

## Supplementary Information

### A Processable Hybrid Supramolecular Polymer Formed by Base Pair

#### Modified Polyoxometalate Clusters

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#### 1. Materials

Ethylbromoacetate and tris(hydroxymethyl)aminomethane (Tris) were purchased from Sinopharm Chemical Reagent Co, Ltd.. Tetrakis(decyl)ammonium (TDA) was purchased from J&K, N,N-dimethyldodecylamine and thymine from Aladdin were used as received.  $[N(C_4H_9)_4]_4[\alpha-Mo_8O_{26}]$  was synthesized according to the literature.<sup>[1]</sup> The other chemicals and solvents were purchased from Beijing Chemical Reagent Industry. Acetonitrile was distilled over  $P_2O_5$  before use. N, N-dimethylformamide (DMF) was dried with  $CaH_2$  before use.

#### 2. Synthetic procedures

**Typical route:** The base groups were modified onto  $MnMo_6$  clusters through an esterification reaction.<sup>[2]</sup> Firstly, the adenine and thymine groups were connected with tris(hydroxymethyl)aminomethane (*Tris*) by amide bonds, and then the resulting *Tris* derivatives were further grafted to  $MnMo_6$  clusters through a following esterification procedure. For the convenient synthesis of  $MnMo_6$  cluster and chemical modification, tetrabutyl ammonium (TBA) was used as the counter cation. To improve the solubility in low-polar solvent that is favorable for the formation of hydrogen bonds, the base pair grafted  $MnMo_6$  clusters were treated by consecutive ion exchange procedures, in which all TBAs were firstly replaced with sodium ions and then tetrakis(decyl) ammoniums (TDAs).

**Monomer 1 with TBA counter ions (1-TBA):** It was synthesized according to the previous publication (Fig. S1a).<sup>[3]</sup>

**Monomer 1 with sodium counter ions (1-Na):** 1-TBA (1.45 g, 0.65 mmol) was dissolved in  $CH_3CN$ , and then the solution was dropped into the  $CH_3CN$  solution of  $NaClO_4 \cdot H_2O$  (1.07 g, 7.59 mmol). The mixture solution was stirred 6 h and an orange precipitation was formed. The solution was filtered and the filter cake was washed several times by  $CH_3CN$  and then dried under vacuum overnight. Yield: 1 g (98.7 %). FT-IR (KBr):  $\nu = 3359(s), 3228(s), 3086(s), 2921(sh), 2873(s), 1693(s), 1645(s), 1581(sh), 1483(sh), 1309(s), 1251(sh), 1109(s), 1035(s), 945(s), 923(s), 823(s)$ ,

796 (s), 665  $\text{cm}^{-1}$  (s). The characteristic vibration bands of  $\text{MnMo}_6$  cluster are observed in the FT-IR spectrum of **1-Na** at 945, 923, 823, and 665  $\text{cm}^{-1}$  (Fig. S2b), indicating the well-retained Anderson-type structure of  $\text{MnMo}_6$  cluster during the ion exchange process. The  $^1\text{H}$  NMR spectrum of **1-Na** is shown in Fig. S3b (500 MHz;  $\text{DMSO-}d_6$ , TMS, ppm): 5.19 (4H, singlet), 7.15 (4H, singlet), 8.06 (2H, singlet), 8.15 (2H, singlet), 64.27 ppm (12H, broad). The proton signals of TBA disappear, which implies a complete ion exchange. The calculated elemental analysis results for  $\text{C}_{22}\text{H}_{26}\text{N}_{12}\text{O}_{26}\text{Na}_3\text{MnMo}_6$  (1574.1  $\text{g mol}^{-1}$ ) are: C 16.79, H 1.66, N 10.68; found C 16.45, H 1.70, N 10.52, which further confirms the existence of three sodium ions on **1-Na**.

**Monomer 1 with TDA counter ions (1): 1-Na** (1.00 g, 0.64 mmol) was dissolved in the mixture solvent (150 mL) of methanol and deionized water (2:1 v/v). The solution was dropped into the solution (180 mL) of methanol and deionized water (2:1 v/v) of tetrakis(decyl)ammonium bromide (4.22 g, 6.4 mmol). The mixture solution was stirred overnight, and then the orange precipitates were separated by centrifuged and dried under vacuum overnight. Yield: 1 g (48.5%). FT-IR (KBr):  $\nu = 3303$  (s), 3253 (s), 3095 (s), 2954 (s), 2925 (sh), 2852 (s), 1699 (s), 1666 (s), 1571 (sh), 1465 (sh), 1421 (s), 1380 (s), 1359 (s), 1323 (s), 1307 (s), 1272 (sh), 1244 (s), 1155 (s), 1109 (s), 1037 (s), 941 (s), 914 (s), 822 (s), 800 (s), 673  $\text{cm}^{-1}$  (s). The characteristic vibration bands of  $\text{MnMo}_6$  cluster appears in the FT-IR spectrum of **1** at 941, 914, 822, and 673  $\text{cm}^{-1}$  (Fig. S2c), which indicates the well-retained Anderson-type structure of  $\text{MnMo}_6$  cluster after the surfactant encapsulating process. The  $^1\text{H}$  NMR spectrum of **1** is shown in Fig. S3c (500 MHz;  $\text{DMSO-}d_6$ , TMS, ppm):  $\delta = 0.86$  (36H, triplet), 1.26 (168H, m), 1.56 (24H, m), 3.15 (24H, m) 5.18 (4H, singlet), 7.14 (4H, singlet), 8.05 (2H, singlet), 8.14 (2H, singlet), 64.42 ppm (12H, broad). The 1:3 integral ratio of the  $-\text{CH}_2\text{O}-$  protons of Tris to the terminal methyl protons of TDA demonstrates that each adenine-grafted  $\text{MnMo}_6$  cluster is averagely accompanied by three TDA counterions. The ESI-MS spectrum of **1** (negative mode,  $\text{CH}_3\text{OH}$ ) is shown in Fig. S4, which exhibits a dominant peak at  $m/z$  of 2662.6  $\text{g mol}^{-1}$ , corresponding to an ionized **1** with two TDA counter ions. This result confirms the molecular composition of **1**. The calculated elemental analysis result for  $\text{C}_{142}\text{H}_{278}\text{N}_{15}\text{O}_{26}\text{MnMo}_6$  (3242.39  $\text{g mol}^{-1}$ ): C 52.60, H 8.64, N 6.48; found C 52.93, H 8.33, N 6.38, which also supports the 1:3 ratio of TDA to  $\text{MnMo}_6$  cluster in **1**.

