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Self-assembly of triangular polyoxometalate–organic hybrid macroions in mixed solvents†

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Triangular-shaped inorganic–organic hybrids with three polyoxometalate (POM) clusters as polar head groups are found to self-assemble into blackberry structures in water–acetone solvent mixtures containing 65–95 vol% acetone. The driving force for the self-assembly of the hybrids is shown to originate from the electrostatic counterion–cluster interactions.

Inorganic–organic hybrids, constructed by covalently linking independent inorganic and organic components together, are not only able to integrate the properties of inorganic (redox activity, magnetism, catalysis, *etc.*) and organic (good processibility, compatible with organic media, *etc.*) components into a single molecule, but also exhibit synergistic effects beyond the individual component, making them new promising materials with a range of modular functions.¹ Polyoxometalates (POMs), a large group of giant metal oxide molecular clusters with rich physical and chemical properties and potential applications as electronic and catalytic materials, are commonly used as inorganic components.² Of equal importance are the incorporated organic components, which can be engineered with specific properties.^{2a,3} Various POM-containing hybrids have been synthesized in the past few years *via* different approaches.³ For instance, inorganic–organic hybrids containing single POM component have been synthesized with one⁴ or two organic tails.⁵ These hybrids show typical surfactant properties with POMs acting as polar head groups and the organic portions acting as hydrophobic tails. They can form regular vesicles⁶ or reverse vesicles⁷ depending on the solvent mixture, with the solvophobic interaction being the driving force for the self-assembly process. Meanwhile, a series of “dumb-bell” shaped POM–organic–POM hybrids also display amphiphilic behaviors,

forming single molecule layer vesicular structures due to the two polar head groups and one central organic linker each hybrid possesses.⁸

It is possible to form “triangular” shaped POM hybrids, with three large polar POM head groups and a central relatively hydrophobic organic component.^{3e} It would be interesting to examine how these hybrids behave in solution. They are still expected to be amphiphilic in nature. However, the hydrophilic portions are more dominant than in conventional amphiphilic compounds, making them similar to giant hydrophilic POM macroions.⁹ As we demonstrated earlier, various hydrophilic POM macroions carrying moderate charges tend to self-assemble into single-layered, hollow, spherical blackberry-type structures due to counterion-mediated attractions.¹⁰ In this communication, the self-assembly behaviours of two “triangular” shaped hybrids containing three identical Wells–Dawson polar head groups (Fig. 1(a)) in water–acetone mixed solvents are investigated to observe the solution behavior of these hybrids with such unique architectures.

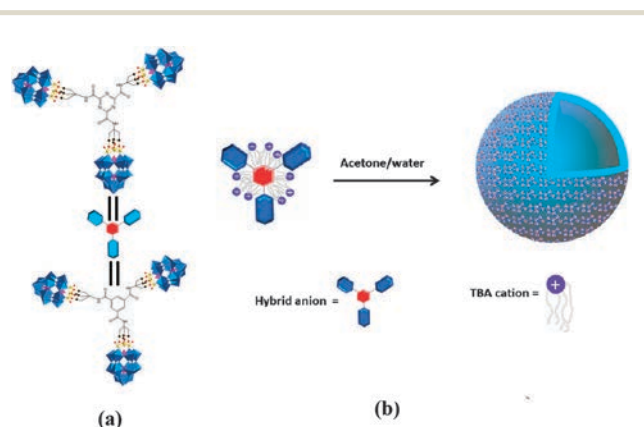


Fig. 1 (a) Molecular structures of two “triangular” shaped inorganic–organic hybrids and (b) self-assembly process cartoon. (a) Top: hybrid **1** $\text{TBA}_{15}\text{H}_3\{(\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{59}(\text{OCH}_2)_3\text{CNHCO})_3\text{C}_3\text{N}_3\}$ with triazine as the organic linker; (a) bottom: hybrid **2** $\text{TBA}_{15}\text{H}_3\{(\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{59}(\text{OCH}_2)_3\text{CNHCO})_3\text{C}_6\text{H}_3\}$ with benzene as the organic linker.

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The organic linkers of these two “triangular” shaped hybrid macroions are a triazine ring (hybrid 1) and a benzene ring (hybrid 2). These two hybrid macroions still possess well-defined hydrophilic and hydrophobic domains, but their hydrophilic portions are more dominant than the “dumb-bell” shaped hybrids previously studied.⁸ Also, their architectures make their external surfaces mainly hydrophilic, possibly making a solvophobic-interaction driven self-assembly more difficult.

