Angewandte Chemie International Edition

DOI: 10.1002/anie.201004143

Polyoxometalates

Smart Self-Assemblies Based on a Surfactant-Encapsulated Photoresponsive Polyoxometalate Complex**

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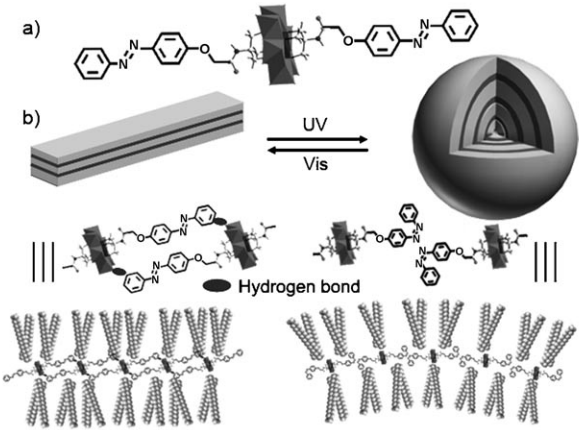
Smart self-assemblies based on photostimulus response have received much attention recently because of their powerful ability to modulate self-assembled structures, morphologies, and functions through remote control of functional groups.[1,2] However, many dynamic supramolecular assemblies based on noncovalent interactions were organic and polymer systems,[3] while systems incorporating inorganic nanoparticles are rarely reported,[4] although such a combination can integrate multiple functional components for synergistic properties.[5] Polyoxometalates (POMs), as a kind of nanosized inorganic cluster, possess versatile potential applications.[6] Most POMs perform the organization feature by virtue of organic components through replacing their counterions with cationic surfactants.[7–9] Self-assemblies for all organically modified POMs with different morphologies have proved to be feasible,[8b] but up to now none of them can carry out a dynamic transition. Therefore, the fabrication of novel aggregate structures and smart POM assemblies will be of topical interest.[9]

To carry out photocontrolled supramolecular assembly in POM-based systems, we combined both organic grafting[10] of photoisomerizable groups and electrostatic encapsulation[7c] onto one POM unit to realize the present proposition. The prepared complex building block can form self-assemblies in solution, and smart morphological changes between fibrous and spherical aggregates are successfully achieved for the first time through tuning the multiple supramolecular interactions by photoirradiation. As expected, the present photoresponsive hybrid system should possess: visible functional potentials in reversible magnetism adjustment of inorganic clusters through photoisomerization;[11] optical property controlling of inorganic clusters through aggregate structure and morphology change; and aggregate morphology-directed transition of the hydrophobic/hydrophilic property.

By grafting the azobenzene (Azo) group[12] covalently onto the Mn-Anderson-type cluster through a tris(hydroxymethyl)aminomethane connector (Figure S1 in the Supporting Information),[10] we prepared a novel photoresponsive surfactant-encapsulated organically grafted polyoxometalate (SEOP), as shown in Scheme 1 a. ^{1}H NMR spectroscopy, mass spectrometry, IR spectroscopy (Figures S2–S4 in the Supporting Information), and full elemental analysis (Table S1 in the Supporting Information) supported the successful synthesis of SEOP-1. To compare the role of the counterion, tetrabutylammonium (TBA) groups with four short alkyl chains in SEOP-1 were replaced by dimethyldioctadecylammonium (DODA) moieties, to yield a new complex named SEOP-2. As DODA with double long alkyl chains would behave in a more well-defined manner than TBA, such replacement can make the POM complexes pack more compactly, thus leading to more favorable self-assembled structures.



Scheme 1. a) Structure of anionic SEOP. b) Reversible morphology change of SEOP-2 between fibrous and spherical structures upon stimulation by light.

According to the ^{1}H NMR spectra (Figure 1 a), at the initial state more than 95 % of Azo groups (calculated from integration of peak area) were in the *trans* form, while after UV (365 nm) irradiation almost all (> 98 %) of the Azo groups were transformed into the *cis* state. UV/Vis spectral study confirmed the photoisomerization of the as-prepared complexes. As shown in Figure 1 b, the strong absorption at

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[**] This work was supported by the National Basic Research Program (2007CB808003), NSFC (20973082, 20703019, 20921003, 20731160002), and Open Project of the State Key Laboratory of Polymer Physics and Chemistry, CAS. We thank the 111 Project for the visit and helpful discussion with Prof. U. Kortz at Jacobs University.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201004143.

