

Supplementary Information

Supramolecular Approach of Modified Polyoxometalate Polymerization and Visualization of Single Polymer Chain

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• Materials

2-Aminoanthraquinone and diglycolic anhydride were purchased from Alfa Aesar. Ethyl 2-ethoxyquinoline-1(2H)-carboxylate (EEDQ) and γ -cyclodextrin (γ -CD) were the products from J&K Chemical Co, Ltd. Tris(hydroxymethyl)aminomethane (NH₂-Tris) was the product of Sinopharm Chemical Reagent Co, Ltd. (SCRC). DMSO-*d*₆, Chloroform-*d* and D₂O were purchased from Sigma-Aldrich or Cambridge Isotope Laboratories, Inc. (CIL). The remaining chemicals were purchased from Beijing Chemical Reagent Company. All the chemicals above were used as received. Doubly distilled water was used in the experiments. The concentrations for An-AlMo₆ were fixed at 2.0 mM and An-MnMo₆ were fixed at 1.0 mM unless otherwise stated.

• Measurements

The UV-Vis spectra were recorded on a spectrometer (Varian CARY 50 Probe) with a 1 mm quartz cell. ¹H NMR spectra were recorded on a Bruker AVANCE 500 MHz spectrometer and 2D NOESY spectrum was recorded on a Bruker AVANCEIII 600MHz spectrometer. The ESI-MS was performed on Agilent1290-microTOF Q II spectrometer. ITC data was collected by GE MicroCal™ iTC200. Organic elemental analysis was carried out on an Elementar Vario micro cube. TEM was conducted on a JEOL JEM-2100F under an accelerating voltage of 200 kV. AFM measurement was carried out on a Bruker FastScan atomic force microscope. Circular Dichroism spectra was recorded on a Biologic PMS 450 with a 1 mm quartz cell and smoothed with the Loess method. The dn/dc value was collected on Brookhaven differential refractometer. SLS was conducted on a ALV/CGS-3 light scattering spectrometer equipped with an ALV/LSE-7004 multiple- τ digital correlator and a 22 mW JDS-Uniphase solid-state He-Ne laser (the wavelength was 632.8 nm). The photo-cycloaddition reaction was conducted under a 365 nm LED UV lamp (6 W) within distance of 2 cm.

• Synthesis of anthracene grafted POMs

The organic part of the grafted POMs was prepared following the route described in Fig. S1.

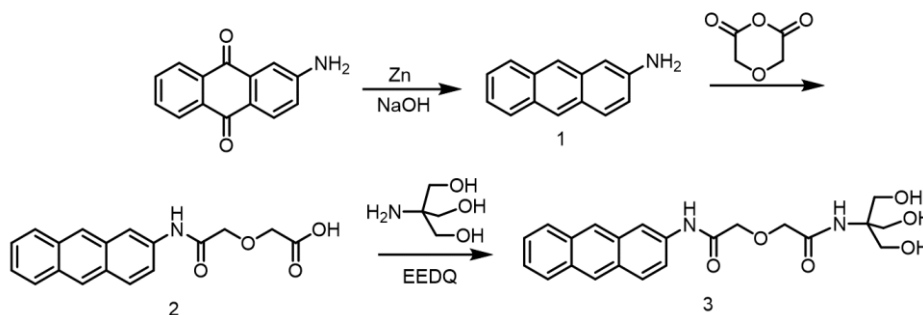


Fig. S1 Synthetic route of anthracene part that is used to graft on to POMs.

2-Aminoanthracene (1). 2-Aminoanthracene was synthesized according to the procedures in literature^[S1]. Briefly, 2-Aminoanthraquinone (15.0 g) was stirred with 10% sodium hydroxide (150 ml) and zinc dust (12.0 g) at room temperature in a round bottom flask. After about 30 min, the reaction solution was slowly heated to about 100°C and another 15.0 g zinc dust was added within 30 min. The mixture was continuously stirred at 100–110°C for 24 h. After cooling to room temperature, the solid

was collected and washed with water for several times. Then, Soxhlet device was used to extract the product with acetone and obtained crude product was recrystallized with toluene in yield 45%. $^1\text{H NMR}$ (500 MHz, CDCl_3 , δ =ppm) 8.30 (s, 1H), 8.13 (s, 1H), 7.96 – 7.86 (m, 3H), 7.39 (dddd, $J = 28.4, 7.9, 6.5, 1.2$ Hz, 2H), 7.11 (d, $J = 2.2$ Hz, 1H), 7.02 (dd, $J = 9.0, 2.2$ Hz, 1H), 3.94 (s, 2H).

2-(2-(anthracen-2-ylamino)-2-oxoethoxy)acetic acid (Anthracene-COOH) (2). The prepared aminoanthracene (0.5 g, 2.59 mmol) and diglycolic anhydride (1.5 g, 12.92 mmol) were dissolved in 20 mL DMF in a round bottom flask equipped with a magnetic stir bar. The solution was heated to 80°C for 6 h. After cooling to room temperature, the solution was poured into 150 mL ethyl acetate and washed with 300 mL water. The organic layer was collected and dried with MgSO_4 . The organic solvent was removed to get yellow solid as target compound (0.7 g, yield 87%). $^1\text{H NMR}$ 500 MHz ($\text{DMSO}-d_6$) δ : 4.27 (4H, s), 7.49 (2H, m), 7.65 (1H, dd), 8.05 – 8.08 (3H, m), 8.47 (1H, s), 8.51 (1H, s), 8.54 (1H, s), 10.15 (1H, s), 12.90 (1H, s)

N-(anthracen-2-yl)-2-(2-((1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)amino)-2-oxoethoxy)acetamide (Anthracene-Tris) (3). Compound (2) (100.00 mg, 0.32 mmol), NH_2 -Tris (48.46 mg, 0.4 mmol) and EEDQ (111.28 mg, 0.45 mmol) were dissolved in 20 mL acetonitrile and the solution was refluxed for 6 h. The acetonitrile was removed by rotary evaporation under reduced pressure. The residue was purified by column chromatography over silica gel (200-300 mesh) with chloroform/methanol (10:1, v/v) as eluent, giving product (3) (90 mg, yield 68.2%) $^1\text{H NMR}$ 500 MHz ($\text{DMSO}-d_6$) δ : 3.63 (6H, d), 4.11 (2H, s), 4.29 (2H, s), 4.78 (1H, t), 7.29 (1H, s), 7.49 (2H, m), 7.63 (1H, dd), 8.05 – 8.08 (3H, m), 8.47 (1H, s), 8.51 (1H, s), 8.54 (1H, s), 10.34 (1H, s)

The $[\text{N}(\text{C}_4\text{H}_9)_4]_3\text{AlMo}_6\text{O}_{18}(\text{OH})_3(\text{OCH}_2)_3\text{CNH}_2$ (TBA- NH_2 - AlMo_6)^[S2], $[\text{N}(\text{C}_4\text{H}_9)_4]_4[\alpha\text{-Mo}_8\text{O}_{26}]$ ^[S3] and $\text{Mn}(\text{CH}_3\text{COO})_3$ ^[S4] were synthesized according the procedures in literatures.

$[\text{N}(\text{C}_4\text{H}_9)_4]_3\text{AlMo}_6\text{O}_{18}(\text{OH})_3(\text{OCH}_2)_3\text{CNHCOCH}_2\text{OCH}_2\text{CONHC}_{14}\text{H}_9$ (TBA-An- AlMo_6). Anthracene-COOH (87 mg, 0.28 mmol), TBA- NH_2 - AlMo_6 (500 mg, 0.28 mmol) and EEDQ (138.5 mg, 0.56 mmol) were dissolved in 15 mL acetonitrile and stirred at 50°C for 18 h. Then poured into plenty of ethyl acetate. The solid was collected and re-dissolved into acetone and then precipitated with isopropyl ether and centrifugalized to get pure TBA-An- AlMo_6 as solid. (350 mg, yield 67.4%). $^1\text{H NMR}$ (500 MHz, $\text{DMSO}-d_6$) δ 10.46 (s, 1H), 8.55 – 8.47 (m, 3H), 8.09 – 8.01 (m, 3H), 7.69 (dd, $J = 9.1, 2.0$ Hz, 1H), 7.51 – 7.44 (m, 2H), 7.31 (s, 1H), 4.72 (s, 6H), 4.22 (s, 2H), 4.02 (s, 2H), 3.57 (s, 3H), 3.22 – 3.12 (m, 24H), 1.56 (td, $J = 11.6, 9.9, 6.0$ Hz, 24H), 1.32 (h, $J = 7.4$ Hz, 24H), 0.94 (t, $J = 7.3$ Hz, 36H). Elemental Analysis: (Calculated: C: 40.45%, H: 6.40%, N: 3.37%, Found: C: 40.57 %, H: 6.40%, N: 3.21%). The synthetic route and structure characterization are listed below (Fig. S2 – S4 and Table S1).