**Monomer 2 with TBA counter ions (2-TBA):** The synthetic route is shown Fig. S1b. Thymine bis(trimethylsilyl)ether was synthesized according to the literatures.<sup>[4]</sup> It was obtained as a colorless oil. Under a  $\text{N}_2$  atmosphere, 20 ml DMF was added to a flask containing the entire portion of thymine bis(trimethylsilyl) ether (3.5 g, 12.96 mmol). And then ethyl bromoacetate (1.5 mL, 13.56 mmol) was added into the mixture slowly. The mixture was further stirred at 60  $^\circ\text{C}$  for 24 h. After evaporating DMF under reduced pressure, ice water (250 ml) was added and the mixture was stirred for 30 min. The white solid products were obtained by filtration, which were dissolved in chloroform and dried with magnesium sulfate, filtered and concentrated by evaporation to yield thymine ester derivative. According to the synthetic method of **1-TBA**, the pure **2-TBA** product was obtained. Yield: 2 g (22 %, based on Mo). IR

(KBr):  $\nu = 3500$  (br), 3284 (s), 3244 (s), 3180 (sh), 3089 (s), 3057 (s), 2962 (s), 2937 (s), 2873 (s), 1689 (s), 1571 (s), 1467 (s), 1421 (sh), 1383 (s), 1350 (s), 1311 (s), 1261 (s), 1243 (s), 1147 (s), 1109 (s), 1039 (s), 941 (s), 920 (s), 900 (s), 835 (w), 768 (s), 671  $\text{cm}^{-1}$  (s). The FT-IR spectrum of **2-TBA** shows the characteristic vibration bands of Anderson-type clusters in which the triple peaks of the terminal Mo=O mode appeared at around 941, 920, 900  $\text{cm}^{-1}$ , and the bridging Mo-O-Mo mode appeared at about 671  $\text{cm}^{-1}$ , confirming the existence of  $\text{MnMo}_6$  moiety in **2-TBA** (Fig. S5a). The  $^1\text{H}$  NMR spectrum of **2-TBA** is shown in Fig. S6a (500 MHz;  $\text{DMSO-}d_6$ , TMS, ppm):  $\delta = 0.93$  (36H, triplet), 1.29 (24H, m), 1.57 (24H, m), 1.73 (6H, singlet), 3.16 (24H, triplet), 4.62 (4H, singlet), 7.40 (2H, singlet), 11.21 (2H, singlet), 64.24 ppm (12H, broad). In comparison with the  $^1\text{H}$  NMR spectra of T-Tris, two distinct changes are observed: the proton signal of the three hydroxyl groups of T-Tris disappears in **2-TBA**; meanwhile, the signal of the three hydroxymethyl groups of T-Tris shifts to downfield 64.24 ppm. These changes indicate a successful esterification reaction in which the three hydroxymethyl groups of T-Tris are covalently grafted to  $\text{MnMo}_6$  clusters. The 1:3 integral ratio of the  $-\text{CH}_2\text{O}-$  protons of Tris to the terminal methyl protons of TBA demonstrates that each thymine-grafted  $\text{MnMo}_6$  cluster is averagely accompanied by three TBAs. The calculated elemental analysis results for  $\text{C}_{70}\text{H}_{136}\text{N}_9\text{O}_{30}\text{MnMo}_6$  (2214.4  $\text{g mol}^{-1}$ ) are: C 37.97, H 6.19, N 5.69; found C 37.82, H 5.94, N 5.26, which further confirms the 1:3 ratio of TBA to  $\text{MnMo}_6$  cluster in **2-TBA**.

**Monomer 2 with sodium counter ions (2-Na):** It was obtained according to the method of **1-Na**. Yield: 1 g (80 %). FT-IR (KBr):  $\nu = 3475$  (br), 3388 (s), 3170 (br), 3066 (s), 2995 (s), 2935 (s), 2817 (s), 1693 (s), 1525 (s), 1475 (s), 1419 (sh), 1373 (s), 1352 (s), 1317 (s), 1245 (s), 1107 (s), 1035 (s), 945 (s), 929 (s), 813 (w), 769 (s), 661  $\text{cm}^{-1}$  (s). The characteristic vibration bands of  $\text{MnMo}_6$  cluster appeared in the FT-IR spectrum of **2-Na** at 945, 929, 813, and 661  $\text{cm}^{-1}$  (Fig. S5b), indicating the well-retained Anderson-type structure of  $\text{MnMo}_6$  cluster after the ion exchange process. The  $^1\text{H}$  NMR spectrum of **2-Na** is shown in Fig. S6b (500 MHz;  $\text{DMSO-}d_6$ , TMS, ppm):  $\delta = 1.73$  (6H, singlet), 4.62 (4H, singlet), 7.41 (2H, singlet), 11.21 (2H, singlet), 64.24 ppm (12H, broad). The proton signals of TBA disappears, which implies a complete ion exchange. The calculated elemental analysis results for  $\text{C}_{22}\text{H}_{28}\text{N}_6\text{O}_{30}\text{Na}_3\text{MnMo}_6$  (1556.0  $\text{g mol}^{-1}$ ) are: C 16.98, H 1.81, N 5.40; found C 16.76, H 1.68, N 5.73, which further confirms the existence of three sodium ions on **2-Na**.

**Monomer 2 with TDA counter ions (2):** It was obtained according to the method of **1**. Yield: 48.3 %. FT-IR (KBr):  $\nu = 3301$  (s), 3251 (s), 3093 (s), 2954 (s), 2925 (sh), 2852 (s), 1699 (s), 1666 (s), 1571 (sh), 1465 (sh), 1421 (s), 1380 (s), 1359 (s), 1323 (s), 1307 (s), 1272 (sh), 1244 (s), 1155 (s), 1109 (s), 1037 (s), 941 (s), 914 (s), 822 (s), 800 (s), 673  $\text{cm}^{-1}$  (s). The characteristic vibration bands of  $\text{MnMo}_6$  cluster appears in the FT-IR spectrum of **2** at 941, 914, 822, and 673  $\text{cm}^{-1}$  (Fig. S5c), which indicates the well-retained Anderson-type structure of  $\text{MnMo}_6$  cluster after the surfactant encapsulating process. The  $^1\text{H}$  NMR spectrum of **2** is shown in Fig. S6c (500 MHz;  $\text{DMSO-}d_6$ , TMS, ppm):  $\delta = 0.86$  (36H, triplet), 1.27 (168H, m), 1.56 (24H, m), 1.73 (6H, singlet), 3.14 (24H, m), 4.62 (4H, singlet), 7.41 (2H, singlet), 11.21 (2H, singlet),

64.24 ppm (12H, broad). The 1:3 integral ratio of the -CH<sub>2</sub>O- protons of Tris to the terminal methyl protons of TDAs demonstrated that each thymine-grafted MnMo<sub>6</sub> cluster is averagely accompanied by three TDA counterions. The ESI-MS spectrum of **2** (negative mode, CH<sub>3</sub>OH) is shown in Fig. S7, which exhibits a dominant peak at *m/z* of 2645 g mol<sup>-1</sup>, corresponding to an ionized **2** with two TDA counter ions. This result confirms the molecular composition of **2**. The calculated elemental analysis results for C<sub>142</sub>H<sub>280</sub>N<sub>9</sub>O<sub>30</sub>MnMo<sub>6</sub> (3224.36 g mol<sup>-1</sup>) are: C 52.89, H 8.75, N 3.91; found C 52.93, H 8.42, N 3.81, which further support the 1:3 ratio of TDA to MnMo<sub>6</sub> cluster in **2**.

