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Surfactants as Promising Media for the Preparation of Crystalline Inorganic Materials

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Given that surfactants can control the shape and size of micro-/nanoparticles, they should be able to direct the growth of bulk crystals. This Minireview summarizes recent developments in the application of surfactants for the preparation of new crystalline inorganic materials, including chalcogenides, metal–organic frameworks, and zeolite analogues. The roles of surfactants in different reaction systems are discussed.

1. Introduction

Surfactants are organic compounds that consist of both polar hydrophilic groups and hydrophobic units.[1] The polar hydrophilic groups ($-OH$, $-NMe_3X$ ($X = Cl$, Br), $-CO_2Na$, and $-SO_3Na$) tend to be water-soluble but oil-insoluble, whereas the hydrophobic units are normally hydrocarbon chains ($-C_nH_{2n+1}$) and are typically oil-soluble and water-insoluble.[2] The amphiphilic behavior of surfactants enables them to self-assemble into diverse aggregates (known as micelles) in solution.[3,4] Their shape strongly determines the morphology and dimensions of the as-formed aggregates, which have been widely used as templates in the preparation of various inorganic materials, including inorganic nanocrystals and mesoporous materials.[5,6] Especially for the synthesis of inorganic nanocrystals, efficient control of the size and shape of the targeted nanocrystals is very important because the physical properties of nanocrystals are highly dependent on their morphology. In the past decade, it has been demonstrated that the aggregates formed in colloidal solution can kinetically control the size and shape of nanocrystals;[7] for example, alkyl phosphonic acids with different alkyl chain lengths can be used to control the morphology of CdSe nanocrystals.[8]

On the other hand, in the case of mesoporous materials, surfactants are usually employed as structure-directing agents to tailor the size and phase of porous materials. For example, the channel dimensions of MCM-41 can be adjusted in the range of 1.6–10 nm by changing the alkyl trimethylammonium surfactant, auxiliary chemicals, and reaction conditions.[9] Moreover, the phase of the as-prepared mesoporous material can be determined on the basis of the liquid-crystal structure of the surfactant. By the use of amphiphilic triblock copolymers, such as poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO-PPO-PEO), as structure-directing agents, hexagonal mesoporous silica (SBA-15) has been synthesized with pore sizes ranging from 4.6 to 30 nm.[10,11] The phase of mesoporous silica can also be controlled by the use of triblock copolymers (PEO-PPO-PEO) with different EO/PO ratios; higher ratios result in the formation of cubic mesoporous silica, whereas lower ratios yield lamellar mesoporous silica. Some specific designed surfactants containing two or more quaternary ammonium groups, such as $C_{22}H_{45}N^+(CH_3)_2C_6H_{12}N^+(CH_3)_2C_6H_{13}Br_2$ ($C_{22\text{-}6\text{-}6}$), have also been employed as structure-directing agents for the formation of MFI (mordenite framework inverted) zeolite nanosheets with lamellar structures.[12–14] The hydrophilic ammonium groups structurally direct the formation of zeolite frameworks, and the hydrophobic alkyl tails can self-assemble into a lamellar structure. The introduction of aromatic groups into the alkyl tails of a surfactant with a single quaternary ammonium group led to π–π stacking of the hydrophobic groups, thus generating strongly ordered aggregates of surfactants and subsequently resulting in the formation of single-crystalline MFI nanosheets with lamellar structures.[15] Furthermore, a fluoride-catalyzed sol–gel process has been used as an efficient approach to enhance the thermal and hydrothermal stability of as-prepared mesoporous silica materials.[16,17] The addition of a fluoride source to the reaction mixture can accelerate the hydrolysis of the silicon precursor, thus suggesting that

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fluoride plays an important role in controlling the condensation of alkoxysilanes.[18]

