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COMMUNICATION

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

Weiming Guan, Gengxin Wang, Jingbo Ding, Bao Li and Lixin Wu*

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An anthracene modified Anderson-Evans polyoxometalate was polymerized *via* supramolecular inclusion and then covalent coupling with the support of γ-cyclodextrin (γ-CD) under the UV light irradiation. The formed mainchain polymers of the inorganic polyanion self-assembled into fibrous bundles and single-strand chain was visualized and characterized *via* TEM and other techniques.

Polyoxometalates (POMs) are a class of inorganic nano-clusters that have abundant topological structures and tuneable negative charges.[1] The rich nanostructures yielding from self-assembly greatly promote POMs' potentials in the fields of catalysis, separation and biomedical materials, and so forth.[2–4] Some POMs, especially Anderson-Evans type clusters, show important features to be grafted with organic groups,[5–7] which extend their functional properties on photo stimulus-response,[8] chiral migration[9] and amplification behaviours.[10] Typically, the polymerization of POMs with the assistance of modified groups allows them to display outstanding synergistic performance beyond the clusters themselves. Since the first grafting POM into polymer chain,[11] cross-linked polymers,[12–14] sidechain polymers[15–17] and mainchain polymers regarding POMs have been realized.[18] Light-triggering polymerization of coumarin modified POMs was reported,[19] and the controllable mainchain growth of POM oligomers was achieved *via* a CuAAC click reaction laterly.[20] The published strategy, however, mainly focuses on direct polymerization of modified POMs like normal polymers and the direct observation of polymers with POMs in main chain has not yet been involved.

The supramolecular polymer that is known as the polymeric array of molecular units *via* a highly preferable noncovalent interaction along the direction of chain growth,[21, 22] has been demonstrated to be a smart combination of self-assembly and supramolecular chemistry over recent years. Well-designed supramolecular polymers can be converted to typical polymers with high efficiency,[23–25] because the polymerizable groups assemble to a favourable position for the following polymerization reactions. For instance, coumarin derivatives pre-included in γ-CD[23] and styrene pyridine derivatives inserting in cucurbit[8]uril have been reported to accelerate their polymerizations.[26] With this route, the photocycloaddition can be more efficient in comparison to those without pre-position controlling.

In this context, our motivation is to combine the organically modified POM monomer with the strategy used in supramolecular assembly and realize a controlled polymerization of modified inorganic clusters. Through grafting an anthracene unit that integrates both roles of guest group and polymerizable moiety onto an Anderson-Evans polyanionic cluster, we build a hybrid cluster monomer. Under the collection of a supramolecular host, the hybrid monomer gets together, forming a supramolecular polymer. After the light triggered coupling reaction, we succeed in achieving covalent polymerization of inorganic nanocluster. Because of the self-assembly induced position locking and staining effect of POMs, shish kebab like single strand polymer chain was observed in POM system.

The Mn-centred Anderson-Evans POM modified with anthracene group on both-sides (abbr. as An-$MnMo_6$) was synthesized following a similar route in previous publications.[7] Al-centred Anderson-Evans POM grafting anthracene group on a single-side (abbr. as An-$AlMo_6$) was also synthesized to simplify the characterization of An-$MnMo_6$ and serve as a reference for coupling model. The preparation procedures and structure characterization data of all samples are summarized in Electronic Supplementary Information (Fig. S1–S9, Table S1–S2, ESI†). Because γ-CD includes two anthracene molecules in one cavity,[26] it is used as a connector for the formation of supramolecular polymer and later photo-polymerization. Following the design (Scheme 1), An-$MnMo_6$ is initially mixed with γ-CD (1.0 mM) at a molar ratio of 1:1. When An-$AlMo_6$ is

