Electronic Supplementary Information

From achiral to helical bilayer self-assemblies of 1,3,5-triazine-2,4,6-triphenol-grafted polyanionic cluster: Countercation and solvent modulation

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Contents

Materials

Trifluoromethanesulfonic acid, 1-bromohexane, ethyl bromoacetate and tris(hydroxymethyl)aminomethane were from Sinopharm Chemical Reagent Co, Ltd. (SCRC) and used as received. $[N(C_4H_9)_4]_4[\alpha\text{-}Mo_8O_{26}]$ and $Mn(OAc)_3{\cdot}2H_2O$ were prepared according to the literature.[1] The other chemicals and solvents were the products from Beijing Chemical Reagent Industry. Acetone, toluene, dichloromethane and acetonitrile were dried over P_2O_5 prior to use. DMSO was dried over CaH_2 for days and distilled prior to use.

Instruments

^1H NMR spectra were recorded on a Bruker AVANCE 500 MHz spectrometer. FT-IR spectra were carried out on a Bruker Vertex 80v FT-IR spectrometer equipped with a DTGS detector (32 scans) with a resolution of 4 cm^{-1} on a KBr pellet. Powder X-ray diffraction (XRD) data were recorded on a Rigaku X-ray diffractometer using Cu K_α radiation at a wavelength of 1.542 Å. Organic elemental analysis (C, H, and N) was performed on a Vario micro cube from Elementar company, while inorganic elemental analysis (Mn, Mo and Na) was performed on an iCAP 7000 inductively coupled plasma atomic emission spectrometer (ICP-AES). Electrospray ionization mass spectrometry (ESI-MS) was obtained on a UPLC-MS/MS (Quattro Premier). The UV-Vis spectra were taken by using a spectrophotometer (Varian CARY 50 Probe). Circular dichroism (CD) spectra were carried out on a Bio-Logic MOS-450 spectropolarimeter with a step size of 1 nm at a speed of 1 nm/s. AFM images were taken with a Dimension FastScan (Bruker, USA) under ambient conditions, operating on the tapping mode with an optical readout using Si cantilevers. Scanning electron microscope (SEM) images were acquired on a JEOL FESEM 6700F electron microscope, and transmission electron microscopic (TEM) images were carried out on a Hitachi H8100 electron microscope. High resolution TEM was conducted on JEOL JEM 2010 under an accelerating voltage of 200 kV.

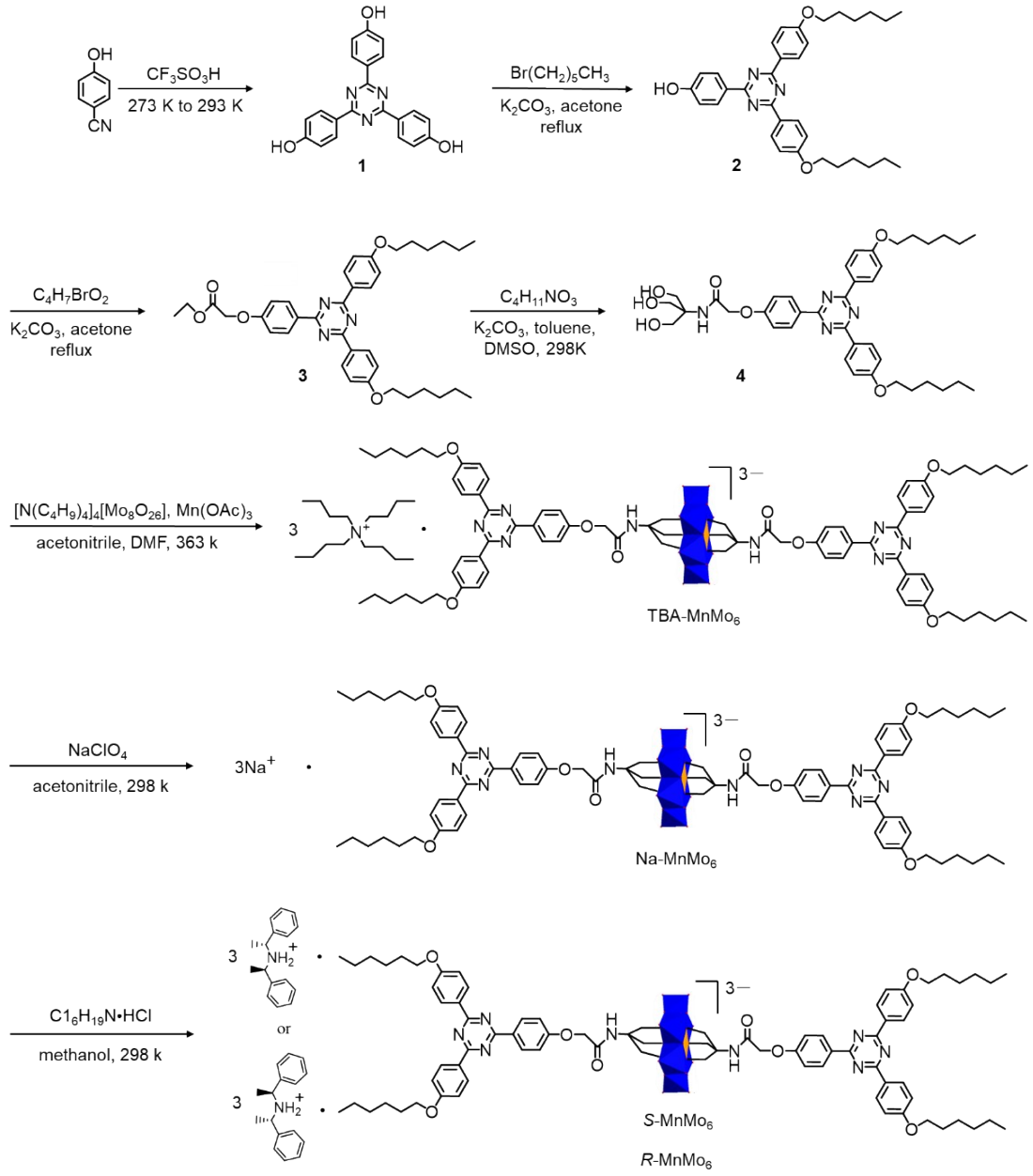
Sample preparation

A typical procedure of sample preparation for TEM was as follows: 0.1 mg sample was added to a 1.0 mL of the mixed solvent in different volume ratios. The solution was sonicated for 20 min at 25 ºC and then was allowed to stand for another 20 min. The obtained self-assembly sample solution was dropped onto carbon-coated copper grids, and then the grids were allowed to dry at room temperature for TEM measurement. The sample preparation for SEM was the same to that for TEM except that the solution was dropped onto a silicon wafer. The samples for AFM measurement were prepared by dropping 10 μL of sample solution onto a silicon wafer and dried gently by blowing nitrogen gas. Samples for XRD was prepared by dropping 10 μL of self-assembly solution onto a silicon wafer followed by drying at room temperature, and this procedure was repeated for ten times to accumulate enough samples for obtaining clear XRD signals.

Synthesis

The synthetic route for the prepared polyanionic cluster with four counter cations in this study is summarized in Chart S1 and the detailed procedures are described as follows.

Chart S1 Synthetic route of the organically modified polyanion with four countercations.



Synthesis of 2,4,6-Triazinetriphenol (1). Trifluoromethanesulfonic acid (10.1 mL, 121.8 mmol) was added to a stirred dichloromethane solution of 4-cyanophenol (5.0 g, 42.0 mmol) slowly at 0 °C under N_2 atmosphere. After stirring for 24 h at room temperature, ammonia water was added. And then, yellow precipitate was obtained after filtration. Finally, the yellow precipitate was washed with deionized water and dried to obtain white powder product (**1**) (12.9 g, 86.0%). ^{1}H NMR (DMSO-d_6, 500 MHz, 298K): δ (ppm)= 10.26 (s, 2H), 8.56−8.55 (d, 6H) 6.99−6.97 (d, 6H). Elemental analysis Calc. for $C_{21}H_{15}N_3O_3$ (357.37 g/mol): C, 70.58%; H, 4.23%; N, 11.76%, found: C, 70.43%; H, 4.35%; N, 11.66%.

Synthesis of 4-(4,6-bis(4-(hexyloxy)phenyl)-1,3,5-triazin-2-yl)phenol (2). To a stirred solution of (**1**) (5.0 g, 14.0 mmol) and K_2CO_3 (1.9 g, 14.0 mmol), 1-bromohexane (4.6 g, 28.0 mmol) were added to acetone (200 mL) under N_2 atmosphere, and the reaction mixture was allowed to reflux for 12 h. Then the reaction solution was cooled to room temperature and the formed salt was removed

by filtration. The crude product was purified by column chromatography with mixture eluent petroleum ether:dichloromethane (1:1, in *v*/*v*), obtaining pure compound (**2**) as a white powder (1.4 g, 19.3%). ^{1}H NMR ($CDCl_3$, 500 MHz, 298K): δ (ppm)= 8.72−8.69 (t, 6H), 7.07−7.00 (m, 6H), 5.10 (s, 1H), 4.12−4.09 (t, 4H), 1.90−1.84 (m, 4H) 1.55−1.50 (m, 1H) 1.42−1.39 (m, 1H), 0.97−0.94 (t, 1H). Elemental analysis Calc. for $C_{33}H_{39}N_3O_3$ (525.69 g/mol): C, 75.40%; H, 7.48%; N, 7.99%, found: C, 75.23%; H, 7.41%; N, 8.17%.

Synthesis of 1-(4-(4,6-bis(4-(hexyloxy)phenyl)-1,3,5-triazin-2-yl)phenoxy)butan-2-one (3). A mixture of (**2)** (1.42 g, 2.7 mmol), K_2CO_3 (0.74 g, 5.4 mmol) and ethyl bromoacetate (1.78 g, 10.7 mmol) in dry acetone (60 mL) was refluxed for 4 h with stirring under N_2 atmosphere. After removal of the formed salt by filtration, the crude product (**3)** was obtained. The crude product was washed with ethanol and pure product was obtained as a white solid in yield 95.7% (1.54 g). ^{1}H NMR ($CDCl_3$, 500 MHz, 298K): δ (ppm) = 8.72−8.68 (m, 6H), 7.07−7.03 (m, 6H), 4.73 (s, 2H), 4.33−4.29 (m, 2H) 4.09−4.06 (t, 4H) 1.87−1.81 (m, 4H), 1.54−1.48 (m, 4H), 1.40−1.36 (m, 8H), 1.34−1.31 (t, 3H) 0.94−0.91 (t, 6H). Elemental analysis Calc. for $C_{37}H_{45}N_3O_4$ (595.78 g/mol): C, 74.59%; H, 7.61%; N, 7.05%, found: C, 74.68%; H, 7.41%; N, 7.00%.