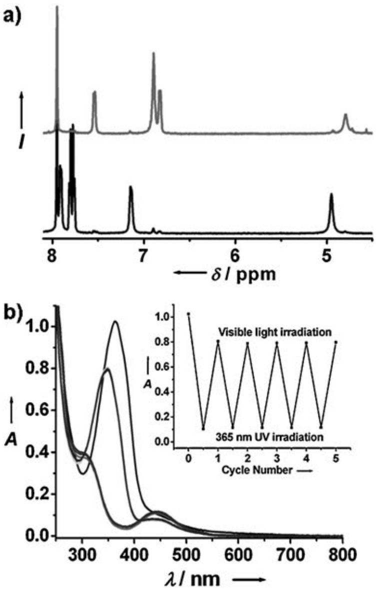

Figure 1. a) ^{1}H NMR spectra of SEOP-1 in [D$_6$]DMSO before (bottom) and after (top) 365 nm UV irradiation. b) UV/Vis spectra of SEOP-2 in CHCl$_3$/CH$_3$OH (4:1 v/v) encountering five cycles of alternate UV and visible light irradiation. Inset: plot of absorbance at 350 nm upon five cycles of alternating irradiation with UV and visible light.

350 nm corresponding to the π→π* transition of the *trans* state decreases upon UV irradiation, while the band at approximately 450 nm (n→π* transition) increases slightly. The photostationary state can be attained within 30 min of irradiation. The reversibility of the *trans–cis* isomerization of Azo groups in SEOPs was evaluated through alternate irradiation with 365 nm and visible light. Except for the initial state, the spectra display almost complete isomerization reversibility with considerable stability, even after five cycles of alternate irradiations. The highly reversible transformation efficiency implies less packing interaction between Azo groups, which is favorable for carrying out such transformation in the aggregate state.

As expected, SEOP-1 cannot form regular self-assemblies in solution because of the short and irregular shape of TBA. Only a smooth thin film was obtained upon evaporation of the solvent to dryness. In contrast, SEOP-2 can form regular self-assemblies, just as those aggregates found in the DODA-encapsulated POMs,[8a] probably as a result of the fine balance of the amphiphilicity and spatial organization provided by DODA such that the complexes would automatically reorganize themselves into layered structures.

Before irradiation, the initial SEOP-2 in CHCl$_3$/CH$_3$OH (4:1 v/v) presents an orange oil stripping-like solution, while after UV irradiation, the color becomes deeper and the solution becomes clearer than the initial state (Figure S8 in the Supporting Information). When laser light passes through the virgin solution, Tyndall scattering can be observed clearly due to a strong light path, whereas it becomes weaker after UV irradiation. These phenomena confirm that SEOP-2 is in its aggregate state and irradiation can definitely influence the self-assemblies in solution.

Scanning electron microscopy (SEM) was employed to depict the aggregate morphology change. When SEOP-2 was dissolved in the mixed solvent of CHCl$_3$ and CH$_3$OH, a mass of cross-linked fibrous assemblies (Figure 2a) was clearly found in the scale of hundreds of nanometers in length, 20–40 nm in width, and less than 100 nm in height (Figure S9 in the Supporting Information). Interestingly, when UV light was applied, the fibers tended to disentangle and shorten their length (Figure 2b), while the fibrous morphology was still preserved. Further irradiation made the short fibers aggregate and twist into clewlike structures, then to rough spheres, in which some intermediate states with rough surfaces could be observed (Figure 2c and d). With prolonged irradiation, continued assembly occurred (Figure 2e), which finally led to spheres with smooth surfaces (Figure 2f). Transmission electron microscopy (TEM) images support the morphology change of the initial and final SEOP-2 self-assemblies. As shown in Figure S10 in the Supporting Information, one can see the fiberlike aggregates initially, which then change to the final spherical assemblies with size of 150 nm after irradiation with 365 nm light.

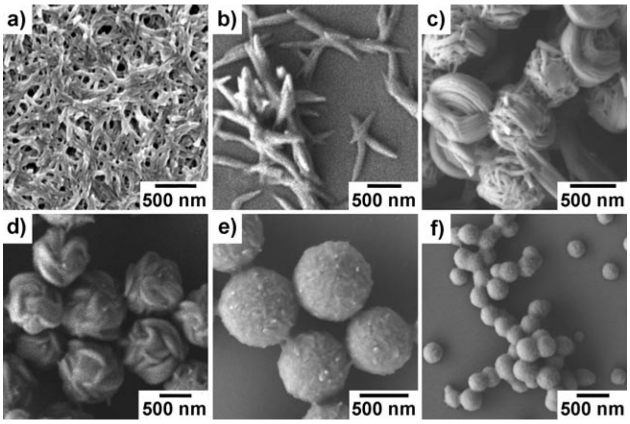

Figure 2. SEM images of SEOP-2 self-assemblies in CHCl$_3$/CH$_3$OH (4:1 v/v) solution after a) 0, b) 1, c) 5, d) 15, e) 30, and f) 120 min of irradiation at 365 nm.

