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Magneto-Adaptive Surfactants Showing Anti-Curie Behavior and Tunable Surface Tension used 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 of extreme value for the synthesis of diverse nanomaterials. Their self-assembly dictated by microphase separation, 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 about surfactants with heads containing tightly bound transition metal centers. The magnetic moment of the head is varied systematically while keeping shape and charge constant. It is proven the magnetic moment of the head leads to notable difference in features like surface tension, aggregate size, contact angle and can also be altered by an external magnetic field. The most astonishing result is, that magnetic surfactants used as structure-directing agents can lead to 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 scientist since decades. Nature leads the way to an enormous potential since many of the unexcelled properties of biological matter originate from the ability to achieve adaptive self-assembly.[1] Full exploration of this potential in materials science is remote because, yet, most examples of self-assembly reported in the literature are dictated by internal measures, thermodynamic equilibrium.[2] Systems reaching a state of higher order only under constant consumption of energy (dissipative, non-equilibrium state) have been reported seldom.[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, e.g. dispersions of superparamagnetic colloids,[4] demonstrate manipulation using magnetism is promising, because it can be applied in a static or dynamic way and unlike to electric fields magnetism is not damped in aqueous electrolytes. Thus, it is worth to discuss, if alternative, molecular systems capable of self-organization can also be triggered by external magnetic fields.

As model systems for self-assembling soft matter, surfactants are in focus of current interest. Surfactants are molecular species, which contain two moieties of opposite solvent compatibility arranged in dipolar geometry. When given into polar solvents, usually water, concentration-dependent self-organization takes. The amphiphilic properties of surfactants make them suitable for the stabilization of interfaces of many kinds, for instance for the generation of nanoparticles or nanoporous materials.[5] The typical head-group of surfactants is organic in nature and, thus, it is diamagnetic. For making a surfactant magnetic one of its constituents should contain a paramagnetic metal species. This emerging field was reviewed very recently by Eastoe and coworkers.[6] It can be seen that most examples known from the literature involve surfactant-like systems with paramagnetic ions as counter-ions for a charged head-group.[7] A nice case was described in 2012 on cationic surfactants with $M(III)X_4^-$ counter-anions.[8] In 2014 Degen et al. investigated organic surfactants with the paramagnetic $FeCl_4^-$ as a counter-ion and concluded that there is no special "magnetic surfactant effect".[9] The latter paper underlines our motivation, that it is important to invest the effort to prepare compounds in which the transition metal species is an integral part of the head group.[10] One can expect that a magnetic toque will direct act on the surfactant molecule under appropriate conditions. This is, what we intend to explore in our current paper.

We recently described the unusual self-assembly of Dy^{3+} coordinated to a multidentate ligand (DOTA) modified by a long alkyl chain.[11] The net charge of deprotonated DOTA was fully neutralized by Dy^{3+} and this reduced the surfactant character.[11] For realizing better surfactant-like character a charged head group is preferred. Thus, one should either coordinate DOTA to M^{2+} or to M^{4+}. Because plenty of redox-stable metal cations M^{2+} are available and robust complexes of DOTA exist also with d-block metals,[12] many of them paramagnetic, here, we describe the series shown in **chart 1**. A table summarizing all compounds prepared for the current study is given in the supporting information (SI) table S1.
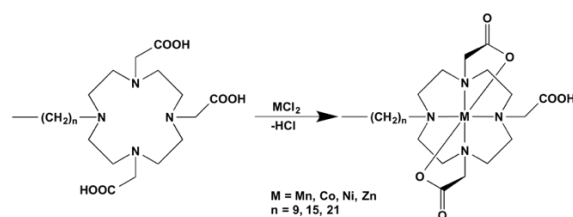
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       the document.

Chart 1. Synthesis of MC_nDOTA (M = Mn, Co, Ni, Zn) surfactants.