Given that surfactants can control the morphologies of materials on the micro-/nanoscale, it is logical to believe that these surfactants should also be able to direct the growth of bulky crystals of inorganic materials (chalcogenides, metal–organic frameworks (MOFs), zeolite analogues, oxides). However, research into such processes remains rare. Although crystalline inorganic materials can be synthesized under hydro(solvo)thermal conditions, whereby water or molecular solvents are employed as solvents,[19,20] the use of surfactants instead of water and molecular solvents is highly desirable, as they should be able to direct the formation of crystalline inorganic materials through strong interactions with the inorganic species. In fact, cationic surfactants have been used as charge-balancing agents or space-filling templates in the preparation of crystalline chalcogenides and zeolites at room temperature and under hydrothermal conditions, respectively.[21–26] However, the resulting structures were very simple, and the inorganic clusters or frameworks were known. Recently, the research groups of Wang and Lii reported a number of new crystalline metal phosphites with two- and three-dimensional structures, which were synthesized by using alkyl monoammonium or alkyl trimethylammonium surfactants as structure-directing agents under hydro(solvo)thermal conditions.[27,28]

Besides the utilization of surfactants as templates in reaction systems, surfactants also possess good solvent properties, which make them promising reaction media to control the crystal growth of inorganic materials. As compared with traditional molecular solvents, surfactants have the advantages of low vapor pressure and high thermal stability; as compared with ionic liquids, which have been well recognized as promising solvents for the preparation for crystalline inorganic materials,[29,30] surfactants have several advantages, including their cheap price, wide commercial availability, and varying properties (cationic, anionic, neutral, basic, acidic). However, surfactants had never been applied as reaction media in the preparation of crystalline inorganic materials until very recently, when exploratory research on the use of surfactants as reaction media for the synthesis of new crystalline chalcogenides and MOFs was carried out by our group.[31,32]

In this Minireview, we summarize the recent application of surfactants to the preparation of crystalline inorganic materials, including chalcogenides, MOFs, and zeolite analogues, and discuss the roles of surfactants in different reaction systems. Surfactants used in the synthesis of these crystalline materials are shown in Scheme 1.

2. Chalcogenides

Crystalline chalcogenides derived from diverse metals in combination with chalcogen elements are among the most important inorganic materials owing to their extensive technological applications in the fields of the photoelectric effect,[33] ion exchange,[34,35] nonlinear optics,[36] photocatalysis,[37] and thermoelectric materials.[38] Generally, four synthetic methods have been widely used in the preparation of crystalline chalcogenides, including high-temperature solid-state synthesis, molten-flux techniques, room-temperature solution processing, and hydro(solvo)thermal synthesis.[39–41] Except for high-temperature solid-state synthesis, which depends on the solid–solid diffusion process at high temperature, reaction media (such as molten salts, water, organic solvents, or organic amines) are usually used in these synthetic strategies, in which alkali (alkaline earth) metal cations, metal complexes, and organic amines act as counterions, structure-directing agents, and templates in the construction of chalcogenide frameworks.[42–46] Although the research groups of Kanatzidis and Ozin demonstrated that a large number of mesostructured chalcogenides could be built up by the linkage of discrete chalcogenide clusters (such as $[M_4Q_{10}]^{4-}$, $[M_2Q_6]^{4-}$, $[MQ_4]^{4-}$ ($M = Ge, Sn$; $Q = S, Se$)) and a variety of metal ions (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Pt^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ga^{3+}, In^{3+}, Sn^{4+}, Sb^{3+}, Pb^{2+})[47–53] by the use of various quaternary alkyl ammonium and alkyl pyridinium cationic surfactants as templates, research involving surfactants as templates or structure-directing agents in the preparation of crystalline chalcogenides is relatively rare. Only recently, our group demonstrated that surfactants can serve as promising reaction media for the preparation of crystalline chalcogenides and can also act as counterions and templates (owing to their cationic, anionic, and neutral properties) in the formation of chalcogenide frameworks.[54]

