A supramolecular gel based on an adenine symmetrically grafted Anderson-type polyoxometalate complex

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An Anderson-type polyoxometalate was covalently decorated by using adenine on both sides. Through cation substitution, we obtained a new hybrid building block with long alkyl chains for supramolecular gels. According to the synergetic effect of hydrogen bonding of inter adenine units and van der Waals interaction of side alkyl chains, the $\text{DODA}_3[\text{A-MnMo}_6\text{-A}]$ gelator can stabilize solvent and self-assemble into fibrous structure, forming supramolecular gel. In addition, the reversible sol-gel transformation was achieved by controlling environmental temperature. Scanning electron microscopy, transmission electron microscopy and X-ray diffraction were used to characterize the gel morphology and structure. As a result, we proposed the possible mechanism of gel formation and sol-gel transformation.

polyoxometalate, supramolecular gel, synergetic effect, hydrogen bonding, network

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Supramolecular gels, as a class of nanostructured soft materials, exhibit wide potential applications in the construction of one-dimensional nanostructured template [1], photonic and electronic materials [2], bio-medical materials [3] and carriers of selective catalysis [4]. The introduction of various functional components is favorable for the gel functionalization, and one of the most important routes is the addition of inorganic functional units into organic gel systems, obtaining organic-inorganic hybrid gels [5–8]. Therefore, attempts have been made to incorporate a variety of inorganic materials into the gel systems to achieve specific functions. Polyoxometalates (POMs) are one of the typical functional polyanions with diverse properties such as catalysis, optic and magnetism. A strategy for designing functional responsive hybrid gels has been developed. The anisotropic supramolecular gel bearing high mechanical intensity was obtained through the coordination of metal ions to the pyridyl covalently grafted Anderson-type POM [9]. Because of the strong binding force, this type of gel did not show responsive properties. Through electrostatic interac-

tions, we used organic cationic surfactant molecules to encapsulate a variety of POMs. By use of the amphiphilicity and intermolecular interactions of the obtained hybrid complexes, we developed the general method to prepare POM contained organic-inorganic supramolecular gels. In addition, the influence factors of gel formation, such as synergetic effect of organic and inorganic components, density and length of organic alkyl chains, and structure of POM, were found to be the important factors for gel formation [10]. A recent report made use of an Anderson-type POM grafted by dendritic organic components on both sides for the formation of a hybrid gel [11]. However, the POM based gels bearing the reversible gel-sol transformation were also rarely reported, though it is important for constructing POM hybrid materials possessing response properties for the stimulus from the external environment. We have prepared pyridyl modified Anderson-type POM gelators to build supramolecular network structures under the assistance of organic dicarboxylic acids. The reversible sol-gel transformation can be successfully performed under the stimuli of adding organic acids and alkalis [12]. However, the POM based hybrid supramolecular gels derived

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from single molecular component are still desired because of the requirement for the simple gel structure with higher stability.

Base on the above work, we designed an adenine (A) symmetrically modified POM (MnMo_6) as the gelator to build network structure that can stabilize solvents. In the formed supramolecular gel, we did not introduce any additional connecting molecular components, but just made use of synergetic effect of hydrogen bonding of inter adenine units and the van der Waals interaction between dioctadecyldimethylammonium (DODA) counterions with long alkyl chains. In the gel system, the high sensitivity for the sol-gel transformation is realized through the change of environmental temperature.