Electron spray ionization mass spectrometry (ESI-MS) is a powerful tool for investigating the molecular composition of hybrid surfactants.[11, 13] **Fig. 1a,b** shows the anion patterns are in agreement with masses for the deprotonated molecular ions $[MC_{30}H_{55}N_4O_6]^-$. By ESI-MS alone one cannot prove with certainty the metal cation is coordinated as depicted in **chart 1**. It could also be just a counter-ion. The latter question could be clarified by X-ray diffraction analysis of single crystals, which could be grown for compounds with short alkyl chain, e.g. $NiC_{10}DOTA$ given in **Fig. 1c**. Ni^{2+} adopts an octahedral coordination and the carboxylic group in para position to the alkyl chain is free (see also **SI-1**) making the surfactants anionic. From further data given in **SI-2** one can infer that the coordination is the same for all MC_nDOTA. Compounds with M ≠ Zn are high-spin complexes with ($Mn^{II}_{J=5/2}$ > $Co^{II}_{J=3/2}$ > $Ni^{II}_{J=2/2}$) as confirmed by superconducting quantum interference device (SQUID) measurements and electron paramagnetic resonance (EPR) spectroscopy shown in **SI-3**.
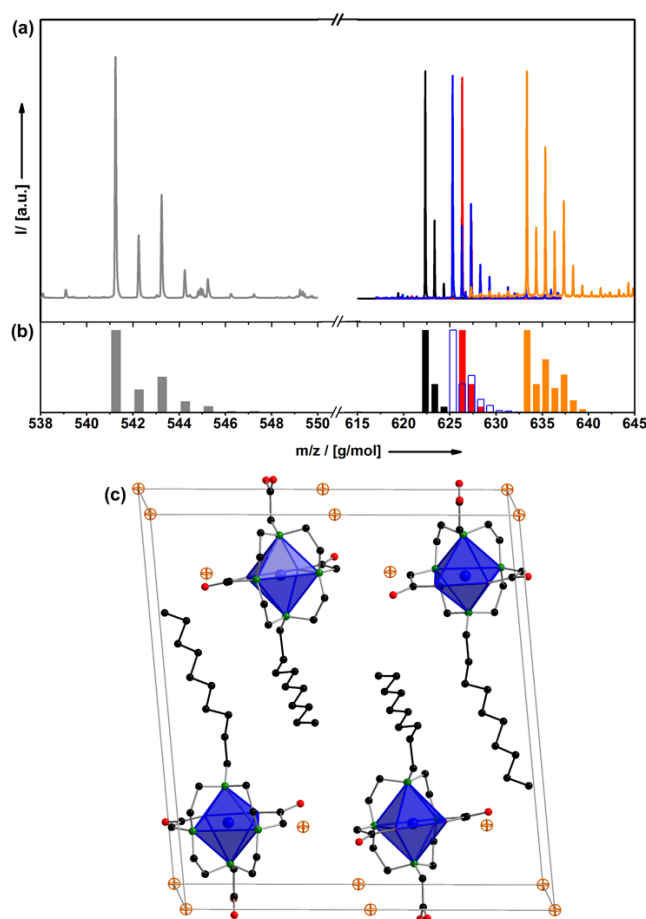

Figure 1. Experimental (a) and simulated (b) ESI-MS patterns of $NiC_{10}DOTA$ (gray) and $MC_{16}DOTA$ (Mn=black, Co=red, Ni=blue, Zn=orange). (c) Packing diagram of $NiC_{10}DOTA$.[14] C ≅ black; N ≅ green; O ≅ red; O (water) ≅ orange; Ni ≅ blue; H-atoms omitted; unit cell ≅ gray line.

Tests were performed for probing typical surfactant properties (see **SI-4**). For all MC_nDOTA we found the formation of fairly stable foams. Further, water/oil emulsions can be made, and their stability is satisfactory as examined by dynamic light scattering (DLS). Our focus is now on $MnC_{16}DOTA$ because it has the