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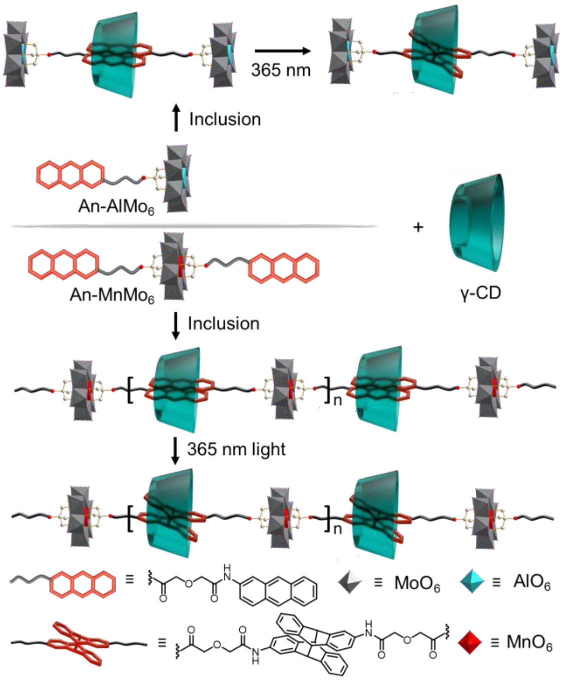
† Electronic Supplementary Information (ESI) available: Synthesis procedures, additional spectra and experimental details. See DOI: 10.1039/x0xx00000x



Scheme 1. Schematic illustration for host-guest interaction induced inclusion of γ-CD with POM and photo-coupling triggered polymerizations.

used, its molar ratio to γ-CD (1.0 mM) is set at 2:1 at the same concentration. After gently shaking samples and culturing, the formed solutions are then characterized. In the case of photo-polymerization, the samples undergo a 365-nm light irradiation.

By taking An-AlMo$_6$ cluster grafting one anthracene group as an example, the host-guest inclusion is firstly evaluated by ^{1}H NMR in D_2O. The proton chemical shifts of anthracene group and connecting groups are shifted upfield in the presence of γ-CD while the chemical shifts from γ-CD also move upfield in comparison to the isolated hybrid guest and CD host (Fig. 1A). This result indicates strong inclusion interaction between anthracene and CD, as described in literature.[27] In addition, the ^{1}H-^{1}H nuclear Overhauser effect spectra (NOESY) (Fig. S10, ESI†) show the proton correlations between anthracene and CD as well as between remote positions that can be attributed to different anthracene groups, demonstrating the inclusion and packing interaction of anthracene. Isothermal titration calorimetry (ITC) is used to calculate the detailed binding ratio. Because the solubility of An-AlMo$_6$ is not as high as γ-CD in water and the yielded aggregation under higher concentration may influence the calorimetry, γ-CD solution is filled in syringe (4.00 mM) while An-AlMo$_6$ at lower concentration (0.23 mM) is added in cell. As the ITC curve (Fig. 1B) fits OneSite model, the binding constant and dynamic parameters become not applicable. Yet, the obtained binding ratio (N value) of 0.51 points out that An-AlMo$_6$ is included in γ-CD at a molar ratio of 2:1, in perfect line with ideal inclusion state and supporting the analysis for the correlation of anthracene unit.

When the An-MnMo$_6$ bearing two anthracene groups was used to combine with γ-CD, the NMR spectrum also points out strong host-guest inclusion (Fig. S11, ESI†). Most of proton peaks sourcing from organic moiety shift upfield while the chemical shifts from CD move upfield and become broadened, indicating the same host-guest interaction as that of An-AlMo$_6$. ITC experiment of An-MnMo$_6$ (Fig. S12, ESI†) versus the addition of γ-CD displays N value of 1.09, indicating the binding ratio of 1:1. This result is in agreement with that one γ-CD accommodates two anthracene groups. Considering that the two grafting anthracene groups in An-MnMo$_6$ locate at opposite sides, it is impossible for them to insert into the same γ-CD and thus, the supramolecular polymer can be concluded to form in water successfully through a host-guest inclusion (Scheme 1).

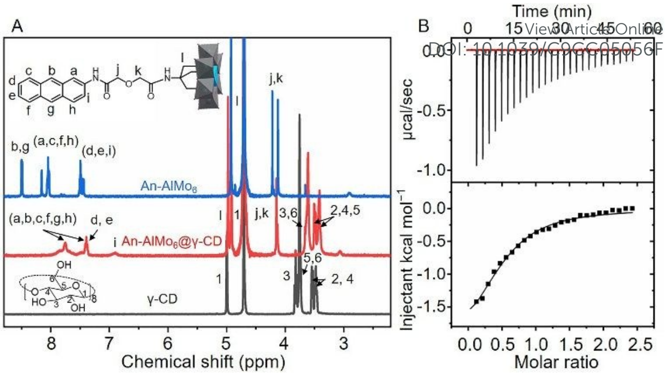


Fig. 1. (A) ^{1}H NMR spectra of An-AlMo$_6$ before and after inclusion with γ-CD in D_2O, and (B) ITC behaviour and fitting curve of γ-CD (4.00 mM) titrating An-AlMo$_6$ (0.23 mM) in water.