Synthesis of 2-(4-(4,6-bis(4-(hexyloxy)phenyl)-1,3,5-triazin-2-yl)phenoxy)-N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)acetamide (4). Tris(hydroxymethyl)aminomethane (0.45 g, 3.7 mmol) and (**3)** (1.52 g, 2.6 mmol) were dissolved in a mixture of toluene and DMSO (1:4, v/v, 10 mL), then potassium carbonate (0.51 g, 3.6 mmol) was added. The mixture was stirred under N_2 atmosphere for 48 h at room temperature. The product (**4**) was precipitated by adding deionized water in yield 86.2% (1.51 g).^{1}H NMR ($CDCl_3$, 500 MHz, 298K): δ (ppm)= 8.74−8.68 (m, 6H,), 7.68 (s, 1H), 7.10−7.04 (m, 6H), 4.65 (s, 2H), 4.09−4.07 (t, 4H), 3.74−3.73 (d, 6H), 3.52 (s, 3H), 1.87−1.81 (m, 4H), 1.52−1.48 (m, 4H), 1.39−1.36 (m, 8H), 0.94−0.91 (t, 6H). Elemental analysis Calc. for $C_{39}H_{50}N_4O_7$ (686.85 g/mol): C 68.2%, H 7.34%, N 8.16%; found C 68.17%, H 7.30%, N 8.33%.

Synthesis of $[N(C_4H_9)_4]_3\{MnMo_6O_{18}[(OCH_2)_3CNHCOC_{34}H_{43}N_3O_3]_2\}$ (TBA-$MnMo_6$). The Anderson-type polyoxometalate TBA-$MnMo_6$ was synthesized through a modified method reported in the literature.[2] A mixture of $[N(C_4H_9)_4]_4[\alpha\text{-}Mo_8O_{26}]$ (1.05 g, 0.5 mmol), $Mn(OAc)_3{\cdot}2H_2O$ (0.12 g, 0.5 mmol) and compound (**4)** (1.20 g, 1.6 mmol) was heated to reflux in acetonitrile with a small amount of DMF for 24 h. The resulted black precipitate was removed by filtration. Through diffusion of diethyl ether into the filtrate at room temperature, TBA_3MnMo_6 was obtained after several days in yield 69.6% (1.03 g, based on Mo). ^{1}H NMR (DMSO-d_6, 500 MHz, 298K): δ (ppm)= 64.32 (br, 12H), 8.67−8.66 (d, 12H), 7.95 (br, 2H), 7.16−7.15 (d, 12H), 4.97 (br, 4H), 3.17−3.14 (t, 8H), 3.14 (t, 24H), 1.81−1.77 (m, 8H), 1.57−1.54 (t, 24H), 1.48 (br, 8H), 1.34−1.29 (m, 40H), 0.95−0.90 (m, 48H). ESI-MS (m/z) $[M\text{-}2TBA]^{2-}$: calculated for $C_{94}H_{136}N_9O_{32}MnMo_6$: 1267.4, found: 1267.7; $[M\text{-}TBA]^-$: calculated for $C_{110}H_{172}N_{10}O_{32}MnMo_6$: 2777.2, found: 2777.6. Elemental analysis Calc. for $C_{126}H_{208}N_{11}O_{32}MnMo_6$ (3019.63 $gmol^{-1}$): C, 50.12%; H, 6.94%; N, 5.10%; Mn, 1.82%; Mo, 19.06%; found: C, 50.27%; H, 6.64%; N, 5.03%; Mn, 1.93%; Mo, 19.1%. IR (KBr): ν = 2958 (s), 2933 (s), 2871 (s), 1701 (s), 1604 (s), 1583 (s), 1506 (s), 1471 (s), 1419 (s), 1369 (s), 1303 (s), 1251 (s), 1174 (s), 1147 (s), 1110 (s), 1070 (s), 1027 (s), 943 (s), 914 (s), 900 (s), 858 (s), 817 (s), 771 (w), 748 (w), 727 (w), 667 (s), 617 (w), 592 (w), 567 (w), 526 (w), 503 (w), 478 (w), 459 (w), 435 (w), and 414 (w) cm^{-1}.

Synthesis of $Na_3\{MnMo_6O_{18}[(OCH_2)_3CNHCOC_{34}H_{43}N_3O_3]_2\}$ (Na-$MnMo_6$). The powder of TBA-$MnMo_6$ (0.50 g, 0.2 mmol) was dissolved in 60 mL of acetonitrile and the solution was stirred

for 1 h and then the solution was added dropwise to a clear solution with large excess amount (0.18 g, 1.5 mmol) of sodium perchlorate in acetonitrile (50 mL). Orange precipitate formed immediately and was centrifuged, drying under vacuum for several days. Yield 82.4% (0.33 g, based on Mo). ^{1}H NMR (DMSO-d_6, 500 MHz, 298K): δ (ppm) = 64.43 (br, 12H), 8.68−8.67 (d, 12H), 7.17−7.16 (d, 12H), 4.98 (br, 4H), 4.14−4.11 (t, 8H), 1.81−1.76 (m, 8H), 1.50−1.44 (m, 8H), 1.37−1.34 (m, 16H), 0.92−0.80 (t, 12H). ESI-MS (m/z) $[M\text{-}2Na]^{2-}/2$: calculated for $C_{78}H_{100}N_8O_{32}NaMnMo_6$: 1257.6, found: 1157.0; $[M\text{-}Na]^-$: calculated for $C_{78}H_{100}N_8O_{32}Na_2MnMo_6$: 2338.2, found: 2338.0. Elemental analysis Calc. for $C_{78}H_{100}N_8O_{32}Na_3MnMo_6$ (2361.21 gmol^{-1}): C, 39.68%; H, 4.27%; N, 4.75%; Mn, 2.33%; Mo, 24.38%; found: C, 39.33%; H, 4.38%; N, 4.87%; Mn, 2.43%; Mo, 24.40%. IR (KBr): ν = 2927 (s), 2867 (s), 2357(s), 1683 (s), 1606 (s), 1585 (s), 1504 (s), 1418 (s), 1369 (s), 1303 (s), 1251 (s), 1173 (s), 1148 (s), 1110 (s), 1053 (s), 1026 (s), 947 (s), 924 (s), 900 (s), 860 (s), 820 (s), 667 (s), 565 (w), 519 (w), and 457(w) cm^{-1} .

Synthesis of $[C_{16}H_{20}N]_3\{MnMo_6O_{18}[(OCH_2)_3CNHCOC_{34}H_{43}N_3O_3]_2\}$ (*S*-MnMo$_6$). The powder of Na-MnMo$_6$ (0.50 g, 0.2 mmol) was dissolved in 100 mL of methanol and the solution was stirred for 1 h and then the solution was added dropwise to a clear solution of large excess amount (0.20 g, 0.8 mmol) of (-)-bvis[(S)-1-phenylethyl]amine hydrochloride (*S*-BPEA·Cl) in methanol (50 mL). Orange precipitate formed immediately and was centrifuged, drying under vacuum for several days to give the product in yield 79.2% (0.49 g, based on Mo). ^{1}H NMR (DMSO-d_6, 500 MHz, 298K): δ (ppm) = 64.16 (br, 12H), 9.23 (s, 6H), 2.75−2.74 (d, 6H), 1.80−1.75 (m, 8H), 1.53−1.45 (t, 26H), 1.36−1.33 (m, 16H), 0.91−0.89 (m, 12H). ESI-MS (m/z) $[M-2Helix]^{2-}/2$: calculated for $C_{94}H_{120}N_9O_{32}MnMo_6$: 1259.3, found: 1259.0. Elemental analysis Calc. for $C_{126}H_{160}N_{11}O_{32}MnMo_6$ (2971.25 gmol^{-1}): C, 50.93%; H, 5.43%; N, 5.19%; Mn, 1.85%; Mo, 19.37%; found: C, 50.63%; H, 5.68%; N, 5.35%; Mn, 1.91%; Mo, 19.50%. IR (KBr): ν = 3062 (s), 2930 (s), 2856 (s), 2495 (s), 1666 (s), 1606 (s), 1585 (s), 1506 (s), 1467 (s), 1420 (s), 1369 (s), 1300 (s), 1250 (s), 1173 (s), 1147 (s), 1111 (s), 1057 (s), 1026 (s), 947 (s), 920 (s), 860 (s), 820 (s), 762 (w), 669 (s), 565 (w), 542 (w), 518 (w), 459 (w), 433 (w), and 412(w) cm^{-1}.

Synthesis of $[C_{16}H_{20}N]_3\{MnMo_6O_{18}[(OCH_2)_3CNHCOC_{34}H_{43}N_3O_3]_2\}$ (*R*-MnMo$_6$). The po wder of Na-MnMo$_6$ (0.50 g, 0.2 mmol) was dissolved in 100 mL of methanol and the so lution was stirred for 1 h and then the solution was added dropwise to a clear solution of large excess amount (0.20 g, 0.8 mmol) of (R,R)-(+)-bis[alpha-methylbenzyl]amine hydroch loride (*R*-BPEA·Cl) in methanol (50 mL). Orange precipitate formed immediately and was centrifuged, drying under vacuum for several days to give the product in yield 80.0% (0.5 0 g, based on Mo). ^{1}H NMR (DMSO-d_6, 500 MHz, 298K): δ (ppm)= 64.15 (br, 12H), 9. 23 (s, 6H), 2.75−2.74 (d, 6H), 1.80−1.76 (m, 8H), 1.53−1.45 (t, 26H), 1.35−1.33 (m, 16H), 0.92−0.89 (m, 12H). ESI-MS (m/z) $[M-2Helix]^{2-}/2$: calculated for $C_{94}H_{120}N_9O_{32}MnMo_6$: 12 59.3, found: 1260.0. Elemental analysis Calc. for $C_{126}H_{160}N_{11}O_{32}MnMo_6$ (2971.25 gmol^{-1}): C, 50.93%; H, 5.43%; N, 5.19%; O,17.23%; Mn, 1.85%; Mo, 19.37%; found: C, 50.95%; H, 5.44%; N, 5.22% O, 17.11%; Mn,1.81%; Mo, 19.32%. IR (KBr): ν = 3063 (s), 2930 (s), 2855 (s), 2495 (s), 1666 (s), 1606(s), 1587 (s), 1506 (s), 1467 (s), 1420 (s), 1368 (s), 13 00 (s), 1250 (s), 1173 (s), 1147 (s), 1111 (s), 1057 (s), 1025 (s), 947 (s), 920 (s), 860 (s), 820 (s), 762 (w), 669 (s), 565(w), 542 (w), 518 (w), 459(w), 433(w), and 413 (w) cm^{-1}.

