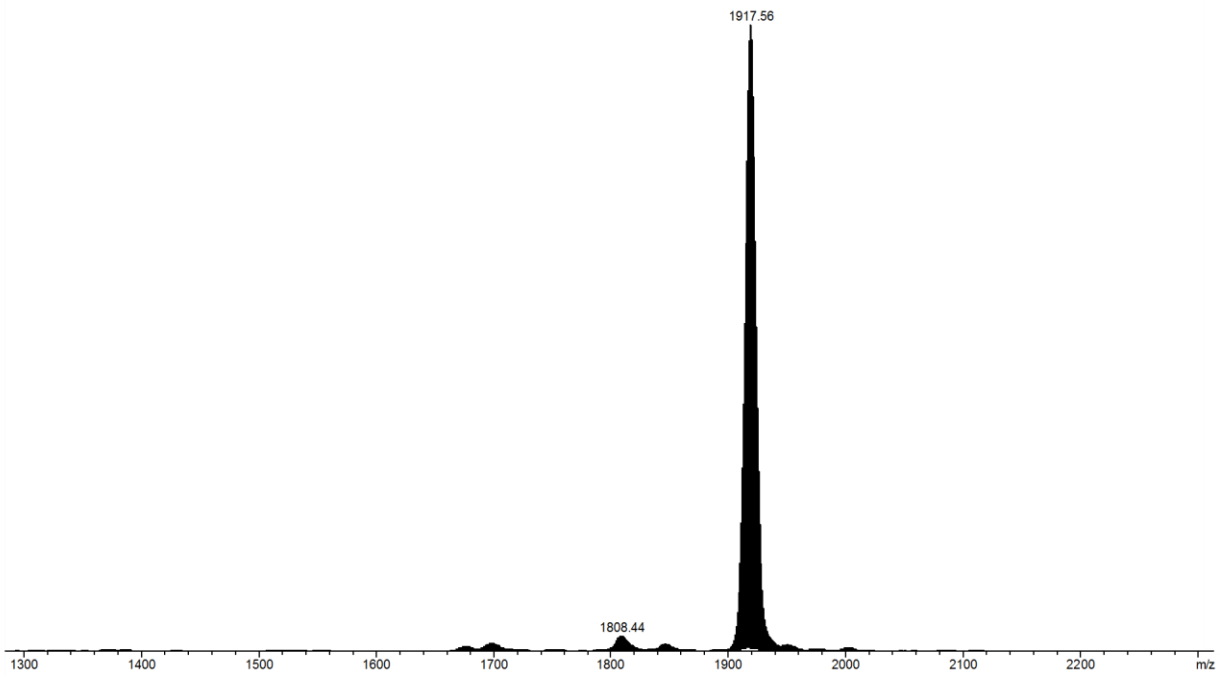


Fig. S37: ESI-MS spectra of the intermediate product. See Table S11 for peak assignments.

Formula assigned	z	m/z calculated	m/z observed
$[MnMo_6O_{24}(C_7H_{12}NO)(C_{19}H_{18}NO_2)]_2(C_{16}H_{36}N)_3Na$	-2	1808.40	1808.44
$[MnMo_6O_{24}(C_7H_{12}NO)(C_{19}H_{18}NO_2)](C_{16}H_{36}N)_2$	-1	1918.05	1917.56
Potential by-products (not observed)	**z**	**m/z calculated**	
$[MnMo_6O_{24}(C_4H_8N)(C_{19}H_{18}NO_2)](C_{16}H_{36}N)_1H$	-1	1620.74	
$[MnMo_6O_{24}(C_4H_8N)(C_{19}H_{18}NO_2)](C_{16}H_{36}N)_2$	-1	1862.02	

Table S11: Assignment of the peak envelopes found in the ESI-MS spectrum of the intermediate product, shown in Fig. S36. Expected peak envelopes belonging to by-products (not observed) are indicated; their absence demonstrates the purity of the sample.

