

Supporting Information:

Asymmetric Modification of Anderson-type Polyoxometalates Towards Organic-inorganic Homo- and Hetero-Cluster Oligomers

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1. General

Single-crystal X-ray diffraction (single-crystal XRD) data were collected on a Rigaku SupperNova diffractometer (λ (CuK α) = 0.1542 Å). Structure solution and refinement were carried out with SHELXT¹ and SHELXL² using Olex2 software package³. ¹H-NMR data were recorded on a Bruker AVANCE 400 MHz NMR instrument. 2D TOCSY NMR was obtained on a Bruker AVANCE 300 MHz NMR instrument. The electrospray time-of-flight mass spectroscopy (ESI-TOF-MS) was conducted on a Thermo Scientific Q Exactive mass spectrometer, and all experiments were performed in negative mode using acetonitrile as solvent. The MALDI-TOF-MS spectrum was collected on a Bruker ultrafleXtreme spectrometer using 2,5-dihydroxybenzoic acid (DHB) as matrix. Dynamic light scattering experiment was carried out on a Malvern Nano-ZS90 instrument at room temperature. Fourier transform infrared (FT-IR) spectra were carried out on a Bruker Vector 22 infrared spectrometer using KBr pellet method. Element analyses of C, N and H contents were determined by the elemental UNICUBE.

2. Synthesis

$[(C_4H_9)_4N]_3\{Al(OH)_3Mo_6O_{18}[(OCH_2)_3CC_6H_4NO_2]\} (Al-NO_2)$:

Na₃[Al(OH)₆Mo₆O₁₈](H₂O)₆·2H₂O (2.4 g, 2 mmol) was dissolved in 40 mL water and heated at 100 °C for 30 min. Tris-NO₂ (454 mg, 2 mmol) dissolved in a small amount of water was then added into the above solution, and reacted at 100 °C for 24 hours. After cooling down to room temperature, 2 g of tetrabutylammonium bromide (abbreviated as TBA-Br) was added, and a large number of precipitates formed. The resulting white product was obtained by filtration and dried in air. Yield: 72.6%. ¹H-NMR (400 MHz, DMSO-*d*₆): δ = 8.26 (d, *J* = 9.0 Hz, 2H), 7.52 (d, *J* = 9.0 Hz, 2H), 4.76 (s, 6H), 3.78 (s, 3H), 3.25 - 3.06 (m, 24H), 1.58 (p, *J* = 7.9 Hz, 24H), 1.32 (h, *J* = 7.3 Hz, 24H), 0.94 (t, *J* = 7.3 Hz, 36H). FT-IR (KBr, cm⁻¹): 3447 (br), 2961 (s), 2874 (s), 1648 (m), 1605 (w), 1522 (m), 1483(s), 1380 (m), 1171 (w), 1152 (w), 1095 (m), 1028 (w), 940 (vs), 921 (vs), 904 (vs), 853 (m), 663 (vs), 577 (m), 515 (m), 448 (m).

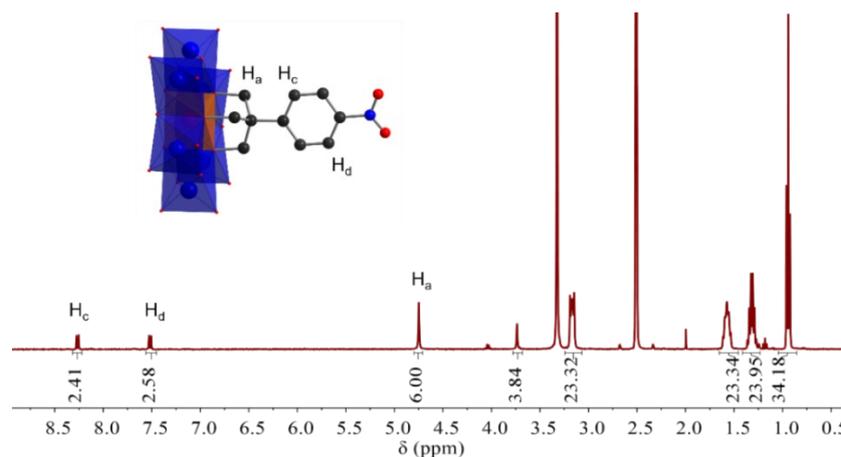


Fig. S1 ¹H-NMR spectrum of Al-NO₂ in DMSO-*d*₆.

$[(C_4H_9)_4N]_3\{AlMo_6O_{18}[(OCH_2)_3CC_6H_4NO_2]_2\} (NO_2-Al-NO_2)$:

Al-NO₂ (946.5 mg, 0.5 mmol) and Tris-NO₂ (136.2 mg, 0.6 mmol) were dissolved in 30 mL ethanol. The resulting solution was refluxed for 16 hours and then cooled down to r.t. The white

precipitates formed during refluxing were filtered off and dried to give the target product. Yield: 80.0%. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ = 8.27 (d, J = 9.0 Hz, 4H), 7.54 (d, J = 9.0 Hz, 4H), 4.78 (s, 12H), 3.21 - 3.11 (m, 24H), 1.57 (p, J = 7.9 Hz, 24H), 1.32 (h, J = 7.3 Hz, 24H), 0.94 (t, J = 7.3 Hz, 36H). FT-IR (KBr, cm^{-1}): 3465 (br), 2963 (s), 2877 (s), 1641 (m), 1601 (w), 1522 (m), 1479(s), 1382 (m), 1347 (m), 1173 (w), 1075 (m), 941 (vs), 925 (vs), 904 (vs), 853 (m), 670 (vs), 580 (m), 529 (m), 470 (m), 448 (m).

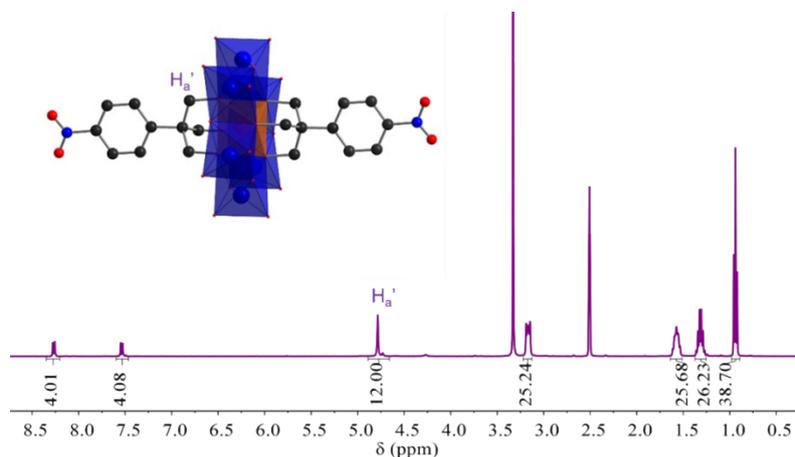


Fig. S2 $^1\text{H-NMR}$ spectrum of $\text{NO}_2\text{-Al-NO}_2$ in $\text{DMSO-}d_6$.

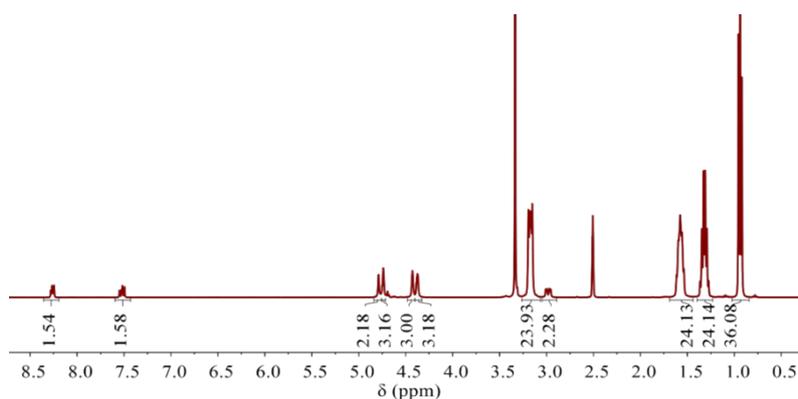


Fig. S3 $^1\text{H-NMR}$ spectrum of the crude product obtained *via* **Route 1**.

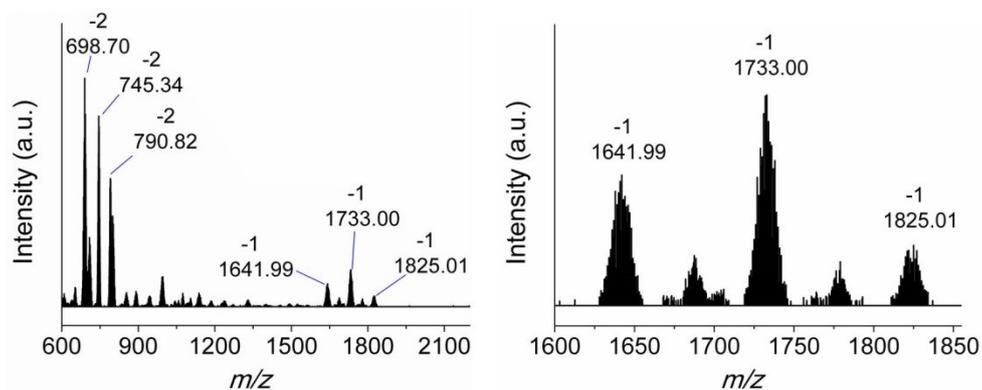


Fig. S4 ESI-TOF-MS spectra of the crude product **1** obtained *via* **Route 1**: full spectrum (left) and the enlarged molecular ion peaks (right).

