

Amphiphilic hybrids containing inorganic constituent: More than soap

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A B S T R A C T

Amphiphiles and surfactants are indispensable compounds in industry, scientific research and everyday life, such as emulsification agents, detergents, etc. The vast majority of currently used amphiphiles are organic in nature, and are composed of two molecular parts joined together, one hydrophilic and one hydrophobic. The current article highlights some of the recent developments in the emerging field of hybrid amphiphiles, focusing on systems with at least one inorganic constituent. Different classes of amphiphiles can be defined, depending on if the inorganic entity is molecular or has particle character, and depending on the strength of interaction between the inorganic and organic phase. It is seen that in addition to typical amphiphilic properties, most importantly the formation of self assembled structures like micelles or lyotropic liquid crystals, the hybrid amphiphiles exhibit additional, functional features like special magnetic or catalytic properties. Ultimately, systemic features can be observed, leading to the emergence of new properties which none of the constituents of hybrid amphiphile could have on its own.

Keywords:

Self-assembly
Polyoxometalates
Organic–inorganic hybrids
Amphiphiles
Janus particles

1. Introduction and background

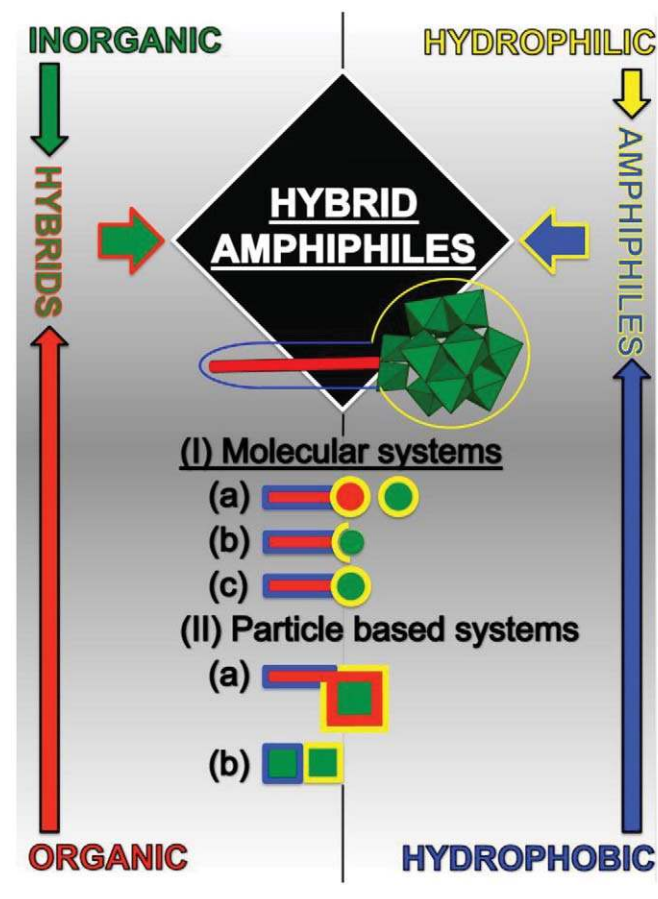
The persistent, general question in materials science is, how novel materials with unique and ultimately unprecedented properties can be found. A strategy, proven to be quite successful, is to combine seemingly opposite entities, hoping for systemic features. A very superficial description of systemic features is that the whole is more than the sum of its parts, found for instance in swarms of certain ensembles e.g. particles [1]. A very obvious choice for joining opposites is to combine organic and inorganic constituents, and this has resulted in the vast field of 'organic inorganic hybrids' with numerous examples of synergistic properties [2]. Another prominent case for a chemical antagonism joined together in one system is represented by surfactants, the latter term representing an abbreviation for surface active agents.

Surfactants are defined as molecular compounds containing one water compatible, hydrophilic part, the so called head group, and a water incompatible, hydrophobic part covalently linked to each other. The hydrophobic unit of a classical surfactant is typically a simple alkyl chain, whereas the hydrophilic part can be cationic (e.g. ammonium), anionic (e.g. carboxylic acid, sulfonic acids) or neutral (e.g. oligoethylene glycol) in nature. The resulting amphiphilic nature of surfactants leads to a range of fascinating and valuable properties for applications in industry and nanotechnology [3], which are connected to their ability to occupy interfaces and with that lowering surface energy. For instance, for ternary systems (water, organic solvent, surfactant) they are known to effectively stabilize different kinds of emulsions. A fascinating property of surfactants

and amphiphiles is their ability for self organization above a certain threshold concentration, the so called cmc (critical micelle concentration). The observed structures, micelles, liquid crystals and inverse phases, are also a function of the so called packing parameter introduced by Israelachvili et al. more than 30 years ago [4]. In the meantime more advanced theories for the self assembly of surfactants and other amphiphiles such as amphiphilic block copolymers have been developed [5], and they consider the modes of intermolecular interaction to explain the formation of the structures. Therefore, one can eventually expect new and exciting self assembled structures, if additional interaction modes come into play.