Structural characterizations of synthetic molecules

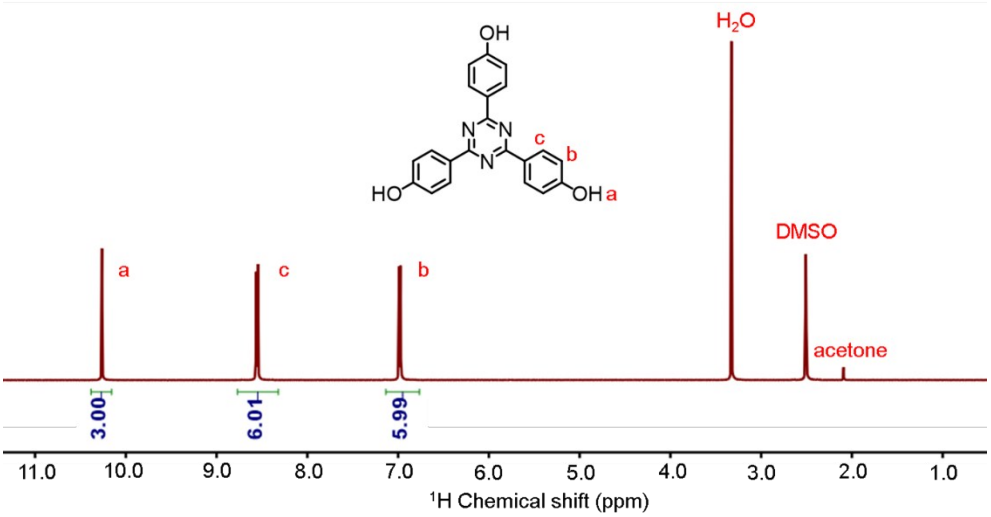


Fig. S1 ^{1}H NMR spectrum of 2,4,6-triazinetriphenol (**1**) in DMSO-d_6.

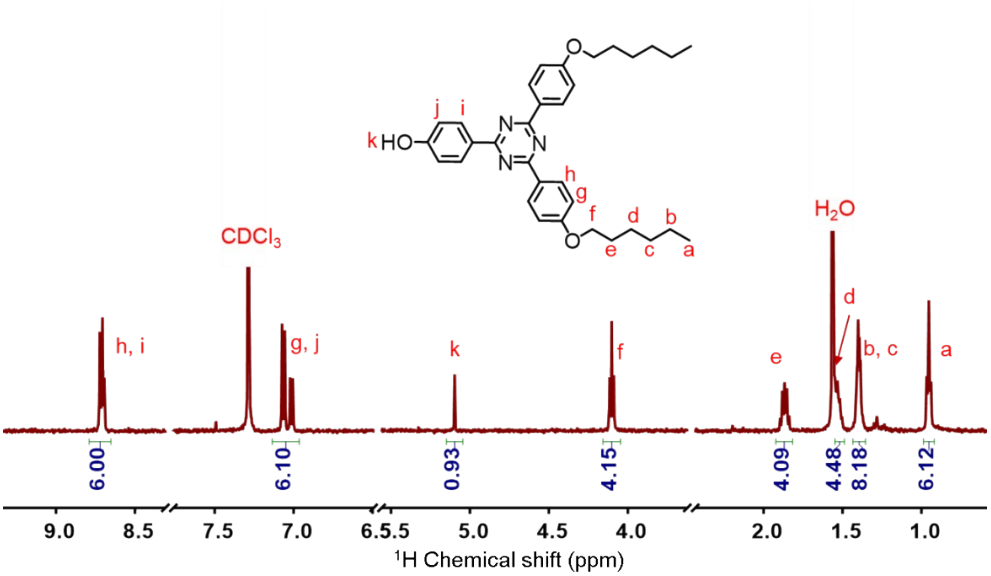


Fig. S2 ^{1}H NMR spectrum of 4-(4,6-bis(4-(hexyloxy)phenyl)-1,3,5-triazin-2-yl)phenol (**2**) in $CDCl_3$.

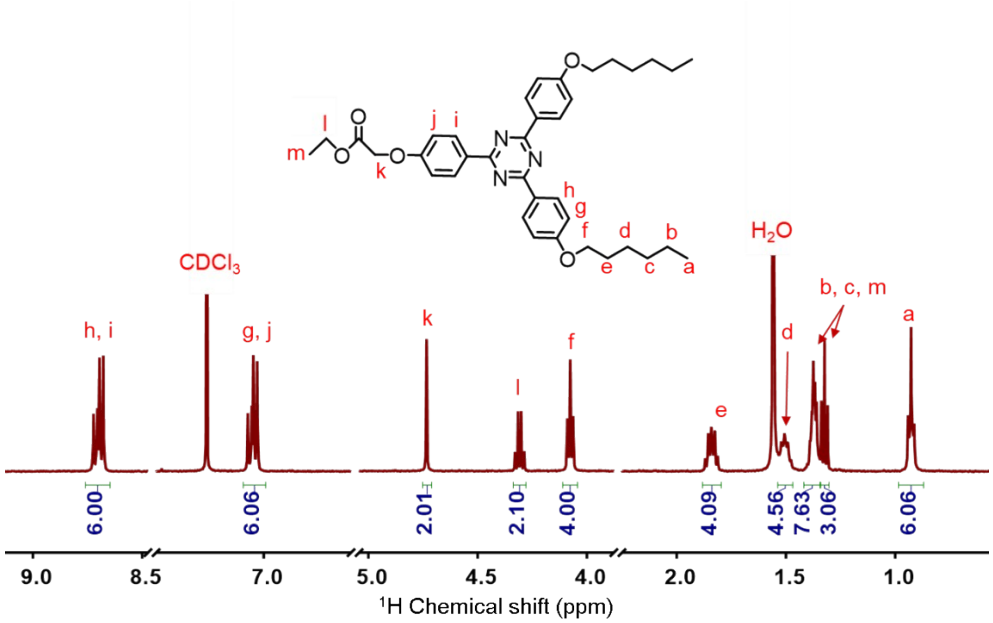


Fig. S3 ^{1}H NMR spectrum of 1-(4-(4,6-bis(4-(hexyloxy)phenyl)-1,3,5-triazin-2-yl)phenoxy)butan-2-one (**3**) in $CDCl_3$.

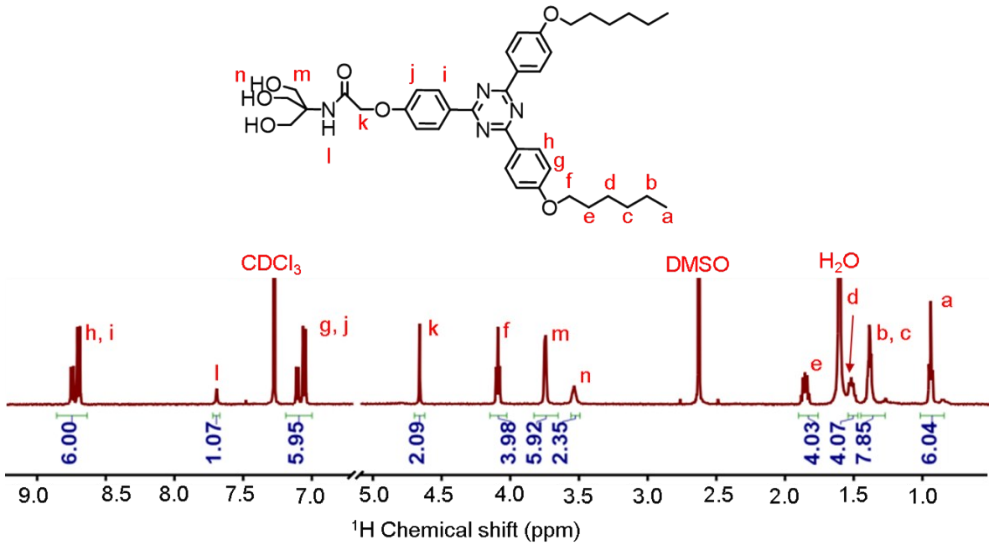


Fig. S4 ^{1}H NMR spectrum of 2-(4-(4,6-bis(4-(hexyloxy)phenyl)-1,3,5-triazin-2-yl)phenoxy)-N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)acetamide (**4**) in $CDCl_3$.

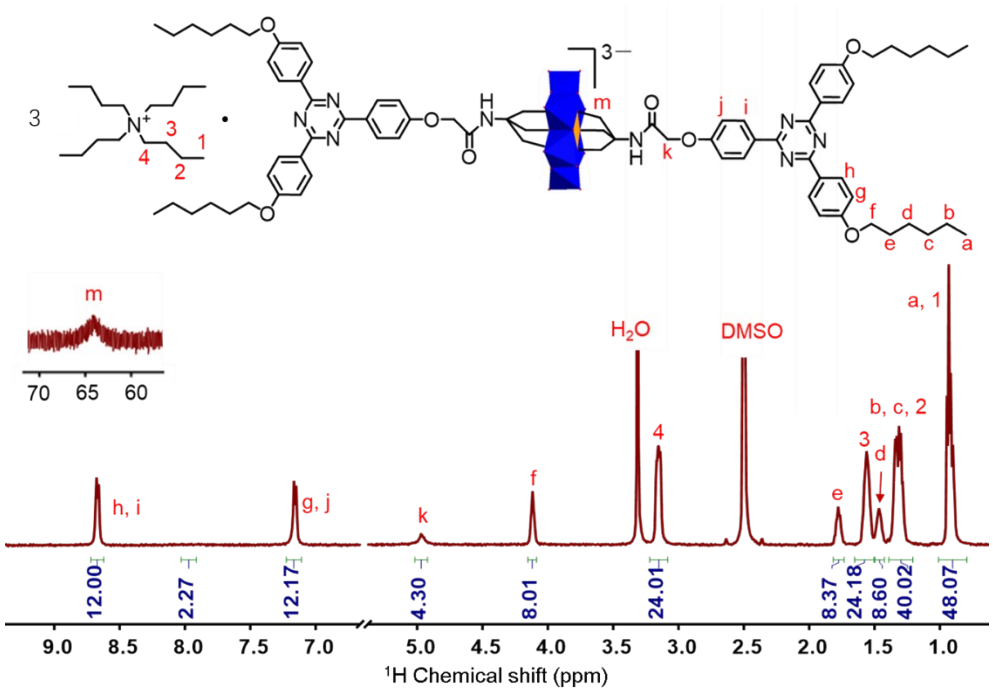


Fig. S5 ^{1}H NMR spectrum of TBA-MnMo$_6$ in DMSO-d_6.