biggest magnetic moment in the discussed series. The critical micelle concentration (cmc) (40 mg/l) was determined from tensiometry shown in **SI-5**. Magnetic properties of the micellar dispersion were examined using EPR (**Fig. 2a**). 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 causes six narrow, equidistant lines. Compared to free Mn^{2+} in aqueous solution,[15] there is a broadening of the signals caused by dipolar coupling and the proximity of the head groups in the micellar corona.
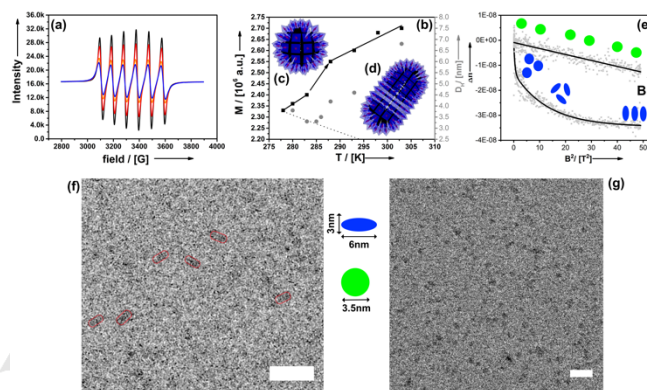

Figure 2. (a) EPR spectra of $MnC_{16}DOTA$ micellar solutions recorded at 278K (blue), 283K (orange), 293K (red), 303K (black). (b) Magnetization (black) and aggregate size (grey). Ordinary Curie behaviour (grey, dotted line). Transition from isotropic (c) to anisotropic micelles (d). (e) Optical birefringence measurements for $MnC_{16}DOTA$ micellar solutions (lower points) and $ZnC_{16}DOTA$ as a reference (upper points). Corresponding cryo-TEM data for $MnC_{16}DOTA$ (f) and $ZnC_{16}DOTA$ (g); scalebars = 20nm.

The T-dependent magnetic behavior is surprising. Unlike to normal paramagnets obeying Curies law (M ∝ χ_M = C/T), magnetization of $MnC_{16}DOTA$ increases with increasing temperature (**Fig. 2b**). It is also worth noting there is a crossing in the temperature region 285-287K, also seen by DLS (**Fig. 2b**). One aggregate species exists in solution whose size is almost constant between 278-287K and fits to micelles (**Fig. 2c; SI-6**). Notable growth follows at T>287K. A suitable idea is there is a transition from spherical micelles to rod-like micelles (see **Fig. 2d**). Other than spherical micelles, rod-like micelles possess magnetic anisotropy and, thus, an increased response to an external magnetic field. In addition to DLS data (see also **SI-6b**) our hypothesis is supported by investigation of the optical birefringence in an external magnetic field (Cotton-Mouton effect).[16] For the diamagnetic $ZnC_{16}DOTA$ there is the expected linear change of the difference in refractive index (Δn) (**Fig. 2e**). $MnC_{16}DOTA$ behaves differently. The pronounced and non-linear correlation fits to the formation of anisotropic micelles aligning with the magnetic field.[17] Finally, with high-resolution transmission electron microscopy (HRTEM) under cryo conditions it is proven $MnC_{16}DOTA$ truly forms anisotropic micelles, while the micelles of $ZnC_{16}DOTA$ remain spherical (**Fig. 2f,g**). Because the surfactants are almost identical in shape, effective head group area and charge, the effects cannot be explained by geometrically considerations (see also **SI 6-c**).