**Monomer 3 with TBA counter ions (3-TBA):** The synthetic route is shown in Fig. S1c. A mixture of trimethylolpropane (0.50 g, 3.73 mmol), Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O (0.43 g, 1.60 mmol), and [N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>]<sub>4</sub>[α-Mo<sub>8</sub>O<sub>26</sub>] (2.29 g, 1.07 mmol) were stirred at 85 °C in CH<sub>3</sub>CN for 24 h in a N<sub>2</sub> atmosphere. The reaction solution was cooled to room temperature and the precipitate was removed by filtration. The orange filtrate was exposed to diethyl ether vapor for after several days and orange crystals were obtained. Yield: 1.63 g (80%, based on Mo). FT-IR (KBr):  $\nu$  = 2960 (s), 2935 (sh), 2875 (s), 1631 (s), 1479 (sh), 1446 (sh), 1382 (s), 1346 (s), 1112 (s), 1041 (s), 937 (s), 919 (s), 900 (s), 663 cm<sup>-1</sup> (s). The FT-IR spectrum of **3-TBA** showed the characteristic vibration bands of Anderson-type clusters in which the triple peaks of the terminal Mo=O mode appeared at around 937, 919, 900 cm<sup>-1</sup>, and the bridging Mo-O-Mo mode appeared at about 663 cm<sup>-1</sup>, confirming the existence of MnMo<sub>6</sub> moiety in **3-TBA** (Fig. S10a). The <sup>1</sup>H NMR spectrum of **3-TBA** is shown in Fig. S11a (500 MHz; DMSO-*d*<sub>6</sub>, TMS, ppm):  $\delta$  = 0.94 (36H, triplet), 1.31 (24H, m), 1.57 (24H, m), 3.16 (24H, m), 59.98 ppm (12H, broad). The signal of the three hydroxymethyl groups of Et-Tris shifts to downfield 59.98 ppm. This change indicates a successful esterification reaction in which the three hydroxymethyl groups of ethyl-Tris are covalently grafted to MnMo<sub>6</sub> clusters. The 1:3 integral ratio of the -CH<sub>2</sub>O- protons of Tris to the terminal methyl protons of TBAs indicates that each ethyl-grafted MnMo<sub>6</sub> cluster is averagely accompanied by three TBA. The calculated elemental analysis results for C<sub>60</sub>H<sub>130</sub>N<sub>3</sub>O<sub>24</sub>MnMo<sub>6</sub> (1908.3 g mol<sup>-1</sup>) are: C 37.76, H 6.87, N 2.20; found C 38.18, H 6.66, N 2.18, which further confirm the 1:3 ratio of TBA to MnMo<sub>6</sub> cluster in **3-TBA**.

**Monomer 3 with sodium counter ions (3-Na):** It was obtained according to the method of **1-Na**. Yield: 0.72 g (95 %). FT-IR (KBr):  $\nu$  = 2960 (s), 2935 (sh), 2875 (s), 1639 (s), 1465 (sh), 1448 (s), 1388 (s), 1101 (s), 1018 (s), 937 (s), 918 (s), 897 (s), 651 cm<sup>-1</sup> (s). The characteristic vibration bands of MnMo<sub>6</sub> cluster appear in the FT-IR spectrum of **3-Na** at 937, 918, 897, and 651 cm<sup>-1</sup> (Fig. S10b), which indicates the well-retained Anderson-type structure of MnMo<sub>6</sub> cluster after the ion exchange process. The <sup>1</sup>H NMR spectrum of **3-Na** in Fig. S11b shows that the proton signals of TBA disappears, which implies a complete ion exchange. The calculated elemental analysis results for C<sub>12</sub>H<sub>22</sub>O<sub>24</sub>Na<sub>3</sub>MnMo<sub>6</sub> (1249.8 g mol<sup>-1</sup>) are: C 11.53, H 1.77; found C 11.29, H 2.17, which further confirms the existence of three sodium ions on **3-Na**.

**Monomer 3 with TDA counter ions (3):** It was obtained according to the preparation method of **1**. Yield: 0.30 g (51.4 %). FT-IR (KBr):  $\nu$  = 2956 (s), 2923 (sh), 2854 (s),

1481 (sh), 1467 (s), 1379 (s), 1112 (s), 1041 (s), 937 (s), 919 (s), 898 (s), 665  $\text{cm}^{-1}$  (s). The characteristic vibration bands of  $\text{MnMo}_6$  cluster appears in the FT-IR spectrum of **3** at 937, 919, 898, and 665  $\text{cm}^{-1}$  (Fig. S10c), indicating the well-retained Anderson-type structure of  $\text{MnMo}_6$  cluster after the surfactant encapsulating process. The  $^1\text{H}$  NMR spectrum of **3** is shown in Fig. S11c (500 MHz;  $\text{DMSO-}d_6$ , TMS, ppm):  $\delta = 0.87$  (36H, triplet), 1.25 (168H, m), 1.55 (24H, m), 3.14 (24H, m), 60.19 ppm (12H, broad). The 1:3 integral ratio of the  $-\text{CH}_2\text{O}-$  protons of Tris to the terminal methyl protons of TDAs demonstrates that each ethyl-grafted  $\text{MnMo}_6$  cluster is averagely accompanied by three TDA counterions. Elemental analysis (%) calculated for  $\text{C}_{132}\text{H}_{274}\text{N}_3\text{O}_{24}\text{MnMo}_6$  (2918.2  $\text{g mol}^{-1}$ ): C 54.33, H 9.46, N 1.44; found C 54.67, H 9.11, N 1.52, which further confirm the 1:3 ratio of TDA to  $\text{MnMo}_6$  cluster in **3**.

**Bola-surfactant:** Under a  $\text{N}_2$  atmosphere, 1, 12-dibromododecane (1 g, 0.003 mol) and N, N-dimethyldodecylamine (3.84 g, 0.018 mol) was dissolved in ethanol and stirred at 85  $^\circ\text{C}$ . The mixture was further stirred for 72 h. After evaporating most of the solvent under reduced pressure, the remained solution was dropped into ethyl ether. The resulting white precipitate was collected as the crude product by filtration, which was further purified by silica gel chromatography with chloroform: methanol (30:1, 20:1, 10:1 v/v) as eluent. Finally, the pure product was obtained as a white solid, the yield was 1.18 g (52.1 %). Its  $^1\text{H}$  NMR spectrum is shown in Fig. S13 (500 MHz;  $\text{CDCl}_3$ , TMS, ppm):  $\delta = 0.88$  (6H, triplet), 1.26-1.41 (52H, m), 1.72 (8H, m), 3.38 (12H, triplet), 3.47 (4H, triplet), 3.69 (4H, triplet). Elemental analysis (%) calculated for  $\text{C}_{40}\text{H}_{86}\text{Br}_2\text{N}_2$  (754.9  $\text{g mol}^{-1}$ ): C 63.64, H 11.48, N 3.71; found C 63.27, H 11.66, N 3.60.

### 3. Measurements

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  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectra were recorded on a Bruker AVANCE 500 MHz spectrometer. Organic elemental analysis (C H N) was performed on a Flash EA1112 from ThermoQuest Italia S.P.A. Thermal gravimetric analysis (TGA) measurements were performed on a Q500 Thermal Analyzer (New Castle TA Instruments) in flowing  $\text{N}_2$  with a heating rate of 10  $^\circ\text{C min}^{-1}$ . Electrospray ionization mass spectrometry (ESI-MS) was obtained on UPLC-MS/MS (Qattro Premier). Scanning electron microscope (SEM) images were acquired on a JEOL FESEM 6700F electron microscope. Energy-dispersive X-ray (EDX) spectra, and EDX elemental mapping were collected on a FEI Tecnai F20 microscope operating at an accelerating voltage of 200 KV. The specific viscosity is calculated through the data of flowing time which were carried out on an Ubbelohde viscometer at room temperature in chloroform. The shearing viscosity values were measured on a LVDV-2 digital rotation viscometer with a small sample adapter. Electrospun supramolecular polymer nanofibers were obtained under the following conditions, 18 kV, 15 cm working distance, from a concentrated solution (60 mM) of SP in chloroform.