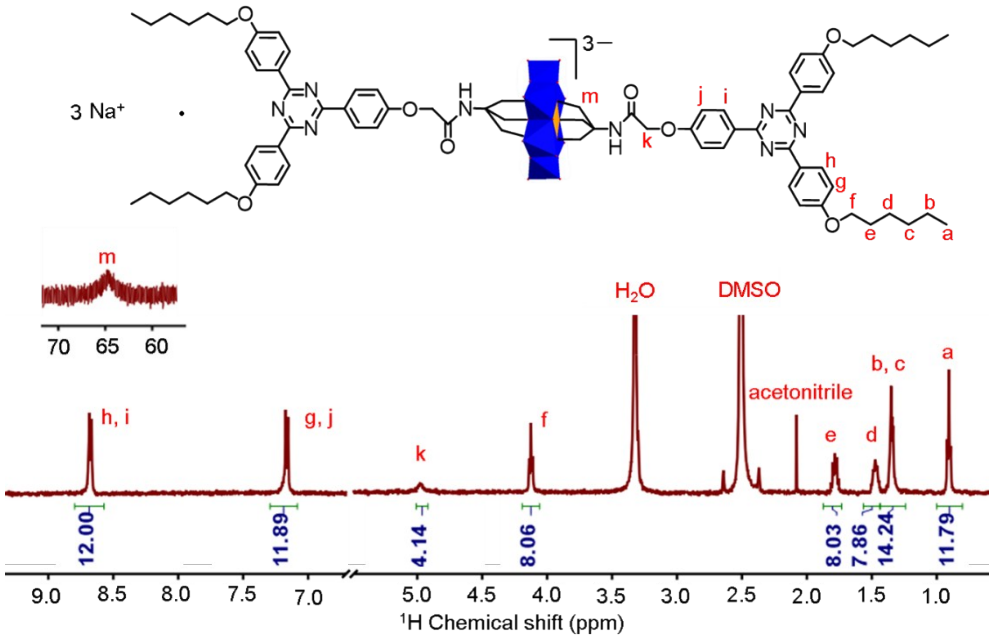


Fig. S6 ^{1}H NMR spectrum of Na-MnMo$_6$ in DMSO-d_6.

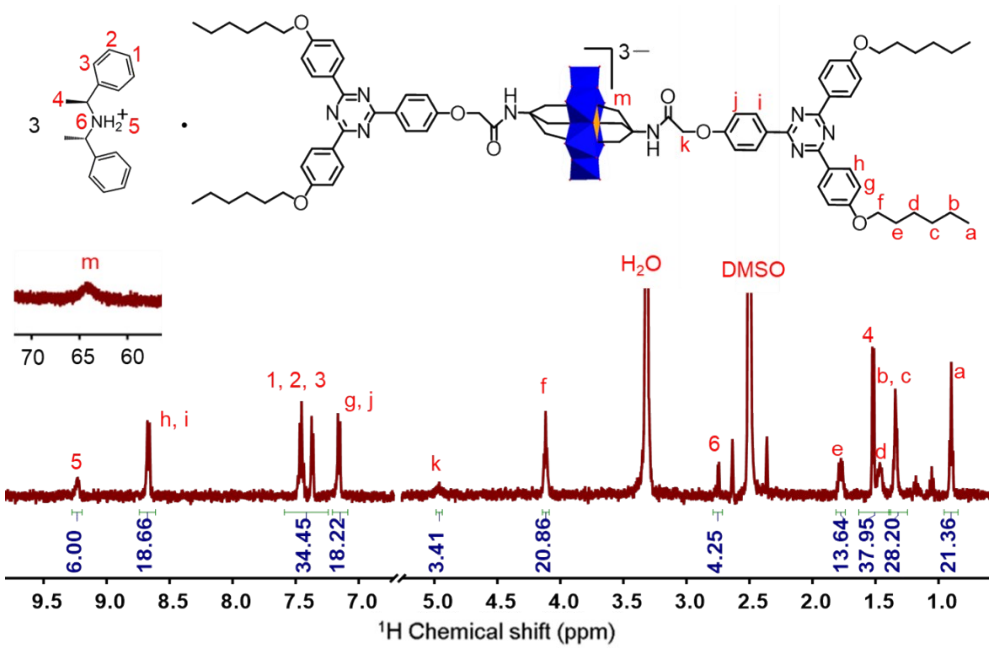


Fig. S7 ^{1}H NMR spectrum of *S*- $MnMo_6$ in DMSO-d_6.

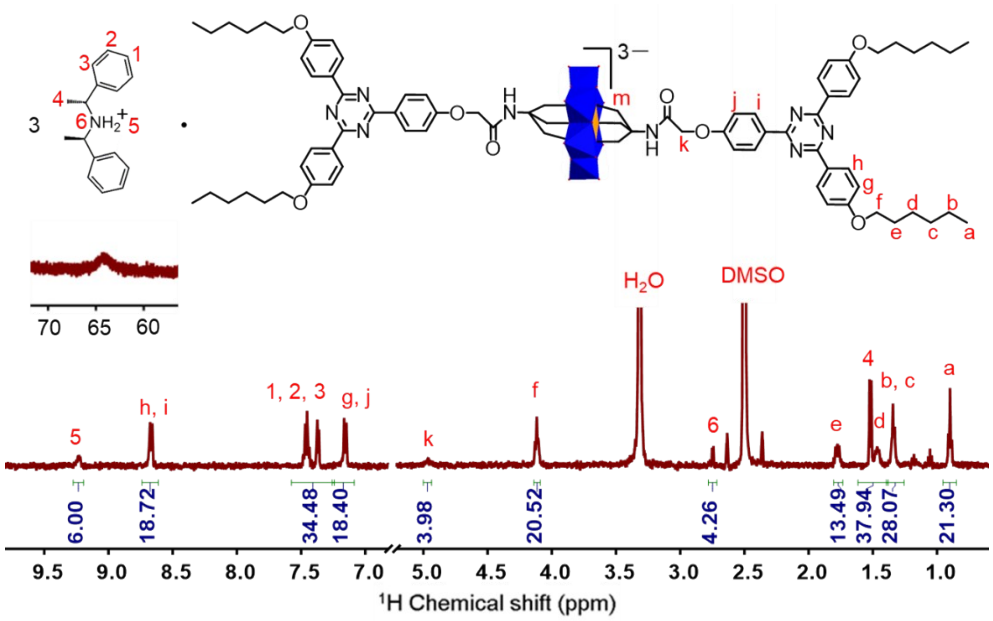


Fig. S8 ^{1}H NMR spectrum of *R*-$BPEA_3MnMo_6$ in DMSO-d_6.

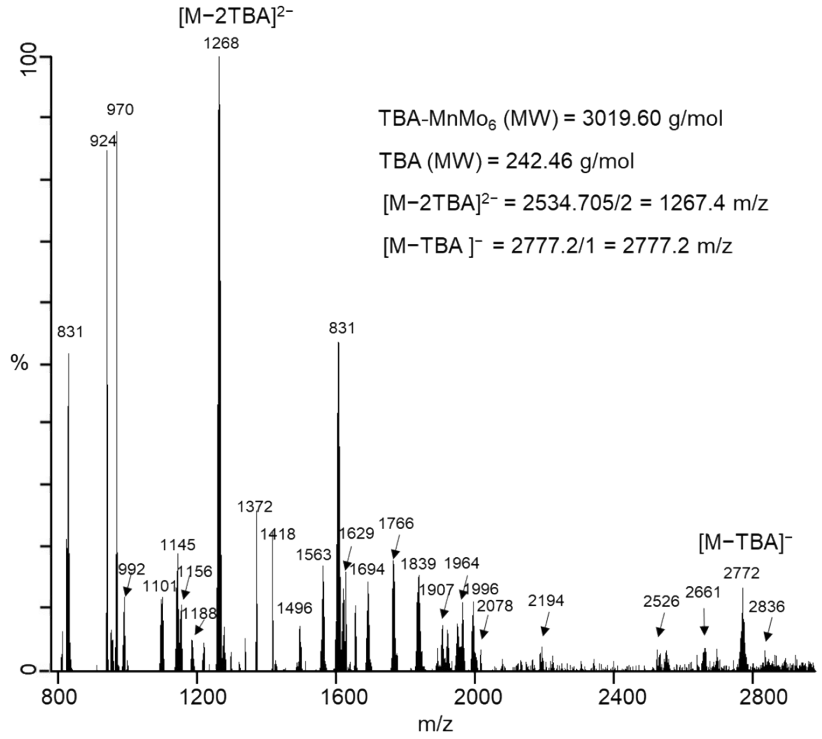


Fig. S9 ESI-MS spectrum of TBA-$MnMo_6$.

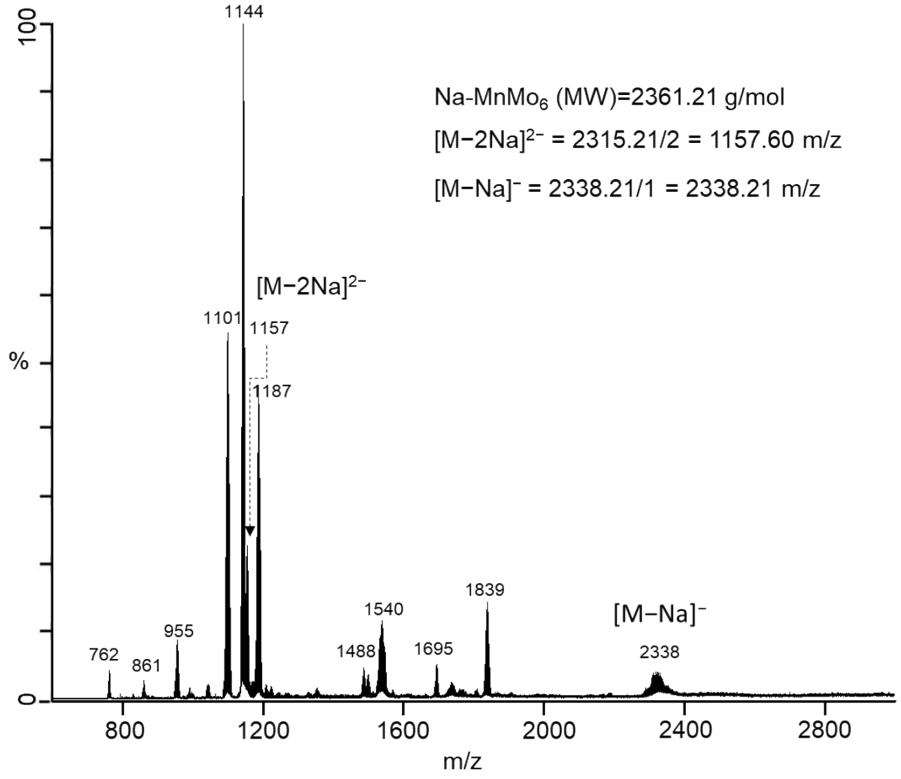


Fig. S10 ESI-MS spectrum of Na-$MnMo_6$.

