Magneto-Adaptive Surfactants Showing Anti-Curie Behavior and Tunable Surface Tension as Porogens for Mesoporous Particles with 12-Fold Symmetry

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Abstract: Gaining external control over self-organization is of vital importance for future smart materials. Surfactants are extremely valuable for the synthesis of diverse nanomaterials. Their self-assembly is dictated by microphase separation, the hydrophobic effect, and head-group repulsion. It is desirable to supplement surfactants with an added mode of long-range and directional interaction. Magnetic forces are ideal, as they are not shielded in water. We report on surfactants with heads containing tightly bound transition-metal centers. The magnetic moment of the head was varied systematically while keeping shape and charge constant. Changes in the magnetic moment of the head led to notable differences in surface tension, aggregate size, and contact angle, which could also be altered by an external magnetic field. The most astonishing result was that the use of magnetic surfactants as structure-directing agents enabled the formation of porous solids with 12-fold rotational symmetry.

The spontaneous formation of organized patterns as an intrinsic property of a system containing discrete constituents, a process termed self-assembly, has fascinated scientists for decades. Nature shows the enormous potential of such behavior, since many of the unexcelled properties of biological matter originate from its capacity for adaptive self-assembly.[1] Full exploration of this potential in materials science is still remote, as most reported examples of self-assembly so far are dictated by internal factors, such as

thermodynamic equilibrium.[2] Systems reaching a state of higher order only under constant consumption of energy (dissipative, non-equilibrium state) have seldom been reported.[3] A premise for advancing research in this direction is that compounds capable of adaptive self-assembly can be equipped with the ability to be actuated externally. Examples from particle research, such as dispersions of superparamagnetic colloids,[4] demonstrate the promise of manipulation by the use of magnetism, because it can be applied in a static or dynamic way, and unlike electric fields, magnetism is not damped in aqueous electrolytes. Thus, it is worth exploring the use of external magnetic fields to trigger the self-organization of molecular systems.

As model systems for the self-assembly of soft matter, surfactants are the focus of much current interest. Surfactants are molecular species that contain two moieties of opposite solvent compatibility arranged in a dipolar geometry. In polar solvents, usually water, concentration-dependent self-organization takes place. The amphiphilic properties of surfactants make them suitable for the stabilization of interfaces of many kinds, for example, for the generation of nanoparticles or nanoporous materials.[5] The typical head group of surfactants is organic in nature and, thus, diamagnetic. To make a surfactant magnetic, one of its constituents should contain a paramagnetic metal species. This emerging field was reviewed very recently by Eastoe and co-workers.[6] Most known examples involve surfactant-like systems with paramagnetic ions as counterions for a charged head group.[7] A nice case was described in 2012 involving cationic surfactants with $M^{III}X_4^-$ counteranions.[8] In 2014, Degen et al. investigated organic surfactants with paramagnetic $FeCl_4^-$ as a counterion and concluded that there is no special "magnetic surfactant effect".[9] This last study motivated us to invest effort in preparing compounds in which the transition-metal species is an integral part of the head group.[10] One can expect that a magnetic torque will act directly on the surfactant molecule under appropriate conditions. We intended to explore this effect in our current study.

We recently described the unusual self-assembly of Dy^{3+} coordinated to a multidentate ligand based on 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTA) modified with a long alkyl chain.[11] The net charge of deprotonated DOTA was fully neutralized by Dy^{3+}, thus reducing the surfactant character.[11] For better surfactant-like character, a charged head group is preferred. Thus, DOTA should be coordinated to either M^{2+} or to M^{4+}. Plenty of

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https://doi.org/10.1002/anie.201612416.
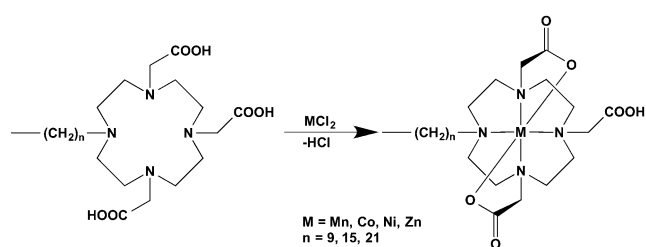
Scheme 1. Synthesis of MC$_n$DOTA surfactants (M = Mn, Co, Ni, Zn).

redox-stable metal cations M^{2+} are available, and robust complexes of DOTA exist also with d-block metals,[12] many of them paramagnetic. We describe herein the series shown in Scheme 1 (see Table S1 in the Supporting Information for all compounds prepared for the current study).

