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Self-Assembly

Smart Inorganic Surfactants: More than Surface Tension**

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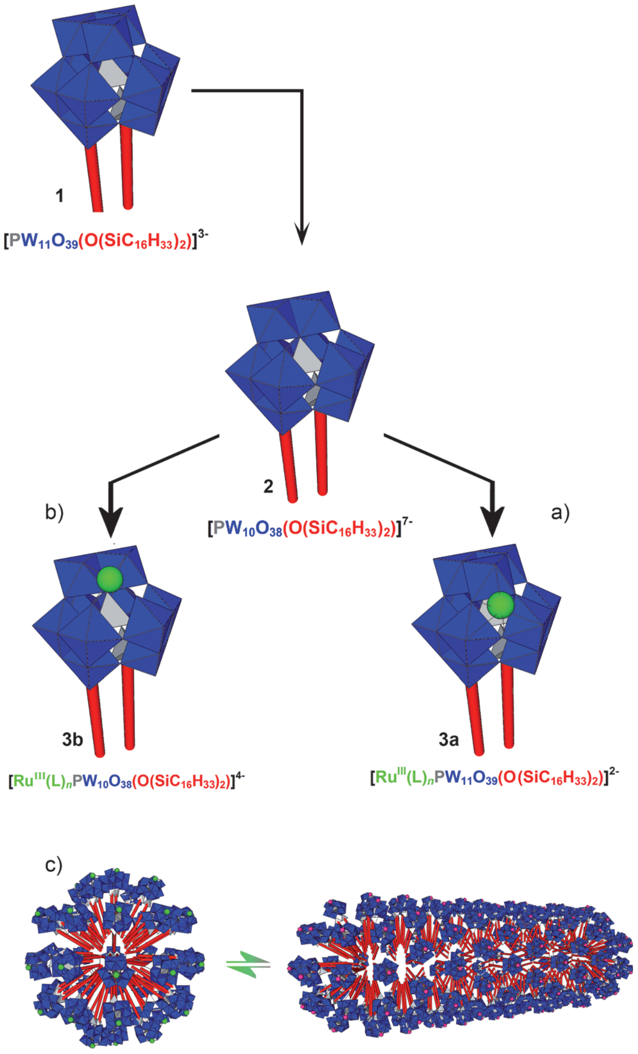
The interconnection to higher length scales, and ultimately to the macroscopic world, is a key for the successful application of functional nanostructures in future technologies.[1] Thus, the development of novel materials that are capable of adapting to environmental conditions is a challenging goal. This special ability of certain materials has been described as either stimuli-responsive, smart, or even intelligent behavior.[2] Smart materials can sense, process, and actuate a response to an external change without assistance. The potential stimuli can be differentiated as physical triggers (for example temperature and magnetic or electric fields) and chemical triggers. Among soft-matter structures, some exciting examples for smart systems can be found. Presumably the best known is the control of the optical properties of thermotropic liquid crystals by electric fields. The related phenomenon has led to an important application in liquid-crystal displays (LCDs).

Liquid-crystalline behavior is also known for amphiphilic molecules, such as surfactants. Conventional surfactants contain a hydrophilic, water-soluble head group and at least one hydrophobic alkyl tail. Because of this antagonism, they self-assemble into defined aggregates when they are brought into contact with a selective solvent, most importantly water. Common structures are micelles, vesicles, and lyotropic phases. The number of studies on the response of amphiphilic aggregates to external factors is relatively small. An interesting example was reported by Winnik, Manners et al.[3] The micellization of a polyferrocenylsilane diblock copolymer was shown to be influenced by redox chemistry.[3] That work shows that the combination of self-assembly with stimuli-responsive properties is a fascinating, rather unexplored area.