The packing modes of these two different morphologies were further identified by X-ray diffraction (XRD; Figure 3a). According to the Bragg equation, it is evident that: 1) both the initial and final packing states of SEOP-2 are in a layered structure; and 2) the layer spacing for the final state after UV irradiation is 3.27 nm, slightly larger than the value

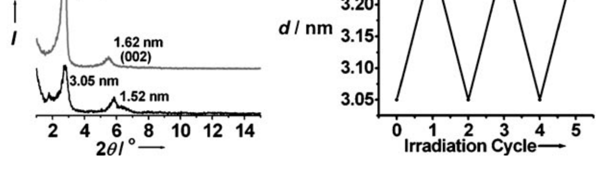

Figure 3. a) XRD patterns of SEOP-2 assemblies in the *trans* (bottom) and *cis* state (top). b) Plot of *d* spacing versus three cycles of UV and visible irradiation.

(3.05 nm) of the initial state. The XRD results can be confirmed distinctly by the onionlike and layered structures found in high-resolution TEM (HRTEM) images (Figure 4 a and b). Considering the photosensitive groups contained in SEOPs and spectral changes, the photoinduced structural transition of the self-assemblies must be derived from the *trans*-to-*cis* isomerization of Azo.[1]

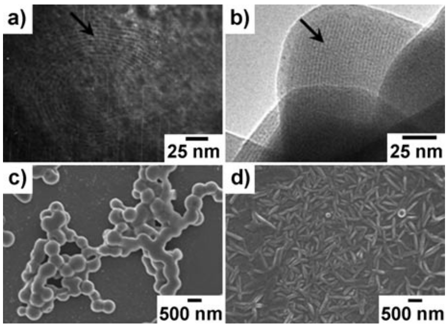

Figure 4. HRTEM images of a) spherical and b) fibrous assemblies. SEM images of SEOP-2 self-assemblies in different states after c) 30 min of UV irradiation; d) 30 min of visible-light irradiation following (c).

Meanwhile, the CH_2 antisymmetric and symmetric stretching of SEOP-2 aggregates before and after UV irradiation appear at 2918 and 2850 cm^{-1}, respectively, in the IR spectra (Figure S13 in the Supporting Information), thus indicating that the alkyl chains on SEOP-2 are in an ordered state and show no sign of change after UV irradiation. Combining the lateral diameter of POM (0.9 nm) and the length of DODA (2.46 nm),[13] the ideal sandwich-type packing structure of SEOP-2 should occupy a bilayer of about 5.82 nm. From the comparison of ideal length with the *d* spacing of 3.05 nm in the *trans* state, an interdigitation of alkyl chains of DODA can be imagined in the assembled structure. On the other hand, the short axis of *trans*-Azo is 0.44 nm,[14a] whereas the value of the *cis* form is 0.55 nm.[14b] Thus, the *trans*-to-*cis* isomerization will lead to a 0.22 nm increase of layer spacing, in good agreement with the *d* spacing change found from XRD results. This estimation also reveals that it is rational for SEOPs lying along their long axes to form a layered structure, similar to those assemblies of other POM complexes.[7d,9a]

From the reversible spectral changes in Figure 1 b, one can also envision the reversible morphology change driven by photoisomerization. We employed SEM to track the morphology change during three cycles of UV and visible irradiation. The initial cross-linked fiberlike assemblies change to spheres after 30 min of UV irradiation (Figure 4 c). In contrast, after visible-light irradiation rodlike assemblies appear accompanied by the disappearance of spherical assemblies, and the fiberlike structure is not found again (Figure 4 d). Following this process, alternate irradiation with UV and visible light led to a morphology change between rod- and spherelike assemblies lasting several cycles without significant changes based on SEM (Figure S14 in the Supporting Information), IR spectroscopy, and UV/Vis spectra. All of these observations prove that the morphology change is reversible and is photocontrolled.

Interestingly, the morphology change of SEOP-2 can be identified to originate from the layer spacing alternation driven by photoisomerization. Through the XRD examination of the assemblies encountering irradiation cycles, as shown in Figure 3 b and Figure S15 in the Supporting Information, we find that the layer spacing changes reversibly between 3.05 nm for the *trans* state and 3.27 nm for the *cis* state.

Besides the photocontrolled reversible morphology change, we also observed an interesting morphology evolution of the final spherical structure. As is known, *cis*-Azo can readily return to the more stable *trans* form in the dark due to thermally induced *cis*–*trans* isomerization.[15] Through deposition of the spherical assemblies (Figure 5 a) in the dark for 20 hours, the spheres were found to be elongated and linked together (Figure 5 b). Willow-leaf-like aggregates were observed after about 48 hours (Figure 5 c). After 96 hours, the willow-leaf-like aggregates were transformed into a beltlike morphology (Figure 5 d). The narrow belt structure grows into a wide and smooth one after 144 hours (Figure 5 e). Although the belt structure keeps its shape, the surface becomes rough and its edge becomes granular after more than 30 days (Figure 5 f). Furthermore, the leaflike aggregate is still in a layered structure with a layer spacing of 3.0 nm (Figure S16 in the Supporting Information). This evolutionary process proves that the self-assembly of SEOP-2 is dynamic in solution and is governed by the existing state of the Azo group.