Electron spray ionization mass spectrometry (ESIMS) is a powerful tool for investigating the molecular composition of hybrid surfactants.[11,13] The anion patterns observed were in agreement with the masses for the deprotonated molecular ions [MC$_{30}$H$_{55}$N$_4$O$_6$]$^-$ (Figure 1 a,b). By ESIMS alone one can not prove with certainty that the metal cation is coordinated
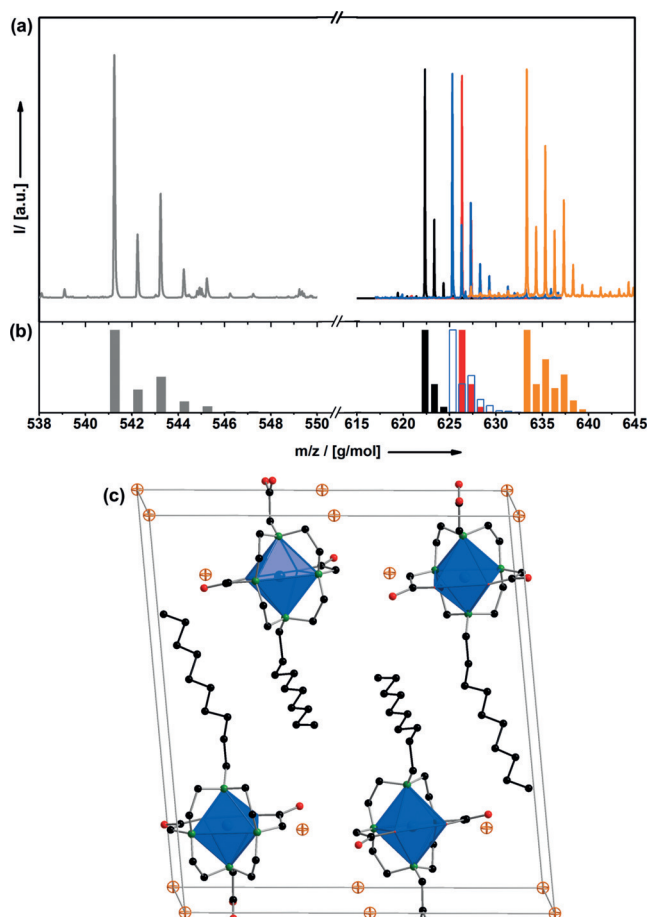

Figure 1. a) Experimental and b) simulated ESIMS patterns of NiC$_{10}$DOTA (gray) and MC$_{16}$DOTA (Mn = black, Co = red, Ni = blue, Zn = orange). c) Packing diagram of NiC$_{10}$DOTA.[14] C black, N green, O red, O (water) orange, Ni blue; H atoms are omitted; gray lines denote the unit cell.

as depicted in Scheme 1. It could also be just a counterion. The latter question could be clarified by X-ray diffraction analysis of single crystals, which could be grown for compounds with a short alkyl chain, for example, NiC$_{10}$DOTA (Figure 1 c). Ni^{2+} adopts an octahedral coordination, and the carboxylic group in the *para* position to the alkyl chain is free (see also SI-1 in the Supporting Information), thus making the surfactants anionic. From further data (see SI-2), we concluded that the coordination was the same for all MC$_n$DOTA complexes. Compounds with M ≠ Zn were high-spin complexes (Mn$^{II}_{J=5/2}$ > Co$^{II}_{J=3/2}$ > Ni$^{II}_{J=2/2}$), as confirmed by super-conducting quantum interference device (SQUID) measurements and electron paramagnetic resonance (EPR) spectroscopy (see SI-3).

We performed a series of tests to probe typical surfactant properties (see SI-4). All MC$_n$DOTA complexes formed fairly stable foams. Furthermore, water/oil emulsions could be made, and their stability was satisfactory, as examined by dynamic light scattering (DLS). We focus herein on MnC$_{16}$DOTA because it has the biggest magnetic moment in the discussed series. The critical micelle concentration (cmc) of MnC$_{16}$DOTA was determined by tensiometry to be 40 mg L^{-1} (see SI-5). The magnetic properties of the micellar dispersion were examined by EPR spectroscopy (Figure 2 a). Mn^{2+} is ideal because there exists only one stable isotope, the *g* and hyperfine tensors are almost isotropic, and hyperfine coupling of the ^{55}Mn nuclear spin with the unpaired electrons leads to six narrow, equidistant lines. As compared to the spectrum of free Mn^{2+} in aqueous solution,[15] broadening of the signals is observed as a result of dipolar coupling and the proximity of the head groups in the micellar corona.