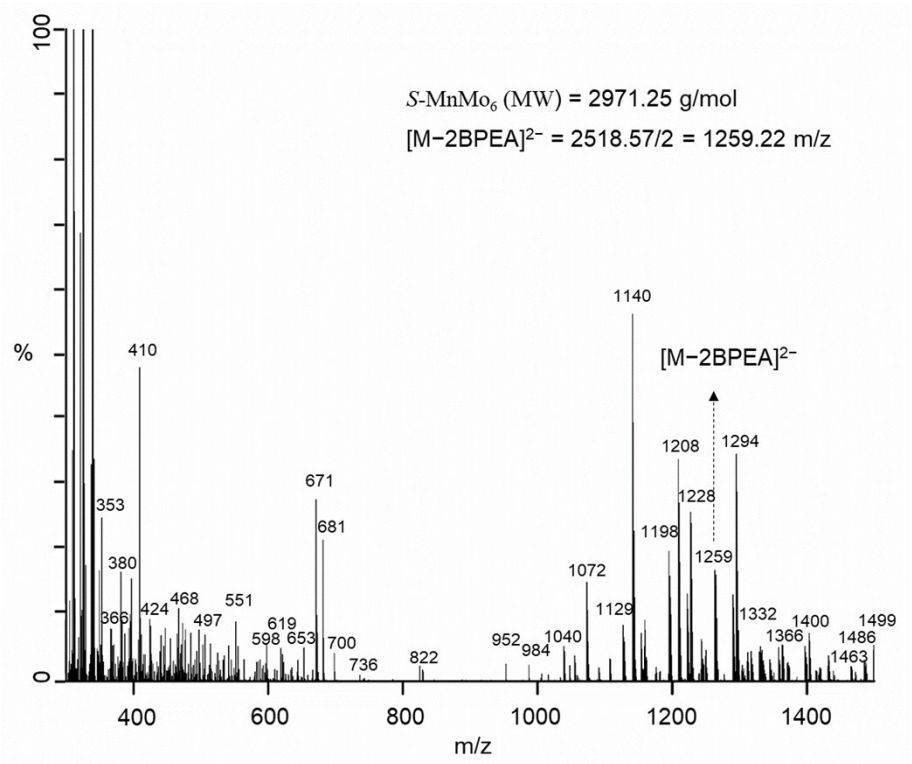


Fig. S11 ESI-MS spectrum of *S*-$MnMo_6$.

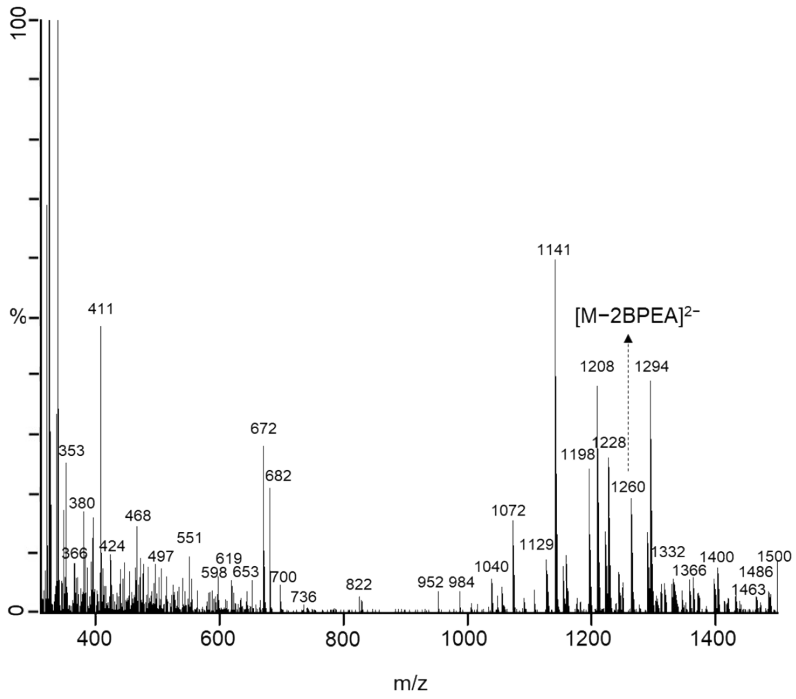


Fig. S12 ESI-MS spectrum of R-$MnMo_6$.

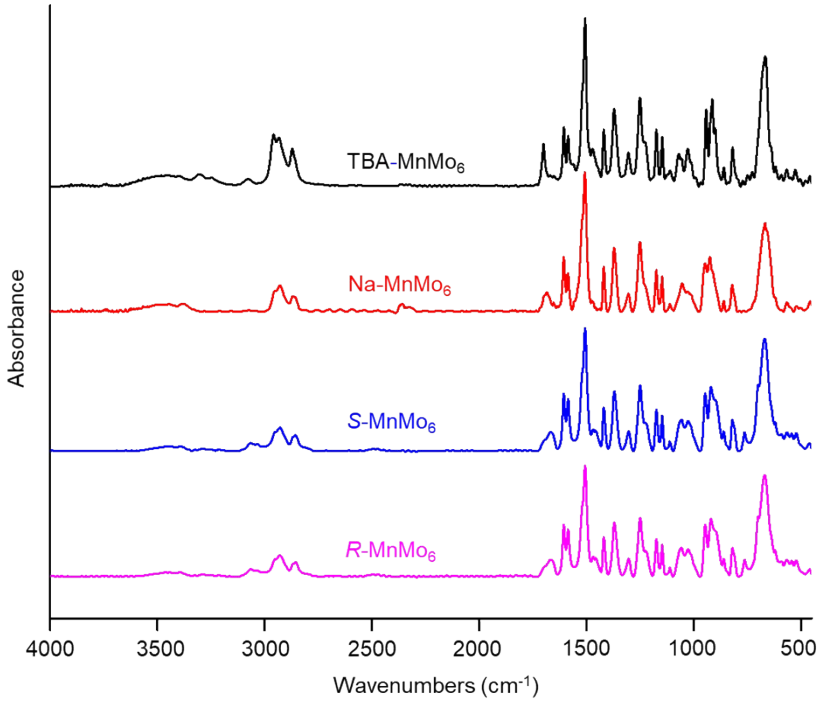


Fig. S13 IR spectra of synthetic hybrid clusters with counter cation (a) TBA^+, (b) Na^+, (c) *S*-$BPEA^+$ and (d) *R*-$BPEA^+$ in KBr pellet.

Table 1 Summary of elemental analysis for the prepared hybrid polyanions.

Sample		C%	H%	N%	Mo%	Mn%	Na%
TBA-$MnMo_6$	Found	50.11	6.94	5.10	19.06	1.82	
	Calcd.	50.27	6.54	5.03	19.10	1.93	
Na-$MnMo_6$	Found	39.68	4.27	4.75	24.38	2.33	2.92
	Calcd.	39.33	4.38	5.33	24.40	2.43	2.91
S-$MnMo_6$	Found	50.93	5.43	5.19	19.37	1.85	
	Calcd.	50.63	5.68	5.35	19.50	1.91	
R-$MnMo_6$	Found	50.93	5.43	5.19	19.37	1.85	
	Calcd.	50.95	5.44	5.22	19.32	1.81	