The latter is only one argument, why amphiphiles containing inorganic parts are thrilling, e.g. thinking of magnetic interactions due to paramagnetic species. There are many more reasons, why it could be highly tempting to combine amphiphilic design and the concept of organic inorganic hybrids (see also Scheme 1). The incorporation of metal cations to the head group of an amphiphile i.e. metallosurfactant [6], now gives interfacial surfactant systems a means to link the associated metal ion functionality to its amphiphilic structure. Inorganic matter provides numerous features (magnetism, redox variety, catalytic properties, higher electronic contrast, etc.), which are hard to realize for organics, but which would be highly desirable, if e.g. a surfactant/amphiphile has them [7]. Thus, surfactants with inorganic constituents (I SURFs) can be seen as belonging to the larger class of so called metallomesogens [8]. The term metallomesogens was introduced by Bruce et al. for molecular species showing the ability to form liquid crystalline (LC) phases comprising coordination complexes as building blocks [9]. In most of this early work one has concentrated on systems with thermotropic LC characteristics, for instance rod like or plate like

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Scheme 1. Classification and genesis of the emerging field 'hybrid surfactants and amphiphiles'.

metal compounds [10]. In the meantime, also some metal containing polymers and even inorganic particles forming LC phases or some supracrystals can be seen as belonging to metallomesogens [11].

However, this area still stands at the beginning and will be highlighted in the current article. In this sense, it should be noted that the aim of our manuscript is not to give a comprehensive overview here, but we have selected some of the most important, recent developments in this emerging research field dating back to the last decade. For further discussion, it makes sense to differentiate between two classes of amphiphilic hybrids (see scheme 1), dependent on, if the system has pure molecular character (class I), or, if constituents with nanoparticle characteristics are involved (class II). Three scenarios can be discussed for class I. The simplest strategy is to start from a conventional surfactant system (Scheme 1; Ia) and just add a metal component to it. The metal component is at most weakly bound to the surfactant. Typically, the inorganic metallic species is the counter ion of the surfactant head group (see also Section 2.1 of this paper). In alternative (Ic) the metal containing unit is the hydrophilic head group covalently linked to the hydrophobic tail. Thus, it has become an integral part of the surfactant (see Section 2.3). The situation in scenario (Ib) is somehow in between, and is best represented by a metal cation coordinated by a ligand linked to a hydrophobic chain (see Section 2.2). Hybrid amphiphilic systems can also be achieved when inorganic nanoparticles are combined with suitable molecular species as shown in Scheme 1/IIa. Another interesting case is realized, when two different nanoparticles with different solvent compatibilities can be joined together like shown in Scheme 1/IIb, or as a result form particles with Janus type characteristics [12]. The latter two topics will be highlighted in Section 3 of this article. It should also be noted that the assignments of the cases discussed in the

following to the defined classes are not absolutely strict, but the junctions from one area to the other are rather smooth.

2. Molecular hybrid amphiphiles

2.1. Surfactants with weakly bound metallic species

It is obvious that anionic surfactants with metal cations as counter ions represent the imaginable simplest I SURF system (see Scheme 1) [13]. The first examples for I SURFs (type Ia) were presented by Mirnaya et al. back in 1989, when the LC formation of alkali metal alkanoate ($M(OOCnH_{2n+1})$) ionic melts was discovered [14]. An interesting case was reported by Weber about the influence of self organization/packing on spin transition on Fe(II) I SURFs [15]. However, also cationic or neutral surfactants in combination with metal species deserve attention. The interaction of the cationic cetyltrimethylammonium surfactant with anionic, silicate species has led to the development of ordered mesoporous materials via the so called synergistic co assembly mechanism [16]. The hybrid surfactant/inorganic phase forms a lyotropic liquid crystal, which acts as a template for the generation of pores. Mesoporous materials have then defined an entirely new field by themselves.

Another interesting area is the combination of anionic metal species like palladates, aluminates etc. with cationic surfactants ions [17]. These form molecular systems that are very similar to surfactants with large, cationic heads. A nice demonstration of how the properties of the amphiphilic systems are enriched by inorganic constituents, comes from the area of ionic liquids (ILs) with metal containing counter ions [18]. Particular impressive examples have been published, when a magnetic counter ion was present [19]. For example, Eastoe showed in a nice paper in 2012 how magnetic ILs could be used to establish responsive surface properties [20]. Also other, less common counter ions like ferrocenyl anions can be used [21]. Some spectacular results, which deserve special attention, could be obtained by using the so called polyoxometalates (POMs) as negative counter anions for cationic ammonium surfactants [22].

POMs consist of multinuclear metal oxide building blocks $[MO_x]$ and are widely known for their interesting properties in catalysis and magnetism [23]. Because polyoxometalates as a class includes thousands of specific compounds, it is beyond the scope of the current paper to give a comprehensive overview of the POM field [23a]. POM SURF hybrid systems represent excellent examples for so called surfactant encapsulated clusters (SECs). Kurth and co workers created SECs by replacing the counter cations of anionic molybdovanadato POMs by long alkyl chained cationic ammonium surfactants [22b,24]. A close packing of the alkyl chains was observed, and it was concluded that there is a compact shell around the POM. The surfactant shell improves the stability of the embedded POM and its solubility in nonpolar, aprotic organic solvents. Our group presented a unique system [22e], which was some years later "adapted" by Cronin and coworkers [25]. Giant, donut shaped POMs were treated with a cationic, double tailed surfactant. It was found that the surfactant binds exclusively on the periphery of the inorganic POM cluster. A novel species forms with special, quadrupolar amphiphilic properties (hydrophilic, hard, inorganic core and hydrophobic, soft, organic shell). Self organization into columnar lyotropic liquid crystal (LLC) phases was reported. Noro et al. used a very similar system to demonstrate gas and vapor adsorption and catalytic properties in addition to the self organization properties [25]. In recent time surfactant complexes with smaller POM cores like the Keggin structure have moved into the focus of research. Zhang reported in 2013 the reversible redox controlled switching of the morphology of a SEC containing the $[Mo_6O_{19}]^{2-}$ (see Fig. 1) [26]. This example gives an idea of the complex self assembly characteristics and opens the door for manifold adjusting for tailor made liquid crystal phases, as not only the encapsulating surfactant but also the core can have an impact on self assembly behavior. Wu and Wang contributed extensively on this topic with their

