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Deprotonations and Charges of Well-Defined $\{Mo_{72}Fe_{30}\}$ Nanoacids Simply Stepwise Tuned by pH Allow Control/Variation of Related Self-Assembly Processes

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Abstract: The solution behavior of the largest inorganic acid known thus far, the neutral, spherical iron/molybdenum/oxide nanocluster $\{Mo_{72}Fe_{30}\}$ ($\equiv\{(Mo^{VI})Mo^{VI}_5\}_{12}Fe^{III}_{30}$ **1a**), including the pH-controlled deprotonation, is reported. The acidic properties are due to the 30 peripheral, weakly acidic $Fe^{III}(H_2O)$ groups that form a unique Archimedean solid with all edges and dihedral angles being equal, the icosidodecahedron, and therefore an "isotropic" surface. Interestingly, the aqueous solutions are stable even for months because of the inertness of the spherical solutes and the presence of the hard Fe^{III} and Mo^{VI} centers. The stability can be nicely proven by the very characteristic Raman spectrum showing, because of the (approximately) icosahedral symmetry, only a few lines. Whereas the $\{Mo_{72}Fe_{30}\}$ clusters exist as discrete, almost neutral, molecules in aqueous solution at pH < 2.9, they get deprotonated and self-associate into single-layer blackberry-type structures at higher pH while the assembly process (i.e., the size of the final species) can be controlled by the pH values; this allows the deliberate generation of differently sized nanoparticles, a long-term goal in nanoscience. The average hydrodynamic radius (R_h) of the self-assembled structures decreases monotonically with increasing number of charges on the $\{Mo_{72}Fe_{30}\}$ macroanions (from $\sim$45 nm at pH $\approx$ 3.0 to $\sim$15 nm at pH $\approx$ 6.6), as studied by laser light scattering and TEM techniques. The $\{Mo_{72}Fe_{30}\}$ macroions with high-stability tunable charges/surfaces, equal shape, and masses provide models for the understanding of more complex polyelectrolyte solutions while the controllable association and dissociation reported here of the assembled soft magnetic materials with tuneable sizes could be interesting for practical applications.

Introduction

Several types of molecules self-assemble in solution into supramolecular structures (e.g., surfactants and membrane lipids into complex micelles, liposomes, or hollow vesicles) owing to their amphiphilic character.[1] The kind of assembly formation depends on the specific functionalities of the species in connection with the cooperativity between these, an effect that is influenced by the respective solvent. The special case of formation of hollow spherical structures, potentially capable of encapsulating various substrates and valid also for the present situation, is of great interest not only for modeling the emergence of protocell assemblies on the primordial earth, but also in context with the related isoperimetric problem (optimal/smallest surface to volume ratio). The respective self-assembly processes may result from different driving forces. Hydrophilic−hydrophobic interactions, for example, are responsible for the self-assembly of amphiphilic surfactants, and attractive van der Waals forces are responsible for the aggregation of large colloidal particles. Different groups, including ours, recently reported a new type of self-assembly behavior[2−12] (i.e., that of soluble, hydrophilic giant molybdenum/oxide-based spherical and wheel-shaped species).[13] These nanosized clusters can be

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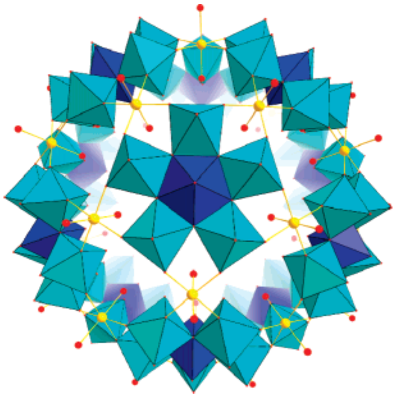

Figure 1. Structure of the spherical $\{Mo_{72}Fe_{30}\}$-type cluster built up by 12 pentagonal $(Mo)Mo_5$-type units spanning an icosahedron (in polyhedral representation) and 30 $Fe(H_2O)_2$ groups acting as linkers and spanning the unique icosidodecahedron with not only all vertices but also all edges equal (in ball and stick representation).