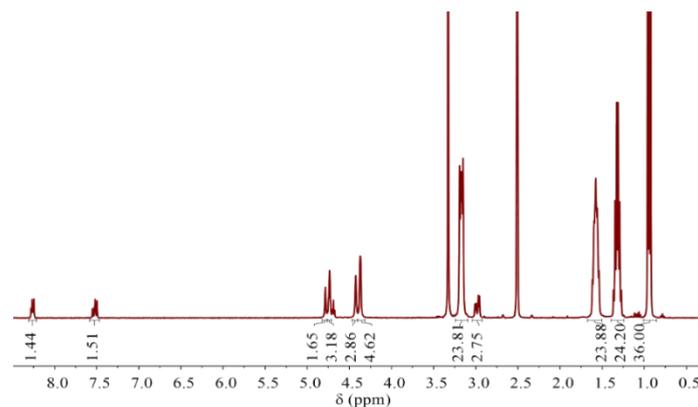


Fig. S5 $^1\text{H-NMR}$ spectrum of the crude product obtained *via Route 2*.

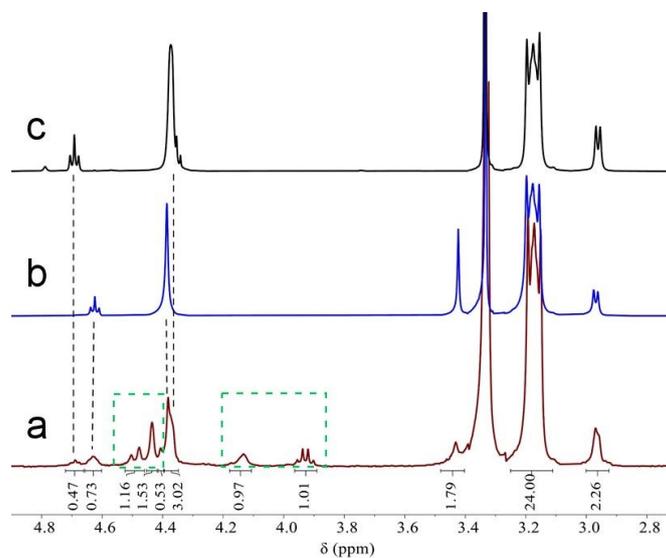


Fig. S6 $^1\text{H-NMR}$ spectra of a) Al-OH after refluxing in ethanol for 3 hours, b) Al-OH, and c) symmetric HO-Al-OH. The black dotted line clearly indicates the formation of symmetric HO-Al-OH, and the newly formed proton peaks (in green dotted box), which cannot be assigned, might be generated from the decomposition or reassembly of the Al-OH.

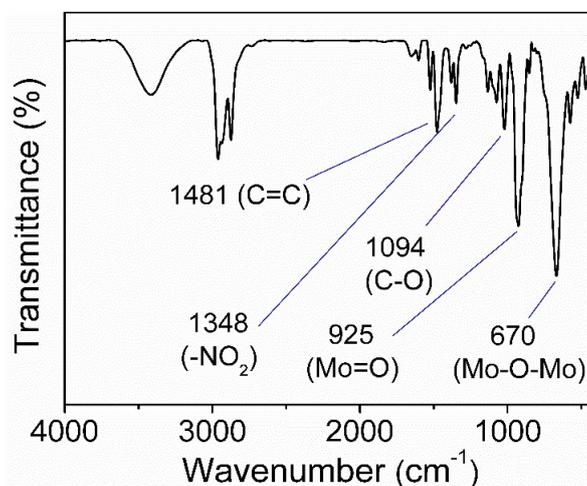


Fig. S7 FT-IR spectrum of the asymmetric **1**.

One-pot Synthesis of $[(C_4H_9)_4N]_3\{AlMo_6O_{18}[(OCH_2)_3CCH_2OH][(OCH_2)_3CC_6H_4NO_2]\}$ (1):

$[(C_4H_9)_4N]_3[Al(OH)_6Mo_6O_{18}]$ (172 mg, 0.1 mmol) was dissolved in a mixture of 12 mL ethanol and 3 mL acetonitrile upon heating. To this solution, Tris-NO₂ (22.7 mg, 0.1 mmol) and pentaerythritol (13.6 mg, 0.1 mmol) was added and refluxed for 24 hours. After reaction, the color of the solution changed to light blue (suggesting the reduction of Anderson cluster), and a large amount of white precipitates formed. The precipitates were collected by filtration and dried in the air. ¹H-NMR shows that the crude product also contains symmetric by-products (Fig. S8).

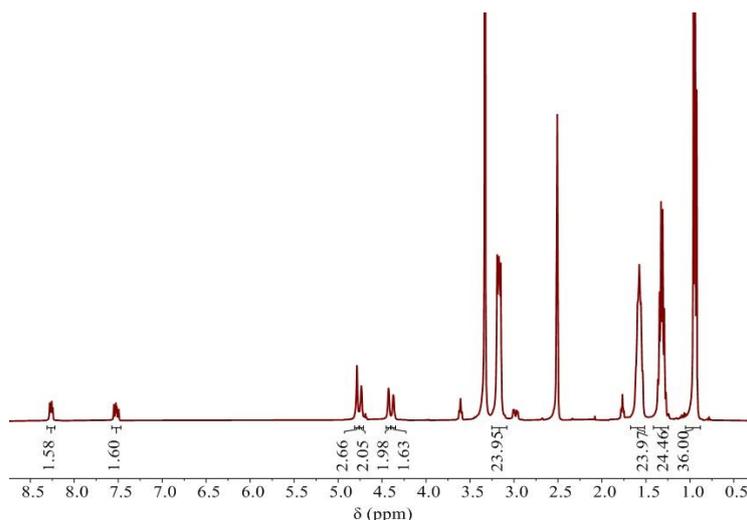
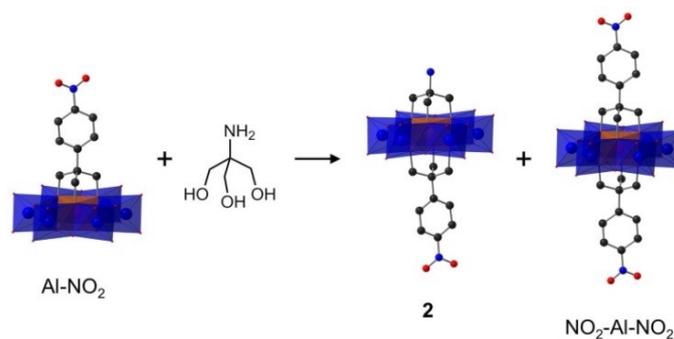


Fig. S8 ¹H-NMR of the crude product obtained by one-pot synthesis.

$[(C_4H_9)_4N]_3\{AlMo_6O_{18}[(OCH_2)_3CNH_2][(OCH_2)_3CC_6H_4NO_2]\}$ (2):



The synthesis of the asymmetrical **2** is similar to that of **1** except the use of Tris instead of pentaerythritol. The resulting crude products contain only the symmetric NO₂-Al-NO₂ byproduct as shown in Fig. S8. ¹H-NMR (400 MHz, DMSO-*d*₆): δ = 8.26 (s, 4H), 7.52 (s, 4H), 4.79 (s, 6H), 4.74 (s, 6H), 4.27 (s, 6H), 3.24 - 3.10 (m, 24H), 1.57 (p, *J* = 8.1 Hz, 24H), 1.31 (h, *J* = 7.3 Hz, 24H), 0.93 (t, *J* = 7.3 Hz, 36H).

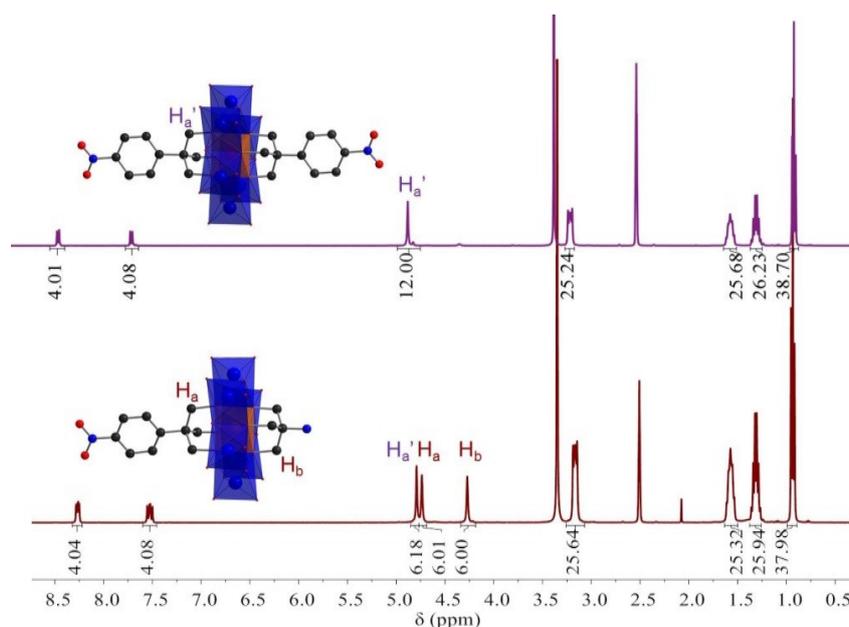


Fig. S9 $^1\text{H-NMR}$ spectra of the crude product **2** (bottom, red) and the symmetric $\text{NO}_2\text{-Al-NO}_2$ byproduct (top, purple).

The purification of **2**:

First, the crude product (1.1 g, *ca* 0.6 mmol) dissolved in 20 mL acetonitrile was cation-exchanged into sodium salt by adding excessive NaClO_4 (685 mg, *ca* 10 equiv). The resulting sodium salt was collected by centrifuge and re-dissolved in 20 mL water. TBA-Br (213 mg, 0.66 mmol) in 1 mL H_2O was added dropwise into the above solution. White precipitates thus formed were removed by centrifuge. The precipitates were proved to be the symmetric $\text{NO}_2\text{-Al-NO}_2$ by $^1\text{H-NMR}$.