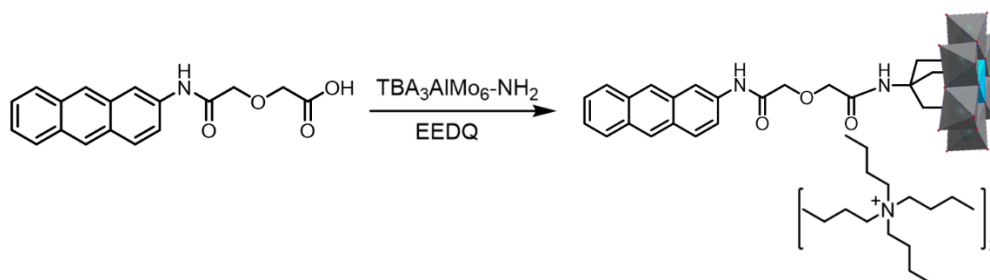


Fig. S2 Synthetic route of anthracene modified Al-centered POM on single side.

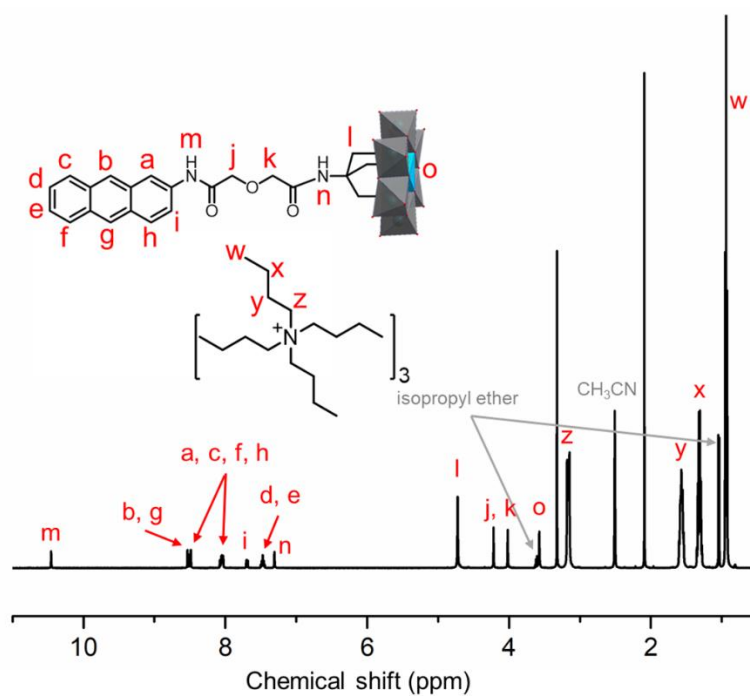


Fig. S3 ^1H NMR spectrum of TBA-An- AlMo_6 in $\text{DMSO-}d_6$.

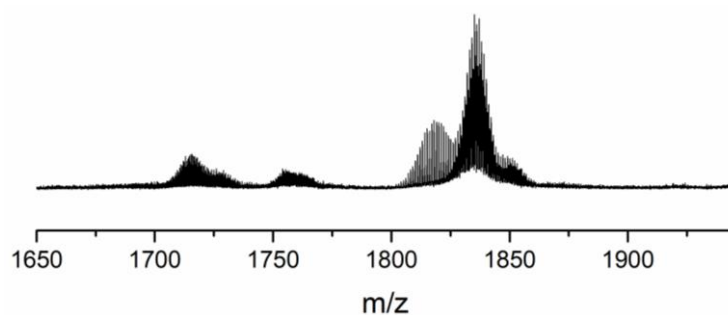


Fig. S4 ESI-MS spectrum of TBA-An- AlMo_6 .

Table S1 Detailed assignment of the ESI-MS of TBA-An- AlMo_6

Chemical formula	Charge	MW* Calculated	MW Found
$[\text{TBA}_3\text{H}[\text{AlMo}_6\text{O}_{18}(\text{OH})_3(\text{OCH}_2)_3\text{CNHCOCH}_2\text{OCH}_2\text{CONHC}_{14}\text{H}_9]_2]^{2-}$	$2e^-$	1715.2	1715.5
$[\text{TBA}_5\text{H}[\text{AlMo}_6\text{O}_{18}(\text{OH})_3(\text{OCH}_2)_3\text{CNHCOCH}_2\text{OCH}_2\text{CONHC}_{14}\text{H}_9]_3]^{3-}$	$3e^-$	1755.3	1755.4
$[\text{TBAH}[\text{AlMo}_6\text{O}_{18}(\text{OH})_3(\text{OCH}_2)_3\text{CNHCOCH}_2\text{OCH}_2\text{CONHC}_{14}\text{H}_9]_1][\text{DMF}]_3^-$	$1e^-$	1813.8	1814.1
$[\text{TBA}_2[\text{AlMo}_6\text{O}_{18}(\text{OH})_3(\text{OCH}_2)_3\text{CNHCOCH}_2\text{OCH}_2\text{CONHC}_{14}\text{H}_9]_1]^-$	$1e^-$	1835.9	1835.1

*MW: Molecular weight.

Na₃AlMo₆O₁₈(OH)₃(OCH₂)₃CNHCOCH₂OCH₂CONHC₁₄H₉ (An-AlMo₆). An acetonitrile solution of TBA-An-AlMo₆ (500.00 mg, 0.24 mmol) was added dropwise to an acetonitrile solution of sodium perchlorate (500.00 mg, 4.08 mmol) and stirred at room temperature for 2 h. The solid was collected by centrifugation and washed with acetonitrile for three times, drying to get water soluble An-AlMo₆. (300 mg, yield 87.9%). ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.45 (s, 1H), 8.56 – 8.47 (m, 3H), 8.09 – 8.01 (m, 3H), 7.69 (dd, *J* = 9.1, 2.0 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.32 (s, 1H), 4.72 (s, 6H), 4.22 (s, 2H), 4.02 (s, 2H), 3.67 (s, 3H). ¹H NMR spectrum is shown in Fig. S5.

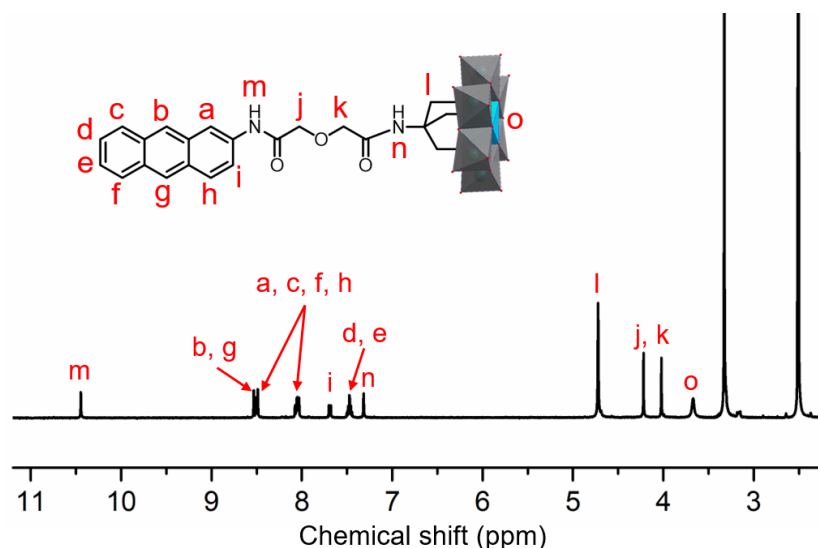


Fig. S5 ¹H NMR spectrum of An-AlMo₆ in DMSO-*d*₆.