categorized into two groups due to their solution behaviors: strong electrolytes and weak electrolytes. Examples of strong electrolytes include anionic giant wheels, especially the $\{Mo_{154}\}$ species[13,14a−c] (and to some extent also the hedgehog-type $\{Mo_{368}\}$),[13,14d,e] which all contain delocalized electrons and are termed therefore “molecular conductors”; these are highly soluble in polar solvents as a result of their negative charges and layers of water ligands, both of which are present on their surfaces. Such macroions tend to self-assemble into single-layered spherical, hollow, vesicle-like structures due to attractive forces resulting essentially from the presence of countercations (alkaline metal and/or H^+). An example of a weak electrolyte is the $\{Mo_{72}Fe_{30}\}$ cluster type with a localized charge distribution (“molecular insulator”) according to the presence of very hard Mo^{VI} and Fe^{III} centers. The related compound **1**[15a] contains in the solid state the neutral icosahedral cluster $\{Mo_{72}Fe_{30}\} \equiv \{(Mo^{VI})Mo^{VI}_5\}_{12}Fe^{III}_{30}$ **1a** (Figure 1), which exhibits a nanometer-sized cavity and 20 small pores equivalent to 20 $Mo_3Fe_3O_6$ rings while the Fe centers span the unique icosidodecahedron (for a discussion, see refs 15n,o). **1a** can be considered as a nanoacid due to the presence of 30 $Fe^{III}(H_2O)$ groups on the surface that allow pH-dependent deprotonations. Clusters of type **1a** which have also unique magnetic properties[15b−o] self-assemble in solution into blackberry-type structures due to unprecedented driving forces[7−10] (see also below), a situation which is significantly different from the above-mentioned “strong electrolyte”-type macroanion case.[2]

$$[Mo^{VI}_{72}Fe^{III}_{30}O_{252}(CH_3COO)_{12}\{Mo_2O_7(H_2O)\}_2\{H_2Mo_2O_8(H_2O)\}(H_2O)_{91}]\cdot ca.\ 150H_2O \equiv \mathbf{1a}\cdot ca.\ 150H_2O \quad (1)$$

Here, we report on several new facets of the solution properties of **1a**. As its skeleton is extremely stable in solution, the related experiments can be easily done over long periods of time. In particular, it was our aim to investigate how the size of these supramolecular structures is affected by a variety of solution conditions, especially the pH. The obtained knowledge was found to be useful in achieving rational/logical control of self-assembled nanostructures, a long-term goal in nanoscience and nanotechnology.

Experimental Section

Static and Dynamic Laser Light Scattering (SLS and DLS). A commercial Brookhaven Instrument LLS spectrometer equipped with a solid-state laser operating at 532 nm was used for SLS and DLS measurements. The basis of the SLS data analysis is the Rayleigh−Gans−Debye equation, which can be used to determine the weight-average molecular weight (M_w) and radius of gyration (R_g) of particles.[16] In our current study, the change of scattered intensity from SLS measurements can be used to monitor the growth of blackberry-type structures in solution.

From DLS measurements,[17] analyzed by the CONTIN method,[18] we can determine the average hydrodynamic radius (R_h) of the particles. We obtain the particle-size distribution in solution from a plot of $\Gamma G(\Gamma)$ versus R_h, with $\Gamma_i G(\Gamma_i)$ being proportional to the angular-dependent scattered intensity of particle i having an apparent hydrodynamic radius $R_{h,i}$. Detailed descriptions on SLS and DLS techniques can be found in our previous publication.[9]

Transmission Electron Microscopy (TEM). For conventional TEM studies, samples were prepared by pipetting 5 μL of the solution of **1** (1 mg/mL) onto a freshly glow discharged carbon-coated EM grid, and after excess liquid was blotted, 5 μL of 2% uranyl acetate aqueous solution was used to negatively stain the sample. The negative stain method provides better sample contrast while keeping the structural details to around 1-nm resolution. Microscopy was done with a Jeol JEM-1200EX microscope. Images were recorded on Kodak SO-163 films and developed with standard procedures. Negative films were digitized with a Nikon Super Coolscan 8000 scanner. For cryo-TEM studies, 5 μL of the sample solution was pipetted onto a glow discharged EM copper grid covered with holey carbon film in a 100% humidity environmental chamber. The grid was blotted and plunge-frozen in liquid ethane cooled by liquid nitrogen. Cryo images were recorded while the sample was kept at −170 °C with a 2 K × 2 K Tietz CCD camera.