Secondly, excessive TBA-Br was adding into the filtration to give the asymmetric **2** as shown in Fig. S9 (black line). Total yield: 31.8%. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ = 8.26 (d, J = 9.0 Hz, 2H), 7.51 (d, J = 9.0 Hz, 2H), 4.74 (s, 6H), 4.36 (d, J = 5.2 Hz, 6H), 3.25 - 3.08 (m, 24H), 1.57 (p, J = 7.9 Hz, 24H), 1.32 (h, J = 7.3 Hz, 24H), 0.94 (t, J = 7.3 Hz, 36H). FT-IR (KBr, cm^{-1}): 3463 (br), 2963 (s), 2875 (s), 1605 (w), 1523 (m), 1480(s), 1381 (m), 1348 (m), 1093 (m), 1049 (m), 943 (vs), 925 (vs), 904(m), 852 (m), 670 (vs), 576 (m), 517 (m), 472 (m), 449 (m). ESI-TOF-MS (neg. mode, MeCN): 1719.00 ($\{(\text{TBA})_2\{\text{AlMo}_6\text{O}_{18}[(\text{OCH}_2)_3\text{CNH}_2][(\text{OCH}_2)_3\text{CC}_6\text{H}_4\text{NO}_2]\}\}^-$, *calcd.* 1717.96), 1475.72 ($\{(\text{TBA})\text{H}\{\text{AlMo}_6\text{O}_{18}[(\text{OCH}_2)_3\text{CNH}_2][(\text{OCH}_2)_3\text{CC}_6\text{H}_4\text{NO}_2]\}\}^-$, *calcd.* 1476.50), and 736.86 ($\{(\text{TBA})\{\text{AlMo}_6\text{O}_{18}[(\text{OCH}_2)_3\text{CNH}_2][(\text{OCH}_2)_3\text{C}-\text{C}_6\text{H}_4\text{NO}_2]\}\}^{2-}$, *calcd.* 737.75). Single-crystals of the asymmetric **2** can be obtained by diethyl ether diffusion into the acetonitrile solution of **2**; however, very weak X-ray diffractions were obtained. In order to get high-quality single-crystals, the asymmetric **2** was cation-exchanged into Mg^{2+} salt (denoted as **2'**). To put it short, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (256 mg, 1 mmol) dissolved in 0.5 mL H_2O was added dropwise into the acetonitrile solution (10 mL) of **2** (195 mg, 0.1 mmol), giving rise to the precipitates of **2'**, which were collected by centrifuge and washed several times by ethanol. Single-crystals suitable for X-ray were obtained by acetone diffusion into the DMF solution of **2'**.

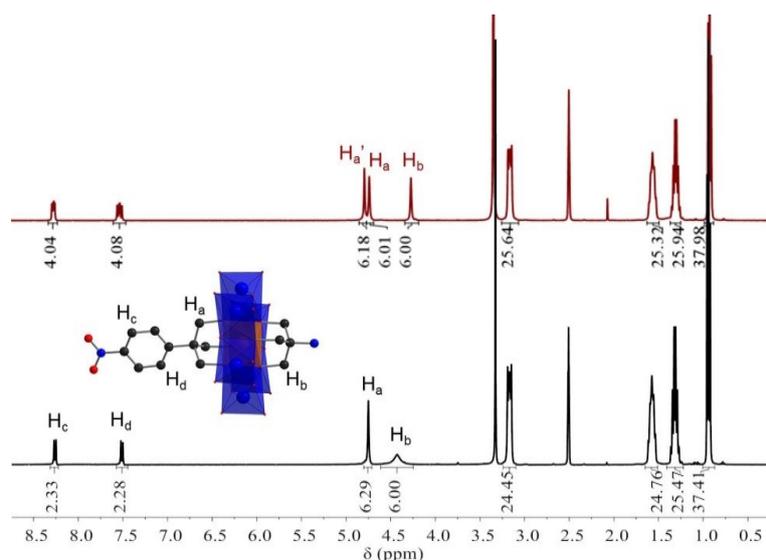
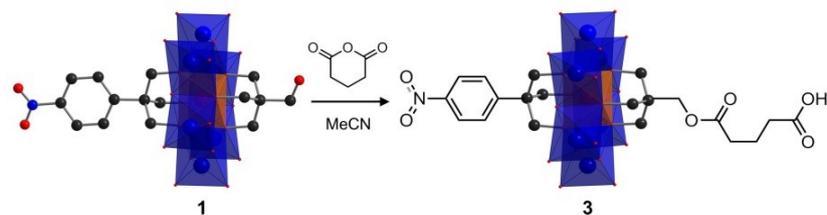


Fig. S10 $^1\text{H-NMR}$ spectra of the purification process of the asymmetric **2**.

$[(\text{C}_4\text{H}_9)_4\text{N}]_3\{\text{AlMo}_6\text{O}_{18}[(\text{OCH}_2)_3\text{CC}_6\text{H}_4\text{NO}_2][(\text{OCH}_2)_3\text{CCH}_2\text{OCO}(\text{CH}_2)_3\text{COOH}]\}$ (**3**):



Compound **1** (2.0 g, 1 mmol), glutaric anhydride (0.3 g, 3 mmol), DIPEA (523 μL , 3 mmol), and a catalytic amount of DMAP were dissolved in dry acetonitrile (20 mL), and refluxed for 24 hours. After cooled down to r.t., the brown solution was set to diethyl ether diffusion. Colorless needle-like single-crystals were obtained after 3 days. Yield: 59.0%. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ = 8.26 (d, J = 9.0 Hz, 2H), 7.51 (d, J = 9.1 Hz, 2H), 4.74 (s, 6H), 4.44 (s, 6H), 3.69 (s, 2H), 3.24 - 3.11 (m, 24H), 2.37 (s, 2H), 2.25 (s, 2H), 1.72 (s, 2H), 1.58 (p, J = 8.0 Hz, 24H), 1.32 (h, J = 7.3 Hz, 24H), 0.94 (t, J = 7.3 Hz, 36H). FT-IR (KBr, cm^{-1}): 3445 (br), 2962 (s), 2876 (s), 1740 (m), 1645 (w), 1605 (w), 1524 (m), 1482 (m), 1383 (m), 1349 (m), 1141(m), 1070 (m), 1028 (w), 943 (vs), 925 (vs), 905 (vs), 853 (m), 670 (vs), 578 (m), 526 (m), 471 (m), 448 (m). ESI-TOF-MS (neg. mode, MeCN): 1846.03 ($\{(\text{TBA})_2\{\text{AlMo}_6\text{O}_{18}[(\text{OCH}_2)_3\text{CC}_6\text{H}_4\text{NO}_2][(\text{OCH}_2)_3\text{CCH}_2\text{OCO}(\text{CH}_2)_3\text{COOH}]\}\}$), *calcd.* 1847.07), 802.37 ($\{(\text{TBA})\{\text{AlMo}_6\text{O}_{18}[(\text{OCH}_2)_3\text{CC}_6\text{H}_4\text{NO}_2][(\text{OCH}_2)_3\text{CCH}_2\text{OCO}(\text{CH}_2)_3\text{COOH}]\}\}^2$), *calcd.* 801.80). Elemental analysis (%) *calcd.* for $\text{C}_{68}\text{H}_{133}\text{AlMo}_6\text{O}_6\text{N}_4\text{O}_{30}$: C 39.05, H 6.37, N 2.68; found: C 37.92, H 5.72, N 2.80.

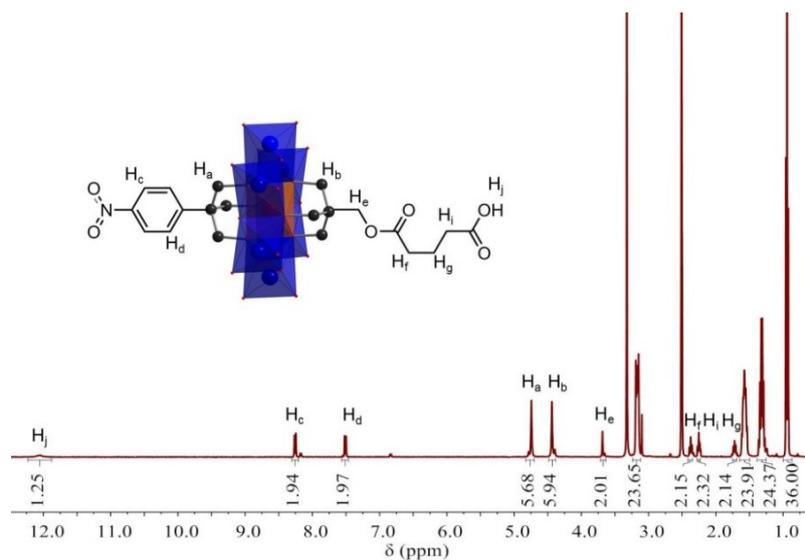


Fig. S11 $^1\text{H-NMR}$ spectrum of **3**.

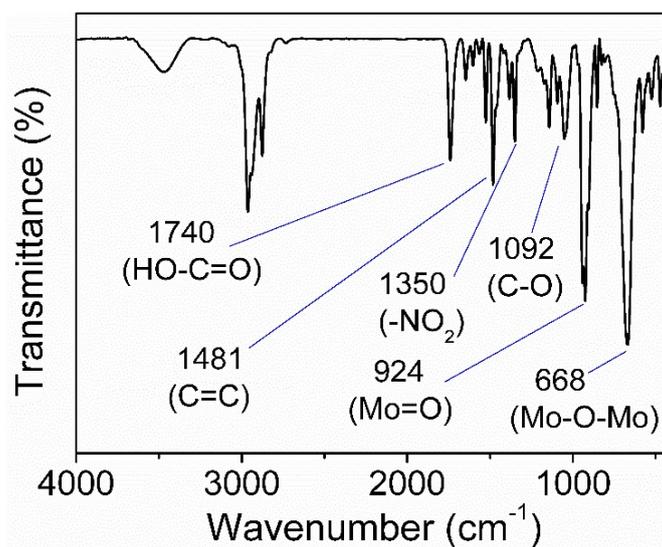


Fig. S12 FT-IR spectrum of **3**.