The creation of a system which can dynamically respond to a chemical trigger would be a significant advance in the field of surfactant and self-assembly science. Conventional surfactants do not allow this possibility to be explored, as they contain chemically inert, organic groups. Surfactant systems incorporating reactive, inorganic building blocks have been described only rarely.[4]

Recently, amphiphilic molecules with a special head group have been reported: polyoxometalate (POM) clusters.[5] POMs are a class of molecular compounds with an amazing variety of physical and chemical properties.[6] Cronin et al. could functionalize a so-called Mn-Anderson cluster with two long alkyl chains in 2008,[7] and they were able to observe the formation of unusual vesicle-like structures. Furthermore, Wu et al.[8] modified Mn-Anderson clusters with two azobenzene groups, which were encapsulated by cationic ammonium surfactants. It was confirmed that the resulting self-assembled structures are sensitive to photo-irradiation.

We have recently presented a new class of surfactants containing the POM cluster [$PW_{11}O_{39}$] as a head group attached to two long alkyl chains (Scheme 1).[9] This unique POM-surfactant (POMSURF) **1** not only behaves as an



Scheme 1. Synthesis of bimetallic Ru-POM surfactants. Ru can either be bound to the surface of the POM (a) or inside a pocket of a lacunary species (b). c) Reversible electrochemical switching from spherical to rod-like micelles.

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amphiphile but at the same time it is catalytically active. The complexity of POMSURF **1** can be increased much more if an additional, functional transition-metal cation could be integrated in the head-group region. In this respect it is important that single W=O entities can be cleaved stepwise from the oxocluster under basic conditions, resulting in so-called lacunary POMs.[10] Various transition metals can coordinate to the oxygen atoms remaining in the vacancy.[11] The reaction of the $[PW_{11}O_{39}]$ surfactant **1** was monitored in situ using ^{31}P NMR spectroscopy ($\delta(^{31}P) = -13.6$ ppm; further data are given in the Supporting Information, S1). The observed chemical shift after alkaline treatment ($\delta(^{31}P) = -12.1$ ppm) indicates that a new, lacunary species with a $[PW_{10}O_{38}]$ head group has formed (see compound **2** in Scheme 1). Next, compound **2** was treated with ruthenium chloride in water with the intention of a defined reaction between the lacunary head group $[PW_{10}O_{38}]^{7-}$ as a ligand and ruthenium(III). There is a change in optical features, as observed by UV/Vis spectroscopy (Supporting Information, S2) that shows the effect on the electronic levels of ruthenium(III) owing to a defined interaction with the POM as a ligand. Clear evidence was obtained from the enforced precipitation of the POMSURF using the organic ammonium cation Bu_4N^+. Because exactly two equivalents of Bu_4N^+ were needed for the quantitative precipitation, it can be concluded that the charge of the head group is 2− after the reaction with $RuCl_3$. Furthermore, the supernatant solution was colorless, meaning that the entire ruthenium(III) is bound to the POMSURF. In agreement to other ruthenium(III)-containing POMs, it was possible to acquire NMR spectra despite the paramagnetism of the compound.[12] ^{1}H, ^{29}Si, ^{31}P, and ^{183}W NMR spectra were measured (Supporting Information, S3). The comparison to the spectra of the starting compound **1** reveals that neither the symmetry nor the structure of the POMSURF has been changed. In particular, the ^{183}W NMR spectrum exhibits six signals with a 2:2:1:2:2:2 pattern, which is characteristic for an intact $[PW_{11}O_{39}]$ head group. The hydrochloric acid released from the hydrolysis of $RuCl_3$ in water and the resulting acidification leads to a back-reaction to **1** before Ru^{III} can enter the coordination pocket of the lacunary species. FTIR (Supporting Information, S4) and FT-Raman spectroscopy show vibration frequencies in the correct range for Ru−O bonds (ca. 800, 690, and 640 cm^{-1}).[13] This means that ruthenium(III) is bound to the outer surface of the POM cluster by WO−Ru links (Scheme 1, compound **3a**). Therefore, the formula $[Ru^{III}(L)_nPW_{11}O_{39}(O(SiC_{16}H_{33})_2)]^{2-}$ can be assigned to POMSURF **3a** (L = additional ligands, such as Cl^-, H_2O), which is also in good agreement with the elemental analysis. The successful incorporation of ruthenium inside the lacunary position of **2** can be achieved by using a more reactive ruthenium complex and avoiding acidification. We have used the labile complex $[\{Ru(p\text{-cymene})Cl_2\}_2]$ according to the method reported by Proust et al.[14] The product was analyzed as before. This time there are clear indications for compound **3b** (for spectroscopic data, see the Supporting Information, S5). In the ^{31}P NMR spectrum, the chemical shift of the phosphorus atom of the head group shifts to $\delta(^{31}P) = -10.80$ ppm in **3b**, and the signals in the ^{183}W NMR spectrum are also shifted significantly. Furthermore, in FTIR and FT-Raman spectra, significant differences can be observed that show that a different POM cluster ($[PW_{10}O_{38}]$) with ruthenium coordinated in the lacunary position has formed. It can be concluded that two bimetallic POMSURFs are available for further studies.