## 4. Figures and Tables

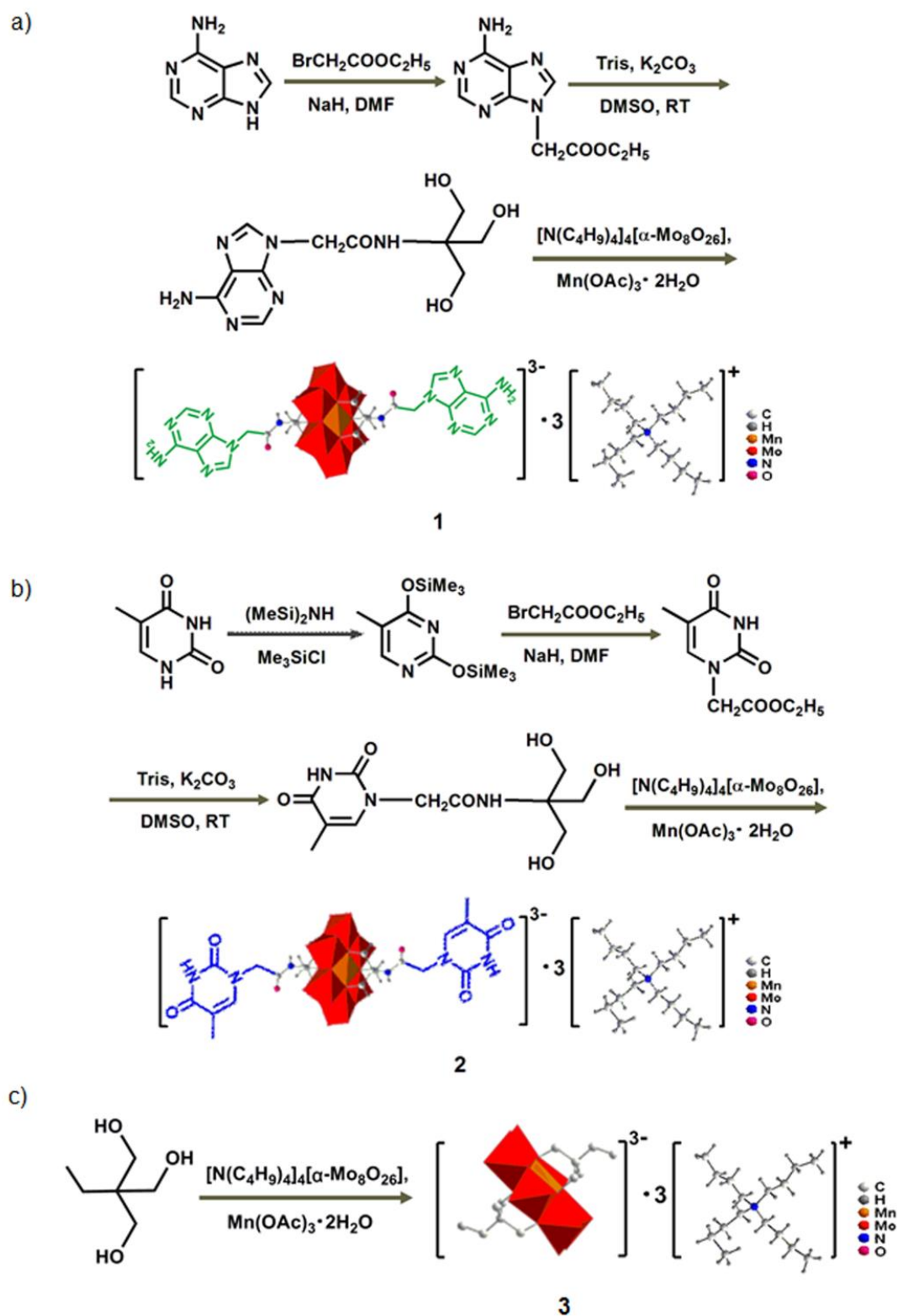
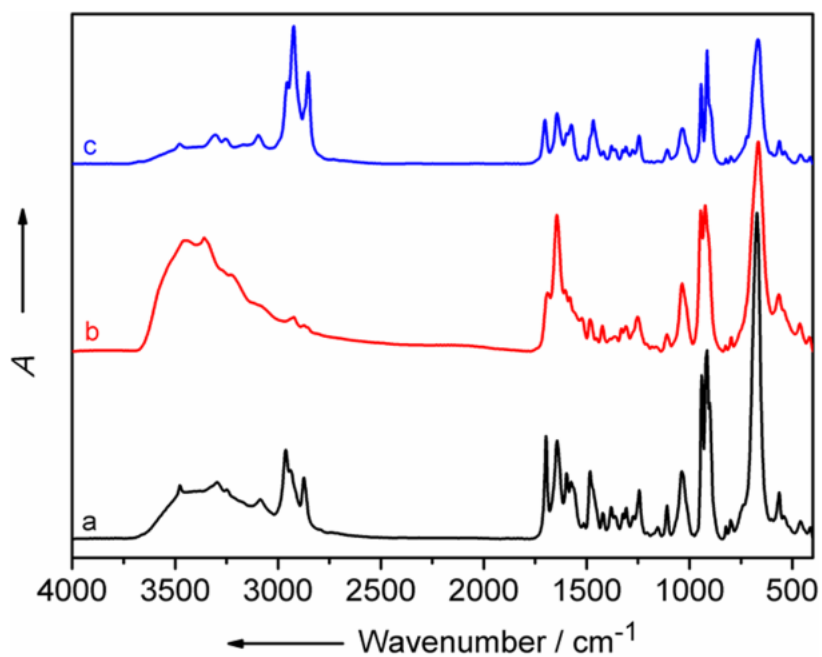
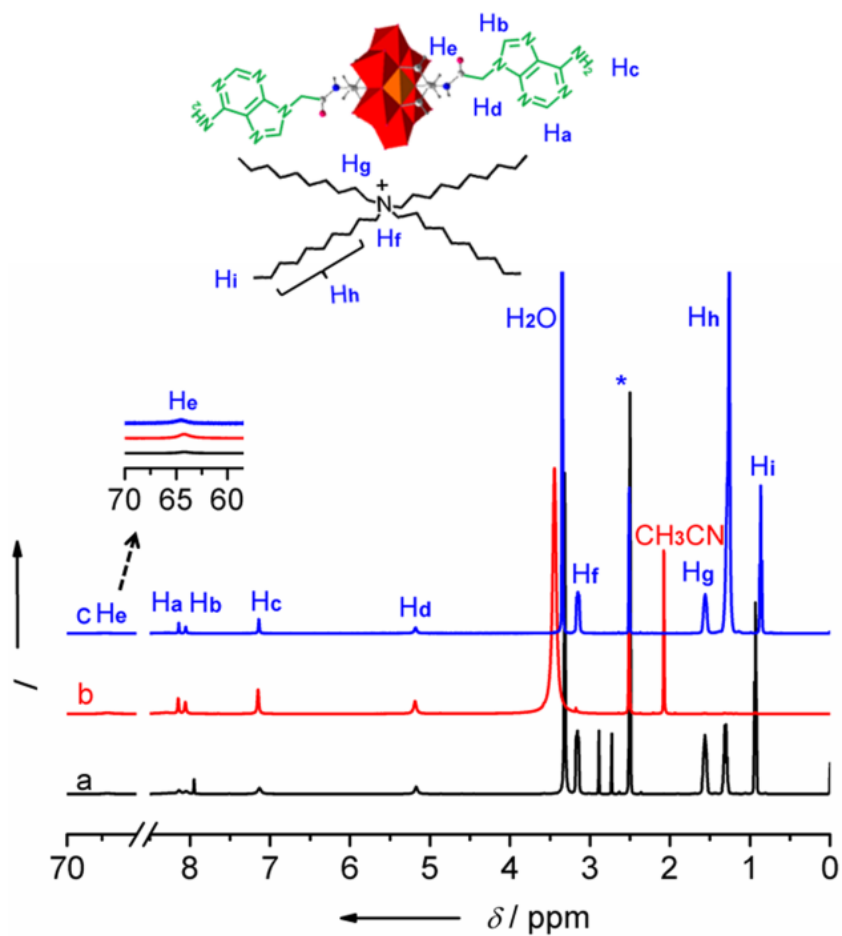