1 Materials and methods

1.1 Chemicals and instruments

All Chemicals were commercial products. Dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were dried by CaH_2 before use. The adenine decorated $\text{TBA}_3[\text{A-MnMo}_6\text{-A}]$ POM complex was synthesized according to the published literature [13]. For structural characterization, the single crystal structure of $\text{TBA}_3[\text{A-MnMo}_6\text{-A}]$ was determined by Rigaku Raxis-Rapid diffraction. Various temperature ^1H NMR spectra of the complex were recorded on a Bruker Avance 500 MHz instrument for the analysis of formation of hydrogen bonds (heating rate $5\text{ }^\circ\text{C min}^{-1}$, interval $5\text{ }^\circ\text{C}$, stabilization time 15 min). IR spectra were performed on a Bruker IFS 66v FT-IR spectrometer with KBr pellets for the analysis of complex composition. The gel morphology images were obtained on a JEOL JSM-6700F field emission scanning electron microscope (SEM) and a Hitachi H8100 transmission electron microscope (TEM). The self-assembly structure of the gel was identified by Rigaku D/MAX-2500 X-ray diffractometer.

1.2 Synthesis and structure characterization of $\text{DODA}_3[\text{A-MnMo}_6\text{-A}]$

$\text{TBA}_3[\text{A-MnMo}_6\text{-A}]$ (50.0 mg, 0.0223 mmol) and excess

$\text{DODA}\cdot\text{Br}$ (42.2 mg, 0.0669 mmol) were added into a vial containing chloroform and deionized water (8 mL) and the mixture solution encountered a long time sonication. After a centrifugation, orange precipitate was collected, and the following vacuum drying gave the target products (Figure 1) in yield 50% (35 mg). ^1H NMR (500 MHz; $\text{DMSO}-d_6$, TMS): 0.84–0.87 (18 H, triple peaks), 1.20–1.30 (180 H, multiple peaks), 1.56–1.67 (12 H, multiple peaks), 2.96 (18 H, single peak), 5.18 (4 H, single peak), 7.14 (4 H, single peak), 8.05 (2 H, single peak), 8.13 (2 H, single peak), 62.89–66.04 (12 H, wide peak). Elemental analysis (%) for $\text{C}_{136}\text{H}_{266}\text{N}_{15}\text{O}_{26}\text{-MnMo}_6$ (3158.2 g mol^{-1}): calculated: C 51.72, H 8.49, N 6.65; found: C 51.35, H 8.26, N 6.70. IR spectra (KBr, cm^{-1}): $\nu = 3323, 3347, 3085, 3032, 2920, 2850, 1697, 1631, 1568, 1468, 1417, 1377, 1355, 1323, 1309, 1298, 1271, 1244, 1149, 1110, 1036, 941, 912, 822, 802$, and 669 cm^{-1} .

1.3 Preparation of sol-gel

$\text{DODA}_3[\text{A-MnMo}_6\text{-A}]$ (20 mg) was added to DMSO (436 μL) and the mixture solution was heated until dissolved completely, obtaining the sol solution with mass fraction of 4%. After cooling to the room temperature ($25\text{ }^\circ\text{C}$), we can observe transformation of solution to gel by inverting the vial (Figure 2). According to the inverted test tube method, by gradually heating or cooling, we can determine the temperature of sol-gel transformation. For preparation of xerogel, the gel was added to an insoluble solvent ethyl ether with shaking, and then spread on copper grids with carbon support film, where the excess solvent was sucked with filter paper. Then, the samples were placed in liquid nitrogen to quickly freeze the surface structure, and then dried to exclude the excess solvent under the low-temperature vacuum condition.

2 Results and discussion

2.1 Formation and structure of gel

For organic supramolecular gels, the gelators stabilize solvents through forming network self-assembly driven by intermolecular forces. Under normal conditions, the self-

Figure 1 Schematic chemical drawing of $[\text{A-MnMo}_6\text{-A}]$ for the substitution of TBA salt with DODA.