The temperature-dependent magnetic behavior of MnC$_{16}$DOTA was surprising. In contrast to normal paramagnets, which obey the Curie law ($M \propto \chi_m = C/T$), the magnetization of MnC$_{16}$DOTA increases with increasing temperature (Figure 2 b). Furthermore, there is a crossing in the temperature region of 285–287 K, as also observed by DLS (Figure 2 b). One aggregate species exists in solution whose size is almost constant between 278 and 287 K and corresponds to micelles (Figure 2 c; see also Figure SI-6). Notable growth follows at $T > 287$ K. We concluded that there is a transition around this temperature from spherical micelles to rodlike micelles (see Figure 2 d). Unlike spherical micelles, rodlike micelles possess magnetic anisotropy and, thus, an increased response to an external magnetic field. In addition to DLS data (see also Figure SI-6b), our hypothesis is supported by the results of our investigation of optical birefringence in an external magnetic field (Cotton–Mouton effect).[16] For diamagnetic ZnC$_{16}$DOTA, there is the expected linear change in the difference in refractive index (Δn; Figure 2 e). MnC$_{16}$DOTA behaves differently. The pronounced and nonlinear correlation is in agreement with the formation of anisotropic micelles aligning with the magnetic field.[17] Finally, by high-resolution transmission electron microscopy (HRTEM) under cryogenic conditions, it was observed MnC$_{16}$DOTA truly formed anisotropic micelles, whereas the micelles of ZnC$_{16}$DOTA remained spherical (Figure 2 f,g). Because the surfactants are almost identical in shape, effective head-group area, and charge, the effects can
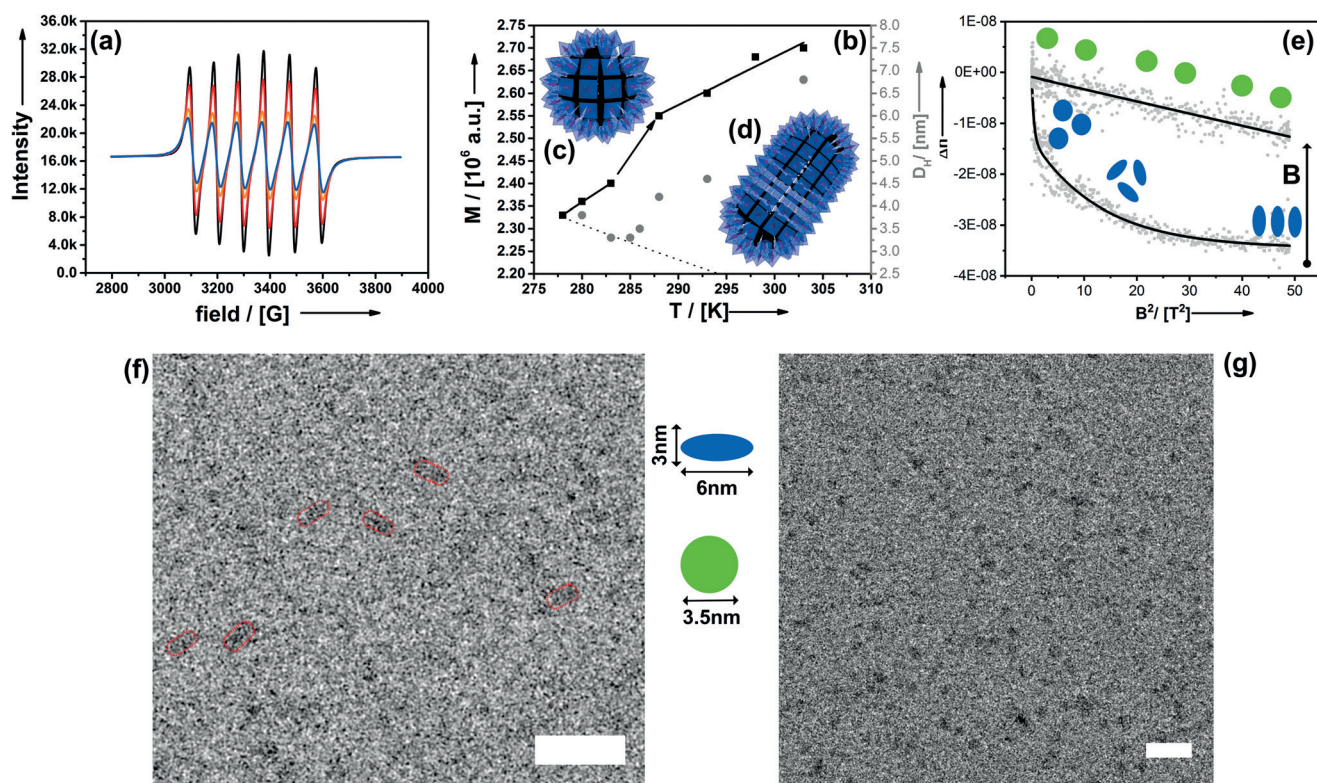
Figure 2. a) EPR spectra of MnC$_{16}$DOTA micellar solutions recorded at 278 (blue), 283 (orange), 293 (red), and 303 K (black). b) Magnetization (black) and aggregate size (gray). Ordinary Curie behavior is indicated by the gray dotted line. A transition from isotropic (c) to anisotropic micelles (d) was observed. e) Optical birefringence measurements for MnC$_{16}$DOTA micellar solutions (lower points) and ZnC$_{16}$DOTA as a reference (upper points). f,g) Corresponding cryo-TEM data for MnC$_{16}$DOTA (f) and ZnC$_{16}$DOTA (g); scale bars: 20 nm.