[N(C₄H₉)₄]₃MnMo₆O₁₈[(OCH₂)₃CNHCOCH₂OCH₂CONHC₁₄H₉]₂ (TBA-An-MnMo₆). A mixture of [N(C₄H₉)₄]₄[α-Mo₈O₂₆] (223.0 mg, 0.104 mmol), Mn(CH₃COO)₃ (42.0 mg, 0.18 mmol) and compound (3) (150.0 mg, 0.36 mmol) in 30 mL acetonitrile with a small amount of DMF (2 mL) was heated to reflux for 17 h. The resulted precipitate was removed by filtration. A diffusion of diethyl ether into the filtrate at room temperature in several days yields the formation of TBA-An-MnMo₆. (320.0 mg, yield 72.9%). ¹H NMR (500 MHz, DMSO-*d*₆) δ 64.52 (br, 12H), 10.44 (s, 2H), 8.59 – 8.46 (m, 6H), 8.00 – 8.10 (m, 6H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.47 (p, *J* = 6.5 Hz, 4H), 4.46 (s, 4H), 4.28 (s, 4H), 3.22 – 3.07 (m, 24H), 1.56 (t, *J* = 8.2 Hz, 24H), 1.31 (h, *J* = 7.3 Hz, 24H), 0.93 (t, *J* = 7.2 Hz, 36H). Elemental Analysis: (Calculated: C: 44.83%, H: 6.13%, N: 3.97%, Found: C: 45.34%, H: 5.93%, N: 4.06%). The synthetic route and structure characterization are listed below (Fig. S6 – S8 and Table S2).

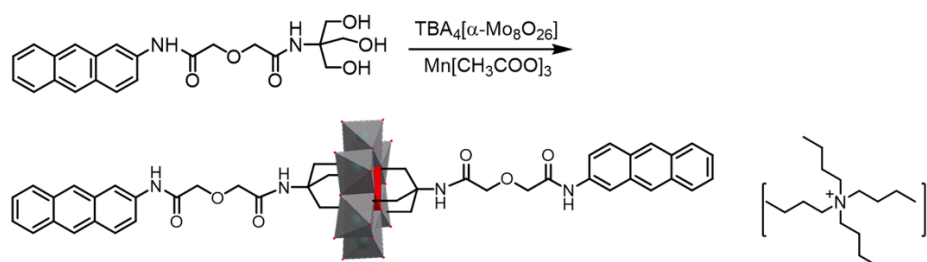


Fig. S6 Synthetic route of anthracene modified Mn-centered POM on double-sides.

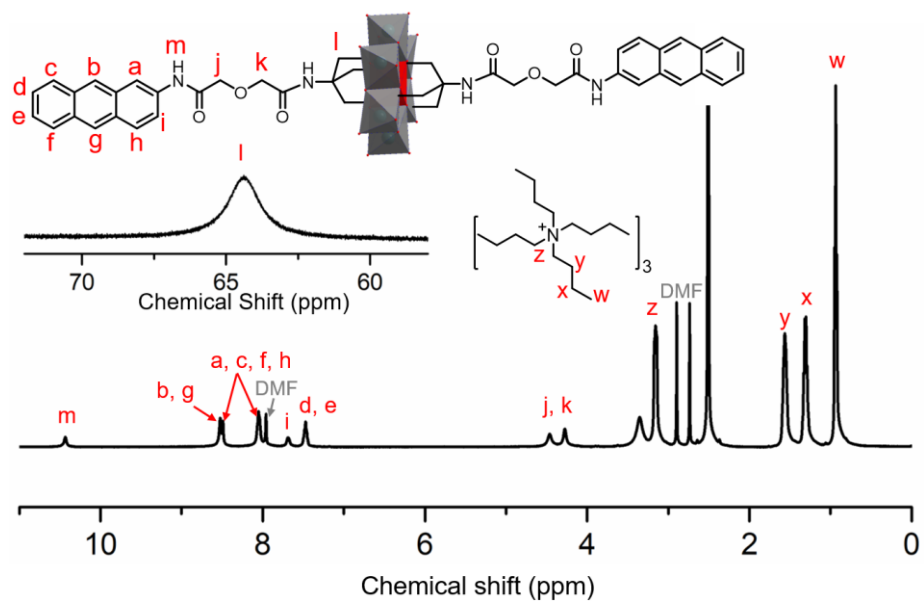


Fig. S7 ^1H NMR spectrum of TBA-An-MnMo₆ in DMSO-*d*₆.

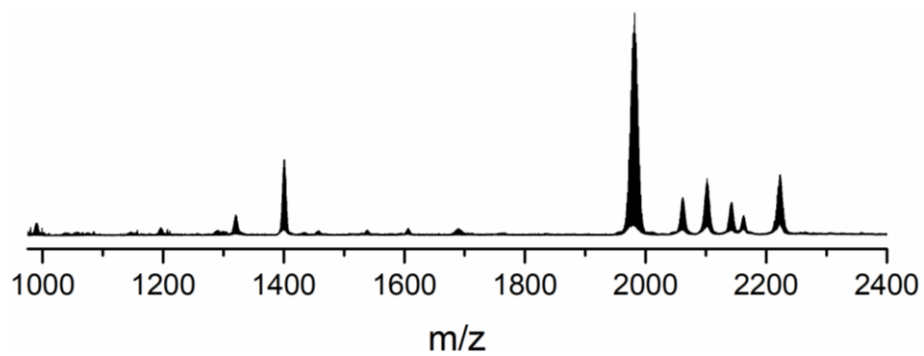


Fig. S8 ESI-MS spectrum of TBA-An-MnMo₆.

Table S2 Detailed assignments for the ESI-MS of TBA-An-MnMo₆

Chemical Formula	Charge	MW* Calculated	MW Found
[TBAMnMo ₆ O ₁₈ [(OCH ₂) ₃ CNHCOCH ₂ OCH ₂ CONHC ₁₄ H ₉] ₂] ²⁻	2e ⁻	989.9	990.0
[TBA ₂ H[MnMo ₆ O ₁₈ [(OCH ₂) ₃ CNHCOCH ₂ OCH ₂ CONHC ₁₄ H ₉] ₂] ₂] ³⁻	3e ⁻	1320.2	1320.3
[TBA ₃ [MnMo ₆ O ₁₈ [(OCH ₂) ₃ CNHCOCH ₂ OCH ₂ CONHC ₁₄ H ₉] ₂] ₂] ³⁻	3e ⁻	1400.7	1400.7
[TBAHMnMo ₆ O ₁₈ [(OCH ₂) ₃ CNHCOCH ₂ OCH ₂ CONHC ₁₄ H ₉] ₂] ⁻	1e ⁻	1980.9	1981.0
[TBA ₄ H ₂ [MnMo ₆ O ₁₈ [(OCH ₂) ₃ CNHCOCH ₂ OCH ₂ CONHC ₁₄ H ₉] ₂] ₃] ³⁻	3e ⁻	2061.3	2061.4
[TBA ₃ H[MnMo ₆ O ₁₈ [(OCH ₂) ₃ CNHCOCH ₂ OCH ₂ CONHC ₁₄ H ₉] ₂] ₂] ²⁻	2e ⁻	2101.6	2101.7
[TBA ₅ H[MnMo ₆ O ₁₈ [(OCH ₂) ₃ CNHCOCH ₂ OCH ₂ CONHC ₁₄ H ₉] ₂] ₃] ³⁻	3e ⁻	2141.7	2141.9
[TBA ₇ H[MnMo ₆ O ₁₈ [(OCH ₂) ₃ CNHCOCH ₂ OCH ₂ CONHC ₁₄ H ₉] ₂] ₄] ⁴⁻	4e ⁻	2162.0	2162.0
[TBA ₂ MnMo ₆ O ₁₈ [(OCH ₂) ₃ CNHCOCH ₂ OCH ₂ CONHC ₁₄ H ₉] ₂] ⁻	1e ⁻	2222.3	2222.3

*MW: Molecular weight.