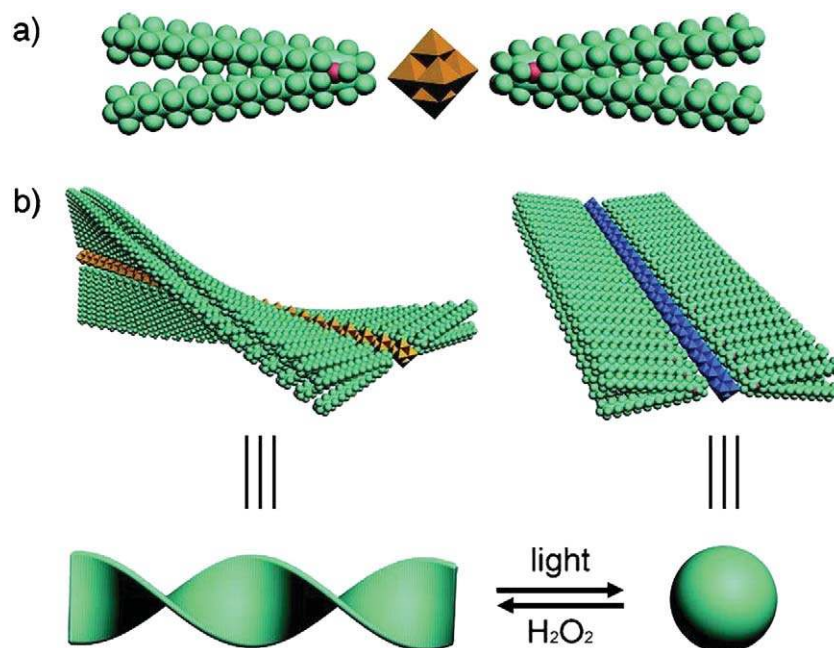


Fig. 1. Schematic of (a) chemical structure of $(\text{DODA})_2[\text{Mo}_6\text{O}_{19}]$ and (b) reversible morphological transformation between helical and spherical assemblies upon UV light reduction and H_2O_2 oxidation. Reproduced from Ref. [26] with permission. Copyright 2013, Wiley-VCH.

publications discussing the liquid crystalline systems. They also increased the complexity of the encapsulated cluster as they use additional transition or rare earth metal substituted POMs [27].

2.2. Amphiphilic ligands with coordinated metals

The access to new hybrid surfactants with a head group containing one single metal center is straightforward at first glance. The basic idea is that a charged metal complex fragment coordinates to a chelating, organic ligand, which is modified by one long alkyl chain. At second glance it becomes apparent that the latter approach is quite demanding. The successive reaction of the metal with a second ligand is generally not preferred, because it leads to compounds with less dipolar and

enhanced hydrophobic character. Consequently, for obtaining 1 SURFs it is favorable if the metal prefers low coordination numbers or the ligand contains a rather high number of chelating donor centers. Further difficulties arise, because it is actually not so easy to prepare asymmetric molecular species. The preparation of the required organic ligands can be quite tedious, and it might be difficult to attach only one hydrocarbon chain.

Macrocyclic cavities such as tetraazamacrocycles are known for complexing various metal cations making them suitable as potential head groups. Over the last decades several methods have been developed for functionalization towards mono alkylation of tetraazamacrocycles or other macrocycles [28]. First examples for the resulting hybrid amphiphiles, were given by Le Moigne et al., who were able to combine the metal binding properties of crown ethers with surfactant design [29].

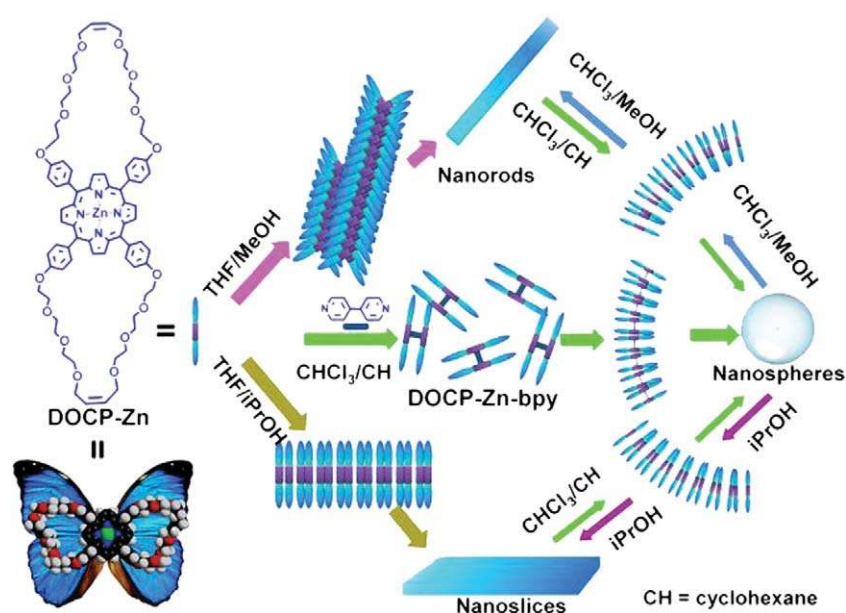


Fig. 2. Conversion between nanoslices (2D), nanorods (1D) and nanospheres (0D) of an amphiphilic Zn(II)-complex. Reprinted (adapted) with permission from Ref. [35]. Copyright (2012) American Chemical Society.