Results and Discussion

$\{Mo_{72}Fe_{30}\}$: Structurally Well-Defined Clusters of 2.5-nm Diameter Acting as Weak Acids in Aqueous Solution.

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Scheme 1

$$\cdots Fe^{III}(OH_2)^{3+} + H_2O \Leftrightarrow \cdots Fe^{III}(OH)^{2+} + H_3O^+$$

Important for the present study is that deprotonations of 30 Fe^{III}-(H_2O) surface groups can be initiated when **1** is dissolved in water while the degree of deprotonation depends in a controlled way on the pH. Such a type of deprotonation behavior is very well-known for the classical complex $[Fe^{III}(H_2O)_6]^{3+}$ containing the same acidic Fe(H_2O) groups (Scheme 1).[19]

In the freshly prepared aqueous solution of **1** (1.0 mg/mL), each cluster releases ~7 H^+ at 20 °C, which leads to pH ≈ 3.4. The deprotonation process becomes of course less favorable with increasing negative surface charges.

Solubility and Stability of the Clusters in Aqueous Solution. **1** has limited solubility in water at room temperature, ~3 wt %. As the dissolution of **1** in water is a very slow process, heating at 50 °C for some time with stirring is needed to obtain solutions of at least ca. 1 wt %. This is quite different from the situation of the above-mentioned a priori charged giant wheel-shaped polyoxometalate clusters (such as $\{Mo_{154}\}$) which release easily H^+ and alkali cations and which therefore can be easily and quickly dissolved in water at room temperature and have much larger solubility. A remarkable property of **1a** is its extreme and, for a nanoparticle, unprecedented stability in (acidic) aqueous solutions, as nicely proven by the very characteristic Raman spectrum (Figure 2), which does not change for months. The reason is that the latter shows only a few intense characteristic lines due to the high (approximately) icosahedral symmetry I_h. (Also the less characteristic UV/vis spectra at room temperature do not change at all over a period of several months.)[7,9] The most intense line in the Raman spectrum at ca. 949 cm^{-1} is due to the totally symmetric ν-(Mo=O) in-phase breathing type vibration. The stability of $\{Mo_{72}Fe_{30}\}$ clusters in aqueous solution allows us to perform interesting special experiments. Although the Raman spectra measured between pH = 3.7−5.9 do not show pronounced changes, some band broadening is observed when the pH of the solution is increased. Furthermore, the wavenumber of the most intense band which has to be assigned to an A_g-type vibration shifts from 949 to 943 cm^{-1} (Figure 2). This type of shift is expected since a small increase of the clusters' negative charge decreases (to some extent) the strength of the terminal Mo=O bonds.

A pH titration experiment was carried out to determine the degree of deprotonation of **1a**. The titration curve (dpH/dV representation, not shown here) has two broad characteristic maxima corresponding to 3.6 ± 0.6 and 22.3 ± 3.0 protons per cluster at pH = 3.2 and 4.9, respectively. This result indicates a significant increase of the charge on the clusters with increasing pH, while it can be assumed that at any given pH somewhat differently protonated/charged clusters coexist in equilibrium. When the pH gets lower than 3.7, precipitation is observed over time at the used concentration (saturated solutions!). At low pH, only uncharged (i.e., completely protonated) clusters exist which are not soluble enough to stay (for a long time) in solution.