Na₃MnMo₆O₁₈[(OCH₂)₃CNHCOCH₂OCH₂CONHC₁₄H₉]₂ (An-MnMo₆). An acetonitrile solution of TBA-An-MnMo₆ (500.0 mg, 0.20 mmol) was added dropwise to an acetonitrile solution containing sodium perchlorate (500.0 mg, 4.08 mmol) and stirred at room temperature for 2 h. The formed solid was collected by centrifugation and washed with acetonitrile for three times, drying to get water soluble product An-AlMo₆. (290 mg, yield 80.3%). ¹H NMR (500 MHz, DMSO-*d*₆) δ 64.52 (br, 12H), 10.43 (s, 1H), 8.58 – 8.46 (m, 3H), 8.05 (m, 3H), 7.68 (s, 1H), 7.47 (m, 2H), 4.46 (s, 2H), 4.28 (s, 2H). ¹H NMR spectrum is shown in Fig. S9.

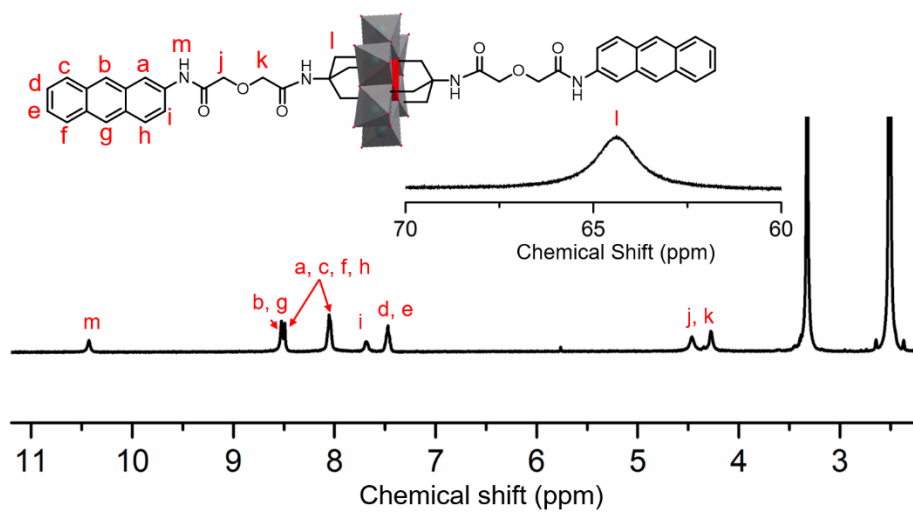


Fig. S9 ^1H NMR spectrum of An-MnMo₆ in DMSO-*d*₆.

- Characterization on host-guest inclusion and formation of An-MnMo₆ polymer

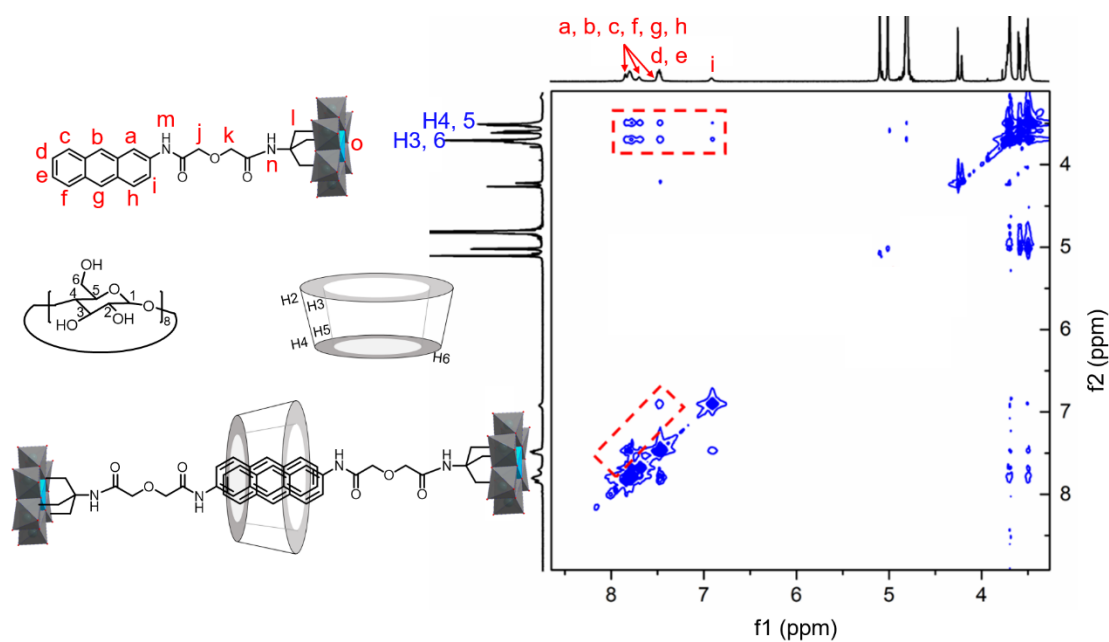


Fig. S10. Nuclear Overhauser effect spectroscopy (NOESY) spectrum of An-AlMo₆ and γ -CD in D₂O

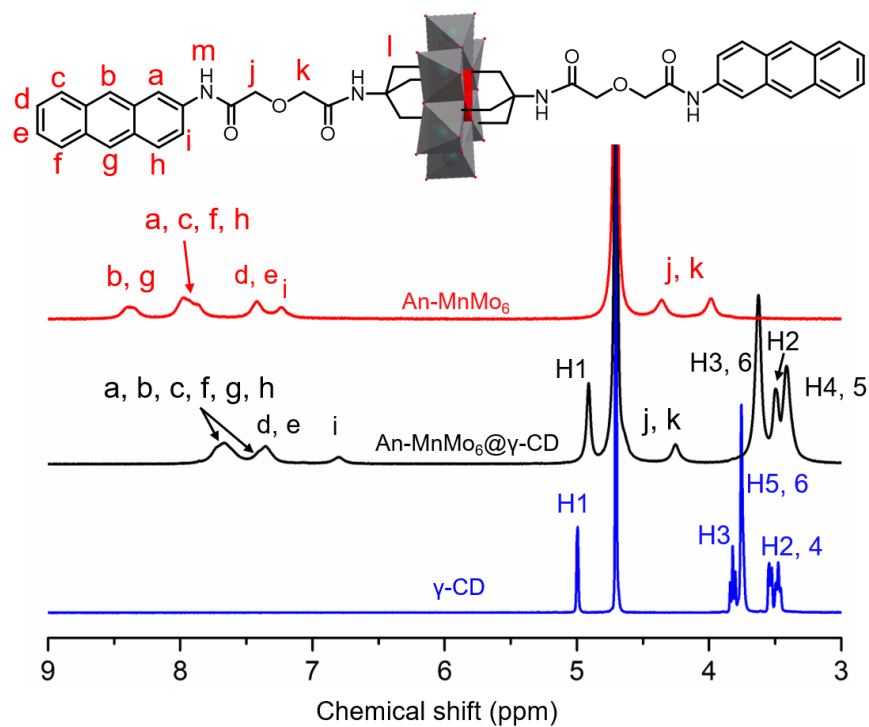


Fig. S11. ¹H NMR spectra of An-MnMo₆ before and after its combination with γ -CD in D₂O.

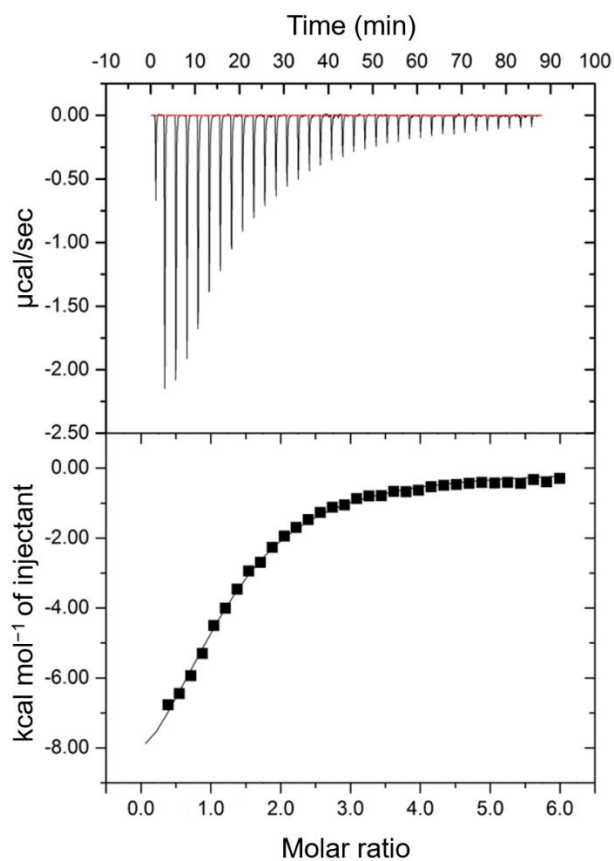


Fig. S12 ITC curves and fittings of γ -CD (3.80 mM) titrating An-MnMo₆ (0.12 mM) in water.