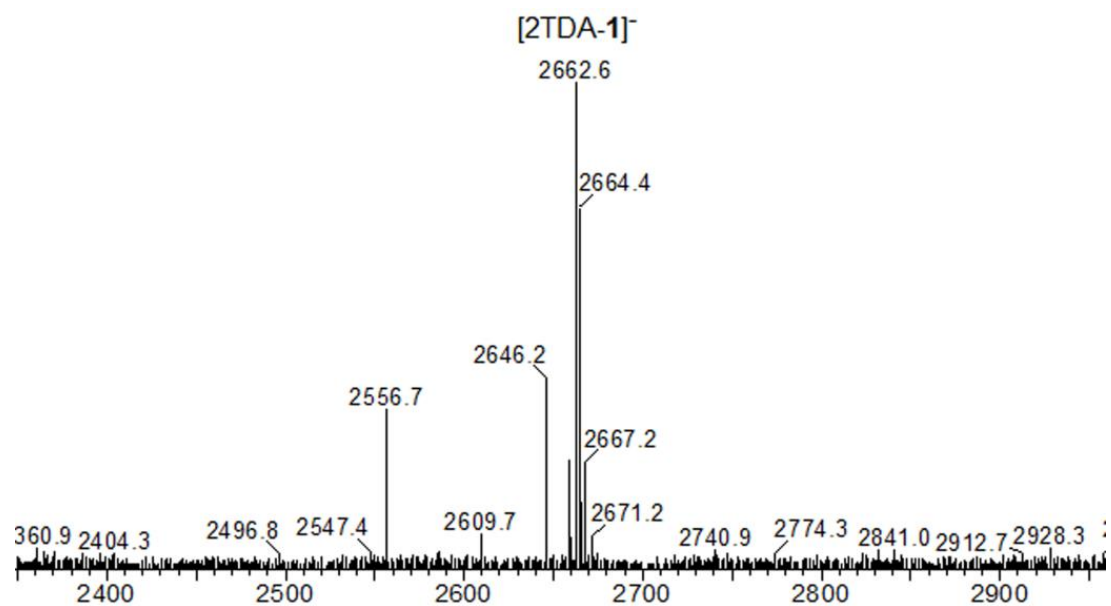
Fig. S1. Synthesis routes of monomer (a) 1-TBA, (b) 2-TBA and (c) 3-TBA.



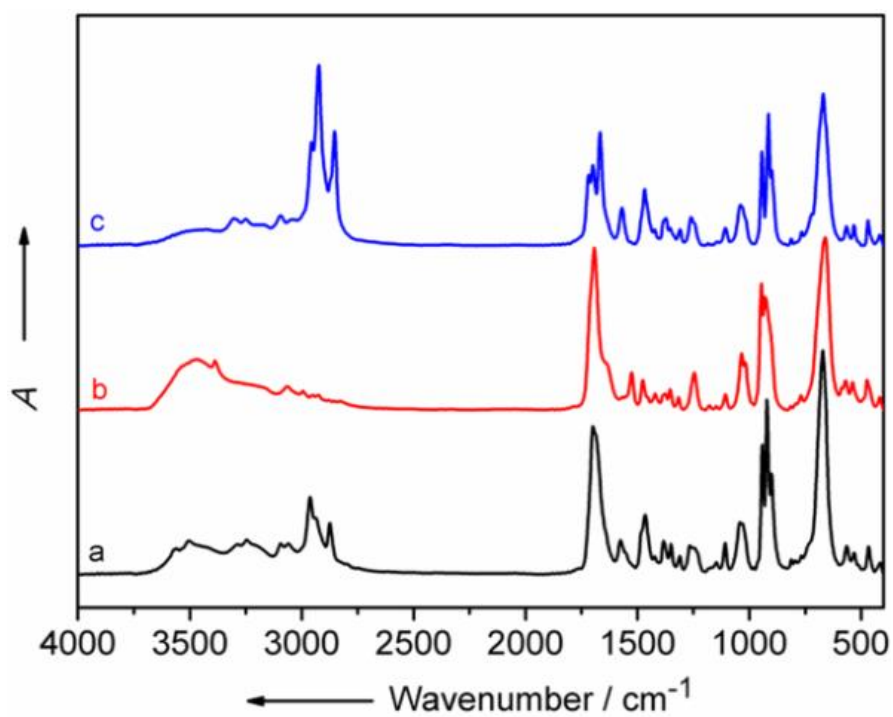
**Fig. S2.** FT-IR spectra of (a) **1-TBA**, (b) **1-Na**, and (c) **1** in KBr pellets.