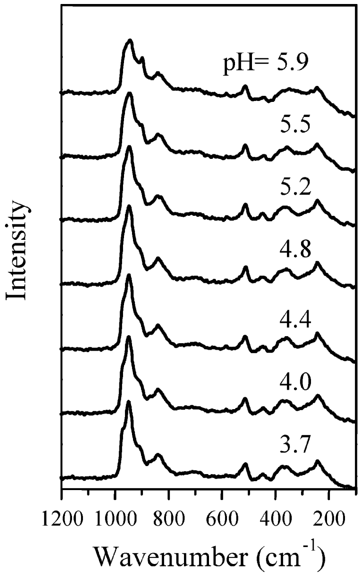

Figure 2. Raman spectra (λ_e = 1064 nm) of $\{Mo_{72}Fe_{30}\}$ clusters in saturated aqueous solutions at different pH values. They show a small shift of the most intense band toward lower wavenumbers as the pH is increased: change from 949 (at pH = 3.7) to 943 cm^{-1} (at pH = 5.9). At pH ≥ 5.5, a decrease of the intensity of this band is observed according to partial decomposition, while a new band appears at ca. 897 cm^{-1}. The concentration used for Raman spectroscopy (nearly saturated solutions) is more than 50 times higher than that for the light scattering measurements (wavenumbers in cm^{-1} of all shown bands: 949, 837, 712, 581, 515, 450, 363, 238).

The variation of deprotonations and of the corresponding (average) net charges on the clusters caused by changes of the pH leads to tunable self-assembly processes discussed below.

Self-Assembly of $\{Mo_{72}Fe_{30}\}$ Macroanions in Aqueous Solution: Basic Facts and pH Dependence. The large size and well-defined surface of the macroanion **1a** is important for the present special solution behavior. In this context, we should also refer to the other above-mentioned molybdenum/oxide-based clusters allowing a nice comparison and better description, that is, to the highly soluble, hydrophilic, wheel-shaped giant mixed-valence $\{Mo_{154}\}$ species which carry quite a few negative charges and delocalized electrons and tend to self-associate into single-layer vesicle-like structures of ca. 45-nm radius with even rather narrow size distribution. The two nearly identical clusters of the related parent mixed-crystal compound/salt contain 14 H^+ counterions as well as 14 or 16 Na^+, respectively.[2,13] The resulting/observed vesicle-like structure is obviously different from that of the (classical) bilayer type formed by amphiphilic surfactants via hydrophobic interactions. This is because the $\{Mo_{154}\}$ macroanions do not have a hydrophobic part. A delicate balance between the repulsive electrostatic interactions and the attractive forces arising from counterion effects, van der Waals forces, and hydrogen bonds is considered to be responsible for the formation of the new type of assemblies. Furthermore, well-defined layers of structured water at the surface of each cluster anion should also play an important role within the overall complex hydrogen-bonding network.[19b]

The present spherical $\{Mo_{72}Fe_{30}\}$ clusters (neutral in the solid state) also form supramolecular structures in solution according to light scattering investigations,[6−12] but of a significantly different type. (These could be called blackberry-type because their structural appearance is reminiscent of this fruit.) The spherical clusters lack (compared to the above-mentioned

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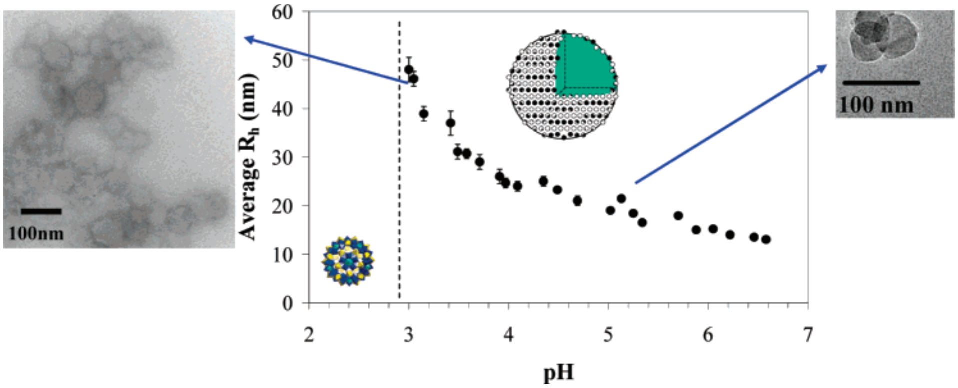

Figure 3. Shown are the average hydrodynamic radii (R_h) of the blackberry-type structures formed in 0.5 mg/mL aqueous solutions of **1a** at different pH, as measured by DLS at 90° scattering angle. For pH < 2.9, the clusters are almost neutral and no supramolecular structures are formed, whereas they are not stable at pH > 6.6. The shown TEM images of the aggregates on carbon film are formed at pH ≈ 3.0 (left; conventional TEM) and pH ≈ 4.6 (right; more appropriate cryo-TEM).