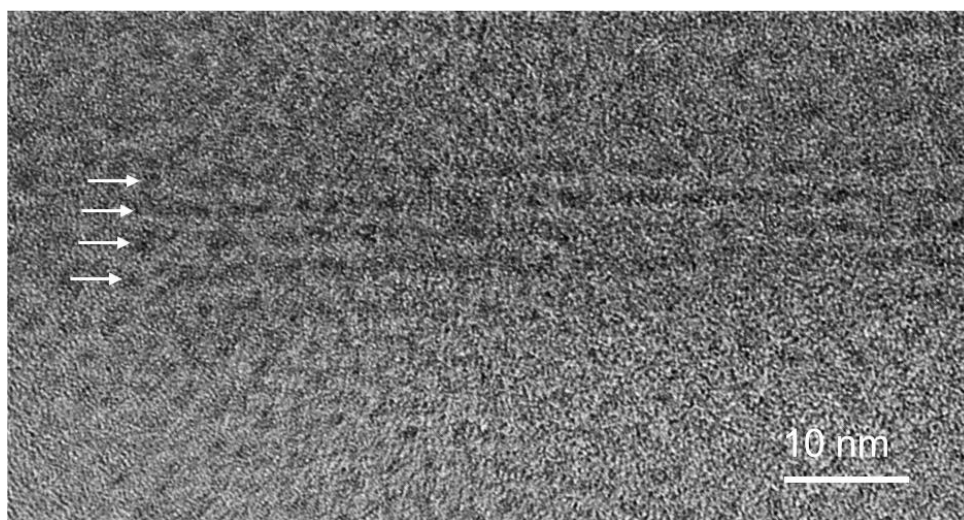


Fig. S13 TEM image of An-AlMo₆@ γ -CD supramolecular polymer at a position of fine fibrous assembly.

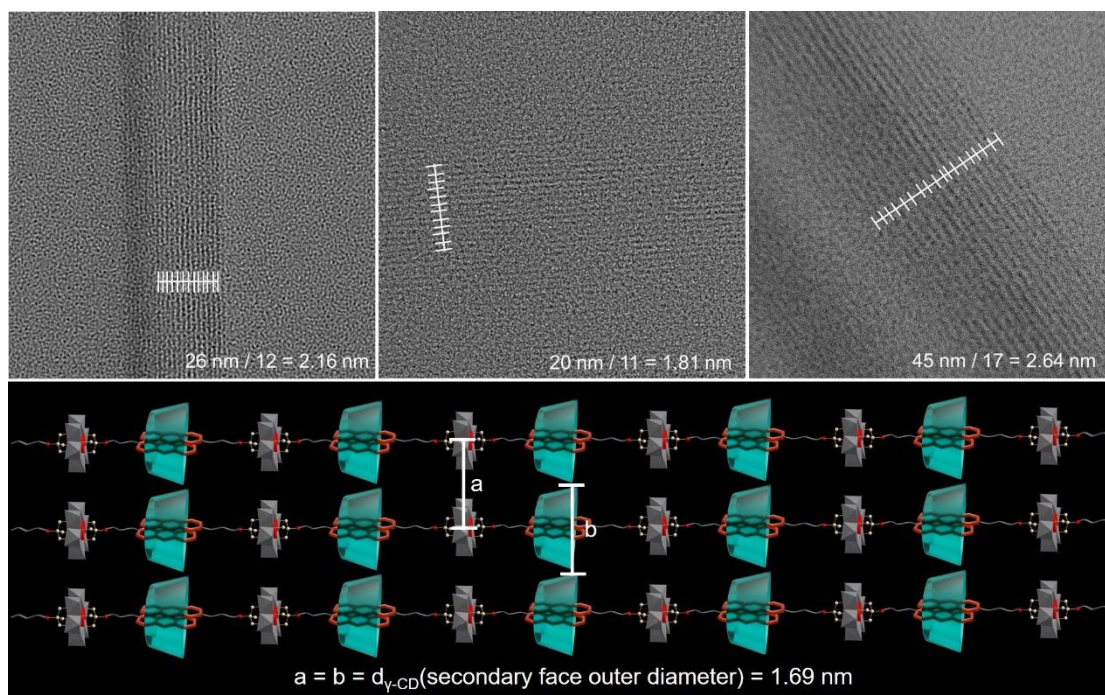


Fig. S14 Estimation and the proposed model for the distance between adjacent supramolecular polymers, based on the observed bundles of polymer chains in TEM images.

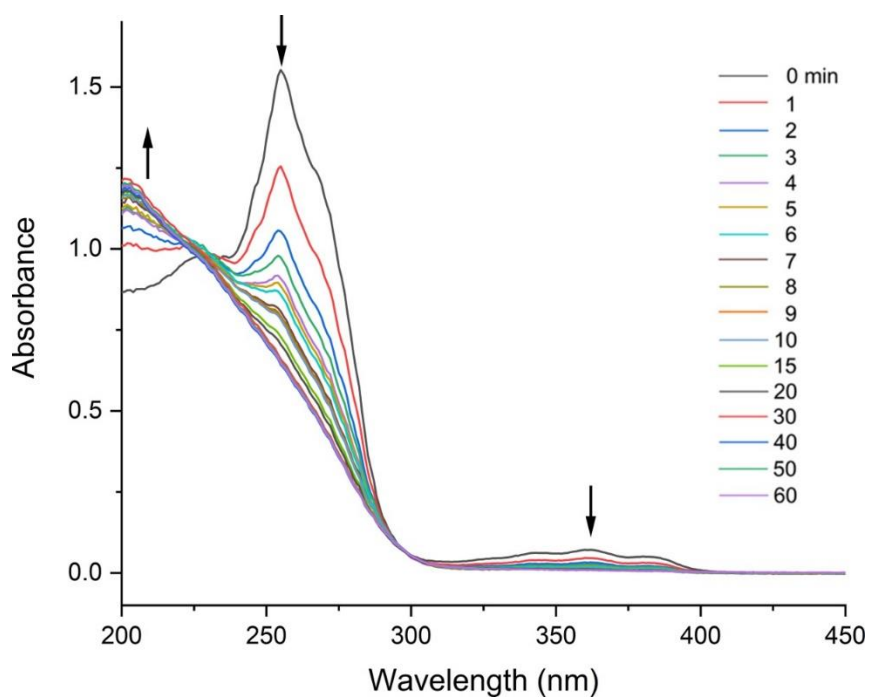


Fig. S15 UV-Vis spectra of An-AlMo₆@ γ -CD versus the irradiation time, in which the concentration of An-AlMo₆ was diluted from 2.0 mM to 0.2 mM for a suitable absorbance.