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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 surface tension drops with the trend in magnetic moment (**Fig. 3a**), one would also expect an increase in aggregation number and,[19] thus, also in 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 using Youngs 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 and in absence and presence of a magnetic field (**Fig. 3b-e**). The contact angle for M=Zn is lower compared to Mn, which fits to the γ_{GL} sequence described before (**Fig. 3a**). More importantly, the shape of the droplet containing ZnC$_{16}$DOTA does not change in the presence of a B field (**Fig. 3b,c**). For MnC$_{16}$DOTA the field leads to an enhanced wetting of the surface (**Fig. 3de**), and the lower contact angle indicates a magnetically-triggered decrease in γ_{GL}. Because of the large binding constants ($\ln\beta = 20.2$) of DOTA free Mn^{2+} in solution can be excluded.[20] Nevertheless, we excluded that similar phenomena are caused by free Mn^{2+} by performing additional reference experiments (see **SI-7**). The incorporation of the paramagnetic metal in the head group is crucial.
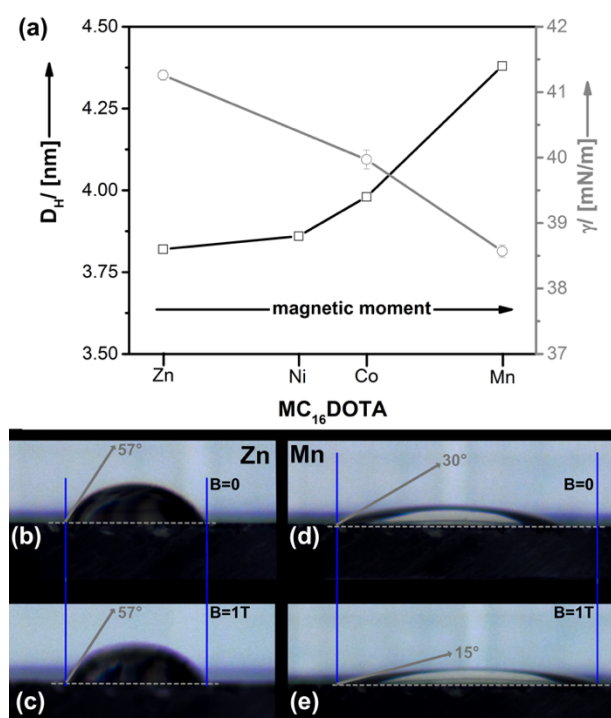

Figure 3. (a) Comparison of micelle diameter (black curve) and γ_{GL} (gray curve) for different surfactants MC$_{16}$DOTA in the absence of an external magnetic field. Contact angle analysis of sessile drops before (b,d) and while applying a magnetic field (c,e) containing ZnC$_{16}$DOTA (left) and MnC$_{16}$DOTA (right).

One of the most prominent applications of surfactants is as porogens for the synthesis ordered mesoporous materials.[21] Methods described in the literature were adapted with either ZnC$_{16}$DOTA or MnC$_{16}$DOTA surfactants as structure directing agents. We begin with the diamagnetic ZnC$_{16}$DOTA (data

summarized in **SI-8**). Polydisperse silica particles with spherical shape have formed. Small angle X-ray scattering, TEM and physisorption reveals those particles have a prototypical mesostructure. When MnC$_{16}$DOTA is used under otherwise identical conditions (**Experimental part; SI**) one finds regularly shaped particles with flat surfaces (**Fig. 4a,b** and **SI-9**). In SEM and TEM analysis one sees the particles consist of densely packed objects ($\approx$ 5nm in size), which according to energy dispersive X-ray spectroscopy (EDX; **SI-9d**) are composed of MnC$_{16}$DOTA. The shape of the mesoporous particles is astonishing because 12-fold rotational symmetry could be an indication for quasicrystals. Final proof of quasicrystallinity is hard to achieve because for materials with nanoscale "periodicities" very sophisticated electron microscopy and diffraction methods have to be applied,[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 rather a 2-D quasicrystal with structural disorder regarding the elongated axis.[24] The work by Gao and coworkers should be noted, who obtained quasicrystalline mesoporous silica with N-myristoyl-L-glutamic acid as a surfactant. The authors discuss a "mesocage-mesocage-interaction", which relies on different protonation degrees of the surfactant controlling the intermolecular interaction. Here, it is not an electrostatic interaction, but a magnetic interaction differentiating the diamagnetic and the paramagnetic from each other, and possibly this 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 effect can also not be excluded.
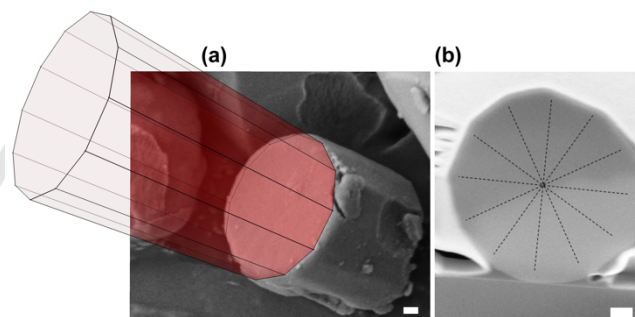

Figure 4. (a) SEM of a silica particle prepared using MnC$_{16}$DOTA as a structure-directing agent; scalebar = 200 nm. (b) Particle cross-section prepared via focused ion beam cutting; scalebar = 200 nm. Dashed lines display the 12-fold symmetry. See also **SI-9** for further EM data.