$\{Mo_{154}\}$ macroions) delocalized electrons, and thus the attractive van der Waals forces are much weaker due to the much lower polarizability. Also, hydrogen bonding and, more importantly, electrostatic interactions are, as expected, much weaker here since solutions of **1** contain much fewer counterions. Fe−O−H···O−Fe interactions between adjacent **1a**-type ions can, in principle, influence the structure formation and could be partly responsible for the comparably broad size distribution; even the formation of a few but temporary(!) Fe−O−Fe links between adjacent clusters at higher pH values cannot be completely ruled out.

Importantly, according to their surface properties, the negative charges on each $\{Mo_{72}Fe_{30}\}$ macroanion change by changing the solution pH due to a variation in the degree of deprotonation. Hence, the strength of the electrostatic interactions can be continuously tuned and correspond to the kind of formation of the related supramolecular structures. In the current experiment, a series of 0.5 mg/mL aqueous solutions of **1** (pH ≈ 3.9) was prepared while their pH values were adjusted in the range between 2.0 and 6.6 by adding small amounts of hydrochloric acid or sodium hydroxide solutions. The solutions were immediately added after dissolving crystalline **1** (i.e., before the very slow formation of the supramolecular structures had started; see below). It should be noted that, when adjusting the pH, small amounts of extra electrolytes such as Na^+ or Cl^- are automatically introduced into the aqueous solutions (but it is known that such small amounts of additional electrolytes do not cause any change in the size of the final supramolecular structures).[9] At a pH ≥ 6.6, the $\{Mo_{72}Fe_{30}\}$ clusters become less stable with the consequence that they are broken while yellow-brown precipitates with the approximate composition ($Fe(OH)_3$) are obtained, as expected.

For the supramolecular structures formed in solutions of **1a** with pH between 3.0 and 6.6, the average hydrodynamic radius (R_h), as observed by DLS measurements, decreases monotonically with increasing pH from ~50 nm (at pH = 3.0) to only ~15 nm (at pH = 6.6), that is, with increasing (average) number of charges on the clusters (Figure 3; cf. also Figure 4). This proves that charges play an important role in the solution behavior of the macroions. As the R_g values obtained by SLS experiments are very similar to the R_h values of DLS studies, there is evidence for the hollow nature of the supramolecular structures (see also ref 6). Under rather high pH conditions, the $\{Mo_{72}Fe_{30}\}$ macroanions should hypothetically carry many more charges, so that the repulsive electrostatic interactions should become very strong and overrun the attractive short-range ones with the consequence that all the macroions should stay as discrete ions in solution. (This would resemble the behavior of many water-soluble proteins.) But this phenomenon at the higher pH conditions cannot be observed since decomposition of **1a** occurs in solutions at pH > 6.6, as expected. Note: all polyoxometalates decompose at high pH values while smaller species are formed.[19c]

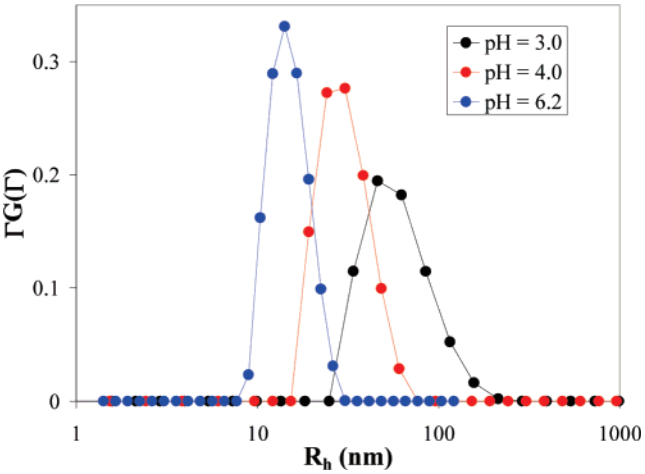

Figure 4. Size distribution of the self-associated structures at different pH values formed in aqueous solutions of **1** as obtained from the CONTIN analysis of DLS measurements. The size distribution becomes broader at low pH conditions.