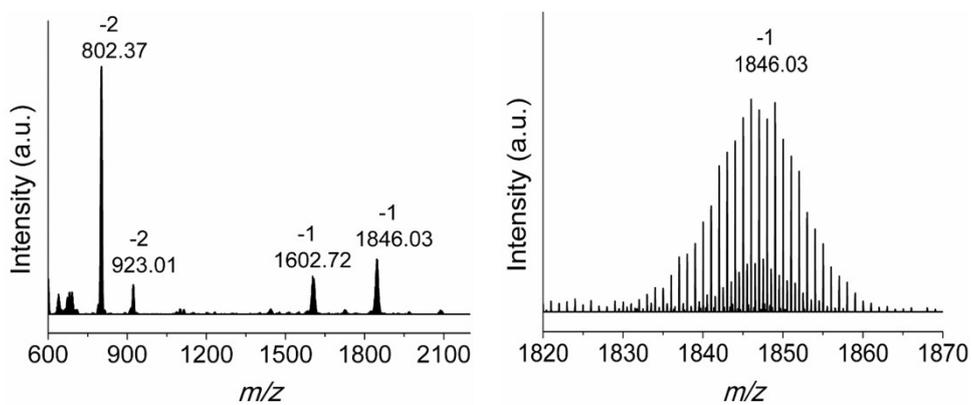
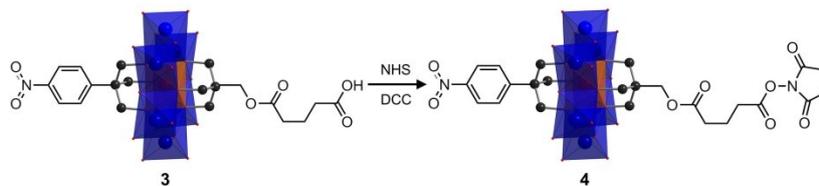


Fig. S13 ESI-TOF-MS spectra of **3**: full spectrum (left) and the molecular ion peak (right).





Compound **3** (2.09 g, 1.0 mmol) was dissolved in 20 mL dry DMF. To this solution *N*-hydroxy succinimide (NHS, 434 mg, 2 equiv) and *N,N'*-dicyclohexylcarbodiimide (DCC, 619 mg, 3 equiv) were added and stirred at r.t. for 24 hours. After reaction, the white precipitates of dicyclohexylurea (DCU) were removed by centrifuge and the resulting light-yellow solution was set for diethyl ether diffusion. Block colorless single-crystals of **4** were obtained after 2 days. Yield: 56.0%. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ = 8.26 (d, J = 9.0 Hz, 2H), 7.51 (d, J = 9.1 Hz, 2H), 4.75 (s, 6H), 4.44 (s, 6H), 3.70 (s, 2H), 3.24 - 3.10 (m, 24H), 2.81 (s, 4H), 2.73 (s, 2H), 2.47 (s, 2H), 1.85 (s, 2H), 1.58 (p, J = 7.9 Hz, 24H), 1.32 (h, J = 7.3 Hz, 24H), 0.94 (t, J = 7.3 Hz, 36H). FT-IR (KBr, cm^{-1}): 3475 (br), 2962 (s), 2876 (s), 1815 (w), 1784 (w), 1740 (s), 1747 (w), 1606 (w), 1524 (m), 1482 (m), 1382 (m), 1349 (m), 1206 (m), 1141 (m), 1069 (m), 942 (vs), 925 (vs), 905 (vs), 853 (m), 670 (vs), 577 (m), 527 (m), 471 (m), 447 (m). ESI-TOF-MS (neg. mode, MeCN): 1944.05 ($\{(\text{TBA})_2\{\text{AlMo}_6\text{O}_{18}[(\text{OCH}_2)_3\text{CC}_6\text{H}_4\text{NO}_2][(\text{OCH}_2)_3\text{CCH}_2\text{OCO}(\text{CH}_2)_3\text{COOC}_4\text{H}_4\text{O}_2\text{N}]\}\}^-$, *calcd.* 1944.14), 848.89 ($\{(\text{TBA})\{\text{AlMo}_6\text{O}_{18}[(\text{OCH}_2)_3\text{CC}_6\text{H}_4\text{NO}_2][(\text{OCH}_2)_3\text{CCH}_2\text{OCO}(\text{CH}_2)_3\text{COOC}_4\text{H}_4\text{O}_2\text{N}]\}\}^{2-}$, *calcd.* 850.84). Elemental analysis (%) *calcd.* for $\text{C}_{72}\text{H}_{136}\text{AlMo}_6\text{N}_5\text{O}_{32}$: C 39.51, H 6.22, N 3.20; found: C 38.92, H 5.74, N 3.38.

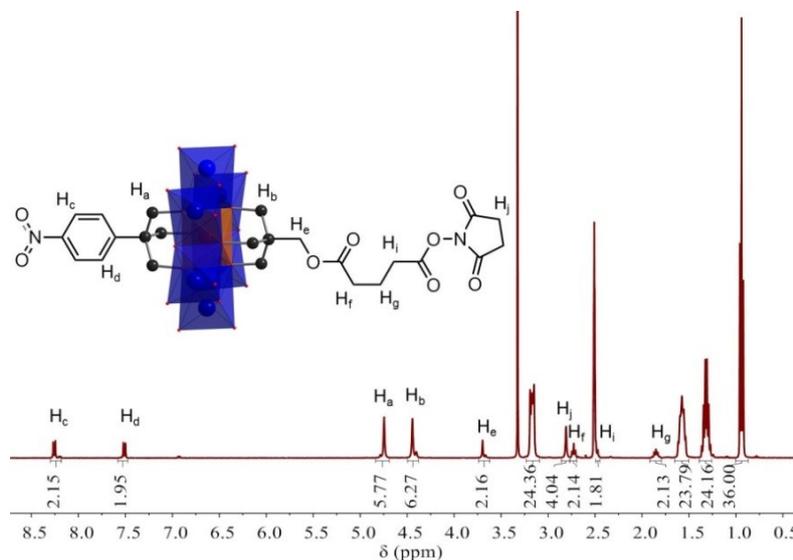


Fig. S14 $^1\text{H-NMR}$ spectrum of **4**.

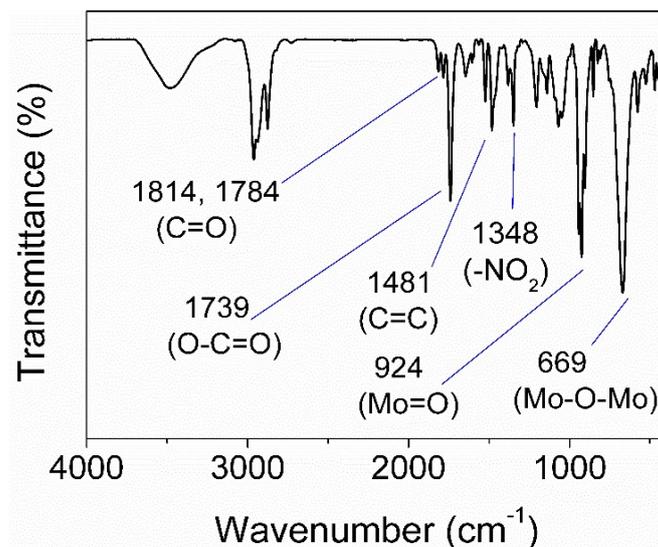


Fig. S15 FT-IR spectrum of **4**.

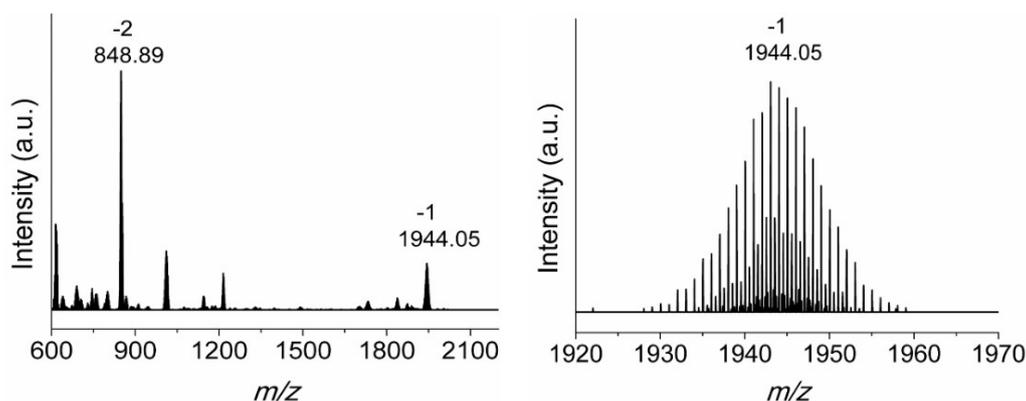
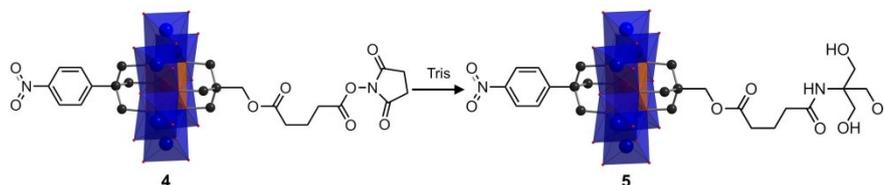


Fig. S16 ESI-TOF-MS spectra of **4**: full spectrum (left) and the molecular ion peaks (right).