Figure 2 Photograph of sol-gel transformation of $\text{DODA}_3[\text{A-MnMo}_6\text{-A}]$ in the process of cooling or heating.

assembled structure is deeply influenced by the solvent environment, due to the change of intermolecular interactions. Besides the method increasing the concentration of gelator to promote the gel formation in a narrow range (10%), the polarity of solvent and preparation condition are also important factors. For the present designed POM complexes, we cannot obtain a supramolecular gel in any soluble solvents by using $\text{TBA}_3[\text{A-MnMo}_6\text{-A}]$ as the gelator, though the intermolecular hydrogen bonds of adenine grafted on the complex can enhance the interaction between molecules. Considering that it is difficult to enhance the intermolecular interactions with TBA as counterions, due to the unfavorable molecular structure, we took the replacement of TBA with DODA. Due to the ordered packing structure of long alkyl chains and stronger interchain interactions of DODA, it can provide stronger driving forces to support the gel formation of the POM complex. Under low polarity solvents condition, DODA-substituted complex is difficult to form gel because of the weaker intermolecular interaction. Increasing the polarity of solvents, such as DMF and DMSO, the gel formation becomes easy due to the increased DODA intermolecular interaction. By continuous increasing gelator content, we can obtain the lowest concentration of gel formation at 4%. Further, the transformation temperature of sol-gel is determined to be about 35°C . When the temperature increases up to 45°C , the gel transforms into sol completely. Importantly, the sol can transform back to gel by decreasing the temperature, exhibiting a thermally reversible sol-gel transformation cycle, which is different from most of the reported POM gel systems. To determine the gel structure, we take the gel system in DMSO as an example and prepare xerogel for morphologic characterization. From the SEM image (Figure 3), we can observe the fibrous structure in the gel state with the diameter of fibrous bind at about 100–200 nm. The fibers form network structure due to their vertical and horizontal twisting, resulting in the stabilization for solvents. According to the molecular composition and the possible intermolecular interaction, we can judge the complex forming the steady linear self-assembly structure.

To identify the above assignment, we carried out TEM measurement of xerogel. From the defined TEM image (Figure 4), we observe the gel fibrous binds with diameter of about 200 nm, which is in accordance with the results of SEM. Interestingly, longitudinal ordered arrangement layer

Figure 3 SEM image of $\text{DODA}_3[\text{A-MnMo}_6\text{-A}]$ xerogel.

Figure 4 TEM image of gel fiber of $\text{DODA}_3[\text{A-MnMo}_6\text{-A}]$.

structure is found in the fibrous bind. By averaging several values of the interlayer distances, we obtained the layer thickness of 3.1 nm. For further understanding the results of TEM and giving the possible internal structure and molecular packing in gel fibers, we took X-ray diffraction measurement to evaluate the gel fiber. Experimental results in Figure 5 give two types of diffraction groups and different interlayer distances, which should correspond to two types of layered packing structures. The first diffraction peak groups give a layer distance of 3.2 nm, which is identical to the layer distance obtained from TEM results. From the literature, we know that the ideal length of DODA cations

Figure 5 The X-ray diffraction spectrum of $\text{DODA}_3[\text{A-MnMo}_6\text{-A}]$ xerogel.

alkyl chains is ca. 2.25 nm in trans tight packing conformation, while the short axis of POM is 0.90 nm derives from the single crystal structure of $\text{TBA}_3[\text{A-MnMo}_6\text{-A}]$. The sum of DODA length and POM diameter is just 3.15 nm, similar to the layer distance of 3.1 nm estimated from TEM and X-ray diffraction results. Based on the chemical composition of $\text{DODA}_3[\text{A-MnMo}_6\text{-A}]$ and the principle of minimum surface energy, the DODA surrounding $[\text{A-MnMo}_6\text{-A}]$ should locate at the out-surface of the layers. The favorable surface energy for DODA packing counterions makes them disperse on both sides of the layers, while POM polyanions locate in the middle part. In this case, the ideal layer thickness should be equal to the sum of POM and double length of DODA, but the value is much larger than the interlayer distance obtaining from the experimental data. From the IR results, we can find that the absorption bands of anti-symmetric and symmetric vibration of CH_2 units appear at 2920 and 2850 cm^{-1} , indicating most alkyl chains in ordered state. Due to the existence of enough space in the short axis of POM, and considering the molecular packing and surface energy, the interdigitation of alkyl chains on the lateral side of POM packing lines should be possible packing style. The entirely interdigitated self-assembled structure just gives an ideal interlayer distance of 3.15 nm, which corresponds to the results of TEM and X-ray diffraction measurement. Considering that the length of $[\text{A-MnMo}_6\text{-A}]$ along its long axis (symmetric adenine direction) is 2.30 nm and the distance of two adenine units is 0.35 nm regarding the formation of hydrogen bonding, according to its single crystal structure, the sum of the above is ca. 2.65 nm, in agreement with the value (2.60 nm) given by the second diffraction peak groups. Though the value of interlayer distance given by the second diffraction peak groups is similar to the length of DODA cations, it is impossible that there is a periodic array of isolated DODA in the POM complex self-assemblies. As the DODA is the counterions of polyanions, it must form periodic ordered structure with POM anions.