A similar surfactant system and its self organization behavior could be presented by Neve et al. [30]. Later Bruce et al. introduced the pioneering concept to use bipyridine derivatives and related compounds as ligands for the synthesis of I SURFs/type Ib (see Scheme 1) [31]. A double tailed surfactant with the vanadyl cation as a magnetic transition metal center was presented by Zhu and Swager [32]. Binnemans et al. have investigated the preparation of surfactants containing lanthanides. They presented tailor made ligands characterized by seven donor centers encapsulating the metal ion [13b,33]. Another nice example is a Tb(III) containing metallosurfactant showing an increase of luminescence as a result of chemical binding of nucleotides [34]. This made it possible to monitor biological processes as it has been observed that the luminescence from the Tb(III) showed a (127 fold) increase due to light energy absorbed by a guanine group of guanine triphosphate and transferred to the Tb(III) center. The nucleotides are able to bind at the vesicular surface and so a sensing system is created, which makes it possible to track the GTP (guanosine 5' triphosphate) to GDP (guanosine 5' diphosphate) conversion. This would not be possible with a classical organic amphiphile, and it is purely due to the nature of the inorganic metal ion that these amphiphilic systems exhibit such interesting properties.

The self assembly of a Zn(II) containing metallosurfactant can reversibly tune via controlled axial coordination of zinc porphyrin with 4,4' bipyridine, which results in 0D, 1D, and 2D structures (see Fig. 2) [35]. This hybrid surfactant has the ability to form different self assembled structure based on the metallosurfactants intramolecular interaction with different solvent that results into the controlled aggregation between nanorods, nanospheres and nanoslices based on a desired solvent combination used [35]. A Ru(II) polypyridyl porphyrin conjugate amphiphile, combines photo induced charge separation and enhanced cellular uptake properties into a single amphiphilic system as an effective photodynamic therapeutic anticancer agent [36]. Another interesting study was published by Iza et al. in 2015. Superior control over the aggregation behavior of a Ru(II) metallosurfactant could be achieved by further influence of cyclodextrins sliding off and on the hydrophobic chain [37]. A novel idea was presented in a paper by Schubert et al., who have linked two parts with different solvent compatibilities to each other via Ru(II) resulting in a unique hybrid block copolymer compound [38].

An investigation of the dynamics process that occurs during stem cell tracking has been achieved via positron emission tomography (PET) *in vivo* with hexadecyl modified DOTA (1,4,7,10 tetraazacyclododecane tetraacetic acid) benzoate labeled with the radioactive nuclide ^{64}Cu , which incorporates into a stem cell membrane and allows *in vivo* observation [39]. These findings are of outstanding interest, because they provide insight in distribution and dynamics *in vivo* without affecting the cell viability in a negative manner. In a case presented by our group, a magnetically susceptible dysprosium Dy(III) cation chelated to a long alkyl chained DOTA ligand, self assembled in panoscopic architecture in nano to macrometer range (see Fig. 3) as a result of the existing magnetic interaction [40]. The orientation dependence with respect to an externally applied magnetic field has a high potential for use in liquid crystal display (LCD) applications and magnetically triggered drug delivery. In addition, the ability to trigger self assembly using an externally applied magnetic field opens a door for the possibility of using different magnetic field strengths to study the aggregation and dynamic of molecular self assembly. Other I SURFs containing strong paramagnetic ions have been of interest due to their potential as contrast agents in magnetic resonance imaging (MRI) rather than for their self assembly properties [41].

Some rare cases of surfactants containing organometallic species (C metal bonds) were described. Many of these compounds comprise complexes with Cp (cyclopentadienyl anion) due to their sufficient stability in protonic solvents, ultimately in water. Li et al. described a Rh Cp I SURF used in enantioselective catalysis [42]. An inverted, hydrophobic hydrophilic motif was presented by Shen et al. with an I SURF containing ferrocene in the hydrophobic moiety [43]. Fascinating work was

also presented by Gohy et al. on ferrocenylsilane block copolymers showing numerous amphiphilic properties [44]. We succeeded in the preparation of another organometallic I SURF containing an alkyl alkoxy zinc cluster attached to two polyethylene glycol as a polar chain [45]. Interestingly, this new organometallic amphiphile self assembles over several length scales. First, the dimers form a lamellar phase via a microphase separation of the hydrophobic oxo cluster entities and the polar PEG domains indicated by polarization microscopy, SAXS and TEM [45]. In contact with apolar solvents like toluene swelling of the hydrophobic domains and further structuring occurs surprisingly into relatively monodisperse spheres.

These spheres agglomerate into a close packing structure, which due to the dimension of the single spheres (200 nm in size) behaves like an optical grating diffracting light in the visible range. The latter leads to the emergence of blue color, although the system does not contain any chromophore. In comparison to traditional amphiphiles, the discussed system is also different because it contains an additional function: the ability to act as a precursor for ZnO [45]. Indeed, a bimodal, macro nano porous ZnO could be generated directly from the nano structured gel and the morphology of the ZnO was directly influenced by the morphology of the $[\text{MeZnOPEG}]_2$ phase.