Next, typical amphiphilic properties were explored. In contact to limited amounts of water, a distorted, polygonal texture is observed with polarization microscopy (Figure 1), which is typical for columnar phases. The nanostructure was investigated by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). The data fit to a liquid crystal comprising an assembly of cylindrical aggregates in a hexagonal fashion (space group *P6mm*; Figure 1 d) and a lattice constant $a = 5.11$ nm.

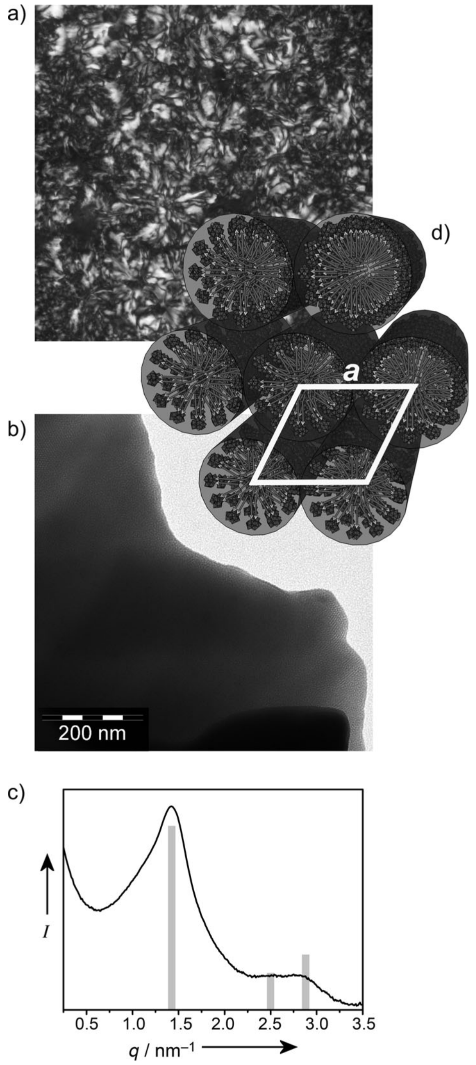

Figure 1. Formation of liquid crystals from the bimetallic POMSURF **3a**. Polarization microscopy (a), TEM (b), SAXS (c), and a model of the LC structure (d).

However, the intriguing feature of the systems presented is that the head group possesses outstanding functional properties. Cyclic voltammetry (CV) of the Ru-POM in acidic aqueous solution reveals three reversible redox couples