We presented a systematic series of surfactants differing regarding the magnetic moment of their hybrid organic-inorganic heads, while shape and charge remain constant. The magnetic moment is not only important regarding surfactant self-assembly, but due to its long-range character and the absence of shielding in aqueous electrolytes magnetism could be shown as a strong tool to control the system externally. We expect magnetic surfactants will find numerous uses various fields e.g. stimuli-responsive micelles and emulsions. One can also imagine, that (nano)particles prepared using magnetic surfactants as capping

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agents could then be separated from the reaction mixture easily, even though the particles themselves are not magnetic.

Experimental Section

Experimental Details are given in the supporting information.

Acknowledgements

[1]   (a) G. A. Ozin, K. Hou, B. V. Lotsch, L. Cademartiri, D. P. Puzzo, F. Scotognella, A. Ghadimi, J. Thomson, *Mater. Today* **2009**, *12*, 12-23; (b) B. A. Grzybowski, C. E. Wilmer, J. Kim, K. P. Browne, K. J. M. Bishop, *Soft Matter* **2009**, *5*, 1110-1128; cA. Wang, W. Shi, J. Huang, Y. Yan, *Soft Matter* **2016**, *12*, 337-357.

[2]   K. J. M. Bishop, C. E. Wilmer, S. Soh, B. A. Grzybowski, *Small* **2009**, *5*, 1600-1630.

[3]   A. C. Mendes, E. T. Baran, R. L. Reis, H. S. Azevedo, *Wiley Interdiscip. Rev.-Nanomed. Nanobiotechnol.* **2013**, *5*, 582-612.

[4]   J. V. I. Timonen, M. Latikka, L. Leibler, R. H. A. Ras, O. Ikkala, *Science* **2013**, *341*, 253-257.

[5]   S. Polarz, B. Smarsly, *J. Nanosci. Nanotechnol.* **2002**, *2*, 581-612.

[6]   P. Brown, T. A. Hatton, J. Eastoe, *Curr. Opin. Colloid Interface Sci.* **2015**, *20*, 140-150.

[7]   (a) R. E. Del Sesto, T. M. McCleskey, A. K. Burrell, G. A. Baker, J. D. Thompson, B. L. Scott, J. S. Wilkes, P. Williams, *Chem. Commun.* **2008**, 447-449; (b) R. Giernoth, *Angew. Chem.-Int. Edit.* **2010**, *49*, 2834-2839.

[8]   P. Brown, A. Bushmelev, C. P. Butts, J. Cheng, J. Eastoe, I. Grillo, R. K. Heenan, A. M. Schmidt, *Angew. Chem. Int. Ed.* **2012**, *51*, 2414-2416.

[9]   P. Degen, E. Zwar, M. Paulus, M. Tolan, H. Rehage, *Langmuir* **2014**, *30*, 11563-11566.

[10]   (a) S. Polarz, S. Landsmann, A. Klaiber, *Angew. Chem.-Int. Edit.* **2014**, *53*, 946-954; (b) K. Binnemans, C. Görller-Walrand, *Chem. Rev.* **2002**, *102*, 2303-2346; (c) Y. Wang, G. A. Voth, *J. Amer. Chem. Soc.* **2005**, *127*, 12192-12193.

[11]   S. Polarz, C. Bährle, S. Landsmann, A. Klaiber, *Angew. Chem. Int. Ed.* **2013**, *52*, 13665-13670.