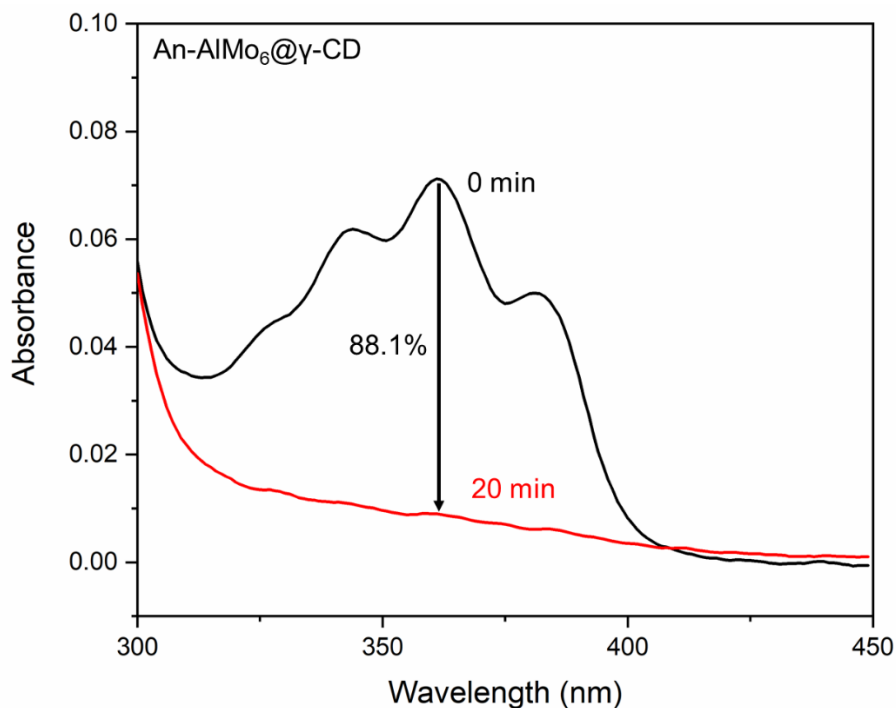


Fig. S16 UV-Vis spectra of An-AlMo₆@γ-CD aqueous solution before and after light irradiation and the calculation of the yield of conversion based on the equation of $A[0 \text{ min}] - A[90 \text{ min}] / A[0 \text{ min}]$ at 355 nm.

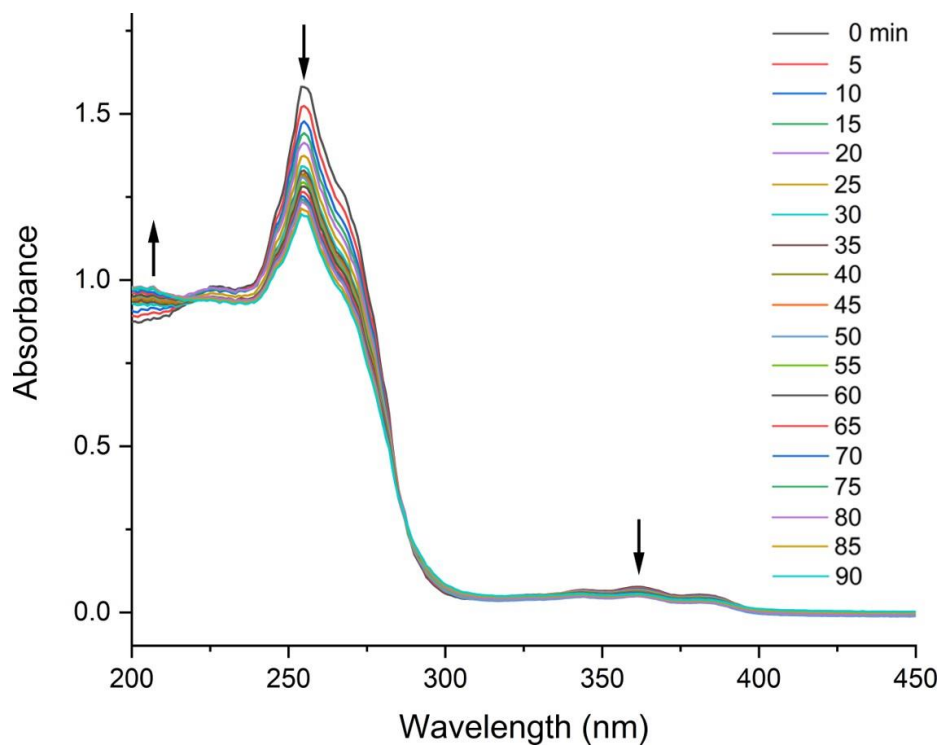


Fig. S17 UV-Vis spectra of bare An-AlMo₆ versus the irradiation time, in which the concentration was diluted from 2.0 mM to 0.2 mM for getting a suitable absorbance.

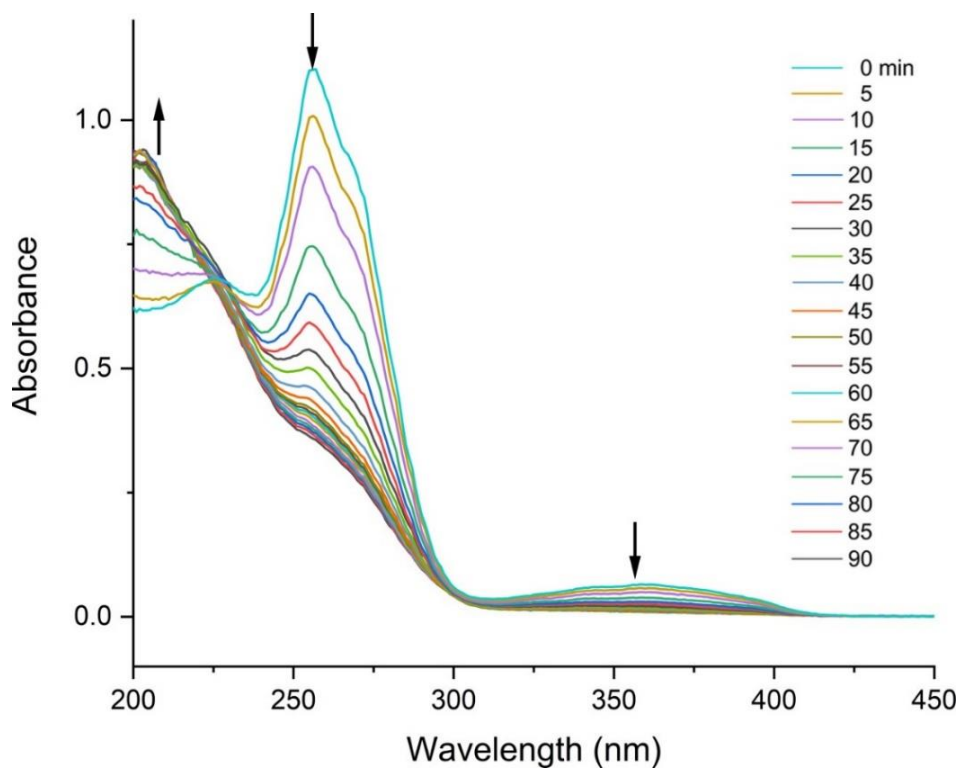


Fig. S18 UV-Vis spectra of An-MnMo₆@ γ -CD versus irradiation time, in which the concentration was diluted from 1.0 mM to 0.1 mM for getting a suitable absorbance.

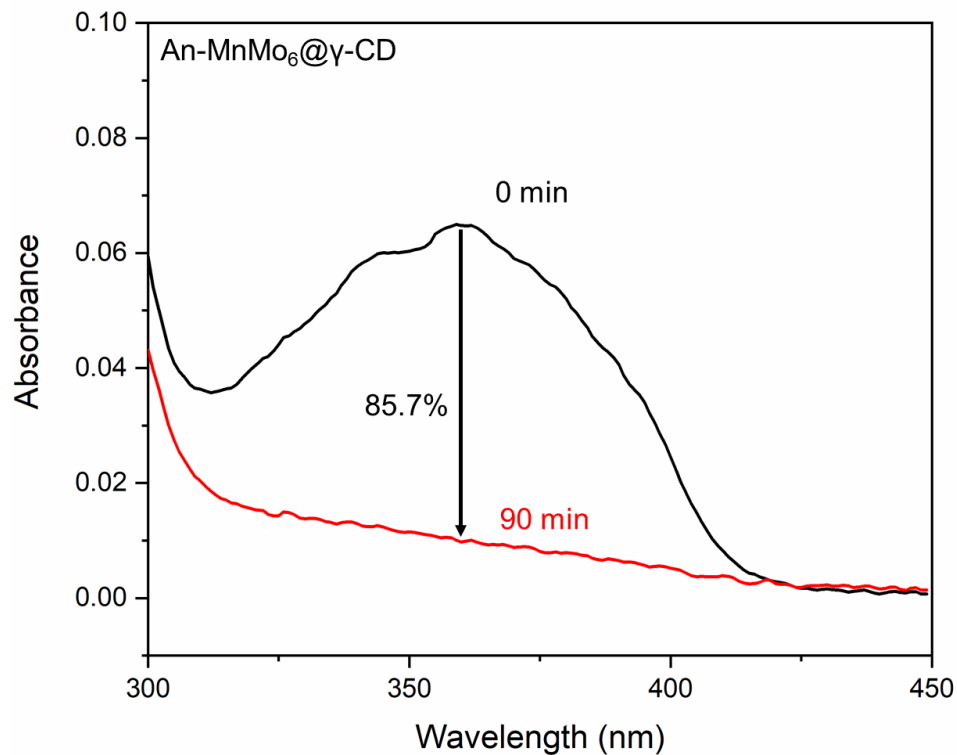


Fig. S19 UV-Vis spectra of An-MnMo₆@ γ -CD aqueous solution before and after light irradiation and the calculation of the yield of conversion based on the equation of $A[0 \text{ min}] - A[90 \text{ min}] / A[0 \text{ min}]$ at 355 nm.