not be explained by geometrical considerations (see also Figure SI-6c).

Surface tension (γ_{GL}) is a key parameter containing information about the intermolecular interaction between surfactants.[18] For an increased attraction between the surfactant molecules (at constant size and shape), not only does the surface tension drop as the magnetic moment decreases (Figure 3a), but one would also expect an increase in aggregation number,[19] and thus in the micelle diameter. Because the interaction between the heads is altered by an external magnetic field, for a paramagnetic surfactant there should be a change in γ_{GL}. $\Delta\gamma_{GL}$ can be determined indirectly from the Young equation ($\Delta\gamma_{GL} = (\gamma_{SG} - \gamma_{SL})/\cos\Delta\theta$). Contact angles were determined from sessile drops of an aqueous phase containing MC$_{16}$DOTA in the presence and absence of a magnetic field (Figure 3b–e). The contact angle for M = Zn is lower than that for Mn, which is consistent with the γ_{GL} sequence described before (Figure 3a). More importantly, the shape of the droplet containing ZnC$_{16}$DOTA did not change in the presence of a B field (Figure 3b,c). For MnC$_{16}$DOTA, the field led to an enhanced wetting of the surface (Figure 3d,e), and the lower contact angle indicates a magnetically triggered decrease in γ_{GL}. Because of the large binding constant ($\ln\beta = 20.2$) of DOTA, free Mn^{2+} in solution does not exist.[20] We also excluded by performing additional reference experiments (see SI-7) that similar can be made for free Mn^{2+}. The incorporation of the paramagnetic metal in the head group is crucial.