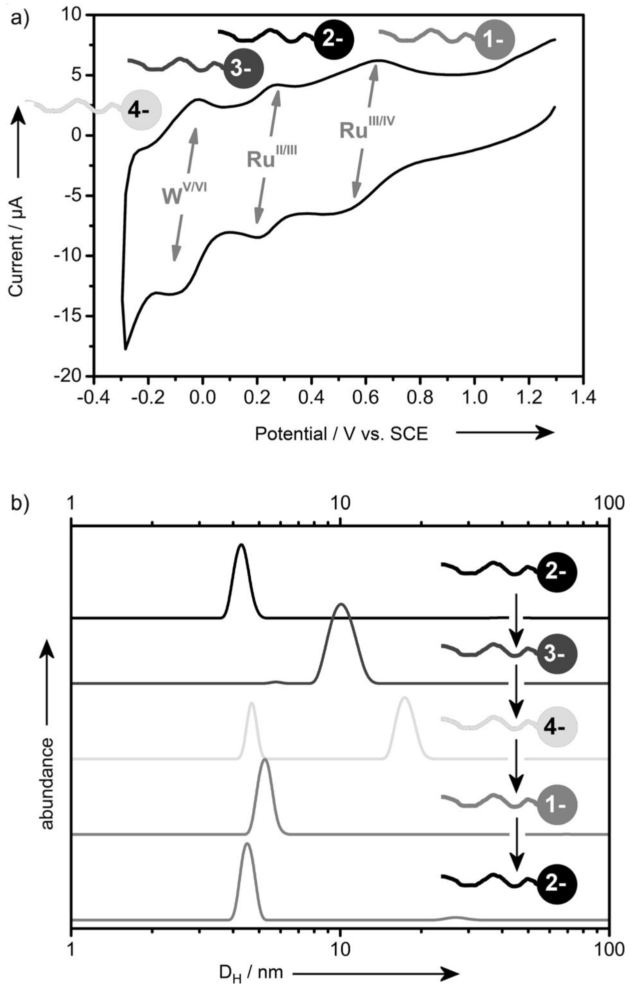

Figure 2. Electrochemical switching of POMSURF **3a** studied by CV (a) and DLS (b). The charge of the head group is also indicated.

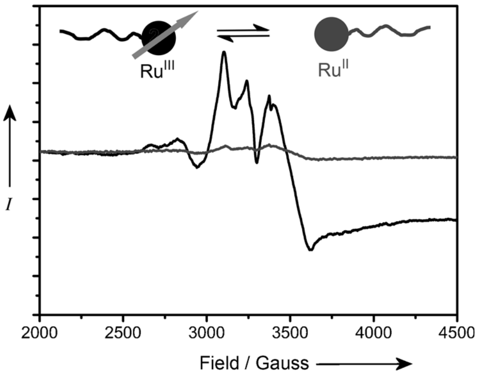

Figure 3. Electrochemical switching of the magnetic properties of the Ru-POMSURF **3a** investigated by EPR spectroscopy before (black) and after reduction (gray).

in the range of +1.3 V to −0.3 V (Figure 2) corresponding to Ru$^{III/IV}$ ($E^0 = 0.545$ V),[15] Ru$^{II/III}$ ($E^0 = 0.239$ V), and W$^{V/VI}$ ($E^0 = -0.069$ V).

The electrochemical activity allows switching from a surfactant head group possessing a magnetic moment (Ru^{III}: d^5 high-spin system) to a non-magnetic state (Ru^{II}: d^6 low-spin) as can be clearly seen from the electron paramagnetic resonance (EPR) spectra shown in Figure 3. The spectrum correlates to a Ru^{III} species. There is no distinctive hyperfine interaction visible owing to the low symmetry of the ligand environment around the ruthenium. Furthermore, the spectrum is broadened by bipolar interactions, which is caused by the proximity of the surfactants in micellar aggregates. Furthermore, electrochemical activity leads not only the change in magnetic properties, but also the charge of the head group can be varied systematically from 2− for **3a** as synthesized to 3−, 4− through reduction, and to 1− through oxidation (Figure 2a). Therefore, the POMSURF system introduced herein allows a key question in surfactant science to be answered: whether (and how) does the head-group charge affect the self-assembly characteristics.