Characterizations for assembled morphologies

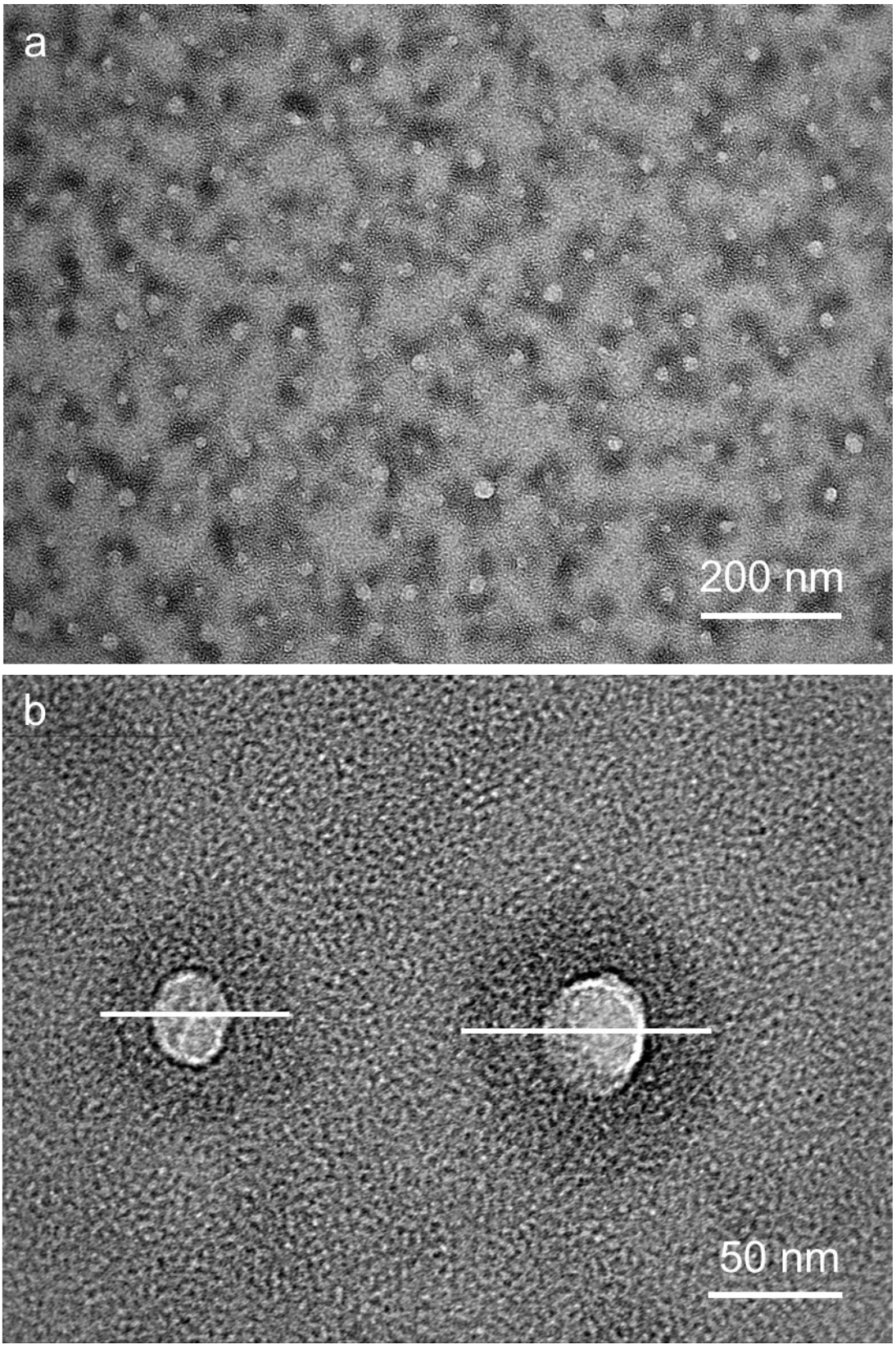


Fig. S14 (a) TEM image and (b) local amplification of Na-$MnMo_6$ in CH_3OH (0.1 mg/mL) at 20

°C.

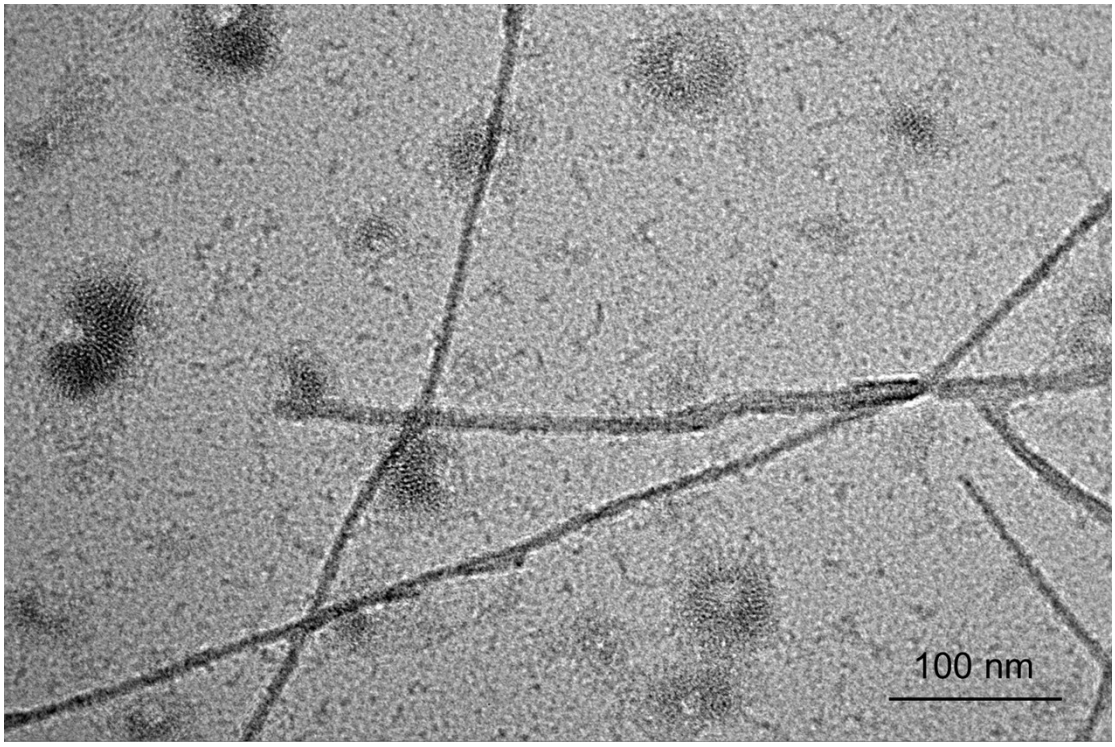


Fig. S15 TEM images of Na-$MnMo_6$ (0.1 mg/mL) in mixed solvent of CH_3OH/H_2O with a volume ratio of 9:1 at 20 °C.

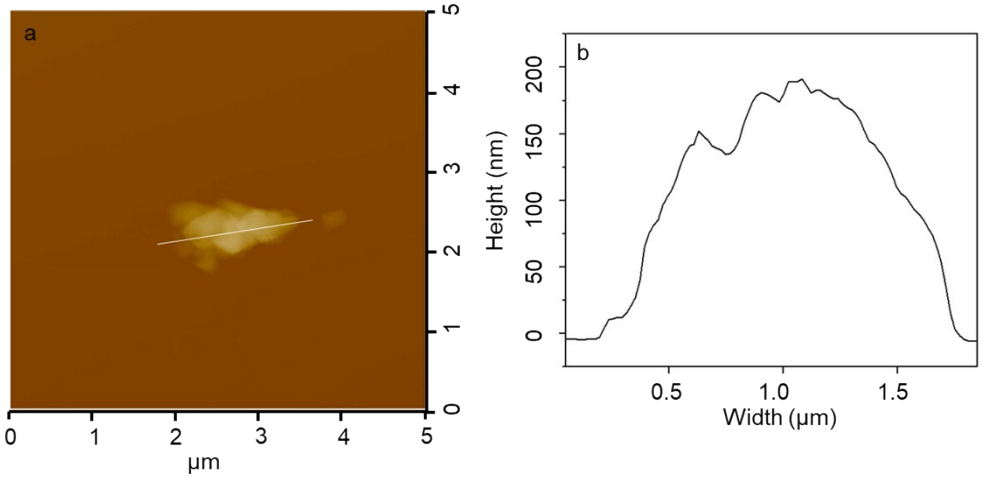


Fig. S16 (a) AFM image in tapping mode and (b) corresponding height profile analysis of Na-$MnMo_6$), prepared from the mixed solvent methanol/H_2O (4:1, v/v) at concentration of 0.1 mg/mL.

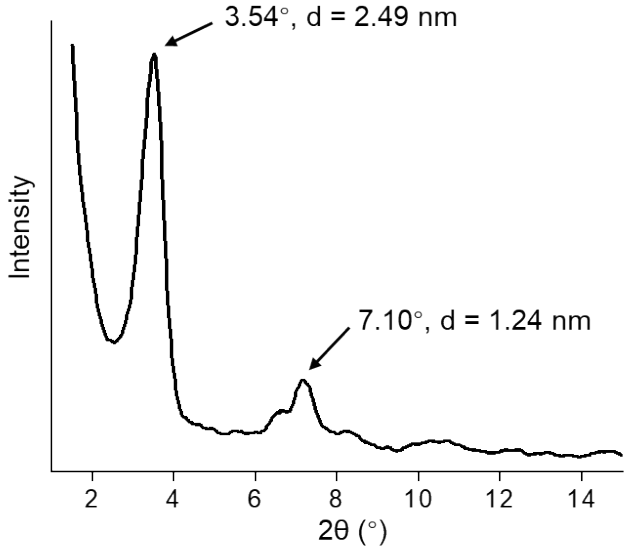


Fig. S17 Powder XRD pattern of Na-$MnMo_6$, prepared from the methanol at the concentration of 0.1 mg/mL.

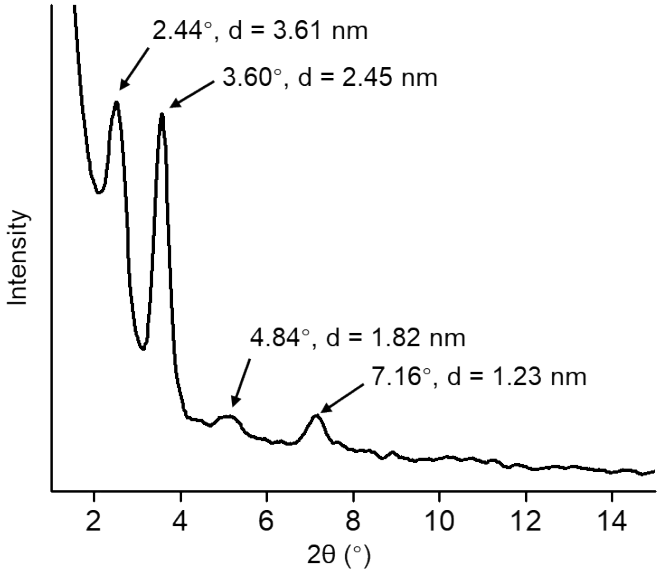


Fig. S18 Powder XRD pattern of Na-$MnMo_6$, prepared from mixed solvent methanol/H_2O (9:1, v/v) at concentration of 0.1 mg/mL.

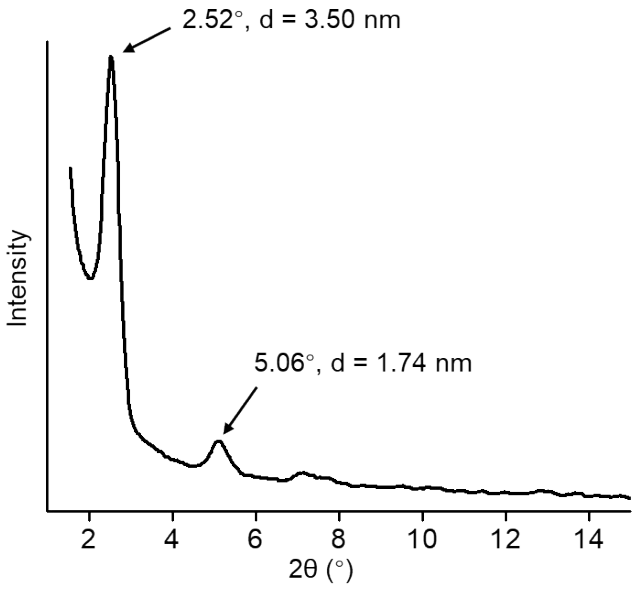


Fig. S19 Powder XRD pattern of Na-$MnMo_6$, prepared from mixed solvent methanol/H_2O (4:1, v/v) at concentration of 0.1 mg/mL.