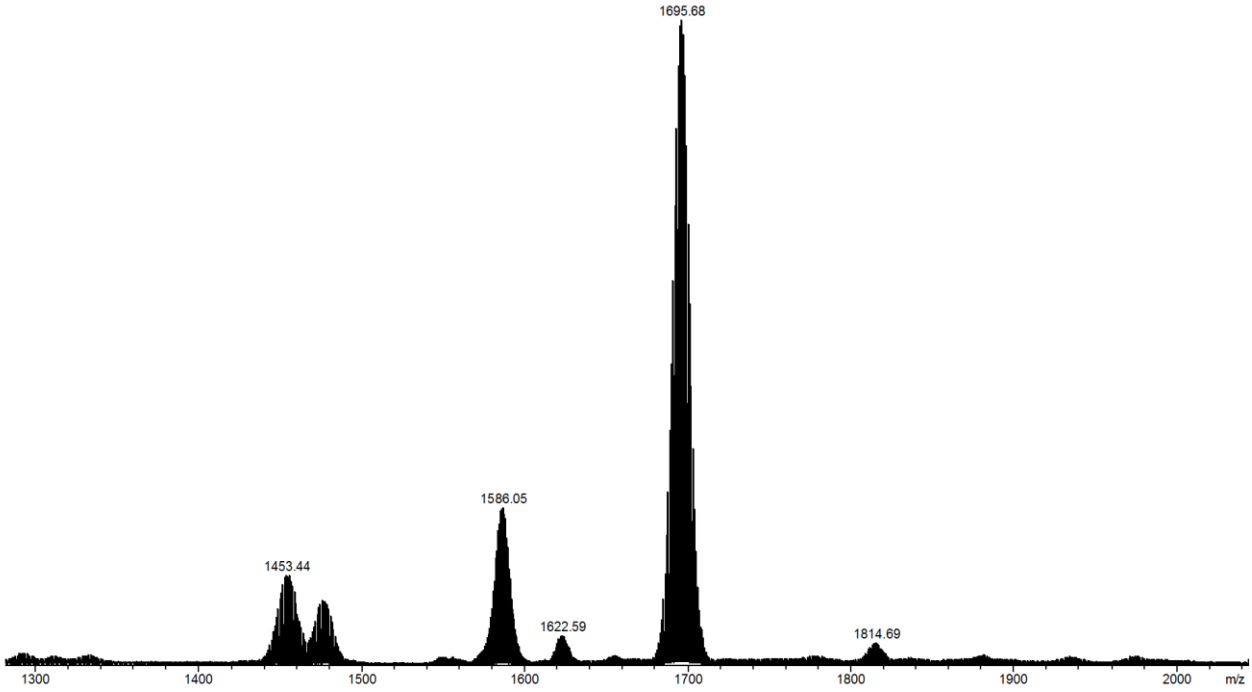


Fig. S38: ESI-MS spectra of pure compound **5**. See Table S12 for peak assignments.

Formula assigned	**z**	**m/z calculated**	**m/z observed**
$[MnMo_6O_{24}(C_7H_{12}NO)(C_4H_8N)](C_{16}H_{36}N)_1H$	-1	1453.70	1453.44
$[MnMo_6O_{24}(C_7H_{12}NO)(C_4H_8N)](C_{16}H_{36}N)_1Na$	-1	1475.68	1475.42
$[MnMo_6O_{24}(C_7H_{12}NO)(C_4H_8N)]_2(C_{16}H_{36}N)_3Na$	-2	1586.33	1586.05
$[MnMo_6O_{24}(C_7H_{12}NO)(C_4H_8N)]_3(C_{16}H_{36}N)_5Na$	-3	1622.54	1622.59
$[MnMo_6O_{24}(C_7H_{12}NO)(C_4H_8N)](C_{16}H_{36}N)_2$	-1	1695.98	1695.68
Potential by-products (not observed)	**z**	**m/z calculated**	
$[MnMo_6O_{24}(C_4H_8N)_2](C_{16}H_{36}N)_1H$	-1	1397.68	
$[MnMo_6O_{24}(C_7H_{12}NO)_2](C_{16}H_{36}N)_1H$	-1	1510.73	
$[MnMo_6O_{24}(C_4H_8N)(C_{19}H_{18}NO_2)](C_{16}H_{36}N)_1H$	-1	1620.74	
$[MnMo_6O_{24}(C_4H_8N)_2](C_{16}H_{36}N)_2$	-1	1639.95	
$[MnMo_6O_{24}(C_7H_{12}NO)(C_{19}H_{18}NO_2)](C_{16}H_{36}N)_1H$	-1	1676.77	
$[MnMo_6O_{24}(C_7H_{12}NO)_2](C_{16}H_{36}N)_2$	-1	1752.01	
$[MnMo_6O_{24}(C_4H_8N)(C_{19}H_{18}NO_2)](C_{16}H_{36}N)_2$	-1	1862.02	
$[MnMo_6O_{24}(C_7H_{12}NO)(C_{19}H_{18}NO_2)](C_{16}H_{36}N)_2$	-1	1918.05	