2.3. Surfactants with pure inorganic heads

Examples of surfactants with purely inorganic head groups (Scheme 1; type Ic) are much more rare, and the first cases have been published only very recently. The attachment of multinuclear transition metal entities as head to an organic alkyl chain is very difficult because many M-X linkages (X = C, O, N) are susceptible to hydrolysis. Obviously, cleavage of the alkyl chain in water would destroy any amphiphilic properties.

However, recent activity in the field of polyoxometalate chemistry (POM) delivered some highly innovative surfactant species that were stable in water, and some nice studies about their self assembly have been published [46]. An important step towards monomolecular POM amphiphiles is the capability of a controlled organic modification of POM clusters to create a fixed amphiphilic molecule. The main route for heteropolyoxometalates starts from lacunary species. Those clusters are lacking one or more $[\text{M} = \text{O}]$ units and therefore present reactive oxygen atoms, where negative charge is localized. At those sites organic groups can easily be attached via condensation reactions. A detailed discussion of functionalization of polyoxometalates would go far beyond the scope of this article. Further information on this topic is provided by Proust et al. and Dolbecq et al. [23b,47].

An early amphiphilic POM system starting from a tris (hydroxymethyl)aminomethane (TRIS) modified Mn Anderson POM was presented by Zhang et al. [48]. Two alkyl chains were capped onto each site of the $[\text{MnMo}_6\text{O}_{24}]$ cluster via amide bonds. It was shown that the amphiphilic system self assembles into large vesicular structures. This was the first example for POM amphiphiles arranging in vesicles. However, the latter system has two disadvantages. The amphiphile is insoluble in water due to the presence of the bulky tetrabutylammonium ions. Self assembly could only occur when significant amounts of acetonitrile were added. Furthermore, the geometry of the amphiphile is unfavorable with respect to the ideal dipolar character of a surfactant, because the hydrophobic tails are symmetrically attached on each site of the head group. As a consequence, the tails have to bend significantly to form a vesicular structure. This makes the vesicle formation more difficult and the self assembly process takes more time compared to classical surfactants. Nevertheless, an amphiphile possessing the latter geometry is more appropriate to self assemble in apolar solvents to form reverse aggregates [49].

Our group has presented polyoxometalate I SURFs with a lacunary $[\text{PW}_{11}\text{O}_{39}]$ head group [50]. It could be shown that this system has all functionalities of classical surfactants, like the ability to form micelles, emulsions, lyotropic liquid crystals, monolayers at the water/air

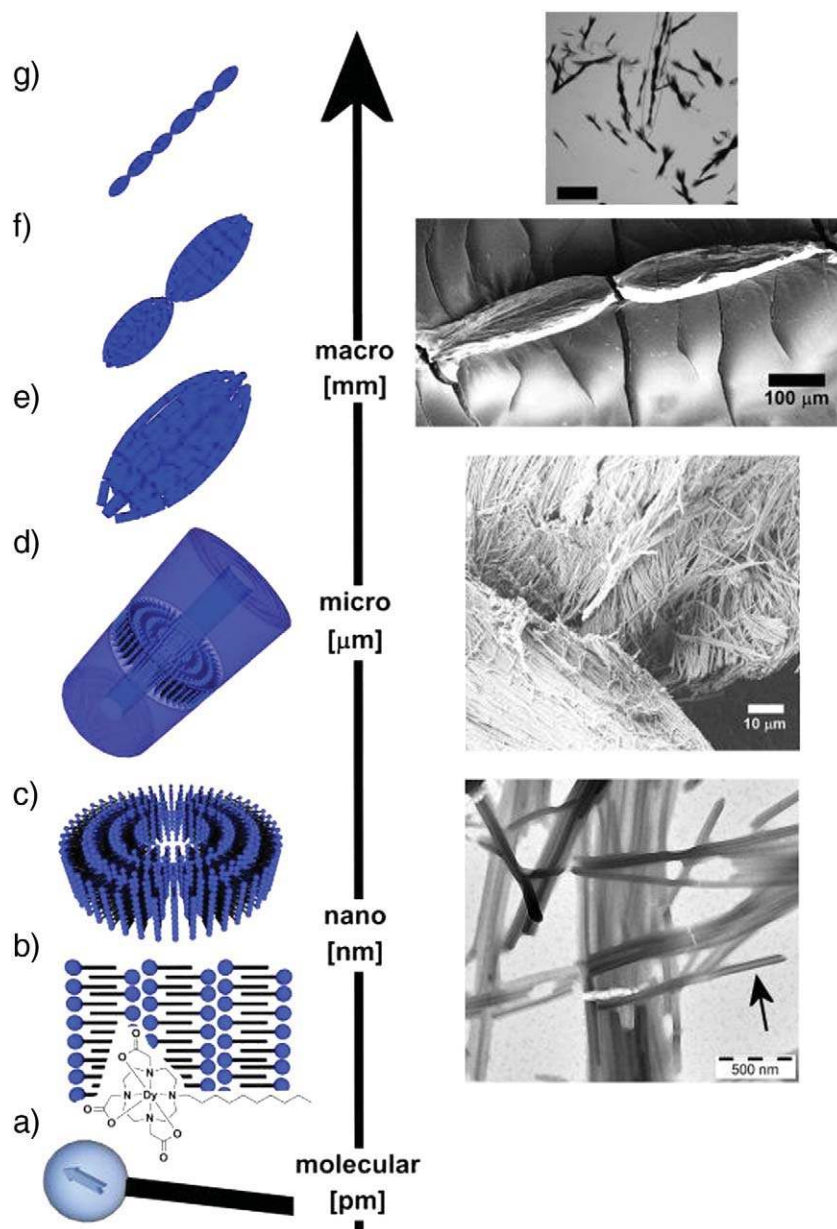


Fig. 3. Panorpic architecture resulting from the hierarchical self-organization of $[\text{Dy-C}_{10}\text{DOTA}]$ and some corresponding analytical data (TEM, SEM, optical microscopy) [40]. (a) The magnetic moment located at the head group is indicated. b) Lamellar structures with interdigitating inorganic surfactants. c, d) Hollow fibers with multilamellar substructure. e) Tactoid. f) Tactoid dumbbell. g) Chains of tactoids.