2.2 Self-assembly structure and driving forces of gel formation

According to the morphologic characterization and structure analysis of the complex gels, we can propose the relation between gel formation and chemical composite. For the present supramolecular gel, in addition to the solvent environment, the interaction force and its style between the gelator molecules must be favorable for the formation of fibrous assembly or network structure. Following above results, here we take the $\text{TBA}_3[\text{A-MnMo}_6\text{-A}]$, the precursor of $\text{DODA}_3[\text{A-MnMo}_6\text{-A}]$, as the model molecule to make an analysis for the intermolecular interactions. From the crystal structure shown in Figure 6, we find clearly that the organic-modified adenine unit can form particular hydrogen bonds each other. The circular double hydrogen bonds

Figure 6 Hydrogen bonding in skeleton and supramolecular chain structure of $\text{TBA}_3[\text{A-MnMo}_6\text{-A}]$.

enhance the interaction between the complexes, giving a one-dimensional ordered self-assembled structure.

For the identification of the hydrogen bonding in the gel system, further characterization is carried out to the gel of $\text{DODA}_3[\text{A-MnMo}_6\text{-A}]$. As mentioned in the published results [14], because of the dependent feature of non-covalent interactions on temperature, we investigate the variation of hydrogen bonding and electrostatic interaction in the formation of gel and the process of gel-sol reversible response. From the variable temperature NMR spectra of $\text{DODA}_3[\text{A-MnMo}_6\text{-A}]$ in the $\text{DMSO-}d_6$ dilute solution (Figure 7), it is found that no chemical shifts occur on non-hydrogen bonding involved protons (H_a and H_b) and very little chemical shifts emerge for weak hydrogen bonding proton (H_d). In contrast to this, obvious chemical shifts to high field for strong hydrogen bonded amino protons (H_c) with the increase of the temperature up to sol state. Interestingly, upon

Figure 7 Variable temperature ^1H NMR spectra of $\text{DODA}_3[\text{A-MnMo}_6\text{-A}]$ in $\text{DMSO-}d_6$ solution with the concentration of 5 mg mL^{-1} , where the heating and cooling rates are 5 $^{\circ}\text{C min}^{-1}$, with measurement interval of 5 $^{\circ}\text{C}$.

decreasing the temperature to the gel state, the chemical shifts for those hydrogen bonded protons move to the opposite direction and reach back to the original state at room temperature. This phenomenon is consistent with the sol-gel transformation, and can be attributed to hydrogen bonding weakening induced electron shielding effect on the H-amino protons of the adenine on the both side of POM cluster. More interestingly, we observed obvious changes of the peak attributed to three $-\text{CH}_2-$ groups connected to POM [15] and organic functional components at high chemical shift with the change of temperature for the first time. Because these protons are far from the hydrogen bonding interaction site and the yielded chemical shift is very large (ca. 10 ppm), the change should be attributed to electrostatic interaction weakening induced electron shield effect and deshield effect on the POM cluster during the temperature change, considering this unit connected to the POM directly. The above results of temperature-dependent chemical shifts not only indicate the strong hydrogen bonding and electrostatic interaction, but also prove the influence of temperature to the two types of interactions. When the intermolecular interactions become weak, the network structure becomes loose and decreases the ability for stabilizing the solvents, resulting in the transformation from gel to sol. The NMR results also identify that the reversible transformation of sol-gel can be attributed to the reversible change of hydrogen bonding and electrostatic interactions.