Table S12: Assignment of the peak envelopes found in the ESI-MS spectrum of compound **5**, shown in Fig. S37. Expected peak envelopes belonging to by-products (not observed) are indicated; their absence demonstrates the purity of the sample.

3 Crystallographic data

	$(TBA)_3[MnMo_6O_{24}(C_{19}H_{16}NO)(C_4H_8N)]\cdot 3DMF$ (**1**)	$(TBA)_3[MnMo_6O_{24}(C_{19}H_{18}NO_2)(C_4H_8N)]\cdot 3DMF$ (**4**)	$(TBA)_3[MnMo_6O_{24}(C_7H_{12}NO)(C_4H_8N)]\cdot 1DMF$ (**5**)	$(TBA)_3[MnMo_6O_{24}(C_{19}H_{16}NO_2)]\cdot 4MeCN$ (**A**)
Formula	$C_{80}H_{153}MnMo_6N_8O_{28}$	$C_{80}H_{155}MnMo_6N_8O_{29}$	$C_{62}H_{135}MnMo_6N_6O_{26}$	$C_{94}H_{152}MnMo_6N_9O_{26}$
M_r (g mol^{-1})	2305.68	2323.70	2011.34	2454.83
Space group	$P2_1/c$	*Pnma*	*Pcca*	*P*-1
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Triclinic
a (Å)	27.455(3)	28.257(2)	23.3192(17)	18.0136(6)
b (Å)	29.007(3)	21.8128(16)	28.200(2)	26.3164(9)
c (Å)	24.974(2)	16.5796(14)	30.215(2)	26.5199(9)
α (°)	90	90	90	113.089(2)
β (°)	94.450(5)	90	90	102.130(2)
γ (°)	90	90	90	100.729(2)
V (Å^3)	19 829(3)	10 219.1(14)	19 869(3)	10 790.7(6)
Z	8	4	8	4
μ (mm^{-1})	0.932	0.906	0.917	0.861
Refl. Coll	287 148	77 882	135 649	162 444
Indep. Refl.	38 952	10 308	17 492	42 424
R (int)	0.0582	0.0862	0.0842	0.0403
GooF on F^2	1.170	1.068	1.076	1.042
$R_1[I>2\sigma(I)]$	0.0802	0.0823	0.0913	0.0415
$wR_2[I>2\sigma(I)]$	0.1796	0.2554	0.2965	0.0998
R_1 (all data)	0.0924	0.1193	0.1506	0.0646
wR_2 (all data)	0.1843	0.2777	0.3334	0.1170

Table S13: Crystallographic data for the asymmetric hybrid Mn-Anderson POM compounds **1**, **4** and **5** and the symmetric control compound synthesized for the RP-HPLC study : Anthracene Mn-Anderson, **A**.