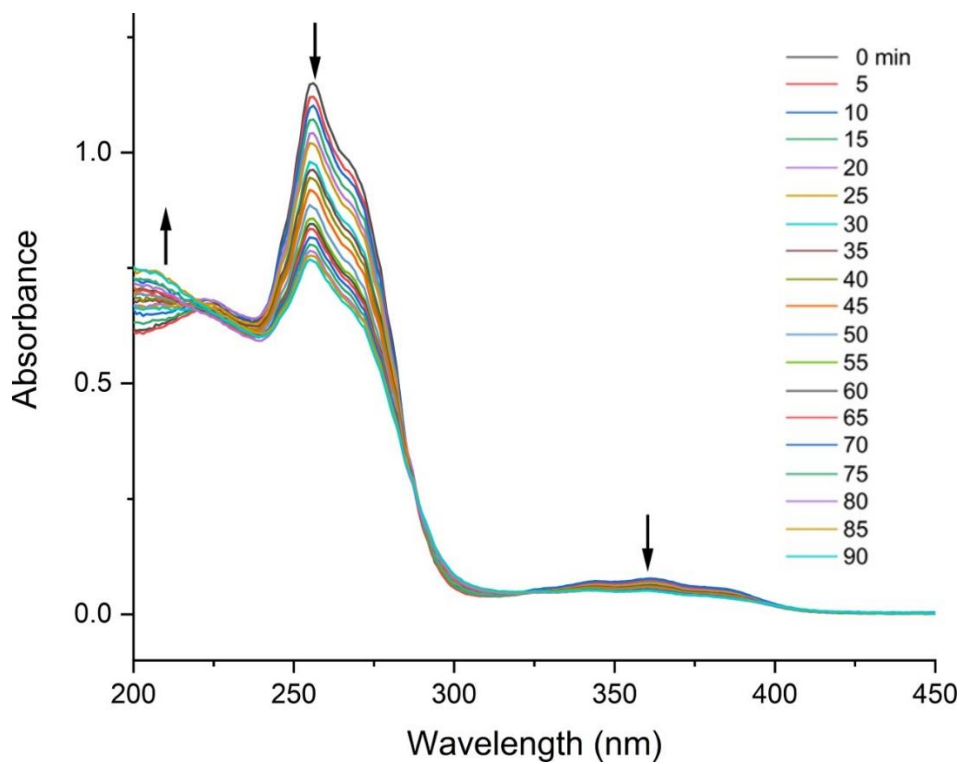


Fig. S20 UV-Vis spectra of bare An-MnMo₆ versus the irradiation time, in which the concentration was diluted from 1.0 mM to 0.1 mM for getting a suitable absorbance.

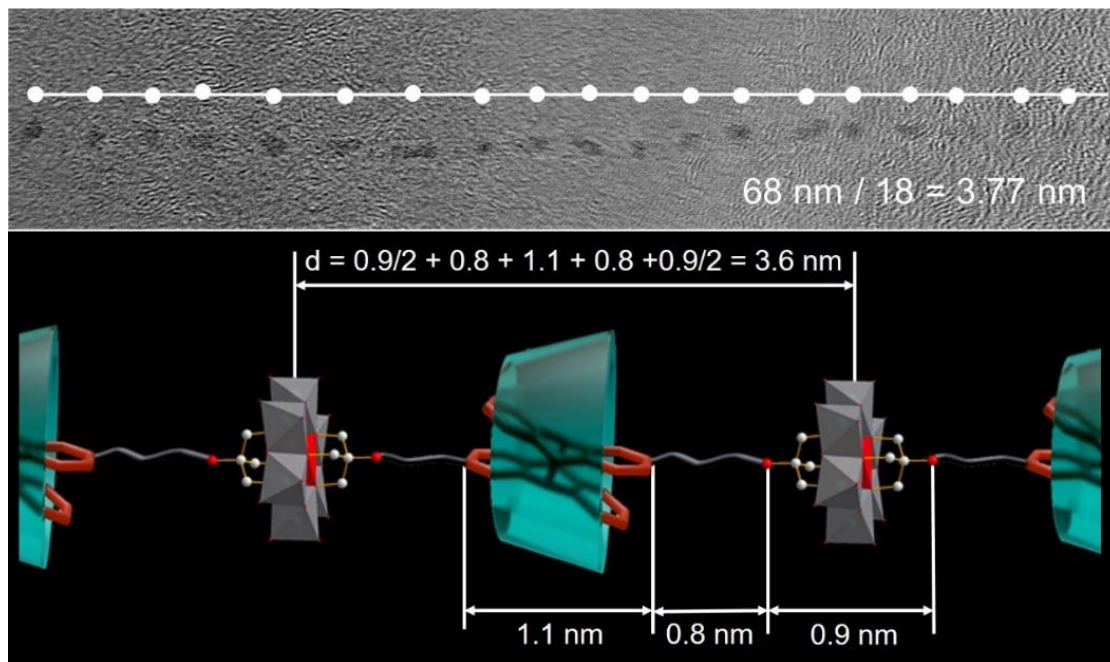


Fig. S21 Calculation for the distance between POMs in covalent polymer, based on polymer chain in TEM image and the ideal size of POM and organic groups.

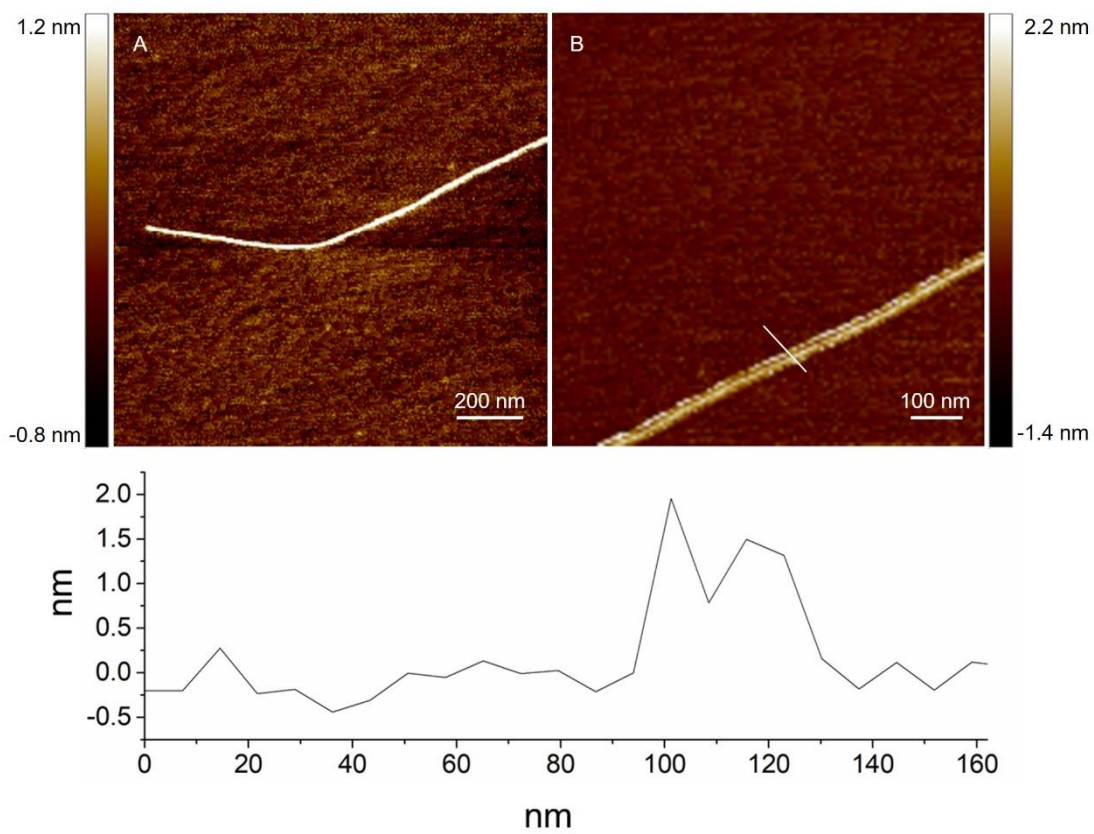


Fig. S22 AFM image of An-MnMo₆ covalently polymer by dropping sample solution on silicon wafer.