On the other hand, on the basis of the present SLS and DLS studies, no supramolecular structures were observed in the macroionic solutions at pH < 2.9 where the clusters, as weak acids, are almost neutral in solution (i.e., when almost no deprotonation occurs). Therefore, these results suggest that the self-assembly of $\{Mo_{72}Fe_{30}\}$ macroions occurs only when they carry a moderate amount of charges, and correspondingly, H_3O^+ counterions are present. Formally, the attractive forces might be called "like-charge attraction", because of the attraction of macroions carrying an identical type of charge. The real reason for this phenomenon is of course the presence of counterions positioned in between the macroions. Quite a few examples are designated by some authors[20−24] as "like-charge attraction" in

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(20) Sogami, I.; Ise, N. *J. Chem. Phys.* **1984**, *81*, 6320.

the case of charged colloids (e.g., latex particles in micrometer size) and sometimes in confined environments.

The total charge on the **1a**-type clusters decreases with decreasing pH, which leads to weaker repulsive interactions between them. If van der Waals forces would be the dominant attractive forces responsible for the self-assembly (considering that this type of force among the macroanions does not change with changing surface charge density), the almost neutral $\{Mo_{72}Fe_{30}\}$ clusters should assemble more efficiently, which could even lead to precipitates. However, experiments show that, at pH < 2.9, the macroions stay as discrete clusters in solution, suggesting that the hydration of the neutral weakly hydrophilic clusters overcomes attractive van der Waals forces, which means for the supramolecular structure formation that a major contribution from the latter types of forces can be ruled out. Let us keep in mind that the interactions of lyophobic colloids, which can as thermodynamically unstable systems only be suspended in solutions due to their charges, can be described by the DLVO theory.[25,26]

Size Distribution of the Blackberry-Type Structures. The size distribution (polydispersity) of the supramolecular structures can be viewed via the $(\mu_2/\Gamma)^2$ values in the CONTIN analysis[27] of DLS measurements, with the smaller values denoting narrower size distributions (Figure 4). The present $(\mu_2/\Gamma)^2$ values are considerably larger than those of the above-mentioned $\{Mo_{154}\}$-type supramolecular structures,[2] signifying (relatively) broader size distributions. This can be elucidated as follows: There is an equilibrium between different $\{Mo_{72}Fe_{30}\}$-type clusters carrying different numbers of charges at each given pH with the consequence that these species form supramolecular structures with different sizes and more complex shapes (Figure 3). The present $(\mu_2/\Gamma)^2$ values show a significant pH dependence with relatively small values (∼0.1−0.2) at higher pH (3.9−6.6) (i.e., indicating narrower size distributions) and larger values (∼0.2−0.3) at lower pH (3.0−3.9) with the reverse result. This could be explained by the fact that, at a higher pH, the macroions carry on average larger numbers of charges; thus, at a given pH the relative change of charge numbers from one cluster to another, being in equilibrium, is comparatively small. On the other hand, at a low pH value the clusters being in equilibrium carry only very few charges with the consequence that a difference of even one charge from cluster to cluster results in quite a comparably large difference in R_h which, correspondingly, leads to a situation with a larger size distribution of the blackberry-type structures.

Further important issues have to be mentioned: because of the presence of the very hard Mo^{VI} and Fe^{III} centers, the electrons/charges are localized on the surfaces, which corresponds to an inhomogeneity of charge distribution (e.g., compared to the above ring-shaped species exhibiting delocalized electrons). The inhomogeneous distribution of negative charges is increased after a few deprotonations on the cluster surfaces, which leads also to an inhomogeneous distribution of counterions such as H_3O^+ around them. Consequently, a large fraction of collisions between the macroions (a condition for association) might become ineffective if there are not enough counterions near the collision site. This effect definitely contributes to the unusual slowness of the $\{Mo_{72}Fe_{30}\}$-type assembly (see below and also ref 7).