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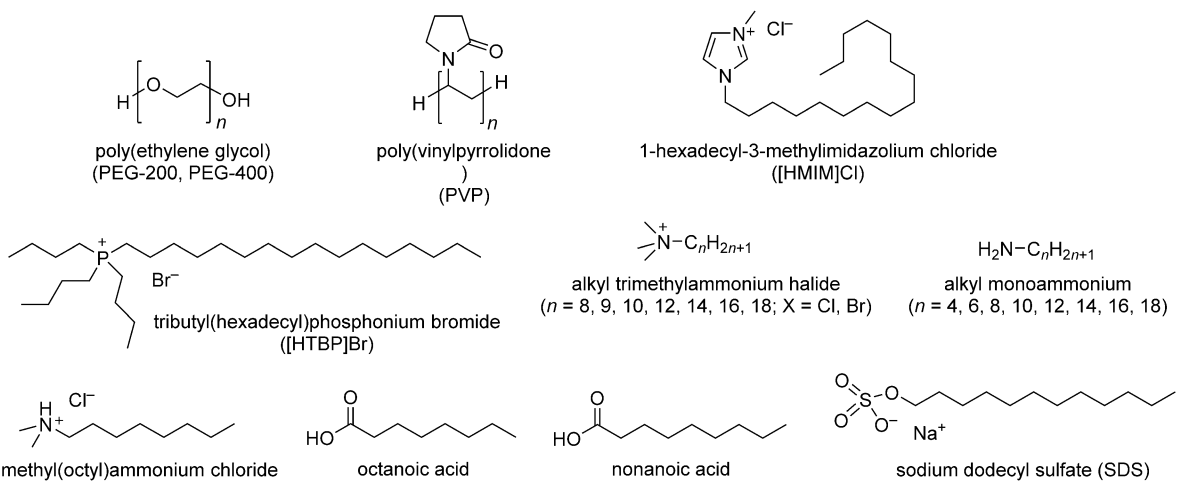
Qichun Zhang obtained his BS degree from Nanjing University and then worked at the research institute of Nanjing Chemical Industry Co. before completing his MS in physical organic chemistry at the Chinese Academy of Sciences (Beijing) and later his MS in organic chemistry at University of California (UC), Los Angeles. He received his PhD in inorganic chemistry from UC Riverside (Prof. Pingyun Feng) in 2007 and then joined the research group of Prof. Kanatzidis at Northwestern University as a postdoctoral fellow. He is currently an associate professor at Nanyang Technological University.



Scheme 1. Surfactants used in the synthesis of crystalline inorganic materials.

In the early years, surfactants were usually used as reactants in reactions with inorganic precursors to produce crystalline chalcogenides under solution conditions at room temperature. In the structures of these crystalline chalcogenides, quaternary alkyl ammonium and alkyl tri-/dimethylammonium surfactants were frequently used as templates to balance the charges of discrete anionic clusters. For example, Kessler and co-workers synthesized the surfactant-templated thiostannate $[C_{12}H_{25}NH_3]_4[Sn_2S_6]\cdot 2H_2O$ by treating $SnCl_4$ with Na_2S and dodecylamine in a mixture of water and ethanol at room temperature.[21] Single-crystal X-ray diffraction analysis indicated that the as-prepared structure featured a discrete $[Sn_2S_6]^{4-}$ anion and four protonated *n*-dodecylammonium cations. The $[Sn_2S_6]^{4-}$ dimers are built up from two edge-sharing $[SnS_4]$ tetrahedra, whereas the *n*-dodecylammonium cations exhibit straight hydrocarbon chains with all nitrogen atoms of neighboring chains pointing in opposite directions.

By using several alkyl trimethylammonium bromides with carbon chains of different lengths as surfactants, Bonhomme and Kanatzidis prepared a series of crystalline surfactant-templated thiogermanates $[C_nH_{2n+1}N(CH_3)_3]_4[Ge_4S_{10}]$ ($n=12$, 14, 16, 18) from an aqueous solution of $Na_4Ge_4S_{10}$ and the alkyl trimethylammonium bromide salt at room temperature.[22] The discrete supertetrahedral T2 cluster $[Ge_4S_{10}]^{4-}$ assembled in parallel inorganic layers, which were charge-balanced by organic bilayers of interdigitated cationic surfactant chains. Then, by replacing alkyl trimethylammonium bromide surfactants with alkyl ammonium chloride surfactants, Rangan and Kanatzidis synthesized a series of crystalline isostructural thiogermanates $[C_nH_{2n+1}NH_3]_4[Ge_4S_{10}]$ ($n=12$, 14, 16, 18) in a mixture of water and ethanol at room temperature.[25] Single crystals of phases with short carbon chains ($n=12$, 14) were obtained. Their structures were determined by single-crystal X-ray diffraction and shown to consist of inorganic layers of $[Ge_4S_{10}]^{4-}$ anionic clusters separated by interpenetrating alkyl ammonium cations. Wachhold and Kanatzidis also reported a series of mesostructured selenogermanates, which were synthesized by the treatment of $K_4Ge_4Se_{10}$ with various alkyl tri- and dimethylammonium halide surfactants $[C_nH_{2n+1}N(CH_3)_{3-m}H_m]X$ ($n=8$, 9, 10, 12, 14, 16, 18; $m=0$, 1; X = Cl, Br).[23] The crystal structures of different phases with shorter alkyl ammonium chains ($n=8$ and 9) were determined by single-crystal X-ray diffraction. Finally, Eichhöfer et al. reported a series of CdSe cluster compounds, in which discrete $[Cd_8Se(SePh)_{12}Cl_4]^{2-}$ anionic clusters were change-balanced by quaternary alkyl ammonium cations with different alkyl chains.[24]