interface and also ultra small monolayer vesicles [51]. The observation of all of the latter structures is aided by the enormous electronic contrast of the tungstate head group [52]. A nice demonstration for the additional functionality of hybrid surfactants was discussed by us in 2012 [53], when the redox properties of a bimetallic Ru POM I SURF were analyzed. It was shown that the charge of the head group could be varied reversibly from $-1 \leftrightarrow -2 \leftrightarrow -3 \leftrightarrow -4$. This unique property of the surfactant enabled triggering of the mode of self assembly via electrochemistry [53]. It goes without saying that the introduction of the polyoxometalate as a head group of an amphiphile has broadened the chemical and physical properties of amphiphiles tremendously and this has opened a door to quite a broad range of applications.

Alternative inorganic entities might be used for the creation of new hybrid surfactants, when linkages stable against water can be used. Two candidates can be identified from the current literature: polyhedral oligomeric silsesquioxane (POSS) and fullerenes. It should be noted that the simple hydrophobic hydrophilic balance can no longer be applied

here directly, because POSS and fullerenes are characterized by substantial hydrophobicity themselves. Therefore, it is important that the attached side chains are different concerning their solvent compatibility. The most common POSS used consists of eight RSiO units that form a highly soluble cage like structure with corner groups that are accessible for further functionalization [54], for instance with polyethylene oxide (PEO) as a polar group [55]. The amphiphilic character created this way also leads to interesting self organization behavior as reported in several other recent publications [56].

Fullerenes, with C_{60} as the most prominent example, are inorganic molecules, which however can be used in organic reactions. They behave like linearly conjugated alkenes, with respect to their chemical reactivity. This makes it possible to apply the addition chemistry known for CC double bonds. Fullerene derivatives that bear aliphatic chains have recently emerged as a new class of hybrid 'hydrophobic surfactants' and the concept was recently discussed by Nakanishi, Schenning et al. and Asanuma et al. [57,58]. The individual head and

tail groups of these amphiphiles are both hydrophobic making these amphiphiles insoluble in water. However, these alkyl fullerenes are compatible in alkyl or aromatic solvents due to the different solvent affinities of the alkyl and fullerene groups of these two solvent types. Note the different self assembled structures shown in Fig. 4 [58a,59]. The amphiphilicity of these alkyl fullerenes arises furthermore due to the electronic gradient between the rigid fullerene head and flexible tail groups. This gradient between head and tail groups results in different solvophobic interactions allowing these amphiphiles to self assemble into different structures. In solution the alkyl fullerene amphiphiles self assemble to minimize contact to its solvophobic parts with the solvent. It is therefore believed that the improved solubility of these hybrid surfactants is caused by the mentioned clustering, which results in unfavorable interactions between the fullerene head group and n alkane molecules [59b].

Furthermore, the self organization of alkyl fullerenes is also governed by a gentle balance between weak $\pi-\pi$ interactions between fullerene head groups and van der Waals intermolecular forces among neighboring hydrocarbon alkyl chains. It is due to these weak interactions that it is possible for this class of amphiphiles to display polymorphism under various externally applied factors such as temperature, solvation effects and concentration, which is an extremely rare phenomenon (see Fig. 5) [57,60]. The self assembly morphologies of alkyl fullerenes range from monolayers [61], bilayer vesicles [59a,62], nanorods and wires [63], thin disks, fibrous, columnar liquid crystal [64], and room temperature liquids [65], to name only a few. Alkyl fullerene systems have potential for multiple molecular and self assembly applications ranging from antioxidant capacity [66], small molecule based bulk heterojunction (BHJ) organic solar cell devices [67], nanocapsules with potential applications as drug delivery systems [68], and emerging photovoltaic and optoelectric devices [69]. It can be concluded that it is appropriate to classify alkyl fullerenes as hybrid amphiphiles, despite the fact that they do not possess the classical hydrophobic/hydrophilic block molecular architecture of surfactant used in water.

3. Particle-based hybrid amphiphiles

It is well known that particles themselves are interfacial active, which is the basis for the formation of pickering emulsions or play a

role in important applications like flotation [70]. However, in line with Scheme 1, here, we only want to consider systems containing at least one nanoparticle and characterized by a substantial amphiphilic, dipolar character, respectively a substantial difference in solvent compatibility. Often these systems are described in the literature as Janus particles, a topic which has already been reviewed extensively in the literature [71]. The term 'Janus' describes anisotropic entities by coupling two or more dissimilar components at a small junction, exposing two regions for optimal expression of their combined functionalities.