The laser light scattering (LLS) technique is commonly used to sensitively detect any possible formation of large assemblies in solution.¹¹ Particularly, dynamic light scattering (DLS) technique with CONTIN analysis¹² measures the hydrodynamic radius (R_h) of large assemblies and static light scattering (SLS)¹³ determines the scattered intensities (I) from solutions and the average radius of gyration (R_g) of the assemblies. The scattered intensity I gives relevant information about assembly status, such as concentration ($I \propto C$) and size ($I \propto R_h^2$).

Both the “triangular” shaped hybrids can be dissolved in acetone at 0.10 mg mL^{-1} to form a clear, stable solution. The scattered intensities were both only $\sim 75 \text{ kcps}$ (for comparison, benzene has a scattered intensity of 85 kcps), suggesting that both hybrids 1 and 2 remain as individual macroions in solution. Whilst keeping the hybrid concentration at 0.10 mg mL^{-1} , but using mixed acetone–water solvent systems, with different solvent compositions, the scattered intensities remained very low ($\sim 70 \text{ kcps}$) in the hybrid solutions with the water content $< 5 \text{ vol\%}$ or $> 35 \text{ vol\%}$, suggesting that the hybrids existed as solvated single macroions under these conditions. In contrast, the scattered intensity of the solution increased to *ca.* 5000 kcps without any precipitation for the mixed solvent containing 10 vol\% water (Fig. 2), suggesting the formation of large assemblies. CONTIN analysis from DLS studies on these solutions indicate the existence of assemblies with average hydrodynamic radius (R_h) of $38 \pm 5 \text{ nm}$ and $69 \pm 5 \text{ nm}$ for hybrids 1 and 2, respectively (Fig. 3), which are angular independent and with narrow size distributions (see ESI 1 and 2†). The average radius of gyration (R_g) of these assemblies obtained from the SLS measurements are $40 \pm 2 \text{ nm}$ and $71 \pm 2 \text{ nm}$ for hybrids 1 and 2, respectively. The R_g values are almost identical to the corresponding R_h values, suggesting hollow, spherical structures

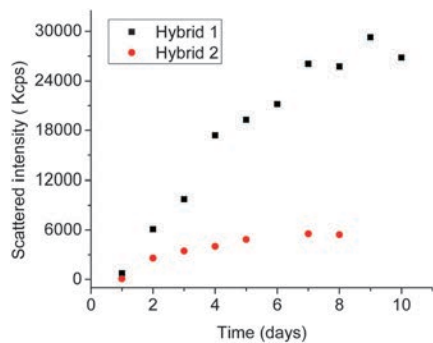


Fig. 2 Change of the scattered intensity from a solution of hybrids 1 and 2 as a function of time in water–acetone mixed solvent containing 90 vol% acetone.

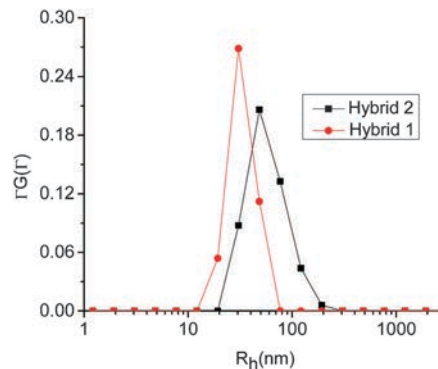


Fig. 3 CONTIN analysis of the R_h distribution of the assemblies of hybrids 1 and 2 in water–acetone mixed solvent containing 90 vol% acetone.

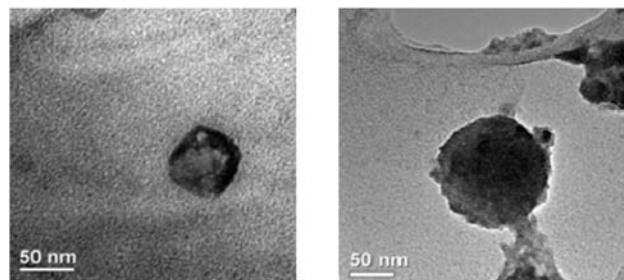


Fig. 4 Typical TEM images of vesicular structures of hybrids 1 and 2 in water–acetone mixed solvent containing 90 vol% acetone: (left) hybrid 1, (right) hybrid 2.

for the assemblies (a hollow sphere would typically have an R_g/R_h ratio of 1). This observation is further confirmed by TEM studies (Fig. 4). The TEM images show that the shape of the assemblies is spherical, and the structure is hollow due to the obvious contrast between the centre area and the shell area, which is consistent with the DLS results. Furthermore, the TEM studies also confirm that the assembly size of hybrid 1 is smaller than that of hybrid 2, which will be explained in the following section.