Besides their use as templates or counterions in the synthesis of crystalline chalcogenides, surfactants can also be used as promising reaction media to control the crystal growth of chalcogenides. The surfactants used in the reaction systems are not in their neat form, but usually a small amount of water or an organic amine is added as an auxiliary solvent to accelerate the reaction process. In our preliminary study, we chose chalcogenidoarsenates as a model system to demonstrate the possibility of synthesizing new crystalline chalcogenides in different surfactants. Indeed, a series of new thioarsenates ranging from a zero-dimensional (0D) cluster to a three-dimensional (3D) framework, $[NH_4]_8[Mn_2As_4S_{16}]$ (0D), $[Mn(NH_3)_6][Mn_2As_2S_8(N_2H_4)_2]$ (1D), $[enH][Cu_3As_2S_5]$ (2D; en = ethylene diamine), and $[NH_4][MnAs_3S_6]$ (3D), were prepared under surfactant–thermal conditions, for which three different surfactants, poly(vinylpyrrolidone) (PVP), poly(ethylene glycol)-400 (PEG-400), and 1-hexadecyl-3-methylimidazolium chloride ([Hmim]Cl), were used as reaction media (Figure 1).[31] No crystals (for the 0D, 1D, and 3D compounds) or only a small amount of crystals (less than 3% yield for the 2D compound) were obtained when the surfactant was not added to the reaction mixture. These studies indicated that the surfactant environment is quite different from molecular-solvent conditions in the preparation of crystalline chalcogenides.

In continuing research, we extended the surfactant–thermal synthetic strategy to the preparation of other metal chalcogenides. Two new one-dimensional mercury selenidostannates, $[DBUH]_2[Hg_2Sn_2Se_6(Se_2)]$ (**1**) and $[DBUH]_2[Hg_2Sn_2Se_7]$ (**2**), were synthesized under surfactant–thermal conditions by the reaction of $HgCl_2$, Sn, Se, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), H_2O, and PEG-400 at