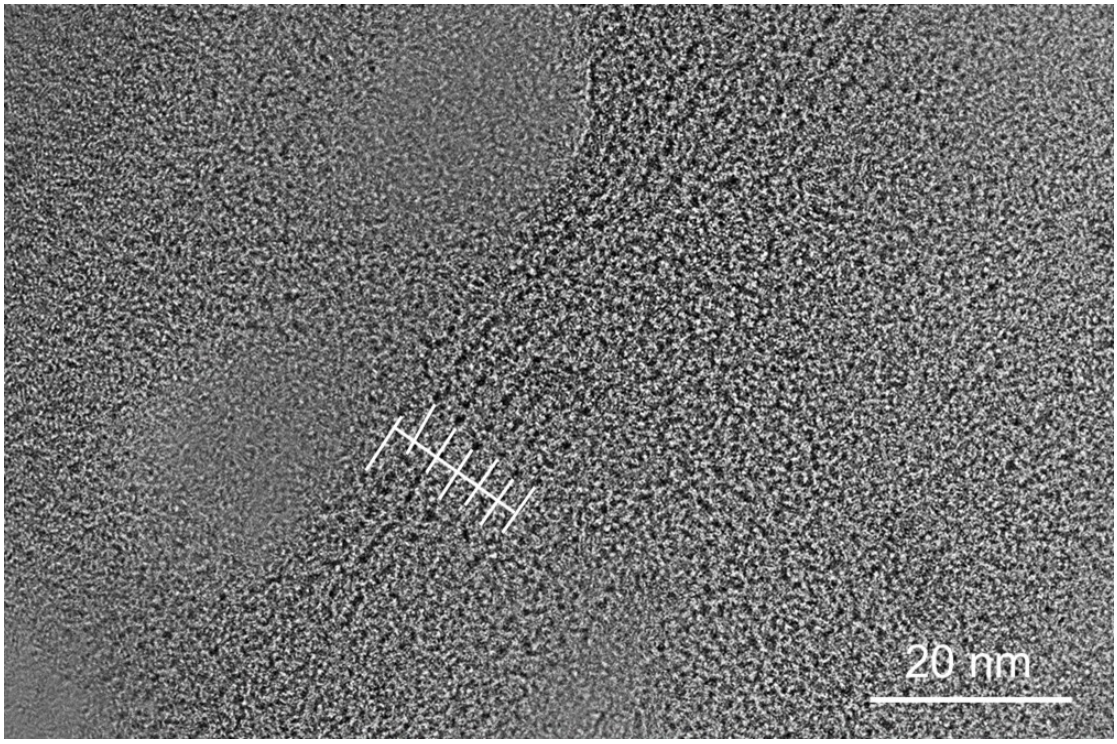


Fig. S20 TEM image for the layer distance estimation of TBA-$MnMo_6$ assemblies in CH_3OH/H_2O (7:3 in v/v) by counting for 6 recognized layers.

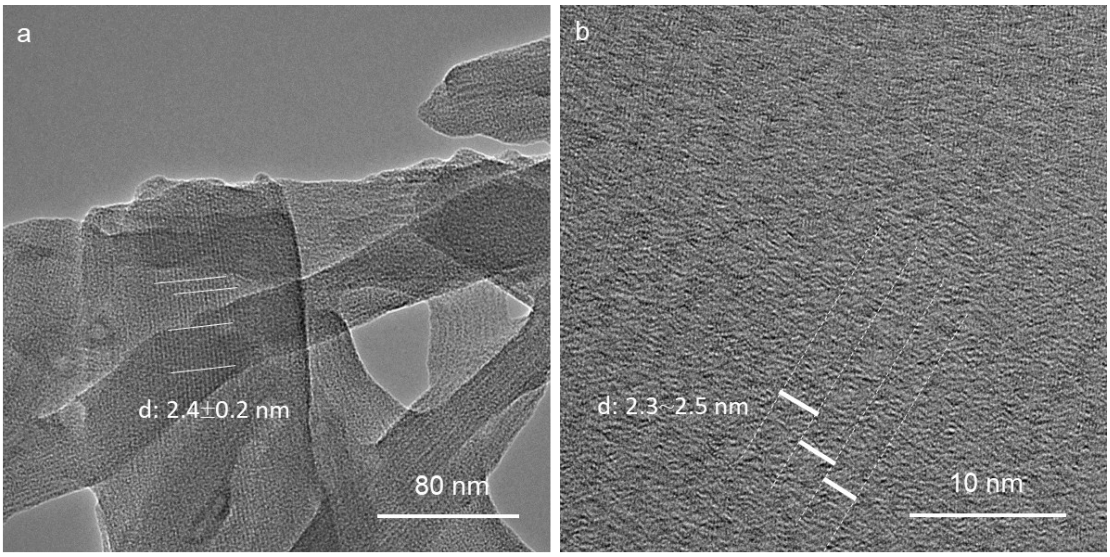


Fig. S21 TEM image for the layer distance estimation of TBA-$MnMo_6$ assemblies in $CHCl_3$/n-C_6H_{14} (3:2 in v/v) by counting for multiple layers shown in Fig. 2f. The concentration is 0.1 mg/mL, and the temperature is 20 °C.

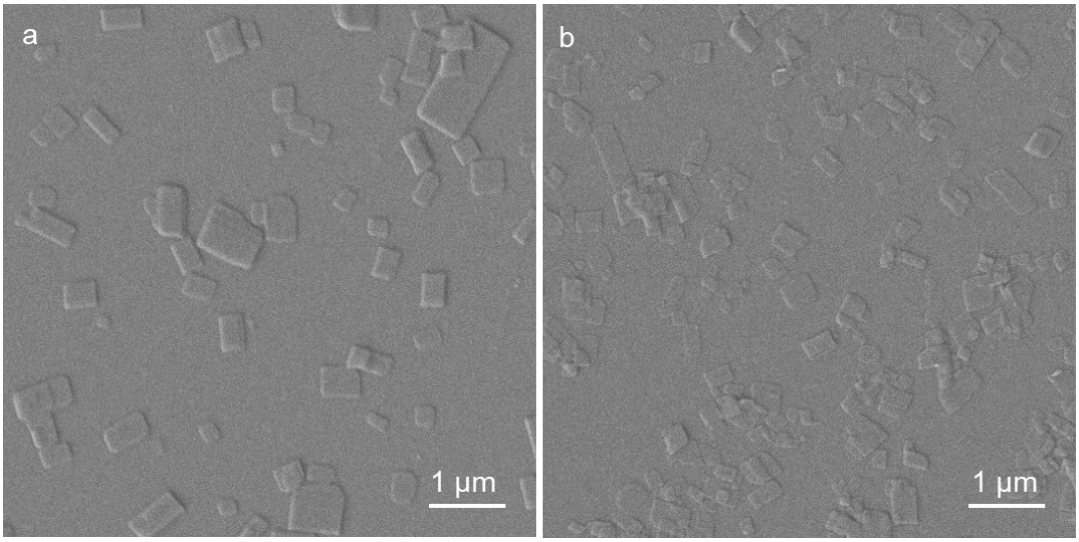


Fig. S22 SEM images of TBA-$MnMo_6$ (0.1 mg/mL) in mixed solvent of $CHCl_3$/n-C_6H_{14} with volume ratio of (a) 1:1 and (b) 2:3 at 20 °C.

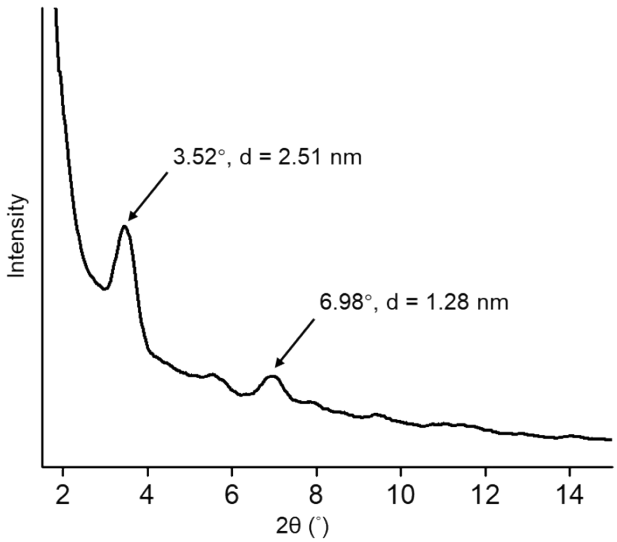


Fig. S23 Powder XRD pattern of TBA-$MnMo_6$ the mixed solvent methanol/H_2O (17:3, v/v) at concentration of 0.1 mg/mL.

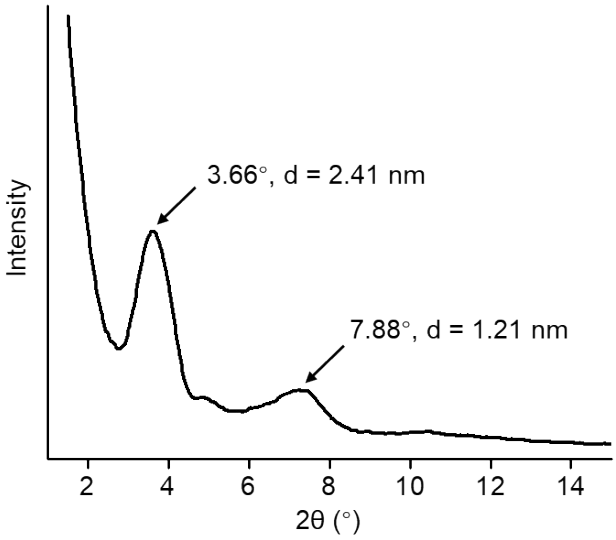


Fig. S24 Powder XRD pattern of TBA-$MnMo_6$, prepared from the mixed solvent methanol/H_2O (7:3, v/v) at concentration of 0.1 mg/mL.