The change in size of the blackberry-type structures with the corresponding pH is confirmed by TEM and environmental scanning electron microscopy (ESEM) measurements. The observed average radii are ∼30−45 and ∼15−20 nm at pH = 3.1 and 4.6, respectively (Figure 3, left and right), a situation comparable to the DLS results. The particles are transparent for the 120 and 200 keV electrons (Figure 3, left and right, respectively), showing the hollow nature of the structures. As shown in Figure 3 as well as by ESEM studies (results not shown), the supramolecular structures are not necessarily in perfect spherical (i.e., blackberry) shape. We attribute this to the presence of differently charged spherical anions of type **1a**, the aggregation of which should lead to different types of assemblies, as mentioned above. In this context, it should be noted that the size derived from TEM images can vary due to specific interactions with the support film and due to shrinking or flattening upon drying.

Characteristics of the Speed of the Self-Assembly: Process Slowness and pH Dependence. One unique property of the structure formation in weak electrolytes such as $\{Mo_{72}Fe_{30}\}$ is that the related self-assembly processes are slow in dilute solutions, especially at low temperatures while the slowness of the process offers the advantage to monitor/follow nicely the structure formation by different types of experiments (e.g., by SLS and DLS).[7] This slowness is due to a high activation energy, corresponding to a very high energy barrier between the two relevant states (i.e., discrete macroions on the one hand and supramolecular structures on the other). The speed is affected by the solution pH. At a given temperature, the self-assembly process, measured by SLS, becomes faster at higher pH (i.e., when the clusters carry more charges), which is more proof for the fact that the charges on the $\{Mo_{72}Fe_{30}\}$ clusters “contribute significantly” to the attractive type of forces: When the clusters contain more charges, they are more easily attracted to each other based on the larger number of counterions in between them, thus allowing more effective collisions.

Transition from Supramolecular Structures to Discrete Macroions Due to pH Change. It is not easy to break down the self-assembled structures into discrete macroions (i.e., once they are formed), due to the high-energy barrier between them. (The addition of a large amount of the cationic surfactant dimethyldioctadecylammonium bromide (DODA-Br), for instance, leads to breaking into single macroions due to forming DODA/$\{Mo_{72}Fe_{30}\}$-type complexes which can be transferred into a $CHCl_3$ phase.)[11] Adding several drops of 1 M hydrochloric acid to an aqueous solution of **1** (pH ≈ 4) (containing a considerable amount of blackberry-type structures) to get a solution with pH ≈ 2 leads to a slow dissociation of the supramolecular assemblies. This was monitored by SLS (continuous and drastic decrease of total scattered intensity from the solution) and DLS measurements (absence of the peak at $R_h \approx 30$ nm in CONTIN analysis characteristic for the disappearance of blackberry structures). The reason for the

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change is due to the protonations of the $\{Mo_{72}Fe_{30}\}$ clusters at low pH. This provides evidence that the supramolecular structure formation is reversible. Heating the solution can significantly accelerate the dissociation. The final solution is still clear/homogeneous, having the characteristic light yellow color of the $\{Mo_{72}Fe_{30}\}$ clusters. Also, a UV/vis and especially the more meaningful Raman study provide almost the same result as that obtained from a freshly prepared solution of **1**, indicating that no significant chemical reaction has occurred during the formation and later dissociation of the assemblies. The result is again a direct proof that the association is dominated by electrostatic interactions. After this type of acidified solution was kept at 50 °C for ca. 2 years, the clusters still exist as individual species according to the characteristic Raman spectra and in agreement with SLS (very weak scattered intensity, indicating no association) and DLS measurements (no peak corresponding to the presence of large structures).

An Unprecedented Process: Assembly upon Dilution. Normally, dilution is expected to bring the solutes further apart from each other, while on the other hand, aggregation or crystallization usually occurs with increasing solute concentration. But this is not the case when a solution containing the $\{Mo_{72}Fe_{30}\}$ clusters is diluted with a larger amount of pure water. Starting with a situation where all clusters are discrete, almost uncharged in a 0.5 mg/mL aqueous solution at pH $=$ 2.7, the following takes place: after dilution of the solution to $\sim$0.1 mg/mL, the pH increases to 3.3, thereby lowering the H^+ concentration with the consequence that their degree of deprotonation increases. After keeping the (diluted) solution at 50 °C (to increase the velocity of association) for only 1 day, a considerable amount of aggregates was detected as the scattered intensity measured by SLS had increased by more than ca. 50 times while DLS studies showed that a new mode ($R_h \approx 40$ nm) with relatively narrow size distribution had appeared. This result further indicates that the transition between the two states (discrete $\{Mo_{72}Fe_{30}\}$ clusters and their assemblies) can be controlled by adjusting only the solution pH. The transition from discrete clusters at pH $=$ 2.7 to the related aggregates at pH $=$ 3.3 is totally consistent with the curve in Figure 3 (center).