**Fig. S3.** <sup>1</sup>H NMR spectra of (a) **1-TBA**, (b) **1-Na**, and (c) **1** in DMSO-*d*<sub>6</sub>.

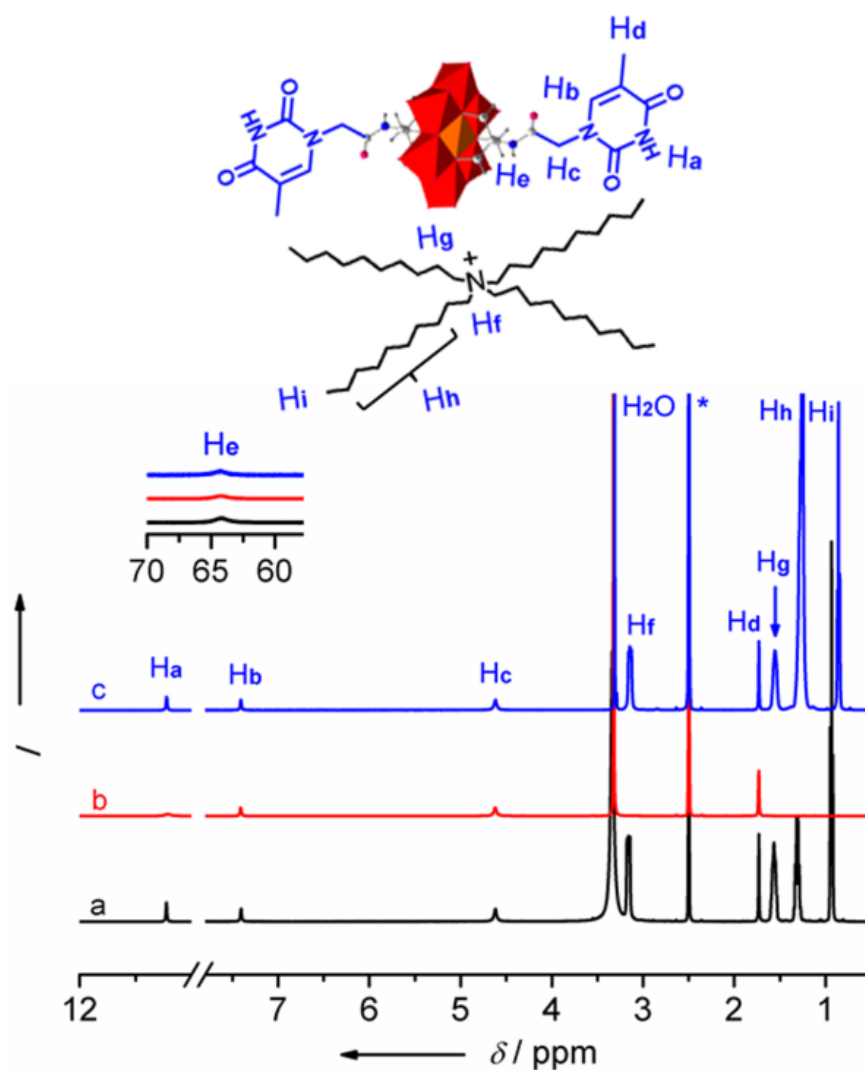


**Fig. S4.** ESI-MS spectrum of **1** in  $CHCl_3$ .

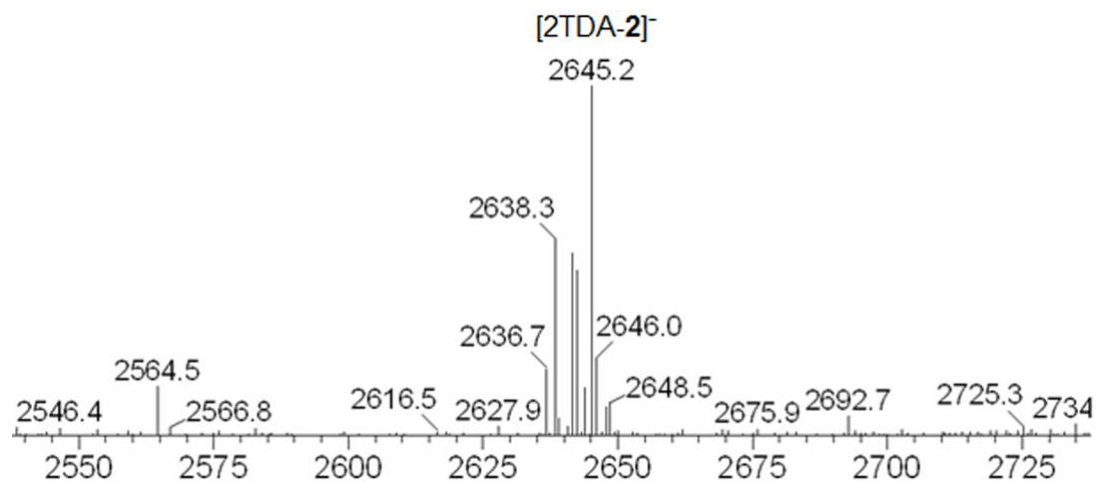


**Fig. S5.** FT-IR spectra of (a) **2-TBA**, (b) **2-Na**, and (c) **2** in KBr pellets.

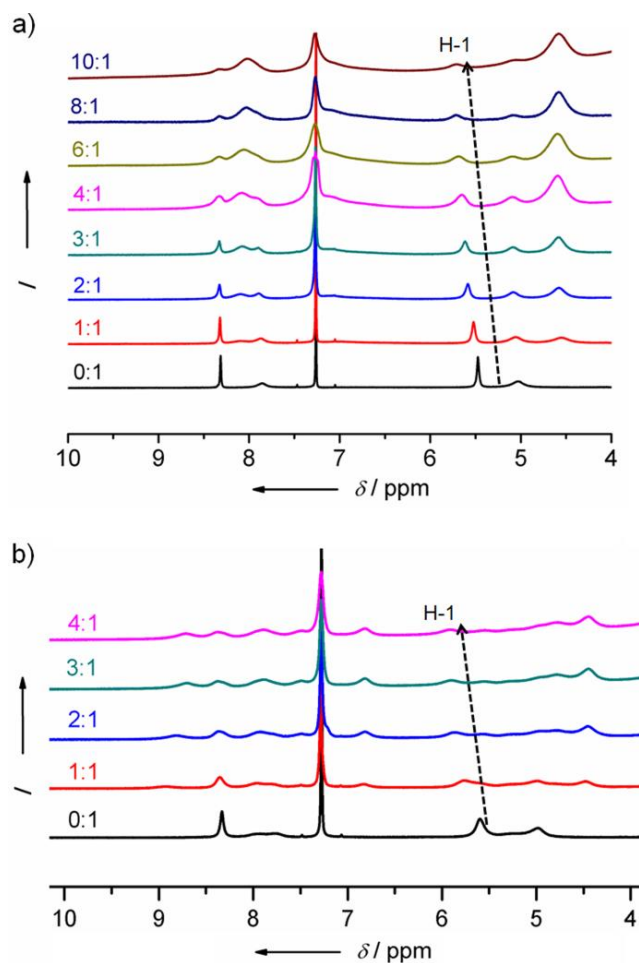




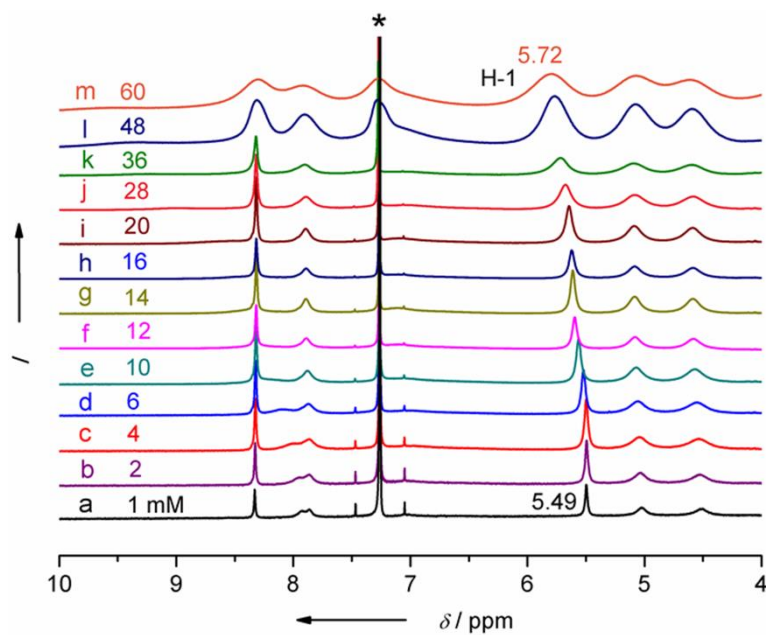
**Fig. S6.** <sup>1</sup>H NMR spectra of (a) 2-TBA, (b) 2-Na, and (c) 2 in DMSO-*d*<sub>6</sub>.



**Fig. S7.** ESI-MS spectrum of 2 in CHCl<sub>3</sub>.



**Fig. S8.** <sup>1</sup>H NMR spectra of 3 mM **1** mixing with **2** in different molar ratios in CDCl<sub>3</sub> at different temperature: a) 25 °C; b) -5 °C.