[12]   (a) S. Wang, T. D. Westmoreland, *Inorg. Chem.* **2009**, *48*, 719-727; (b) A. Riesen, M. Zehnder, T. A. Kaden, *Acta Cryst. C* **1991**, *47*, 531-533.

[13]   (a) S. Polarz, R. Regenspurger, J. Hartmann, *Angew. Chem.-Int. Edit.* **2007**, *46*, 2426-2430; (b) S. Landsmann, C. Lizandara-Pueyo, S. Polarz, *J. Amer. Chem. Soc.* **2010**, *132*, 5315-5321; (c) J. J. Giner-Casares, G. Brezesinski, H. Mohwald, S. Landsmann, S. Polarz, *J. Phys. Chem. Lett.* **2012**, *3*, 322-326; (d) S. Landsmann, M. Luka, S. Polarz, *Nat. Commun.* **2012**, *3*, 6; (e) S. Landsmann, M. Wessig, M. Schmid, H. Cölfen, S. Polarz, *Angew. Chem. Int. Ed.* **2012**, *51*, 5995-5999.

[14]   CCDC-1450242, The crystal data are available free of charge at Cambridge Crystallographic Data Center**.**

[15]   C. C. Hinckley, L. O. Morgan, *J. Chem. Phys.* **1966**, *44*, 898-&.

[16]   G. Maret, G. Weill, *Biopolymers* **1983**, *22*, 2727-2744.

[17]   (a) I. O. Shklyarevskiy, P. Jonkheijm, P. C. M. Christianen, A. Schenning, E. W. Meijer, O. Henze, A. F. M. Kilbinger, W. J. Feast, A. Del Guerzo, J. P. Desvergne, J. C. Maan, *J. Am. Chem. Soc.* **2005**, *127*, 1112-1113; (b) O. V. Manyuhina, I. O. Shklyarevskiy, P. Jonkheijm, P. C. M. Christianen, A. Fasolino, M. I. Katsnelson, A. Schenning, E. W. Meijer, O. Henze, A. F. M. Kilbinger, W. J. Feast, J. C. Maan, *Phys. Rev. Lett.* **2007**, *98*.

[18]   W. Shinoda, R. DeVane, M. L. Klein, *Soft Matter* **2008**, *4*, 2454-2462.

[19]   V. Srinivasan, D. Blankschtein, *Langmuir* **2003**, *19*, 9932-9945.

[20]   S. Chaves, R. Delgado, J. Dasilva, *Talanta* **1992**, *39*, 249-254.

[21]   C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710-712.

[22]   (a) D. V. Talapin, E. V. Shevchenko, M. I. Bodnarchuk, X. C. Ye, J. Chen, C. B. Murray, *Nature* **2009**, *461*, 964-967; (b) C. Xiao, N. Fujita, K. Miyasaka, Y. Sakamoto, O. Terasaki, *Nature* **2012**, *487*, 349-353; (c) S. Fischer, A. Exner, K. Zielske, J. Perlich, S. Deloudi, W. Steurer, P. Lindner, S. Förster, *Proc. Nat. Acad. Sci. USA* **2011**, *108*, 1810-1814.

[23]   L. Pauling, *Phys. Rev. Lett.* **1987**, *58*, 365-368.

[24]   M. E. Zoorob, M. D. B. Charlton, G. J. Parker, J. J. Baumberg, M. C. Netti, *Nature* **2000**, *404*, 740-743.

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Magnetic Soap. Head groups containing paramagnetic transition metals provide surfactants with additional, non-classic long-range interactions. This facilitates new modes of supramolecular self-assembly and control of key parameters of surfactants by external magnetic fields.
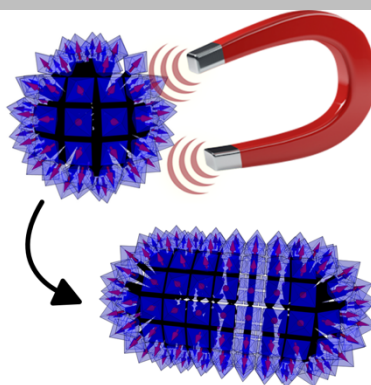
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