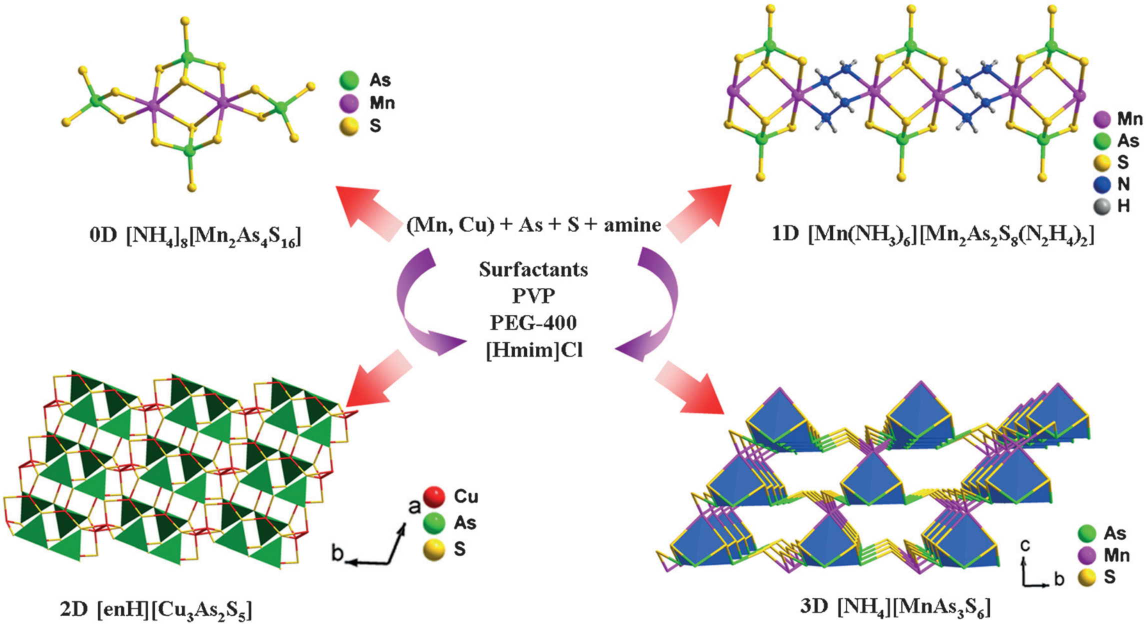


Figure 1. By the use of three different surfactants as reaction media (PVP, PEG-400, and [Hmim]Cl), a series of thioarsenates ranging from a zero-dimensional (0D) cluster to a three-dimensional (3D) framework were synthesized.

160 °C (4 days for **1** and 20 days for **2**).[55] In the presence of the surfactant PEG-400, compound **1** was kinetically stable and could be gradually converted into compound **2** by prolonging the reaction time. However, only compound **2** was obtained at various reaction times when PEG-400 was removed or replaced with an organic molecular solvent, such as *N*,*N*-dimethylformamide (DMF), methanol, or acetonitrile.

By using a cationic surfactant (hexadecyltributylphosphonium bromide) as the reaction medium, we obtained a novel oxosulfide, $(N_2H_4)_2Mn_3Sb_4S_8(\mu_3\text{-}OH)_2$.[56] Its structure features a neutral two-dimensional layer, which contains novel $[Mn_3(\mu_3\text{-}OH)_2]_n$ chains. If the cationic surfactant was removed or replaced with another surfactant (such as the neutral surfactant PEG), no crystals were produced, thus suggesting that it plays an important role in the synthesis of this target compound. Photocatalytic studies demonstrated that this oxosulfide was a stable photocatalyst for continuous H_2 evolution under visible-light irradiation without any cocatalyst.

During our continuing research on the preparation of crystalline metal chalcogenides, a series of manganese chalcogenidogermanates, $Mn_3Ge_2S_7(NH_3)_4$ (2D), $[Mn(en)_2(H_2O)][Mn(en)_2MnGe_3Se_9]$ (1D), $(1,2\text{-dapH})_2\{[Mn(1,2\text{-dap})_2]Ge_2Se_7\}$ (1D), and $(1,3\text{-dapH})(puH)MnGeSe_4$ (1D; pu = propyleneurea), were synthesized in the surfactant PEG-400 in the presence of different organic amines (hydrazine monohydrate, ethylenediamine, 1,2-propanediamine (1,2-dap), 1,3-propanediamine (1,3-dap)).[57] The surfactant PEG-400 was crucial to the formation of these compounds, since no crystal could be obtained without the addition of PEG-400. Magnetic measurements for the two-dimensional compound $Mn_3Ge_2S_7(NH_3)_4$ exhibited a clear antiferromagnetic transition at approximately 9 K. When the neutral surfactant PEG-400 or the anionic surfactant sodium dodecyl sulfate (SDS) was used as the reaction medium, two new neutral two-dimensional manganese thioantimonates, $MnSb_2S_4(N_2H_4)_2$ and $[Mn(tepa)Sb_6S_{10}]$ (tepa = tetraethylenepentamine), were prepared.[58] Photocatalytic investigations indicated that both compounds display hydrogen-evolution behavior under visible-light irradiation. Very recently, we reported the single-crystal growth of a PEG/selenidostannate composite, $[DBNH]_2[Sn_3Se_7]\cdot PEG$, which was synthesized by treating Sn and Se with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), H_2O, ethylene glycol, and PEG-400 at 120 °C for 6 days.[59] In the structure of this compound, the PEG chains are threaded through the nanochannels of the two-dimensional honeycomb $[Sn_3Se_7]_n^{2n-}$ layers (Figure 2). Various hydrogen bonds exist between the PEG chains and inorganic $[Sn_3Se_7]_n^{2n-}$ layers and $DBNH^+$ cations. When the reaction