Transmission electronic microscope (TEM) is used to detect the formation of supramolecular polymer bearing inorganic clusters. The fibrous assembly bundles are clearly observed in lengths from hundreds of nanometres to several micrometres and in widths about dozens of nanometres (Fig. 2A). Interestingly, by enlarging the image of the fibrous assembly, stripe structure with high resolution in bundles is seen (Fig. 2B). Based on the mainchain growing process of the supramolecular polymer, the dark lines can be ascribed to the supramolecular polymer chains because of staining effect from POM clusters. From the amplified image focusing on a thin fibre (Fig. S13, ESI†), cluster chains with a certain interval are observed to pack in parallel with each other, supporting the supramolecular polymer in the fibrous self-assembly. As a common behaviour for the self-assembly of cyclodextrin-based polyrotaxane,[28] we believe the hydrogen bonds among neighbouring γ-CDs holding the formed supramolecular polymers together. The average distance between supramolecular chains is estimated to vary from ca. 1.7 nm to ca. 2.6 nm. Considering the diameter of POM (0.9 nm) and γ-CD (1.7 nm) as well as the possible malposition between POM and CD, such a distance is rational for secondary assembly of supramolecular polymers (Fig. S14, ESI†).[29] Because the alternately arranged structure of POMs and γ-CD blocks the entanglement, the observed fibres here are in rigid straight line and show difference from traditional γ-CD catalysed organic polymers with obvious flexibility.[24]

Following the formation of supramolecular polymer, the post polymerization is then conducted. The [4+4] cyclodimerization of two anthracene groups included in one γ-CD is performed under UV light irradiation.[26] After encountering a 365-nm light radiation to the model supramolecular complex An-AlMo$_6$@γ-

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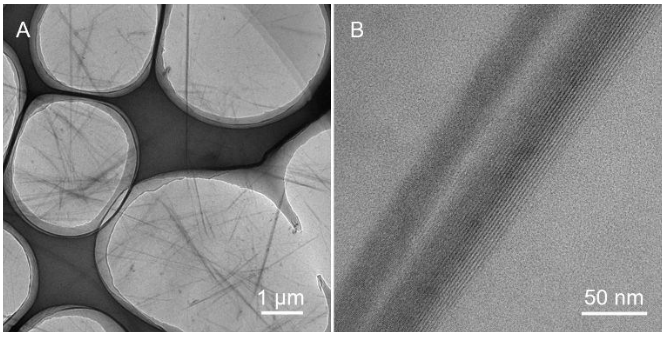

Fig. 2. TEM images of (A) An-MnMo$_6$ supramolecular polymer assembly and (B) local amplification.

CD in aqueous solution, the absorbance at nearby 256 nm and 355 nm belonging to anthracene decreases rapidly and reaches to an equilibrium state within 30 min, indicating the occurrence of photo-coupling reaction (Fig. 3A, Fig. S15, ESI†). The yield of conversion calculated from the absorbance decrease at 355 nm is estimated to be ca. 88.1% (Fig. S16, ESI†). In the ^{1}H NMR spectra (Fig. 3B), the proton peaks belonging to anthracene at 7.0–8.0 ppm decrease apparently while new peaks appear at 6.5–7.0 ppm, confirming that the photo-cycloaddition on two anthracene groups occurs. Meanwhile, the changed proton peaks attributing to γ-CD also indicate the improved host-guest interaction. As a comparison, we evaluate the UV-Vis spectra of An-AlMo$_6$ without addition of γ-CD in water (Fig. 3A, Fig. S17, ESI†). During the irradiation with 365 nm light, the coupling reaction goes very slow and the reaction progress in 90 min is just about the state after 1 min of light radiation in the presence of γ-CD. Obviously, γ-CD inclusion accelerates the reaction and provides an efficient way to build covalently linked POMs.