$[(C_4H_9)_4N]_3\{AlMo_6O_{18}[(OCH_2)_3CC_6H_4NO_2][(OCH_2)_3CCH_2OCO(CH_2)_3CONHC(CH_2OH)_3]\}$ (**5**):



Compound **4** (655.8 mg, 0.3 mmol) and Tris (66 mg, 2 equiv) were dissolved in 10 mL DMF. To this solution, DIPEA (94 μ L, 2.2 equiv) was added and then reacted at 60 $^{\circ}$ C for 12 hours. After cooled down to r.t., the product was obtained by vapour diffusion of diethyl ether for two weeks. Yield: 65.0%. 1 H-NMR (400 MHz, DMSO- d_6): δ = 8.26 (d, J = 9.0 Hz, 2H), 7.51 (d, J = 9.0 Hz, 2H), 7.08 (s, 1H), 4.75 (s, 6H), 4.69 (s, 3H), 4.44 (s, 6H), 3.70 (s, 2H), 3.52 (d, J = 5.7 Hz, 6H), 3.28 - 3.05 (m, 24H), 2.36 (s, 2H), 2.18 (s, 2H), 1.72 (s, 2H), 1.57 (q, J = 11.8, 8.0 Hz, 24H), 1.32 (h, J = 7.2 Hz, 24H), 0.94 (t, J = 7.3 Hz, 36H). FT-IR (KBr, cm^{-1}): 3429 (br), 2962 (s), 2876 (s), 1738 (s), 1650 (w), 1523 (m), 1482 (m), 1382 (m), 1349 (m), 1141 (m), 1093 (m), 1050 (m), 942 (vs), 925 (vs), 905 (vs), 852 (m),

669 (vs), 578 (m), 522 (m), 471 (m), 446 (m).

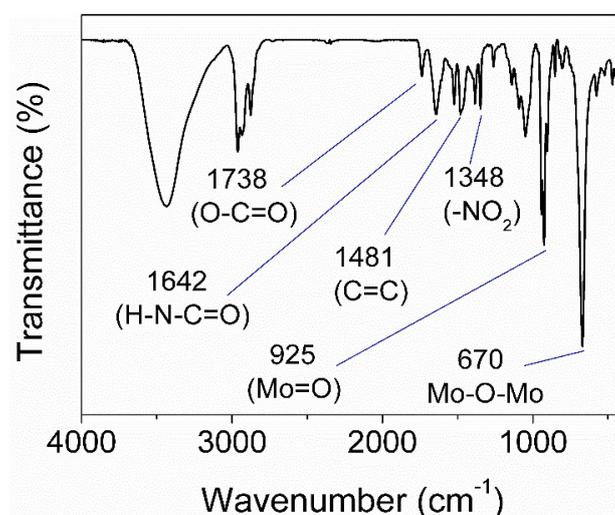
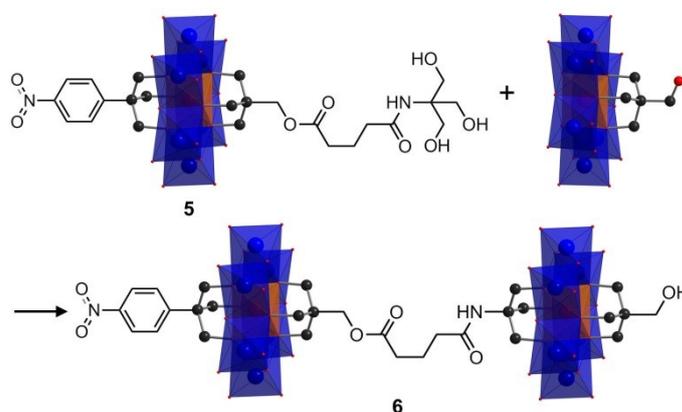


Fig. S17 FT-IR spectrum of 5.

$[(C_4H_9)_4N]_6\{(AlMo_6O_{18})_2[(OCH_2)_3CC_6H_4NO_2][(OCH_2)_3CCH_2OCO(CH_2)_3CONHC(OCH_2)_3][(OCH_2)_3C-CH_2OH]\}$ (6):



Al-OH (360 mg, 0.2 mmol) and **5** (438 mg, 0.2 mmol) were dissolved in 100 mL ethanol and refluxed for 6 hours. After cooled down to r.t., the white precipitates formed during the reaction were collected by filtration and dried in air. The precipitates were then recrystallized by diethyl ether diffusion into the acetonitrile solution for 3 days. Yield: 56.0%. 1H -NMR (400 MHz, DMSO- d_6): δ = 8.25 (d, J = 8.9 Hz, 2H), 7.51 (d, J = 9.0 Hz, 2H), 7.18 (s, 1H), 4.75 (s, 6H), 4.71 (d, J = 5.8 Hz, 1H), 4.59 (s, 6H), 4.42 (s, 6H), 4.37 (s, 6H), 3.63 (s, 2H), 3.29 - 3.07 (m, 48H), 2.97 (d, J = 5.3 Hz, 2H), 2.28 (s, 2H), 2.01 (s, 2H), 1.72 - 1.48 (m, 50H), 1.32 (h, J = 7.2 Hz, 48H), 0.94 (t, J = 7.3 Hz, 72H). FT-IR (KBr, cm^{-1}): 3428 (br), 2962 (s), 2875 (s), 1738 (s), 1679 (w), 1524 (m), 1482 (m), 1381 (m), 1347 (m), 1140 (m), 1095 (m), 1023 (m), 942 (vs), 925 (vs), 904 (vs), 853 (m), 826 (m), 672 (vs), 577 (m), 523 (m), 471 (m), 447 (m). ESI-TOF-MS (neg. mode, MeCN): 1729.01 ($\{(TBA)_4M\}^{2-}$, *calcd.* 1727.98), 1071.25 ($\{(TBA)_3M\}^{3-}$, *calcd.* 1071.16), 741.12 ($\{(TBA)_2M\}^{4-}$, *calcd.* 742.76). Elemental analysis (%) *calcd.* for $C_{125}H_{256}Al_2Mo_{12}N_8O_{54}$: C 38.06, H 6.50, N 2.84; found: C 38.25, H 6.41, N 2.82.

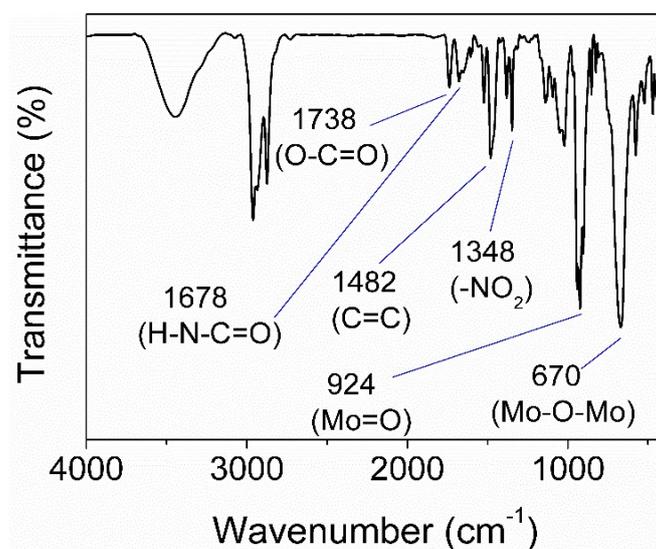


Fig. S18 FT-IR spectrum of 6.

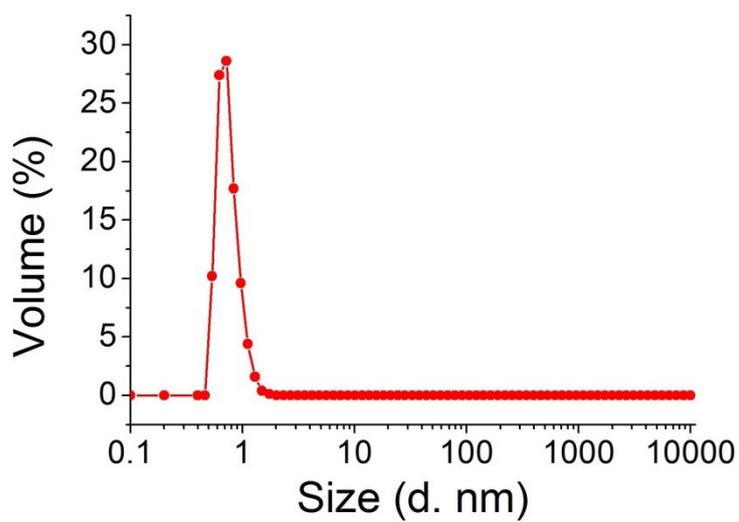
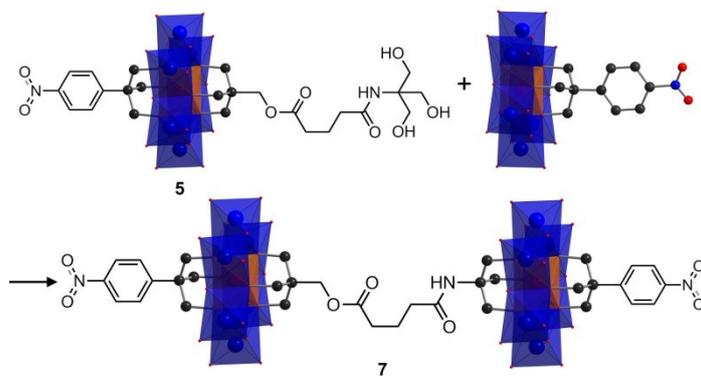


Fig. S19 The DLS spectrum of dimer 6 in acetonitrile.