Changing the Size of Formed Supramolecular Structures by Changing Solution pH. Importantly, the size of the blackberry-type structures is found to be adjustable with pH, even after they are formed. A typical experiment is described as follows. A sample of 1.0 mg/mL $\{Mo_{72}Fe_{30}\}$ solution (pH $=$ 3.5, 10 mL) was heated at 40 °C for a couple of weeks to ensure the completion of self-assembly. In that case, the average R_h of the supramolecular species is around 29.5 ± 1.5 nm, which is consistent with the results presented in Figure 3. After several drops of 1 M sodium acetate (NaAc) solution were added to the reaction medium to adjust the solution pH to 5.0, the size of the blackberry-type structures did not immediately change, proving that they are rather difficult to break. But after heating the solutions at 40 °C for 1 day, DLS measurements clearly showed that the average R_h of the assemblies had decreased to $\sim 16.2 \pm 1.0$ nm, indicating that their sizes have changed in response to the pH change. The present data are in agreement with the R_h vs. pH curve in Figure 3.

Connection between Inorganic Macroions and Long-Chain Organic Polyelectrolytes. There are obvious similarities between the mentioned molybdenum/oxide-based macroions[13,14] and long-chain polyelectrolytes, including some natural biomacromolecules, such as DNAs and proteins (see, for instance, ref 9). Therefore, the inorganic macroions described here can be treated as a simple form of polyelectrolytes and can be used as excellent model systems for studies of more complex charged macromolecules because they are identical in size, shape, and mass, and carry for a well-defined solution condition either an identical (in case of the mentioned $\{Mo_{154}\}$ type species) or a similar number of charges, which can easily be tuned. Moreover, these inorganic clusters have the advantage that they are rigid.

It is well-known that various organic polyelectrolytes tend to form large domains in salt-free or low-salt-concentration solutions. Although there are continuous disputes on the nature of such "large domains" (sometimes called "slow mode"), more and more evidence shows that at least in some cases they are stable while multimacroionic structures are formed by the association of single polyelectrolyte chains;[28−34] rodlike polyelectrolytes, for instance, can form bundlelike aggregates.[29] Sedlák recently reported that, in sodium poly(styrene sulfonate)/H_2O systems, the average size of multimacroionic domains was related to the concentration of the added electrolytes[28] which shorten the screening length between polyelectrolytes while their concentration affects the effective attraction between polyelectrolyte chains. This result shows a certain similarity to our current situation, which indicates that charge distributions play a key role for the attractive forces among the inorganic macroions. Whereas Sedlák noticed that in the presence of additional electrolytes the formation of multimacroionic domains shows an obvious delay process,[33] a similar phenomenon can be observed in the self-assembly process of $\{Mo_{72}Fe_{30}\}$ macroions in NaCl-containing solutions.[35] Even the kinetic curves of the formation of the polyelectrolyte multidomain structures[34] and the type of supramolecular structures described here have similar shapes. To summarize, on the basis of the present results, it can be expected that in the future the present type of assemblies of the inorganic macroionic solutions could lead to a better understanding of the intriguing polyelectrolyte solutions, maybe even of those of the biomacromolecular type.

Summary and Conclusions

$\{Mo_{72}Fe_{30}\}$ clusters act in dilute aqueous solution as nanosized weak inorganic acids that can deprotonate differently depending on the pH, which allows (based on a thermodynamically favored assembly process) to form differently sized soft "nanoparticles". Their sizes monotonically decrease with increasing deprotonation and the related cluster surface charges, suggesting that the charges play an important role in this kind of self-assembly. Furthermore, the self-assembly processes are reversible. The unique solution properties together with the high stability of the clusters in acidic media render them promising materials for both fundamental studies of macroionic solutions as well as for practical applications regarding controllable association and dissociation of nanoscaled soft (magnetic) materials with rationally tunable sizes.

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