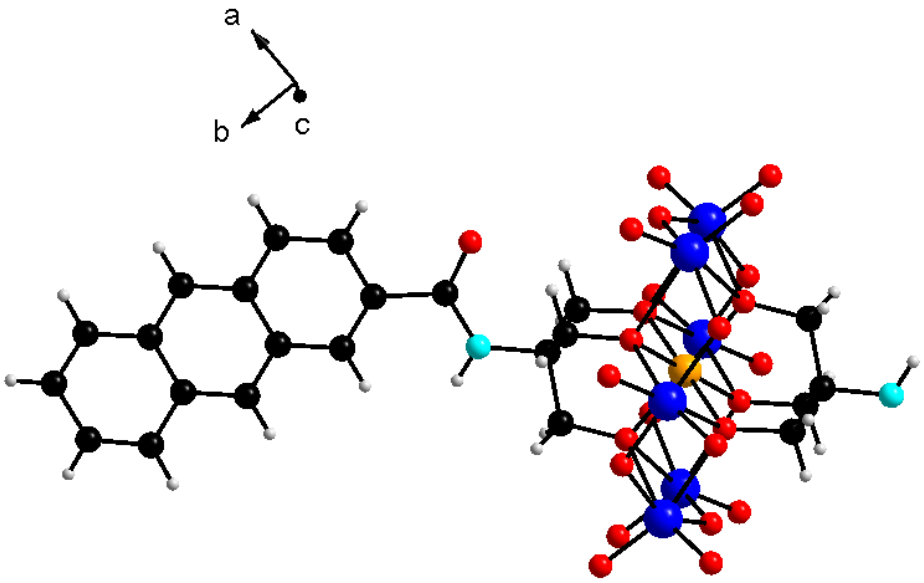


Fig. S39: Crystal structure obtained for the Anthracene-TRIS/TRIS Mn-Anderson compound (**1**). Color scheme: Mo (blue), Mn (orange), O (red), C (black), N (cyan), H (grey), TBA cations and solvent molecules are omitted for clarity.

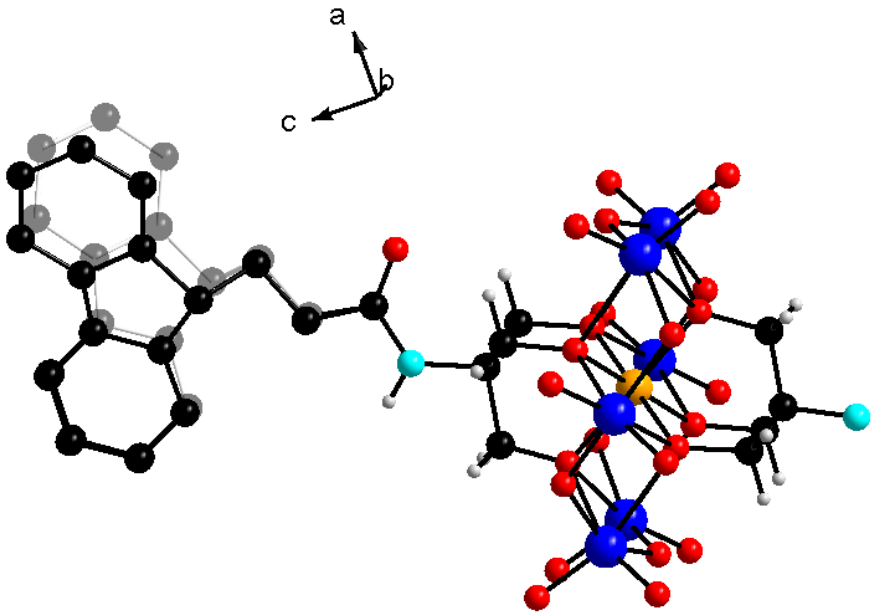


Fig. S40: Crystal structure obtained for the Fmoc-TRIS/TRIS Mn-Anderson compound (**4**). Color scheme: Mo (blue), Mn (orange), O (red), C (black), N (cyan), H (grey), disorder is shown as 50% opacity, TBA cations and solvent molecules are omitted for clarity.