Based on the above characterizations and analysis, we propose the following self-assembly structure changes and the possible mechanism for the sol-gel reversible transformation of $\text{DODA}_3[\text{A-MnMo}_6\text{-A}]$. As shown in Figure 8, in the polarity solvent, $\text{DODA}_3[\text{A-MnMo}_6\text{-A}]$ forms chain-like self-assembly structure under the driven by hydrogen bonding and hydrophobic interactions, which is different from that of $\text{TBA}_3[\text{A-MnMo}_6\text{-A}]$, only hydrogen bonding performs in the solution. In this type of packing arrangement, both layer structured arrangement of alkyl chains vertical to the supramolecular chains due to the van der Waals interaction, and duplicate packing of $[\text{A-MnMo}_6\text{-A}]$ along hydrogen bonding direction contribute to the fibrous gel structure. Considering under the charge balance condition, DODA cannot cover the surface of $[\text{A-MnMo}_6\text{-A}]$ completely, which will result in an unmatched organic-inorganic pack-

ing which is unfavorable for the efficient packing density. Thus, the alkyl chain adopts an interdigitated packing style and becomes the steady assembly structure. In addition, the extension and transverse interaction of one-dimensional chain-like structure promote the formation of fibrous structure. Under heating condition, both the disorder of alkyl chains and dissociation of hydrogen bonding can make the gel structure disassociated. The decrease of the temperature leads to an opposite process, that is, the gel forms again. To identify the above mechanism and the assembled gel structure, we measured the surface energies of the two type complexes. For $\text{TBA}_3[\text{A-MnMo}_6\text{-A}]$, the static contact angle is only 10° due to the short and disordered TBAs on the surface of POM. For close packing $\text{DODA}_3[\text{A-MnMo}_6\text{-A}]$ gel assembly, the contact angle increases up to 96° , which is similar with the value of DODA. This result indicated that the POM has been encapsulated by DODA completely and is also coincident with the tight one-dimensional arrangement of alkyl chains lying on both sides of POM chain.

3 Conclusions

We have successfully incorporated adenine groups into the POM on both sides covalently and the designed $[\text{A-MnMo}_6\text{-A}]$ gelator based on the modifiable character of Anderson-type POM (MnMo_6). When we took DODAs as the counterions, the additional hydrophobic interaction makes the $[\text{A-MnMo}_6\text{-A}]$ gelator form a thermally responsive reversible supramolecular gel by itself. Intermolecular hydrogen bonds between adenine groups along $[\text{A-MnMo}_6\text{-A}]$ maintain the stability of the supramolecular chains. The van der Waals force between the lateral alkyl chains under the assistance of electrostatic interactions further supports the ordered supramolecular chains to form a fibrous structure, while under the same condition, $\text{TBA}_3[\text{A-MnMo}_6\text{-A}]$ molecules cannot form a gel. The present research confirms that the hydrogen bonding between $[\text{A-MnMo}_6\text{-A}]$ POMs, the interaction between alkyl chains, and the interfacial energy all contribute to the gel formation and reversible change to the dissociated state. The present results also validate the understanding of the formation mechanism of gel related to the modified POM system in our previous work [12].

Figure 8 Schematic drawing of the mechanism of sol-gel transformation of the supramolecular complex.

Compared with the previous work, the gel reported in this paper is more convenient, the response is much faster, and sol-gel transformation temperature is lower and more sensitive. In addition, the observed properties provide a valuable implication for controllable catalysis of POMs by use of supramolecular gel characterizations.

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