For hybrids 1 and 2, we speculate that they form blackberry-type structures and this is driven by the counterion-mediated attractions, similar to macroanionic POMs in solution, instead of forming vesicles *via* solvophobic interaction. One obvious piece of supporting evidence for this is the kinetics of self-assembly. The hybrids investigated here take a long time (14 days) to complete their assembly and reach equilibrium (see Fig. 2), while the “dumb-bell” shaped hybrids⁸ reach self-assembly equilibrium within 24 hours under the same conditions, suggesting that there could be a high activation energy that must be overcome during the self-assembly process, similar to the blackberry formation process of the macroanions,¹⁴ but different from the self-assembly of the “dumb-bell” shaped hybrids, driven by solvophobic interaction which reach equilibrium quickly. Furthermore, if the hydrophobic effect is the dominant driving force in this case, the assembly process should be much easier and faster in more polar solvents (higher water content in the acetone–water mixed solvents) than in less polar solvents, because stronger hydrophobic interactions would be expected in

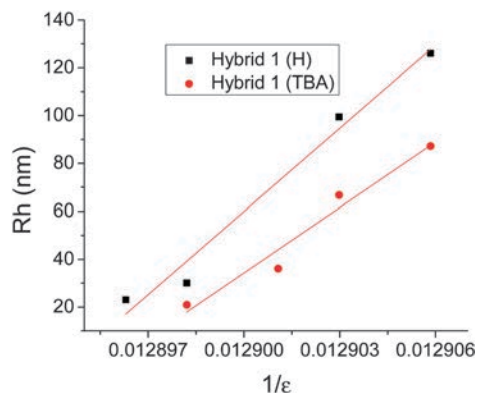


Fig. 5 Plot of the average vesicle radius (R_h) versus the inverted dielectric constant ($1/\epsilon$) of the solvent for hybrid **1** in water–acetone mixed solvent. These systems seem to show a roughly linear relationship.

the former solution (the hydrophobic ligands become better solvated when more acetone is introduced). Although the hydrophobic interactions are not the major driving force for the self-assembly process, we notice that the organic linker still affects the self-assembly process, because hybrid **1** forms smaller assemblies than hybrid **2** under the same conditions. Moreover, the assembly size (R_h) stays fairly constant throughout the whole self-assembly process, as shown in ESI 3,[†] indicating that the structures are quite stable. Therefore, the increment of the scattered intensity (Fig. 2) from solutions over time must be due to the increase in the number of the assemblies rather than an increase in assembly size. This observation is in agreement with our previous studies on the self-assembly of POM macroanions.¹⁵

When the self-assembly reached equilibrium, we found that the assembly size displays a linear relationship with the inverse dielectric constant of the solvent, which implies that size can be determined by controlling charge density of the hybrid macroanion, as shown in Fig. 5.

Another interesting phenomenon being noticed is that the counterions play an important role in this self-assembly process, analogous to POM macroanions. To further study the effect of the counterions on the self-assembly process, the TBA counterions were replaced by protons using a cation-exchange resin column. The experiment can be found in the ESI 4.[†] It was found that, after replacing the TBA counterions with protons, under the same conditions, the average assembly size becomes larger (Fig. 5). The underlying mechanism could be attributed to the decrease of charge density of the polar head groups, caused by the specific hydrogen bonding between the proton donors and the abundant acceptors on the POM's surface, including the terminal oxo, hydroxo and bound water ligands.¹⁶ In the case of the POMs and TBAs, there is no equivalent hydrogen bonding. The low charge density reduces the repulsion between the polar heads on the surface of the assembly. Correspondingly, the curvature of the assemblies decreases, leading to a larger assembly size.

Although the counterion-mediated attractions dominate the self-assembly process, the organic linkers still play a role during the self-assembly. Comparing the two hybrids' organic linkers,

the triazine ring linker is less hydrophobic than the benzene ring. Therefore, the hydrophobic interactions between the TBA tails and benzene rings are stronger than those between the TBA tails and the triazine rings. As a result, the stronger hydrophobic interactions between TBAs and the benzene ring mean the TBAs more effectively shield hybrid **2**, resulting in the lower charge density observed. Consequently, hybrid **2** assembles into larger structures, as has been confirmed experimentally. Once more, compared with the individual inorganic macroions, the self-assembly processes of such hybrids not only can be adjusted by counterions, solvent compositions, but also by the organic linkers.

In summary, the “triangular” shaped POM–organic hybrids can slowly self-assemble into large, hollow, spherical blackberry-type structures in polar solvents (see Fig. 1(b)). Evidence shows that the driving force of the self-assembly is mainly counterion-mediated attraction, similar to the self-assembly process of hydrophilic macroions, instead of the solvophobic interactions which dominate the self-assembly of dumb-bell shaped hybrids.

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