$[(C_4H_9)_4N]_6\{(AlMo_6O_{18})_2[(OCH_2)_3CC_6H_4NO_2]_2[(OCH_2)_3CH_2OCO(CH_2)_3CONHC(OCH_2)_3]\}$ (7):



The synthesis of **7** was similar to that of **6** except the use of Al-NO₂ instead of Al-OH. Yield: 56.0%. ¹H-NMR (400 MHz, DMSO-*d*₆): δ = 8.25 (d, *J* = 9.0 Hz, 4H), 7.51 (d, *J* = 9.1 Hz, 4H), 7.25 (s, 1H), 4.74 (s, 12H), 4.64 (s, 6H), 4.43 (s, 6H), 3.64 (s, 2H), 3.26 - 3.07 (m, 48H), 2.29 (s, 2H), 2.03 (s, 2H), 1.58 (p, *J* = 8.0 Hz, 50H), 1.32 (h, *J* = 7.3 Hz, 48H), 0.94 (t, *J* = 7.3 Hz, 72H). FT-IR (KBr, cm⁻¹): 3471 (br), 2962 (s), 2876 (s), 1738 (s), 1677 (w), 1523 (m), 1482 (m), 1382 (m), 1349 (m), 1142 (m), 1041 (m), 941 (vs), 927 (vs), 905 (vs), 853 (m), 826 (m), 670 (vs), 578 (m), 523 (m), 471 (m), 448 (m). ESI-TOF-MS (neg. mode, MeCN): 1773.51 ({(TBA)₄M}²⁻, *calcd.* 1773.51), 1100.92 ({(TBA)₃M}³⁻, *calcd.* 1101.52), 764.37 ({(TBA)₂M}⁴⁻, *calcd.* 765.52). Elemental analysis (%) *calcd.* for C₁₃₀H₂₅₇Al₂Mo₁₂N₉O₅₅: C 38.69, H 6.37, N 3.13; found: C 38.25, H 6.38, N 2.75.

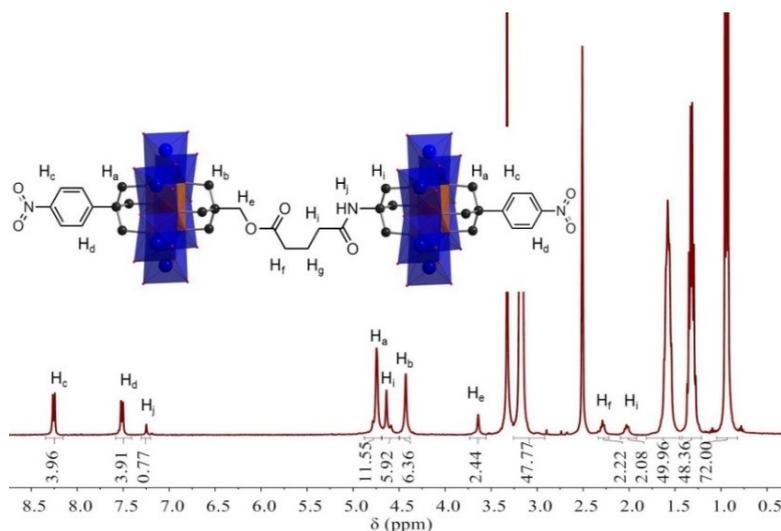


Fig. S20 ¹H-NMR spectrum of **7**.

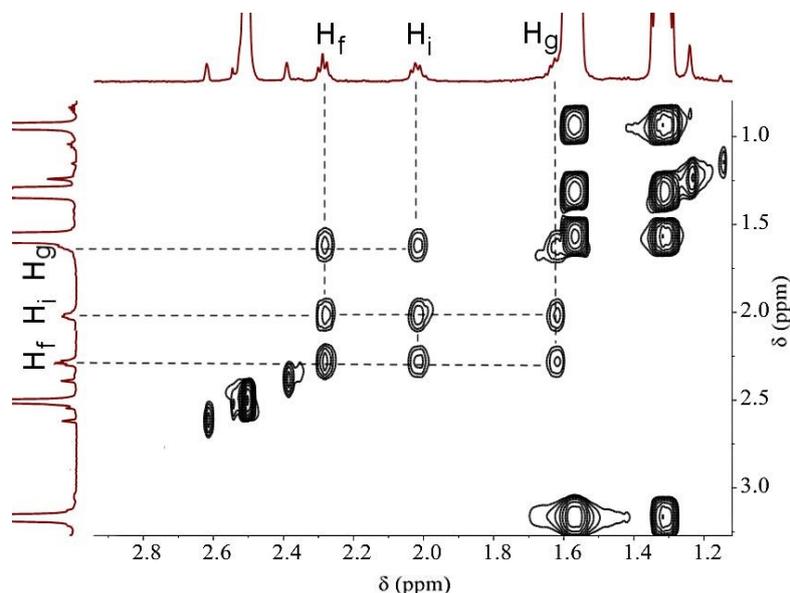


Fig. S21 2D TOCSY NMR spectrum of **7**, which gives the correlations of H_f, H_g, and H_i protons.

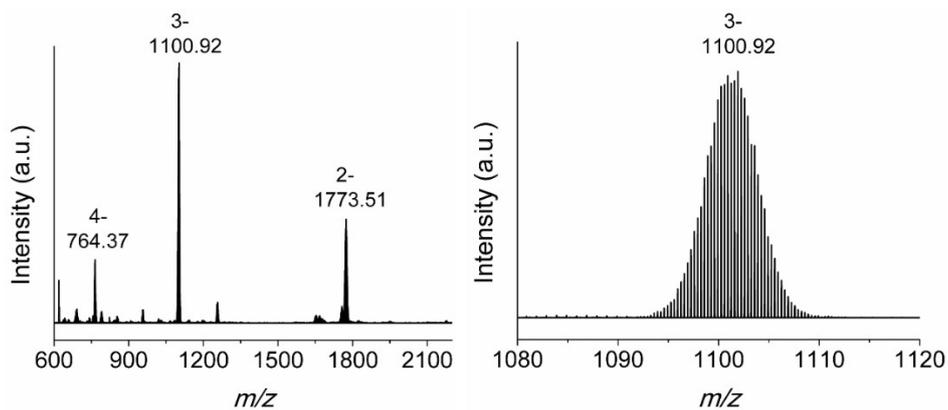
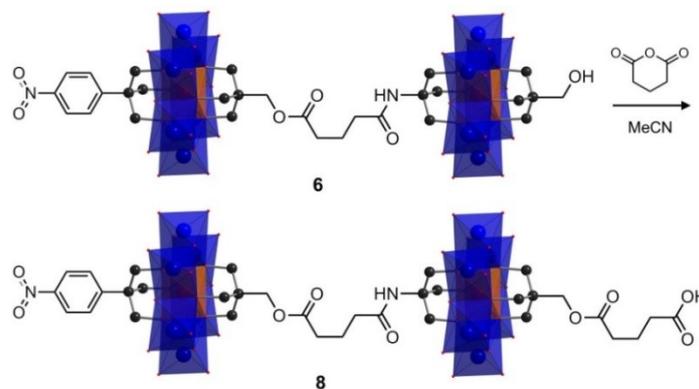


Fig. S22 ESI-TOF-MS spectra of **7**: full spectrum (left) and the molecular ion peak (right).

$[(C_4H_9)_4N]_6\{[AlMo_6O_{18}]_2[(OCH_2)_3CC_6H_4NO_2][[(OCH_2)_3CCH_2OCO(CH_2)_3CONHC(OCH_2)_3][[(OCH_2)_3C-CH_2OCO(CH_2)_3COOH]]\}$ (**8**):



The synthesis of **8** was similar to that of **3** except the use of **6** instead of **1**. Yield: 45.0%. 1H -NMR (400 MHz, DMSO- d_6): δ = 8.25 (d, J = 8.9 Hz, 2H), 7.51 (d, J = 9.0 Hz, 2H), 7.20 (s, 1H), 4.74 (s, 6H), 4.60 (s, 6H), 4.42 (s, 6H), 4.39 (s, 6H), 3.64 (s, 4H), 3.26 - 3.09 (m, 48H), 2.36 (s, 2H), 2.26 (d, J = 7.4 Hz, 4H), 2.01 (s, 2H), 1.71 (s, 4H), 1.58 (p, J = 7.9 Hz, 48H), 1.32 (h, J = 7.3 Hz, 48H), 0.94 (t, J = 7.3 Hz, 72H). FT-IR (KBr, cm^{-1}): 3445 (br), 2962 (s), 2876 (s), 1740 (m), 1645 (w), 1605 (w), 1524 (m), 1482 (m), 1383 (m), 1349 (m), 1141 (m), 1070 (m), 1028 (w), 943 (vs), 925 (vs), 905 (vs), 853 (m), 670 (vs), 578 (m), 526 (m), 471 (m), 448 (m).

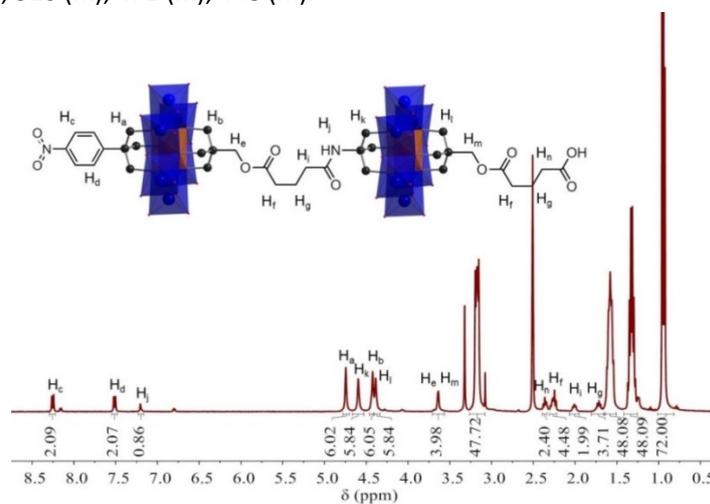
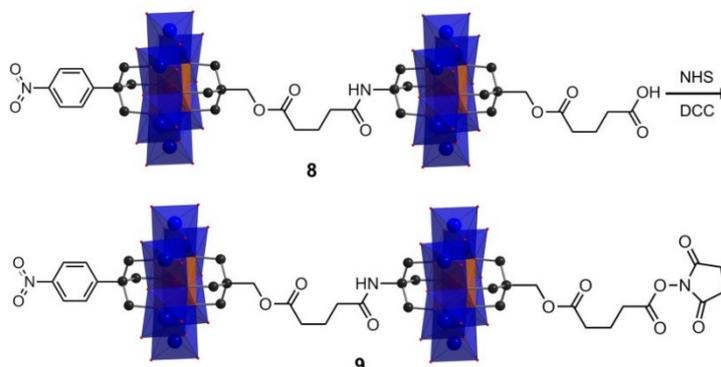


Fig. S23 1H -NMR spectrum of **8**.