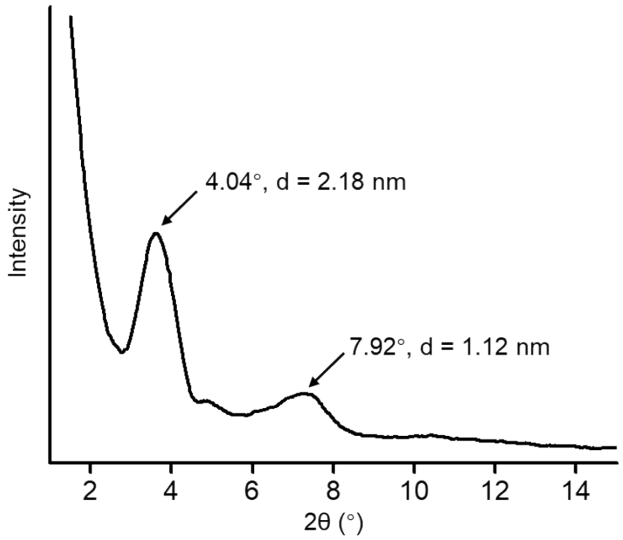


Fig. S25 Powder XRD pattern of TBA-$MnMo_6$, prepared from mixed solvent $CHCl_3$/n-C_6H_{14} (1:1, v/v) at concentration of 0.1 mg/mL.

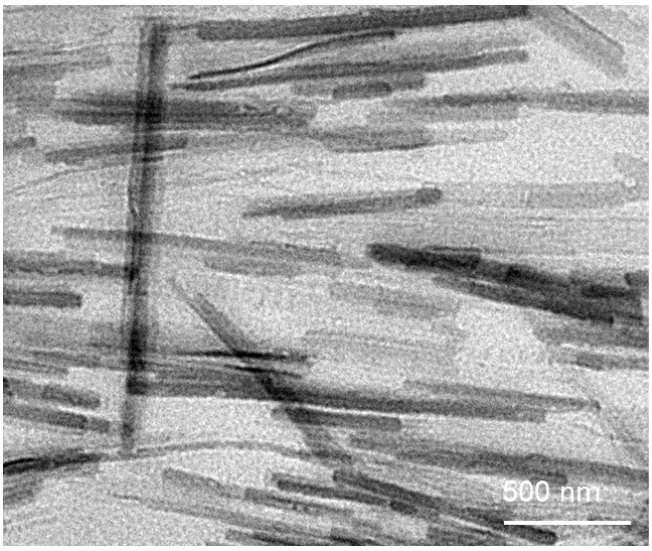


Fig. S26 TEM image of *S*-$MnMo_6$, prepared from the solution of pure $CHCl_3$ at concentration of 0.1 mg/mL.

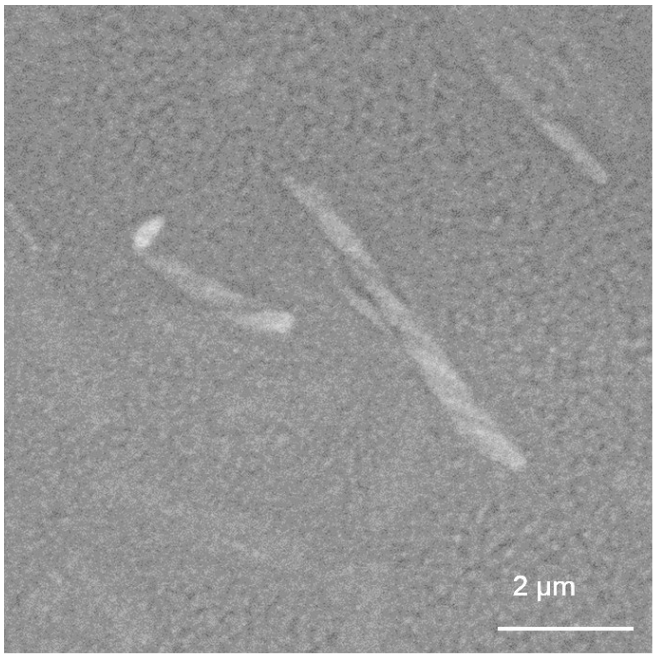


Fig. S27 SEM image of *R*-$MnMo_6$, prepared from the mixed solvent $CHCl_3$/n-C_6H_{14} (9:1, v/v) at concentration of 0.1 mg/mL.

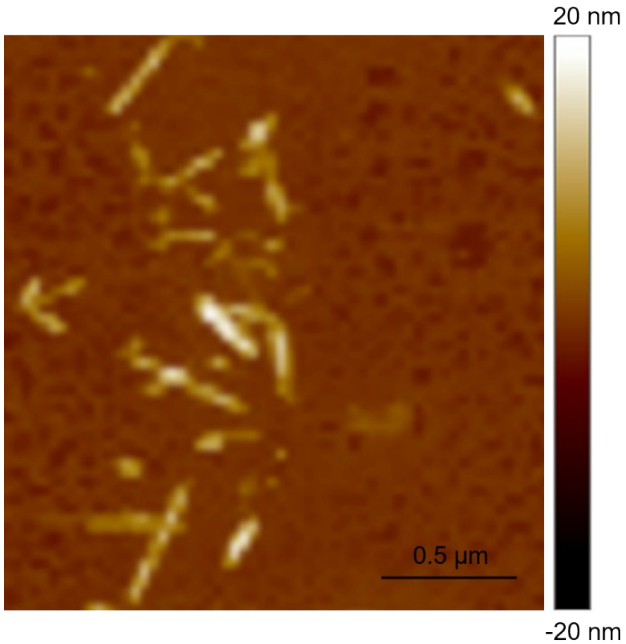


Fig. S28 AFM image of *R*-$MnMo_6$ prepared from the solvent $CHCl_3$/n-C_6H_{14} (9:1, v/v) at concentration of 0.1 mg/mL.

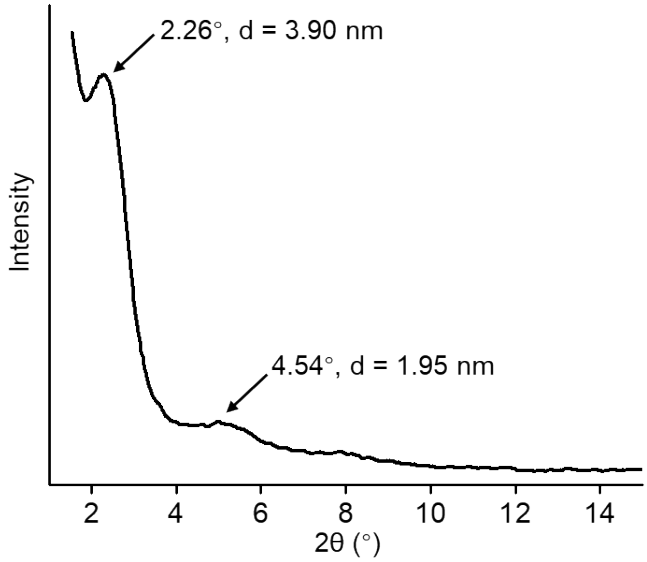


Fig. S29 Powder XRD pattern of *S*-$MnMo_6$, prepared from the mixed solvent $CHCl_3$/n-C_6H_{14} (9:1, v/v) at concentration of 0.1 mg/mL.

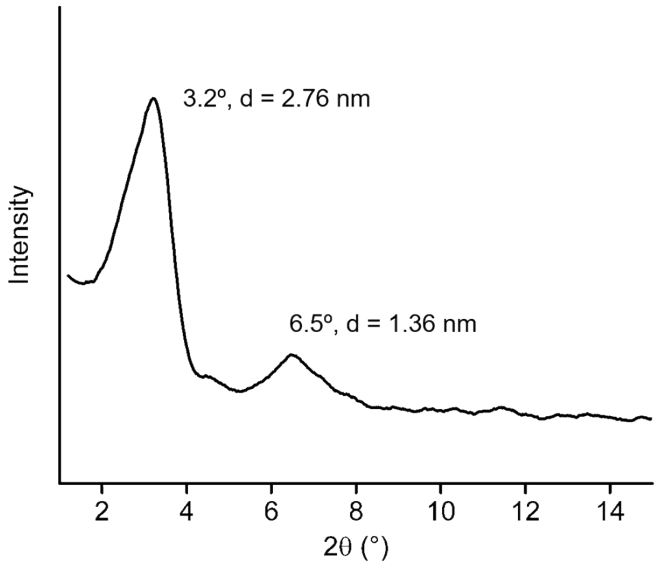


Fig. S30 Powder XRD pattern of racemic *S*-/R- $MnMo_6$, prepared from the solvent $CHCl_3$ at concentration of 0.1 mg/mL.

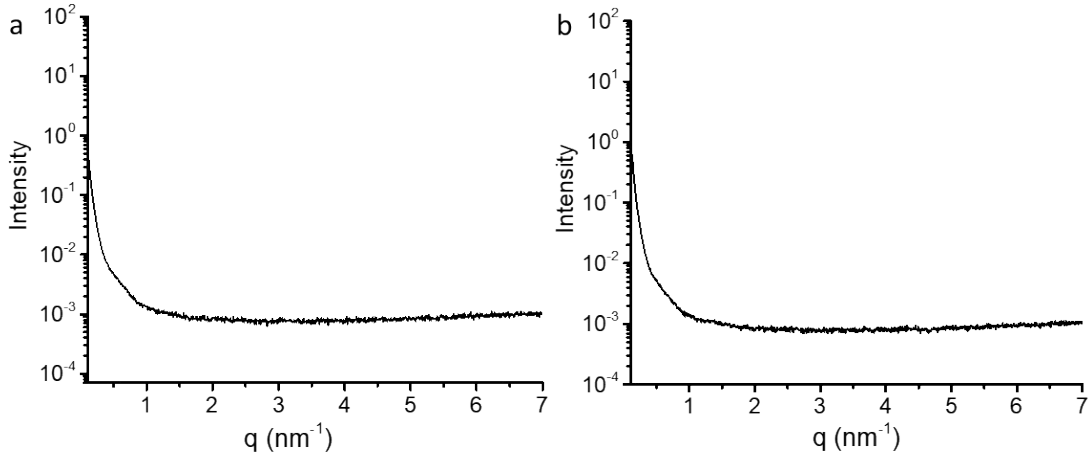


Fig. S31 Small angle X-ray scattering spectra of (a) 0.1 mg/mL and (b) 1 mg/mL of TBA-$MnMo_6$ in CH_3OH:H_2O (17:3 in v/v) at 20°C.

Reference:

1 a) T. C. Hsieh, S. N. Shaikh and J. Zubieta, *Inorg. Chem.*, 1987, **26***,* 4079; b) J. B. Bush Jr. and H. Finkbeiner, *J. Am. Soc. Chem*., 1968, **90**, 5903; c) E. Buncel and S. R. Keum, *Tetrahedron*, 1983, **39**, 1091.

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