Interesting effects were observed using dynamic light scattering (DLS) on micellar solutions of POMSURF **3a** (Figure 2b). The hydrodynamic diameter D_H of the micelles is 4.3 nm, which is in good agreement to the extension of **3a**. Reduction causes growth of the aggregates to $D_H = 10.0$ nm. Then, for a head-group charge of 4−, two values for D_H are detected (4.7 nm, 17.3 nm), which is a sign for the appearance of anisotropic objects, such as worm-like micelles (Scheme 1c). To verify the latter assumption, additional analytical measurements were performed. The large electronic contrast between the [$PW_{11}O_{39}Ru$] head-group region and the alkyl chains allows for the acquisition of reliable SAXS data of the micellar dispersions. Porod and Kratky plots were used to identify the shape (Supporting Information, S6).[16] The slope of the Porod plot $\log I$ versus $\log q$ is close to −1, which indicates the presence of rods. The pattern of a Kratky plot ($q^2 I$) is almost linear in the high-q range, which is also typical for rods. As a third, independent method, analytical ultracentrifugation was performed (Supporting Information, S6). Frictional coefficients of greater than one were observed and the calculated aspect ratio shows that the particles have an elongated morphology. It is important to note that the entire process is reversible. The electrochemical cycle is closed by addressing the head group charge 1− ($D_H = 5.3$ nm) and 2− ($D_H = 4.4$ nm), as shown in Figure 2.

Although it has already been shown that the POMSURF system has stimuli-responsive properties, up to this point the coupling to the macroscopic world is still missing. Therefore, an experiment was designed for the investigation of switching light-harvesting properties of micelles constructed from POMSURF **3a**. Excitation and emission spectra are shown in Figure 4. The excitation spectrum of **3a** has a maximum at $\lambda = 382$ nm. Fluorescence can be detected; the main signals are at $\lambda = 417$ nm and 700 nm (Figure 4b). On the other hand, pyrene absorbs light at about 330 nm and emits at about 385 (Figure 4a). Therefore, the combination of POMSURF **3a** and pyrene is a potential couple for Förster resonance energy transfer (FRET) processes (Figure 4d).[17] When pyrene is incorporated in the hydrophobic domain of POMSURF **3a** aggregates, and an excitation wavelength of $\lambda = 334$ nm is applied, it can be seen that the fluorescence of pyrene is quenched quantitatively. Instead, the 700 nm emission associated with **3a** is observed as the only signal. After electrochemical switching to head-group charge 3−, accompanied by

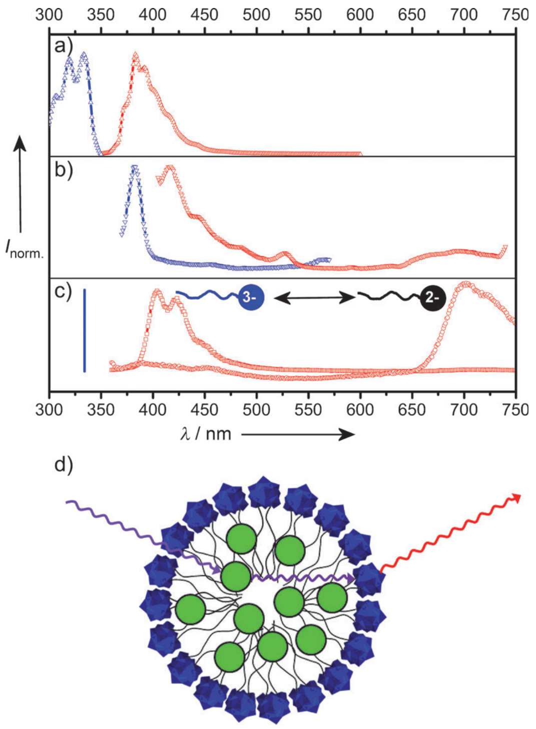

Figure 4. Excitation (blue) and emission spectra (red). a) Pyrene in solution. b) POMSURF **3a**. c) Pyrene in micelles of POMSURF **3a** before (○) and after electrochemical reduction (□); the excitation wavelength was 334 nm (blue vertical line). d) FRET between pyrene (●) and the POMSURF.

the structural transformation of the self-assembled aggregate, the optical response of the system changes significantly. The emission spectrum is now a superposition of the fluorescence signals of pyrene and the POMSURF (Figure 4d). This means that FRET can be switched on and off.

The goal of this work was to extend the conventional properties of surfactants into the area of smart materials. The synthesis of unique surfactants containing an inorganic head group with two different transition metals (W, Ru) led to the emergence of an entire set of new qualities. The magnetic momentum and the charge of the head group can be controlled by electrochemical methods. A reversible switching between two self-assembled structures of different symmetry was demonstrated. Last but not least, the novel surfactant system was facilitated for light-harvesting that could be turned on and off at will.