3.1. Organic inorganic particle hybrids

In case the linkage between the nanoparticle and the molecular species to attach is very strong, like for covalent bonds, various methodologies have been developed for modification of only one side of a particle [71]. For instance, one can immobilize the particle on a substrate, and only its opposite surface is accessible to modifications. However, in most cases the interaction between surfaces of solid inorganic materials and organic compounds has a dative character between low coordinated surface centers (e.g. metal cations) and donor groups in the organic additive (e.g. $-\text{COO}^-$). Because this kind of linkage can be weak, and highly reversible in character, it has proven to be quite difficult to prepare hybrid amphiphiles type IIa (see Scheme 1) using inorganic particles, because sooner or later there would be an equally distributed organic shell all around the particle. It is very hard to maintain an anisotropic distribution. However, two strategies exist, which have to be explored much further in future research.

It is well known that nanocrystals have different surfaces corresponding to different facets of the crystal lattice [11g]. Eventually this can lead to a different density of organic capping agents attached to the different surfaces. As a result there may be a slight anisotropy and amphiphilic character leading to self assembly and the formation of ordered particle superstructures, resembling liquid crystals [72]. Another approach is, if it is possible to partially modify one particle exclusively only with one organic molecule (see Scheme 1/IIa). For larger nanoparticles it is extremely hard to secure that only one species interacts with the surface by avoiding multiple bonding. However, when the inorganic particles are very small, e.g. for inorganic clusters, some successful and interesting cases have been reported in the literature. For instance Fujii et al. have described in 2013, how one side of a 2 nm Au

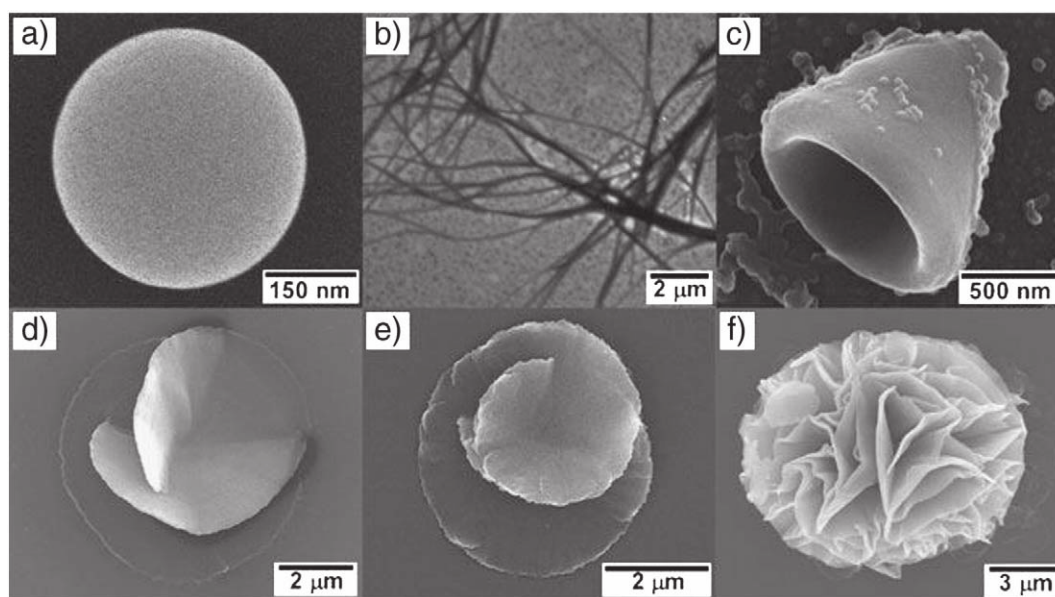


Fig. 4. SEM images of fulleropyrrolidine with 3,4,5-(hexadecyloxy) phenyl amphiphile displaying self-assembly polymorphism (a) vesicular in 2-propanol/toluene, (b) fibrous in 1-propanol, (c) cone-shaped in water/THF (d) left-handed, (e) right-handed spiral object in 2-(R)-butanol and 2-(S)-butanol respectively, and (f) flowerlike assemblies in 1,4-dioxane at 60 °C. Reprint with permission from Ref. [57], Copyright (2010) Royal Society of Chemistry and Copyright 2007, Wiley-VCH.