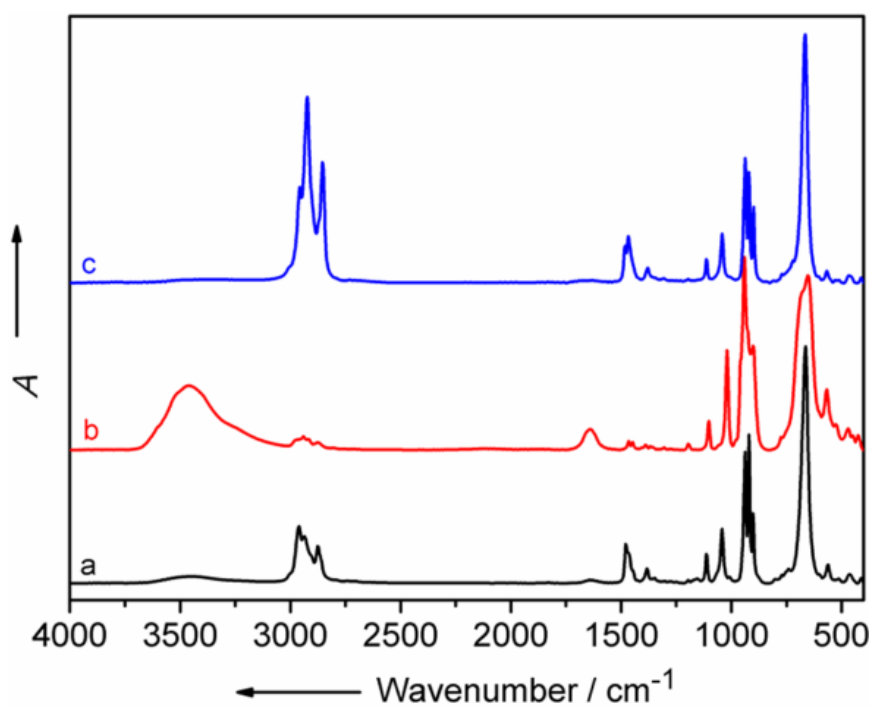


**Fig. S9.** <sup>1</sup>H NMR spectra of the mixture of **1** and **2** with the molar ratio of 1:1 in CDCl<sub>3</sub>. From curve (a) to (n), their total concentrations of **1** and **2** are both increased from 2 to 60 mM.

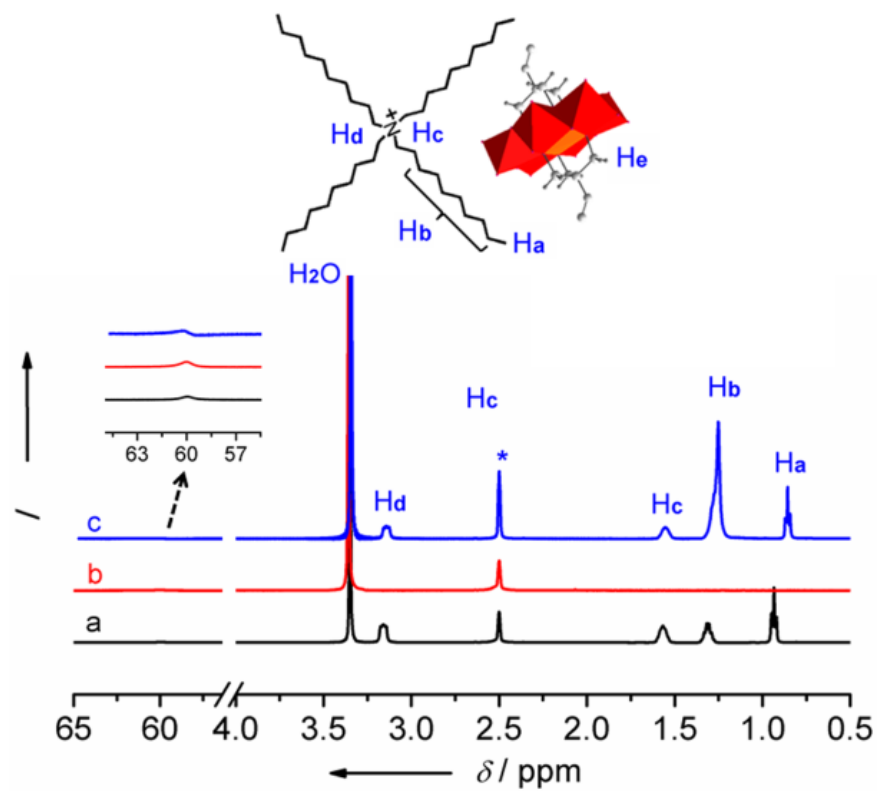
**Table S1.** Calculated values of  $p$  and  $n$  at different initial total concentration of **1** and **2** (which is equal to the concentration of  $\text{MnMo}_6$  clusters) with the molar ratio of 1:1.

| Total concentration / mM | $p^a$ | $n^b$ |
|--------------------------|-------|-------|
| 14                       | 0.419 | 1.72  |
| 28                       | 0.654 | 2.89  |
| 36                       | 0.809 | 5.24  |
| 48                       | 0.963 | 27.03 |

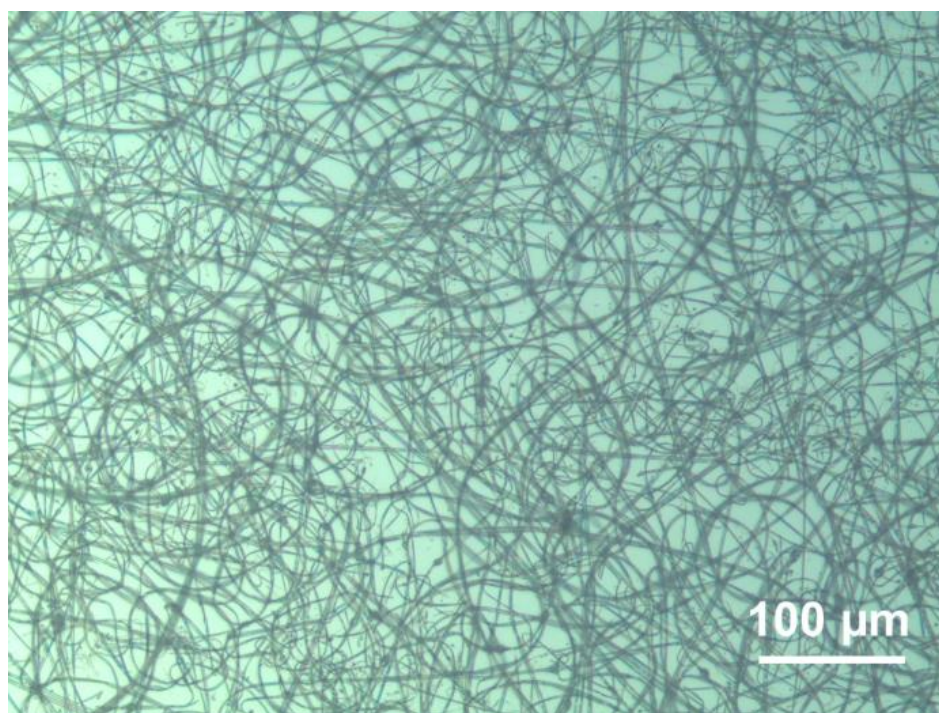
<sup>a</sup> Calculated from  $p = \Delta / \Delta_0$ ; <sup>b</sup> Calculated from  $n = 1/(1-p)$ .