When An-MnMo$_6$@γ-CD is conducted the same photo-cycloaddition reaction, the transformation from POM supramolecular polymer to covalent polymer takes place. The absorption bands at nearby 256 nm and 355 nm (Fig. 3C, Fig. S18, ESI†) decrease versus the 365 nm UV irradiation, which is similar to An-AlMo$_6$ except that the exposure time reaching to equilibrium is extended to about 90 min. The yield of conversion is calculated to be 85.7% (Fig. S19, ESI†). The NMR spectra (Fig. 3D) show largely moving and broadening of proton peaks ascribing to anthracene and γ-CD, indicative of the photo-polymerization. The photo coupling process of An-MnMo$_6$ is compared in the absence of γ-CD (Fig.3C, Fig. S20, ESI†). The reaction after 90 min of irradiation is just like the state undergoing 20–30 min of irradiation in the presence of γ-CD. From the chemical shifting of proton peaks ascribing to γ-CD, it can be concluded that the CD host maintains in the formed polymer chain. In the case of close inclusion, the cyclodextrins bearing intrinsic chirality have the capability to induce supramolecular chirality of guest molecules.[30] Therefore, we use the induced circular chroism (ICD) to evaluate the formed polymer. The model An-AlMo$_6$ included within γ-CD shows obvious ICD signal from anthracene group at inclusion state (Fig. 3E). After 20 min of 365 nm light irradiation, the ICD signals change versus the cyclodimerization reaction, confirming that γ-CD still locates at the binding site and is locked by POM cluster after the dimerization reaction. Identically, the ICD is also observed during the polymerization of An-MnMo$_6$ (Fig. 3F), demonstrating that γ-CD remains in the polymer mainchain and forms a polyrotaxane.

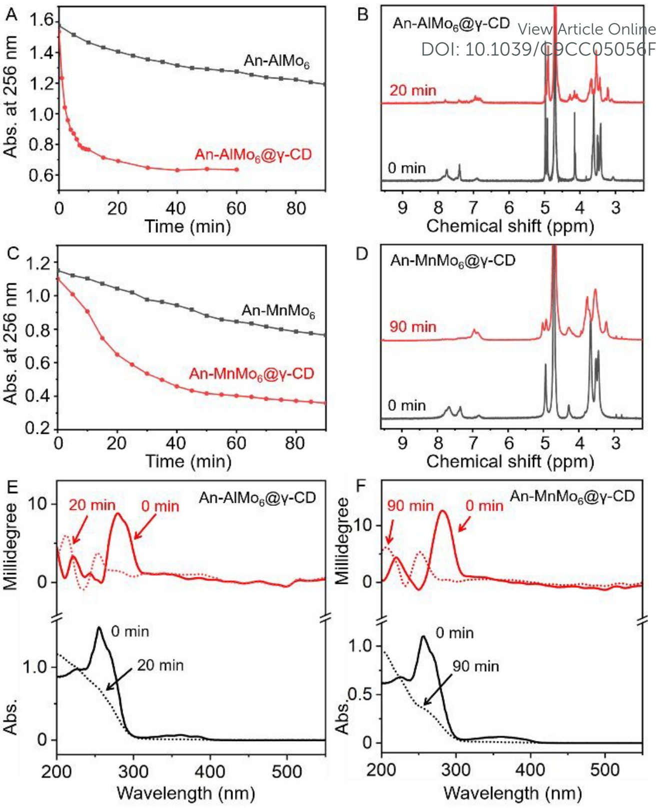

Fig. 3. (A) Absorbance at 256 nm and (B) ^{1}H NMR spectral changes versus 365 nm light irradiation for An-AlMo$_6$, (C) and (D) for An-MnMo$_6$, (E) circular dichroism (0.5 mM) and UV-Vis spectra (0.2 mM) for An-AlMo$_6$, and (F) circular dichroism (0.4 mM) and UV-Vis (0.1 mM) spectra for An-MnMo$_6$.