One of the most prominent applications of surfactants is as porogens for the synthesis of ordered mesoporous materials.[21] Previously described methods were adapted to include either the ZnC$_{16}$DOTA or MnC$_{16}$DOTA surfactant as a structure-directing agent. With diamagnetic ZnC$_{16}$DOTA (see SI-8), polydisperse silica particles with a spherical shape were formed. Small-angle X-ray scattering, TEM, and physisorption analysis revealed that those particles had a prototypical mesostructure. When MnC$_{16}$DOTA was used under otherwise identical conditions (see the Supporting Information), regularly shaped particles with flat surfaces were observed (Figure 4a,b; see also SI-9). By SEM and TEM analysis, we observed that the particles consisted of densely packed objects (ca. 5 nm in size), which according to energy-dispersive X-ray spectroscopy (EDX; see SI-9d) were composed of MnC$_{16}$DOTA. The shape of the mesoporous particles is astonishing because 12-fold rotational symmetry could be an indication for quasicrystals. Conclusive proof of quasicrystallinity is hard to obtain because very sophisticated electron microscopy and diffraction methods have to be applied for materials with nanoscale "periodicities",[22] and even then it is very hard to differentiate a quasicrystal from a twinned system.[23] Furthermore, the prismatic shape indicates that the current system could be a 2D quasicrystal with structural disorder in terms of the elongated axis.[24] Gao and co-workers[25] obtained quasicrystalline mesoporous silica with *N*-myristoyl-L-glutamic acid as a surfactant and discussed a "mesocage–mesocage interaction", which relies on
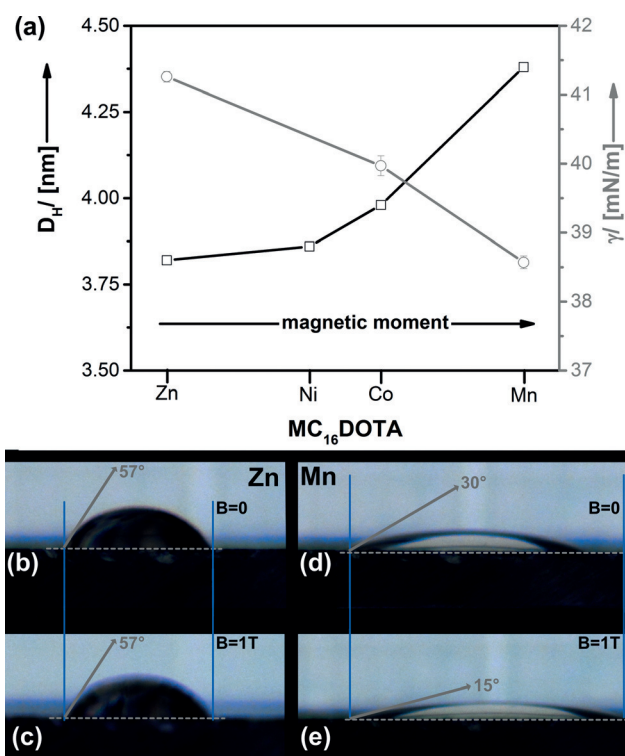
Figure 3. a) Comparison of micelle diameter (black curve) and γ_{GL} (gray curve) for different surfactants MC$_{16}$DOTA in the absence of an external magnetic field. b–e) Contact-angle analysis of sessile drops containing ZnC$_{16}$DOTA (left) and MnC$_{16}$DOTA (right) before (b,d) and during the application of a magnetic field (c,e).
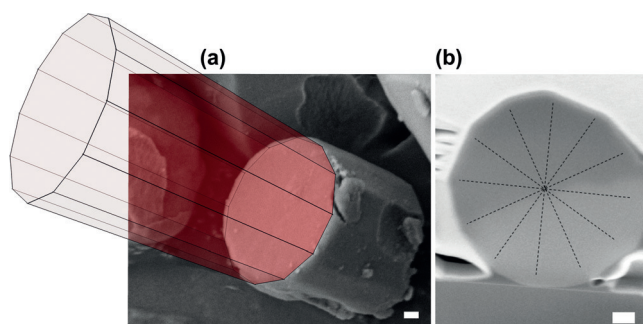

Figure 4. a) SEM of a silica particle prepared by the use of MnC$_{16}$DOTA as a structure-directing agent; scale bar: 200 nm. b) Particle cross-section prepared by focused ion beam cutting; scale bar: 200 nm. Dashed lines show the 12-fold symmetry. See also SI-9 for further electron microscopy data.

different degrees of protonation of the surfactant controlling the intermolecular interaction. In our case the interaction is not electrostatic but magnetic, based on the differentiation of diamagnetic and paramagnetic species, and could also lead to a mesocage effect. Because our surfactants react even to weak magnetic fields, and during preparation the dispersion was magnetically stirred, a potential mesocage effect can not be excluded.

We have presented a series of surfactants, which were varied systematically with respect to the magnetic moment of

their hybrid organic–inorganic heads while their shape and charge remained constant. The magnetic moment is not only important with regard to surfactant self-assembly, but owing to its long-range character and the absence of shielding in aqueous electrolytes, magnetism was shown to be a strong tool for controlling the system externally. We expect magnetic surfactants to be useful in various fields, for example, in the development of stimuli-responsive micelles and emulsions. One can also imagine that (nano)particles prepared by the use of magnetic surfactants as capping agents could then be separated readily from the reaction mixture even though the particles themselves are not magnetic.

Conflict of interest

The authors declare no conflict of interest.

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