**Fig. S10.** FT-IR spectra of (a) **3-TBA**, (b) **3-Na** and (c) **3** in KBr pellets.

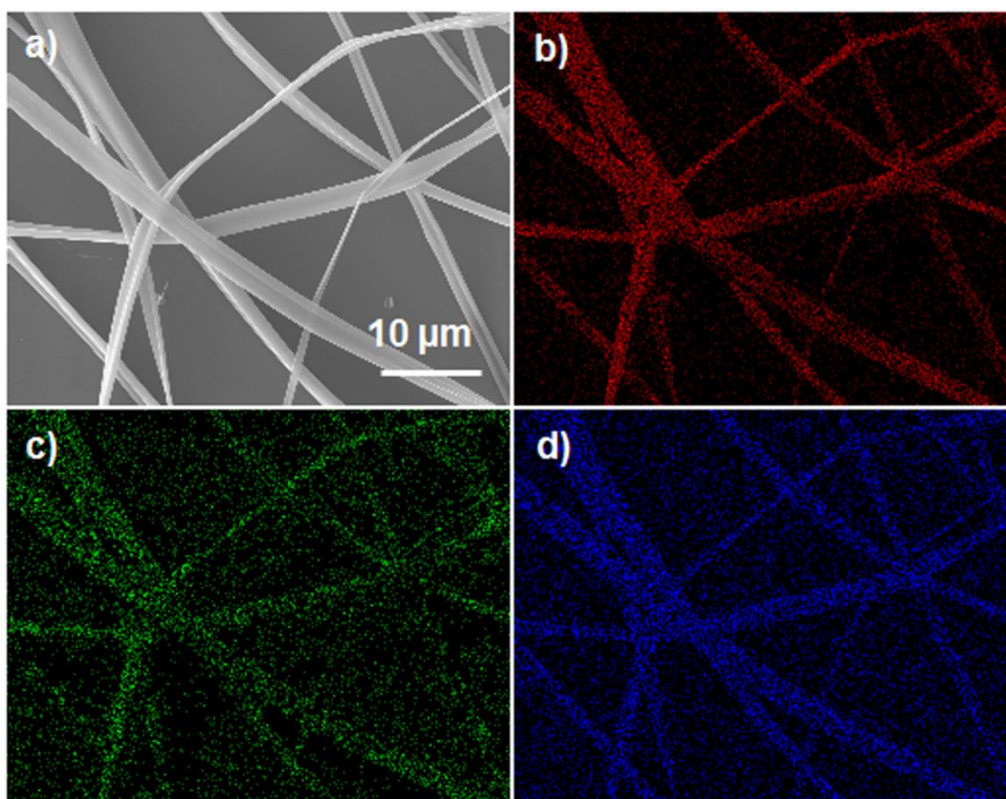


**Fig. S11.**  $^1\text{H}$  NMR spectra of (a) 3-TBA, (b) 3-Na and (c) 3 in  $\text{DMSO-}d_6$ .

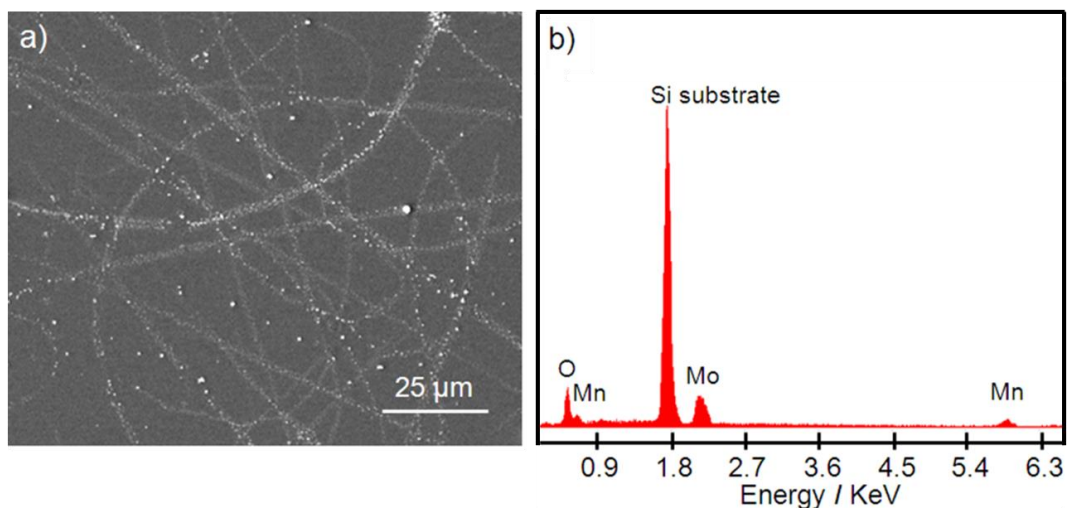


**Fig. S12.** Optical macroscopic photo of the electrospun supramolecular polymer fibers on silica substrate.

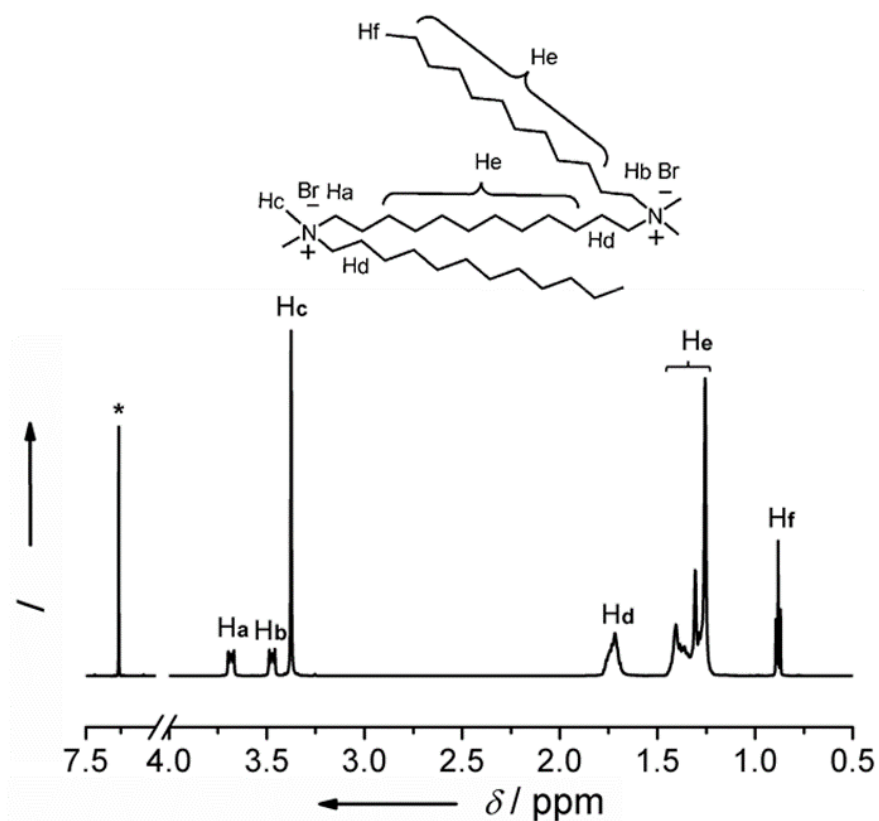




**Fig. S13.** (a) SEM image of the hybrid SP fibers prepared by electrospinning; EDX mapping images of the fibers by analyzing (b) C, (c) O and (d) Mo element.



**Fig. S14.** X-ray energy-dispersive spectroscopy (EDX) analysis of the electrospun supramolecular polymer fibers on silica substrate after calcination at 650 °C in air for 1 h: (a) the SEM image of the retained fibrous assemblies; (b) the binding energy spectrum of the region of image (a), which shows the complete decomposition of the carbon-containing organic part of the electrospun supramolecular polymer.



**Fig. S15.**  $^1\text{H}$  NMR spectrum of the bola-surfactant in  $\text{CDCl}_3$ .

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