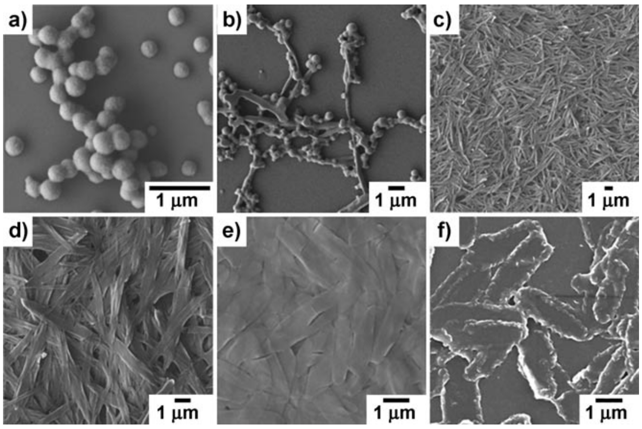

Figure 5. SEM images of the morphological evolution of the spherical self-assembly versus the deposition time in the dark: a) initial state, b) 20 h, c) 48 h, d) 96 h, e) 144 h, and f) 30 days.

To evaluate the concentration dependence of SEOP-2 on the morphology and structure of the self-assemblies, we investigated the possible interaction between Azo groups. From Figure S17 in the Supporting Information it is clear that there is no π–π interaction between Azo groups as no band shift was observed upon increasing the concentration. However, when UV irradiation was applied, the band at 364 nm shifted to 350 nm, which was maintained reversibly at this position. The band shift can be attributed to the existence of some amount of the *cis* form.

In addition to the conformation change of Azo, hydrogen bonds, another possible driving force in the self-assembly, are found between the terminal oxygen atoms of POM and hydrogen atoms of the organic component. X-ray photoelectron spectroscopy (XPS) was used to characterize the existing state of oxygen atoms. As shown in Figure 6, it is apparent that the O1s signals of SEOPs are broad and composed of overlapping peaks emerging at 532.0 and 530.0 eV, which should be contributed from O atoms bearing different chemical environments. Based on previous results,[9a] the peak at 532.0 eV can be attributed to the O atoms linked to Mo atoms, which electrostatically interact with surfactant cations, while the peak at 530.0 eV can be ascribed to the O atoms that are associated with H atoms of organic components through hydrogen bonds. Such kinds of C–H···O hydrogen bonds have also been reported in the literature.[16] Interestingly, the hydrogen bond can be reversibly tuned through alternate photoirradiation. In the *trans* state, the hydrogen bond is strong whereas in the *cis* state, the hydrogen bond is weakened. Therefore, the dynamic supramolecular self-assembly process can be expected as follows (Scheme 1b). In the initial state, SEOP-2 forms fiberlike self-assemblies with a flat bilayer structure resulting from the multiple C–H···O hydrogen bonds between *trans*-Azo groups and POMs; upon UV irradiation, the *trans*-Azo changes to its *cis* state, which results in the destruction of the directional hydrogen bonds, and hence the formation of a spherical structure due to the increased flexibility of the bilayer arrangement.[8a,9a] The steric effect of the *cis* form of Azo would also lead to assemblies with slightly larger layer spacing.

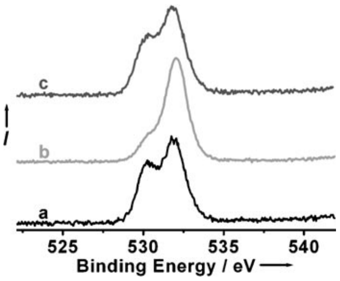

Figure 6. O1s XPS spectra of a) initial SEOP-2 self-assembly cast from $CHCl_3/CH_3OH$ (4:1 v/v) solution; b) initial self-assembly solution with 30 min of UV irradiation and then c) 30 min of visible-light irradiation.

In conclusion, we have designed a new class of nanosized (3.65 nm) hybrids from Anderson-type clusters and photoresponsive ligands. Furthermore, by making use of this building block, we have successfully achieved smart self-assembled architectures that are controlled by reversible destruction and rebuilding of hydrogen bonds through photoirradiation. The novel surfactant-encapsulated Azo-grafted POM complex exhibits a fiberlike morphology in its *trans* state, while upon UV irradiation it displays a spherical structure, thus demonstrating the versatility of this approach in fabricating reversibly responsive POM materials.

Received: July 7, 2010
Revised: September 3, 2010

Keywords: isomerization · photochemistry · polyoxometalates · self-assembly · supramolecular chemistry

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