$[(C_4H_9)_4N]_6\{(AlMo_6O_{18})_2[(OCH_2)_3CC_6H_4NO_2][[(OCH_2)_3CCH_2OCO(CH_2)_3CONHC(OCH_2)_3][[(OCH_2)_3C-CH_2OCO(CH_2)_3COOC_4H_4O_2N]]\}$ (9):



The synthesis of **9** was similar to that of **4** except the use of **8** instead of **3**. Yield: 55.0%. 1H -NMR (400 MHz, DMSO- d_6): δ = 8.25 (d, J = 9.0 Hz, 2H), 7.51 (d, J = 9.0 Hz, 2H), 7.20 (s, 1H), 4.75 (s, 6H), 4.60 (s, 6H), 4.42 (s, 6H), 4.39 (s, 6H), 3.64 (s, 4H), 3.27 - 3.09 (m, 48H), 2.81 (s, 4H), 2.72 (s, 2H), 2.48 (s, 2H), 2.28 (s, 2H), 2.01 (s, 2H), 1.84 (s, 2H), 1.77 (s, 2H), 1.58 (p, J = 8.0 Hz, 48H), 1.32 (h, J = 7.3 Hz, 48H), 0.94 (t, J = 7.3 Hz, 72H). FT-IR (KBr, cm^{-1}): 3475 (br), 2962 (s), 2876 (s), 1815 (w), 1784 (w), 1740 (s), 1747 (w), 1606 (w), 1524 (m), 1482 (m), 1382 (m), 1349 (m), 1206 (m), 1141 (m), 1069 (m), 942 (vs), 925 (vs), 905 (vs), 853 (m), 670 (vs), 577 (m), 527 (m), 471 (m), 447 (m).

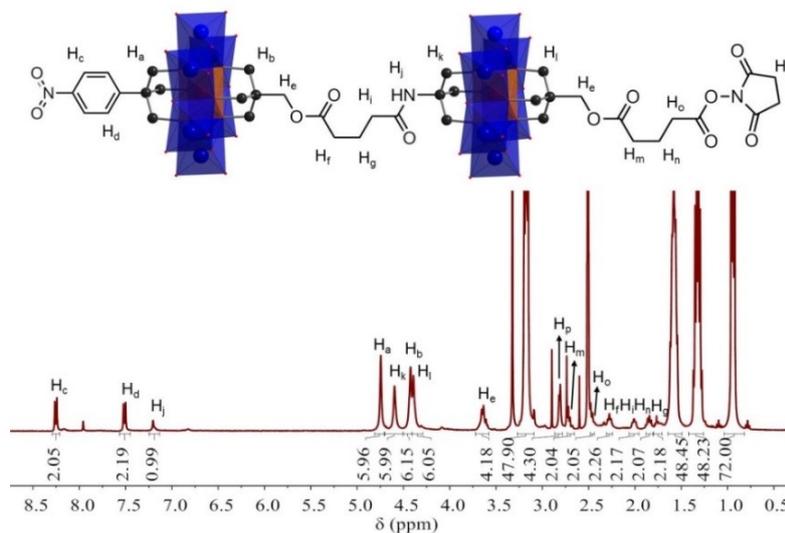
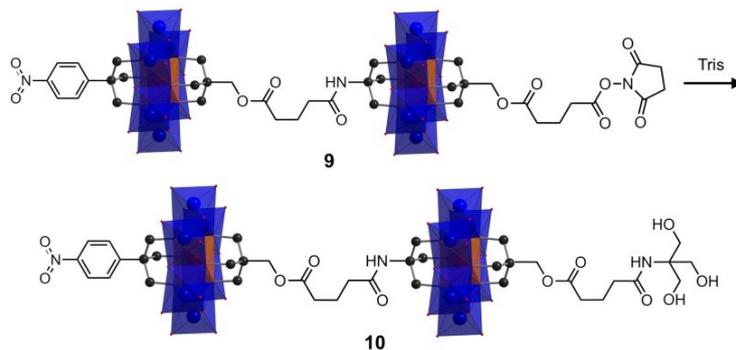


Fig. S24 1H -NMR spectrum of **9**.

$[(C_4H_9)_4N]_6\{(AlMo_6O_{18})_2[(OCH_2)_3CC_6H_4NO_2][[(OCH_2)_3CCH_2OCO(CH_2)_3CONHC(OCH_2)_3][[(OCH_2)_3C-CH_2OCO(CH_2)_3CONH(CH_2OH)_3]]\}$ (10):



The synthesis of **10** was similar to that of **5** except the use of **9** instead of **4**. Yield: 40,0%. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ = 8.25 (d, J = 9.0 Hz, 2H), 7.51 (d, J = 9.0 Hz, 2H), 7.21 (s, 1H), 7.09 (s, 1H), 4.75 (s, 6H), 4.69 (s, 3H), 4.60 (s, 6H), 4.43 (s, 6H), 4.39 (s, 6H), 3.63 (s, 4H), 3.52 (d, J = 5.8 Hz, 6H), 3.26 - 3.07 (m, 48H), 2.35 (s, 2H), 2.28 (s, 2H), 2.17 (s, 2H), 2.01 (s, 2H), 1.72 (s, 4H), 1.58 (p, J = 8.0 Hz, 48H), 1.32 (h, J = 7.3 Hz, 48H), 0.94 (t, J = 7.3 Hz, 72H). FT-IR (KBr, cm^{-1}): 3429 (br), 2962 (s), 2876 (s), 1738 (s), 1650 (w), 1523 (m), 1482 (m), 1382 (m), 1349 (m), 1141 (m), 1093 (m), 1050 (m), 942 (vs), 925 (vs), 905 (vs), 852 (m), 669 (vs), 578 (m), 522 (m), 471 (m), 446 (m).

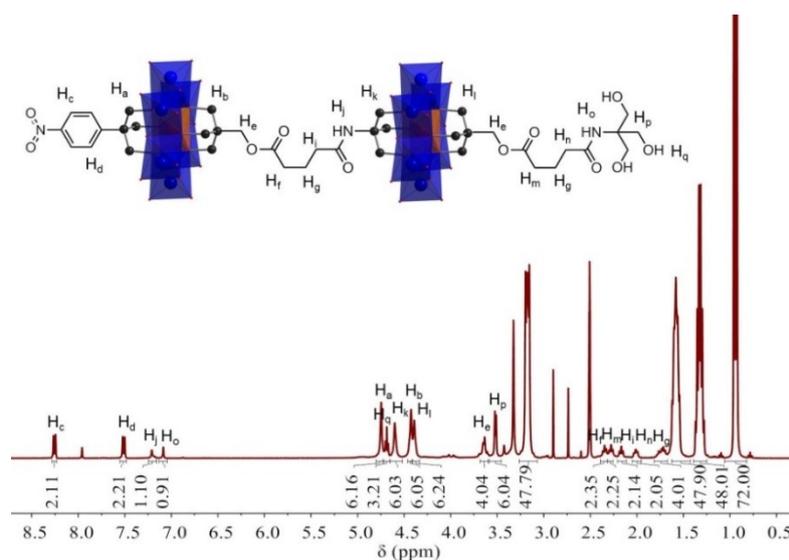
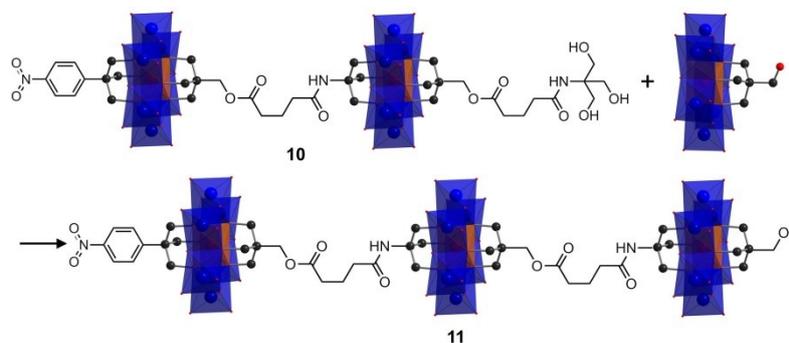


Fig. S25 $^1\text{H-NMR}$ spectrum of **10**.

$[(\text{C}_4\text{H}_9)_4\text{N}]_9\{(\text{AlMo}_6\text{O}_{18})_3[(\text{OCH}_2)_3\text{CC}_6\text{H}_4\text{NO}_2][(\text{OCH}_2)_3\text{CCH}_2\text{OCO}(\text{CH}_2)_3\text{CONHC}(\text{OCH}_2)_3]_2[(\text{OCH}_2)_3\text{C-CH}_2\text{OH}]\}$ (**11**):



The synthesis of **11** was similar to that of **6** except the use of **10** instead of **5**. Yield: 64.0%. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ = 8.25 (d, J = 9.0 Hz, 2H), 7.51 (d, J = 9.0 Hz, 2H), 7.19 (d, J = 9.9 Hz, 2H), 4.75 (s, 6H), 4.70 (s, 1H), 4.59 (s, 12H), 4.42 (s, 6H), 4.37 (s, 12H), 3.63 (s, 4H), 3.18 (dd, J = 10.7, 5.6 Hz, 72H), 2.96 (d, J = 5.3 Hz, 2H), 2.28 (s, 4H), 2.01 (s, 4H), 1.77 - 1.46 (m, 76H), 1.33 (h, J = 7.2 Hz, 72H), 0.94 (t, J = 7.3 Hz, 108H). FT-IR (KBr, cm^{-1}): 3442 (br), 2967 (s), 2876 (s), 1738 (w), 1667 (s), 1523 (w), 1478 (m), 1381 (w), 1348 (m), 1049 (m), 1023 (m), 945 (vs), 928 (vs), 901 (vs), 672 (vs), 575 (w), 471 (w). ESI-TOF-MS (neg. mode, MeCN): 1726.03 ($\{(\text{TBA})_6\text{M}\}^{3-}$, *calcd.* 1726.31), 1653.27 ($\{(\text{Na}(\text{TBA})_5\text{M})^{3-}$, *calcd.* 1654.15), 1234.05 ($\{(\text{TBA})_5\text{M}\}^{4-}$, *calcd.* 1234.12), 1173.48 ($\{(\text{H}(\text{TBA})_4\text{M})^{4-}$, *calcd.* 1173.75), 938.10 ($\{(\text{TBA})_4\text{M}\}^{5-}$, *calcd.* 939.20), 741.37 ($\{(\text{TBA})_3\text{M}\}^{6-}$, *calcd.* 741.92). Element analysis (%) *calcd.* for $\text{C}_{187}\text{H}_{385}\text{Al}_3\text{Mo}_{18}\text{N}_{12}\text{O}_{81}$: C 38.03, H 6.57, N 2.85; found: C 37.96; H 6.24, N 2.80.