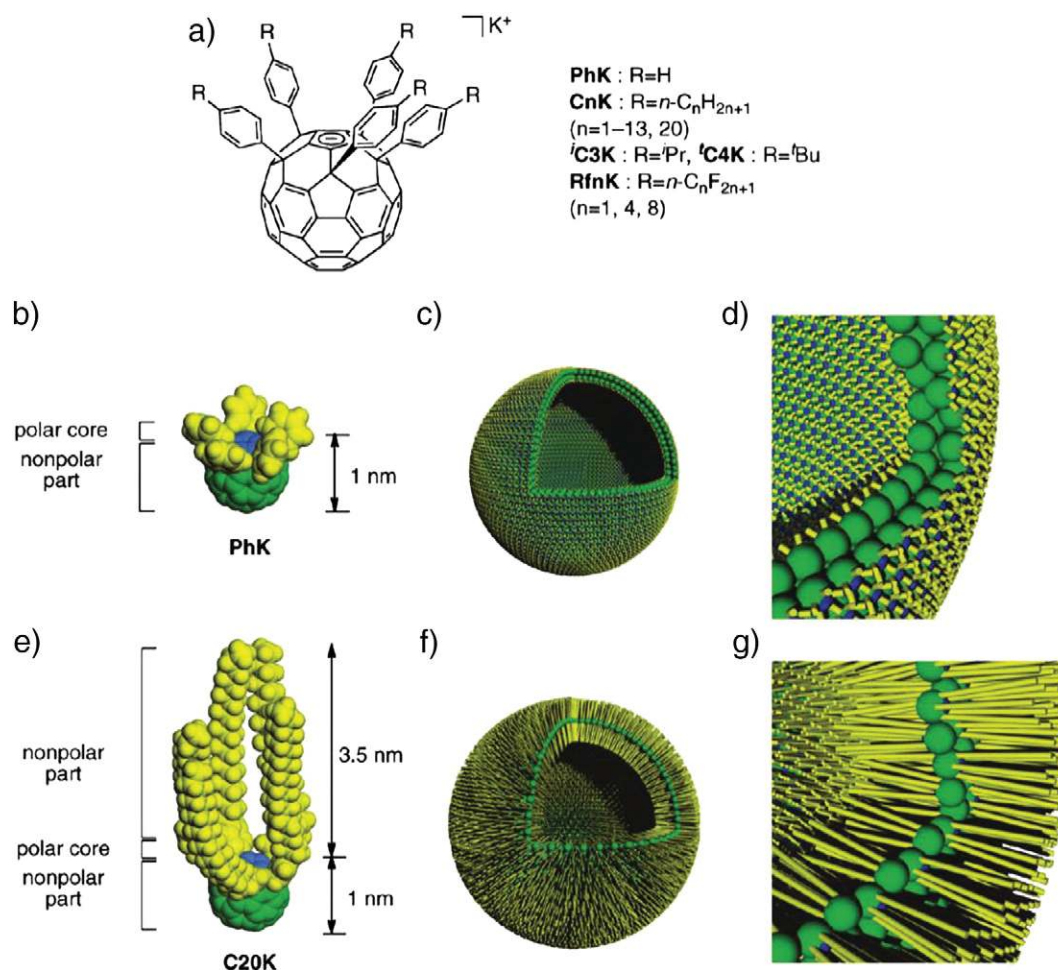


Fig. 5. Schematic images of vesicles made of fullerene anion of surfactants. (a) Chemical structures of potassium complexes of fullerene anions. (b) CPK drawing of PhK. (c) Schematic model of bilayer vesicle of PhK. (d) A magnified image of the bilayer PhK vesicle. (e) CPK drawing of C20K. (f) Schematic model of a vesicle of C20K. (g) A magnified image of the interdigitated bilayer of the C20K vesicle. The fullerene parts are shown in green, the hydrophilic parts in blue, and substituents in yellow. Reprinted with permission from Ref. [35]. Copyright (2011) American Chemical Society.

nanoparticle was stuck inside the cavity of a cysteine modified calixarene [73]. The novel hybrid compound had amphiphilic properties and showed interesting self assembly features. Very recently Yao et al. showed that the capping agents around an Au_{25} could be switched from an isotropic distribution around the cluster core, to an anisotropic state with amphiphilic character [74].

3.2. Particle particle Janus systems

Much more cases have been reported for the combination of two types of particles with each other, often resulting in amphiphilic properties. The number of combinations is almost endless with organic organic, organic inorganic and inorganic inorganic representing only the major classes [71]. However, it is very difficult to join exactly two different particles together to a new hybrid amphiphile (case IIb in Scheme 1). Frequently, one finds in the literature reports about hybrid particles formed by the assembly of several nanoparticles gaining amphiphilicity via a partial microphase separation. A good example for the latter is Janus particles bearing organic inorganic composite such as Fe_2O_3 and TiO_2 , self assembled into dual phase quasi spherical material via introducing amphiphilic polymers [75]. The amphiphilic nature of these particles allows the formation of stable dispersions and higher aggregates in solution.

Only few and very recent examples should be discussed here for situation IIb (Scheme 1). One example is on dumbbell shape amphiphilic Janus $\text{Au}(\text{Fe}_3\text{O}_4@\text{SiO}_2)$ nanoparticles [76], with tunable wettability

and enhanced catalytic properties. The system is capable of cell internalization, which is making it a good material for application in the field of magnetic resonance imaging (MRI) and drug delivery. Furthermore, the availability of anisotropic magnetic susceptibility allows the manipulation of the particle orientation interaction with respect to an externally applied electric and magnetic field inducing rotational motion relative to the applied field. This offers a means to influence the mode of self assembly of these systems due to the inorganic constituent. Li et al. showed in 2014, how an interesting Fe_3O_4 graphene hybrid amphiphile can be prepared, and they indicated how the material could be applied as novel supercapacitors [77]. The amphiphilic properties of $\text{Au}(\text{Fe}_3\text{O}_4)$ Janus nanoparticles were studied by Sahoo et al. in an impressive paper, showing their ability for the colloidal stabilization of WS_2 nanotubes [78]. Very unusual modes of self assembly and superstructure formation were reported by Zhao et al. for a hybrid amphiphile composed of Au and CdSe [79].

4. Conclusions

Despite the fact, that only several cases were highlighted here, the previous paragraphs have clearly shown that the creation and investigation of hybrid amphiphiles are an emerging topic with high potential. Researcher could already obtain some fascinating results. Compared to pure organic surfactants and amphiphiles, one can see that the mode of self assembly is often more complex, sometimes spans several length scales. This is mostly due to additional intermolecular interactions

between the constituents different to van der Waals and electrostatics only. Furthermore, it could be seen that numerous cases exist, showing that there is not only a combination of amphiphilic features with the properties of the inorganic constituent (e.g. special electronic, catalytic properties, etc.), but that the hybrid materials have new characteristics that none of the single components have by themselves, e.g. certain stimuli responsive properties. Thus hybrid amphiphiles are truly fulfilling their promise for the existence of emergent phenomena and systemic features.

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