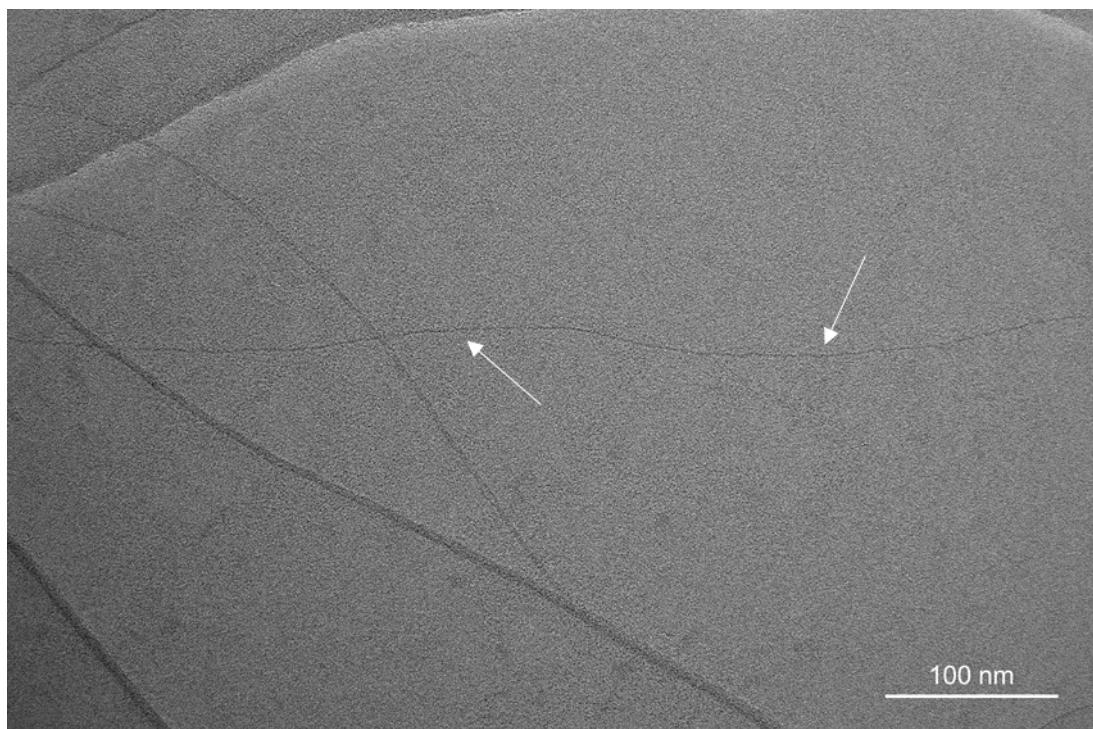


Fig. S23 Length measurement of a single-chain of MnMo₆ polymer.

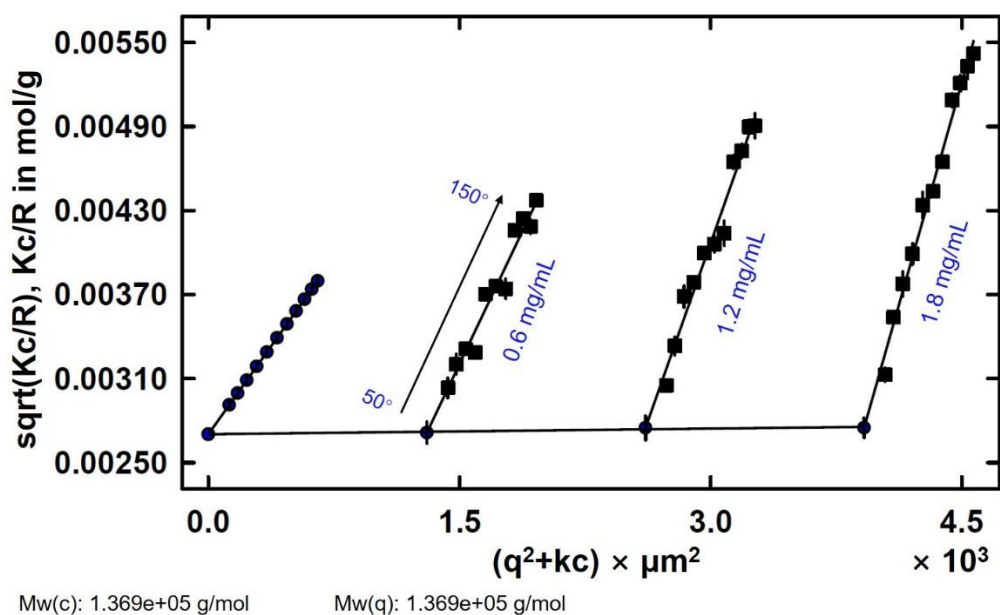


Fig. S24 Static light scattering (SLS) data of An-MnMo₆@ γ -CD in DMSO/water (1/9 in v/v) encountering 90 min of irradiation at 365 nm for weight-average molecular weight (results of Berry-Plot, $dn/dc = 0.1633 \text{ mL/g}$).

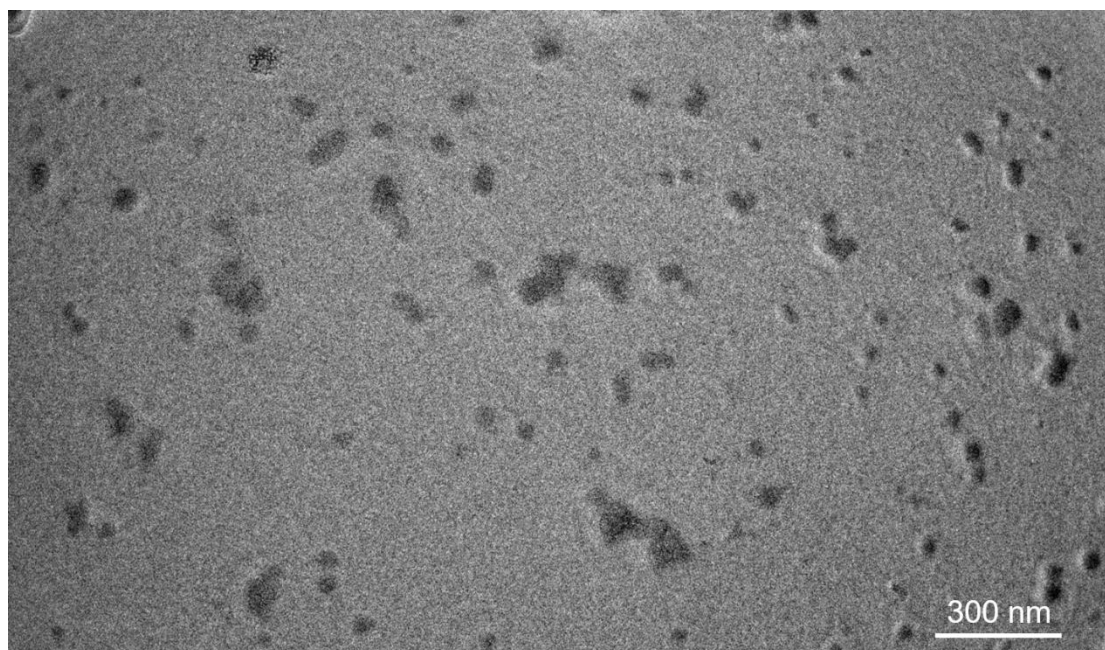


Fig. S25 TEM image of bare An-MnMo₆ polymer without mixing with γ -CD after the irradiation of 6 h.

References

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