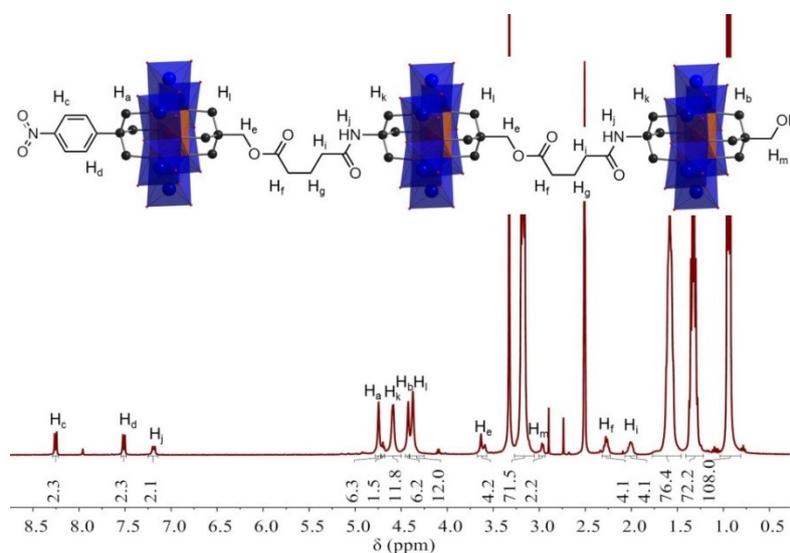


Fig. S26 $^1\text{H-NMR}$ spectrum of **11**.

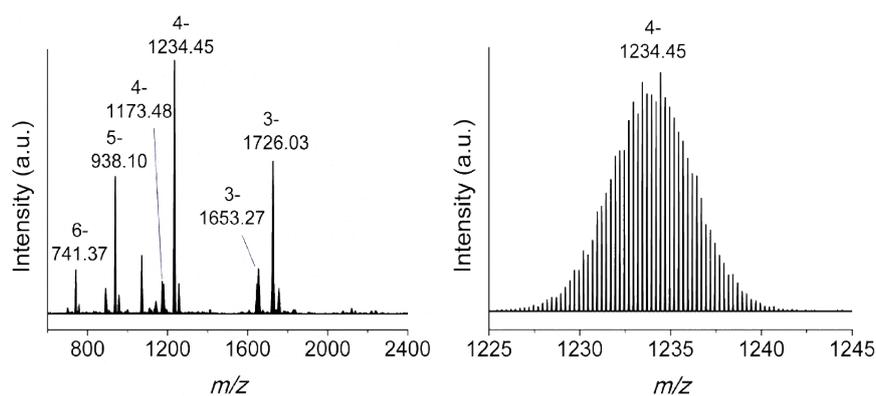


Fig. S27 ESI-TOF-MS spectra of **11**: full spectrum (left) and the molecular ion peak (right).

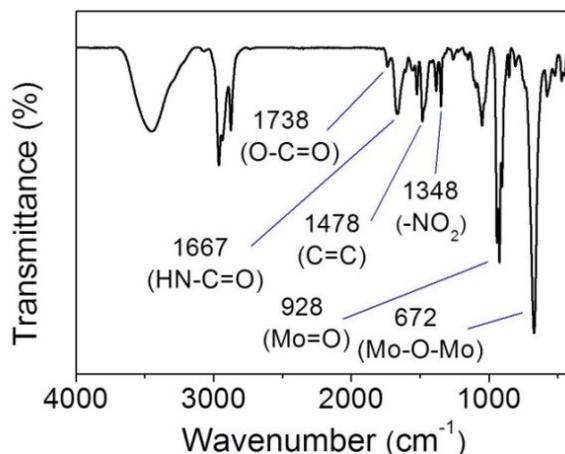


Fig. S28 FT-IR spectrum of **11**.

[(C₄H₉)₄N]₉H{SiW₁₁O₄₀{Si(CH₂)₃NHCO(CH₂)₃COOCH₂C(OCH₂)₃(AlMo₆O₁₈)(OCH₂)₃CC₆H₄NO₂]₂ (12):

SiW₁₁-NH₂ (2.0 g, 0.5 mmol), **4** (2.4 g, 1.1 mmol) and DIPEA (192 μL, 1.1 mmol) were dissolved in 10 mL anhydrous DMF and stirred at r.t. overnight. The undissolved residues were filter off and the filtrate was placed under diethyl ether atmosphere for slow vapor diffusion. Light-brown crystals were obtained after 3 days and were washed several times with acetone. Yield: 49.0%. ¹H-NMR (400 MHz, DMSO-*d*₆): δ = 8.26 (d, *J* = 9.0 Hz, 4H), 7.79 (s, 2H), 7.52 (d, *J* = 9.0 Hz, 4H), 4.75 (s, 12H), 4.44 (s, 12H), 3.66 (s, 8H), 3.28 - 3.09 (m, 68H), 3.04 (s, 4H), 2.32 (s, 4H), 2.10 (s, 4H), 1.70 (s, 4H), 1.58 (p, *J* = 8.1 Hz, 69H), 1.33 (q, *J* = 7.3 Hz, 65H), 0.94 (t, *J* = 7.3 Hz, 100H), 0.52 (s, 4H). FT-IR (KBr, cm⁻¹): 3471 (br), 2963 (s), 2876 (s), 1738 (m), 1650 (m), 1524 (m), 1483 (m), 1382 (m), 1349 (m), 1140 (m), 1044 (s), 964 (s), 943 (s), 926 (s), 905 (s), 853 (m), 807 (s), 755 (w), 672 (s), 577 (m), 530 (m), 472 (w), 448 (w), 419 (w). MALDI-TOF-MS (neg. mode, MeCN): 4002.58 ({(TBA)₁₀(M-2H)}²⁻, *calcd.* 3987.54), 2432.04 ({(TBA)₇M}³⁻, *calcd.* 2423.40), 2334.16 ({(TBA)₆HM}³⁻, *calcd.* 2335.57). Elemental analysis (%) *calcd.* for C₁₉₀H₃₈₇Al₂Mo₁₂N₁₃O₉₈Si₃W₁₁: C 29.51, H 5.03, N 2.35; found: C 29.77, H 4.98, N 2.42.

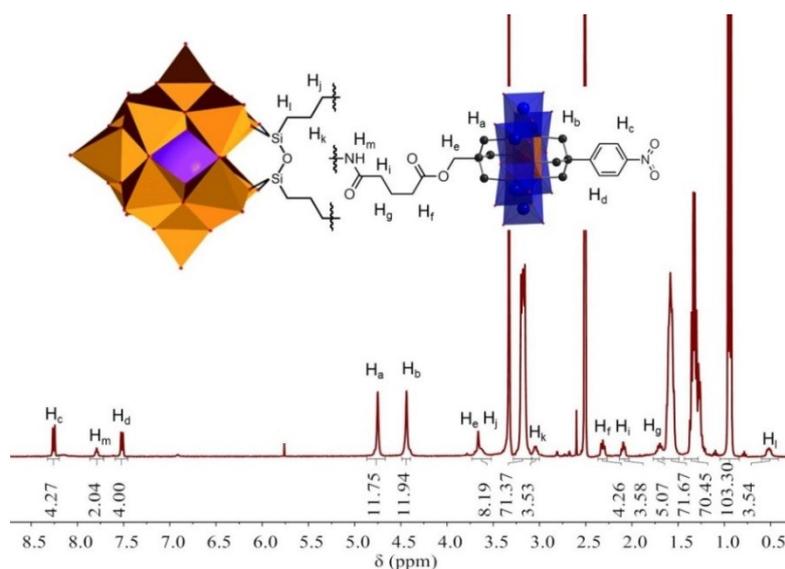


Fig. S29 ¹H-NMR spectrum of **12**.

3. Crystallographic data

Table S1 Summary of crystal data for compound **1** and **2'**.

	1	2'
CCDC NO.	2212865	2212866
formula	C ₆₃ H ₁₂₇ AlMo ₆ N ₄ O ₂₇	C ₆₄ H ₁₂₆ Al ₂ Mg ₃ Mo ₁₂ N ₁₆ O ₆₇
F.W.	1975.30	3469.98
Cryst. Syst.	monoclinic	monoclinic
Space group	<i>P2₁/c</i>	<i>P2₁/c</i>
<i>a</i> /Å	13.9148 (2)	17.15420 (10)
<i>b</i> /Å	13.1920 (2)	34.8516 (2)
<i>c</i> /Å	24.9753 (3)	22.25040 (10)
α (°)	90	90
β (°)	91.8810 (10)	93.4110 (10)
γ (°)	90	90
<i>V</i> /Å ³	4582.10 (11)	13278.87 (12)
<i>Z</i>	2	4
ρ	1.432	1.736
<i>R</i> ₁	0.0623	0.0692
<i>wR</i> ₂	0.1883	0.1840

4. References

1. G. M. Sheldrick, *Acta Cryst.*, **2015**, A71, 3-8.
2. G. M. Sheldrick, *Acta Cryst.*, **2015**, C71, 3-8.
3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, **2009**, 42, 339-341.