Experimental Section

$H_3[PW_{11}O_{39}(SiC_{16}H_{33})_2O]$ (**1**) and $[\{Ru(p\text{-cymene})Cl_2\}_2]$ were prepared as described previously.[9,18]

3a: An aqueous solution of sodium carbonate (2 M, 0.385 mL, 0.771 mmol) was added to a solution of $H_3[PW_{11}O_{39}(SiC_{16}H_{33})_2O]$ (420 mg, 0.128 mmol) in water (6 mL). Subsequently, ruthenium(III) chloride hydrate (28.0 mg, 0.135 mmol) in water (1.5 mL) was added. After 30 min of stirring at room temperature, the solution was poured into acetonitrile (200 mL) and evaporated to dryness. Afterwards, the residue was dissolved in acetonitrile again and centrifuged. The supernatant solution was evaporated to dryness and the product was dried at 80 °C under reduced pressure (380 mg yield).

^{1}H NMR ([D$_6$]DMSO): $\delta = 7.24$ (s, 1H), 6.64 (s, 1H), 1.60–1.10 (m, 56H), 0.85 (t, $J = 6.8$, 6H), 0.71 ppm (t, $J = 7.6$, 4H). ^{31}P NMR ([D$_6$]DMSO): $\delta = -13.82$ ppm. ^{29}Si NMR ([D$_6$]DMSO): $\delta = -51.24$ ppm. ^{183}W NMR ([D$_6$]DMSO): $\delta = -97.81$ (2W), -103.47 (2W), -107.30 (1W), -120.66 (2W), -198.13 (2W), -251.36 ppm (2W). IR (ATR, polyoxometalate region): $\tilde{\nu} = 1112$ (Si-O-Si), 1065 (P-O), 1049 (sh, P-O), 1035 (P-O), 998 (sh, W=O), 981 (sh, W=O), 955 (W=O), 862 (W-O-W), 803 (W-O-W), 774 (W-O-W), 743 (W-O-W), 699 cm^{-1} (W-O-W).

3b: A mixture of $[\{Ru(p\text{-cymene})Cl_2\}_2]$ (67.4 mg, 0.110 mmol) and $AgBF_4$ (85.7 mg, 0.440 mmol) in acetonitrile (2.5 mL) was heated at 40 °C for 2 h. The AgCl was removed by filtration and the filtrate was evaporated to dryness. The resulting oily solid was dissolved in water (2 mL). The filtrated solution was added quickly to a fresh mixture of $H_3[PW_{11}O_{39}(SiC_{16}H_{33})_2O]$ (600 mg, 0.184 mmol) in water (10 mL) and a 2 M aqueous solution of sodium carbonate (0.918 mL, 1.835 mmol). After 15 min of stirring at room temperature, the solution was poured in acetonitrile (250 mL) and evaporated to dryness. Afterwards, the residue was dissolved in acetonitrile again and centrifuged. The residue was redissolved in methanol and centrifuged. The supernatant solution was evaporated to dryness and the product was dried at 80 °C under reduced pressure (490 mg yield).

^{1}H NMR ([D$_6$]DMSO): $\delta = 6.00$–5.00 (m, 4H), 2.11 (m, 3H), 1.60–1.00 (m, 62H), 0.84 (t, $J = 6.8$, 6H), 0.42–0.24 ppm (m, 4H). ^{31}P NMR (D$_2$O): $\delta = -10.78$ ppm. ^{29}Si NMR ([D$_6$]DMSO): $\delta = -53.71$ (1Si), -59.65 ppm (1Si). IR (ATR, polyoxometalate region): $\tilde{\nu} = 1122$ (sh, Si-O-Si), 1085 (P-O), 1060 (sh, P-O), 1039 (P-O), 1020 (P-O), 965 (sh, W=O), 944 (W=O), 844 (W-O-W), 803 (W-O-W), 716 cm^{-1} > (br, W-O-W).

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