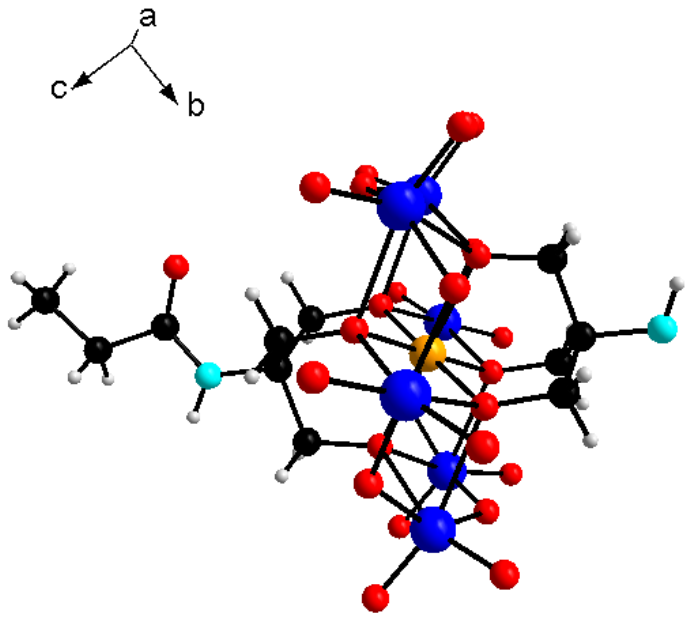


Fig. S41: Crystal structure obtained for the Propylamide/TRIS Mn-Anderson compound (**5**). Color scheme: Mo (blue), Mn (orange), O (red), C (black), N (cyan), H (grey), TBA cations and solvent molecules are omitted for clarity.

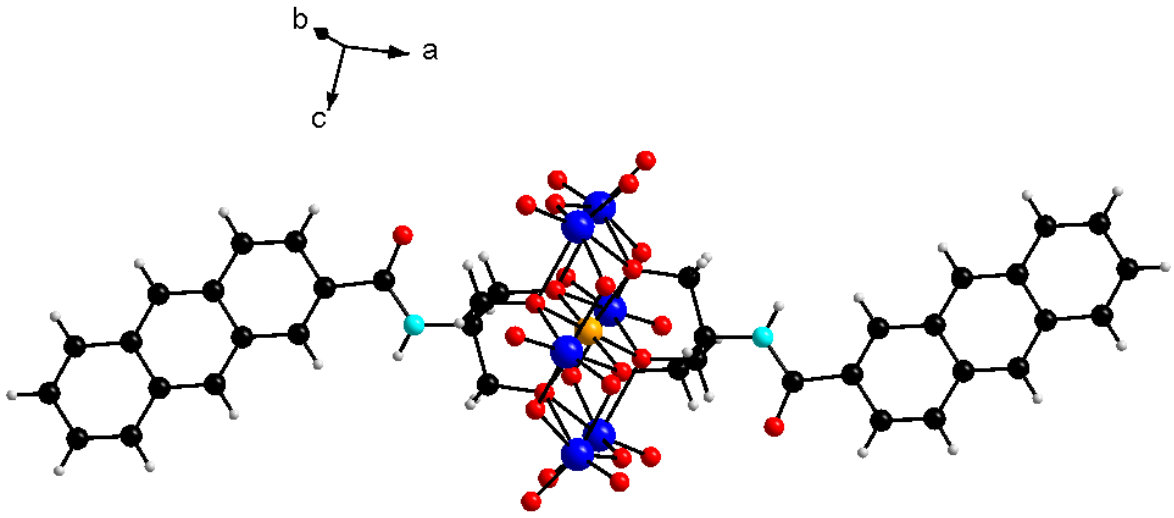


Fig. S42: Crystal structure obtained for the Anthracene Mn-Anderson compound (**A**). Color scheme: Mo (blue), Mn (orange), O (red), C (black), N (cyan), H (grey), TBA cations and solvent molecules are omitted for clarity.

4 References:

1. R. H. Blessing, *Acta. Cryst. A*, 1995, **51**, 33-38.
2. G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112-122.
3. L. J. Farrugia, *J. Appl. Cryst.*, 1999, **32**, 837-838.
4. H. S. Rho, H. S. Baek, D. H. Kim, I. S. Chang, *Bull. Korean Chem. Soc.*, 2006, **27**, 584-586.
5. M. H. Rosnes, C. Musumeci, C. P. Pradeep, J. S. Mathieson, D.-L. Long, Y.-F. Song, B. Pignataro, R. Cogdell and L. Cronin, *J. Am. Chem. Soc.*, 2010, **132**, 15490-15492.
6. W. G. Klemperer, in *Inorganic synthesis*, ed. A. P. Ginsberg, John Wiley & Sons, Inc., 1990, vol. 27, pp. 74-85.
7. Y. F. Song, N. McMillan, D.-L. Long, J. Thiel, Y. L. Ding, H. S. Chen, N. Gadegaard and L. Cronin, *Chem. Eur. J.*, 2008, **14**, 2349-2354.
8. Pierre R. Marcoux, B. Hasenknopf, J. Vaissermann and P. Gouzerh, *Eur. J. Inorg. Chem.*, 2003, **2003**, 2406-2412.