TEM observation shows clear morphology of the polymerized An-MnMo$_6$ mainchains. The assembly structure with length ranging from several to dozens of micrometres figures out highly regular packing driven by covalent bonding (Fig. 4A). Importantly, individual single-strand fibril can be found splitting from the main fibrous bundles (Fig. 4B), indicating that the assemblies are sourced from the packing of isolated polymer chains. By enlarging a single-strand (Fig. 4C), we succeed in observing shish kebab structure of MnMo$_6$ clusters as the dark dots. The average distance between dark dots is about 3.8 nm, consistent with the calculated value (about 3.6 nm) according to the inclusion model and the size of the POM cluster and anthracene group (Fig. S21, ESI†).[31–33] The single polymer chain structure is further identified by AFM on mica (Fig. S22, ESI†). In consistent with the observation from TEM, the single chain fibril is seen at a height of ca. 1.8 nm, in perfect agreement with the periphery diameter of γ-CD (1.7 nm). Based on the observed length of a single-strand polymer in ca. 630 nm in TEM image (Fig. S23, ESI†), the polymerization degree is estimated to reach about at least 175. Static light scattering (SLS) is used to measure the weight- average molecular weight (Mw). For the case of 90 min irradiation, the calculated Mw is 1.37×10^5 g/mol

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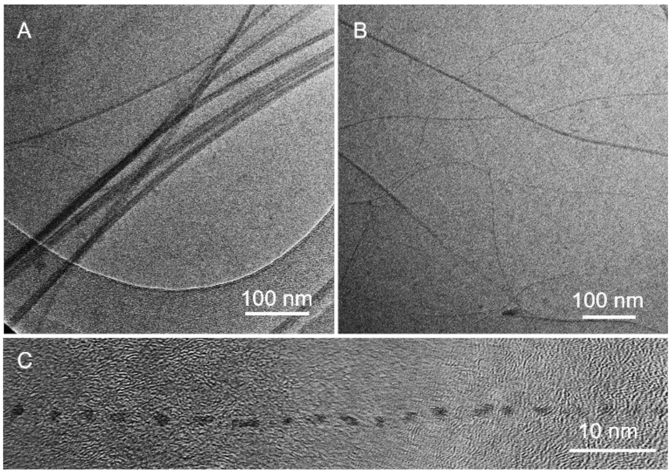

Fig. 4. TEM images of An-$MnMo_6$ covalent polymer in (A) fibrous bundles, (B) isolated single chain and (C) local amplification.

(Fig. S24, ESI†). In the case of further irradiation for 5 h, the Mw value reaches up to 3.240×10^5 g/mol. In contrast to this, when the An-$MnMo_6$ encounters the same photo coupling in the absence of γ-CD, the TEM image (Fig. S25, ESI†) only presents spherical assembly structure. This result implies that the photo coupling reaction without the presence of γ-CD leads to the more flexible polymers and the exposed organic moiety with hydrophobicity makes the polymer less water-soluble, resulting in irregular globular aggregates.

In summary, we demonstrate a supramolecular strategy to polymerize an Anderson-Evans POM cluster *via* a host-guest inclusion and then photo- cyclodimerization procedures. The inclusion and coupling reaction not only trigger the formation of supramolecular and covalent polymers, but also build a shish kebab like mainchain with a polyrotaxane structure in which inorganic cluster and cyclodextrin are threaded together alternately. Owing to the chain rigidity, we firstly observed the morphology of the single-strand and the induced chirality in the hybrid polymer is confirmed. It is sure that such a supramolecular method is extendable for controlled polymerization of POM-contained functional materials and development of two-dimensional structures *via* crosslinking.

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Conflicts of interest

There are no conflicts to declare.

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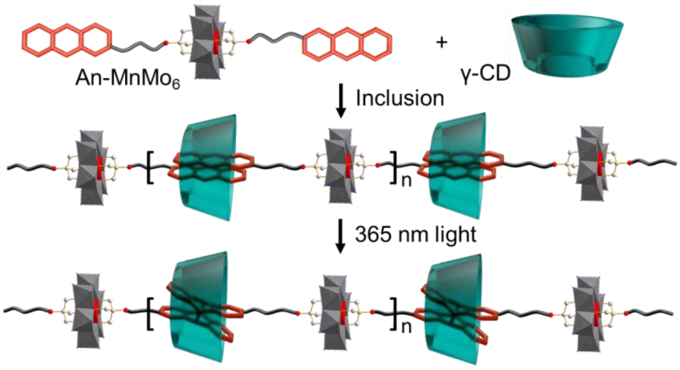

Photo-polymerization based on pre-assembly of anthracene-grafted polyoxometalate through host-guest inclusion of cyclodextrin is realized and single polymer chain is visualized.