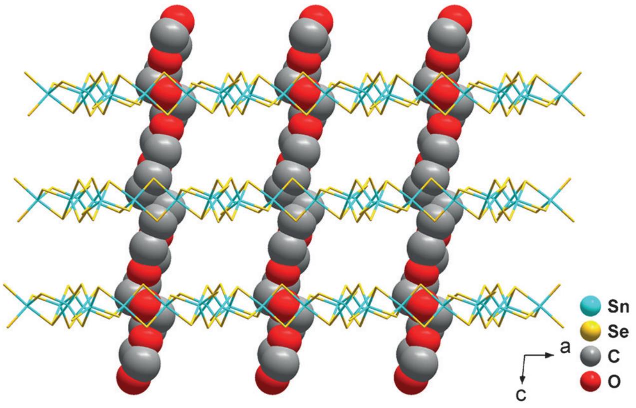


Figure 2. In the structure of the PEG/selenidostannate composite $[DBNH]_2[Sn_3Se_7]\cdot PEG$, the PEG chains are threaded through the nanochannels of the two-dimensional honeycomb $[Sn_3Se_7]_n^{2n-}$ layers. (The $DBNH^+$ cations and hydrogen atoms are omitted for clarity.)

temperature was increased to 190 °C but all other reaction conditions were kept the same, an isostructural selenidostannate, $[DBNH]_3[NH_4][Sn_6Se_{14}]$, was isolated, thus indicating that the preparation of PEG/selenidostannate composites can be controlled thermodynamically. From the syntheses of these crystalline chalcogenides, we conclude that surfactants can play different roles in different reaction systems under different reaction conditions; that is, they can act as solvents or structure-directing agents in various metal chalcogenide reaction systems. Furthermore, phase transformations of chalcogenides under kinetic and thermodynamic control have been discovered in the PEG surfactant environment.[55]

3. Metal–Organic Frameworks

Metal–organic frameworks (MOFs) are crystalline materials constructed by the bonding of metal ions or clusters with organic ligands.[60] The structures of these materials can be designed by the selection of appropriate metal-based coordinating building blocks and multifunctional organic ligands, a large variety of which are available and enable MOFs with diverse structures and rich chemical compositions to be created.[61,62] In fact, MOFs have attracted considerable research interest owing to their potential for application in the areas of gas separation and storage, chemical sensors, nonlinear optics, magnetism, and catalysis.[63–70] Typically, MOFs can be synthesized by applying various mild synthetic methods, such as hydrothermal and solvothermal techniques, which involve the utilization of molecular solvents with low boiling points. The organic solvents used in these methods produce high vapor pressure at high temperature and could cause serious health and environmental problems. In recent years, ionothermal conditions, which are regarded as environmentally friendly, have been employed in the synthesis of MOFs. The particular properties of ionic liquids (high thermal stability, negligible vapor pressure, high ionic conductivity) make them good candidates for the preparation of MOFs. However, their high price has limited the large-scale fabrication of MOF materials. Surfactants have the same characteristics of high thermal stability and low vapor pressure as ionic liquids but are much cheaper. Furthermore, the hydrophilic and hydrophobic groups of surfactants can increase the solubility of metal ions and organic ligands, which would be helpful for the crystal growth of MOFs. Several studies have been reported that concern the synthesis of mesostructured MOFs by the use of surfactants as structure-directing agents under solvothermal or ionic-liquid/CO_2 reaction conditions.[71–73] The structures of these meso-MOFs can be viewed as hierarchical systems containing micro- and mesopores. The surfactants form micelles in the mesopores, whereas the mesopore walls are built up by crystalline microporous frameworks. However, the application of surfactants as reaction media for the synthesis of new crystalline MOFs remains unknown.

Recently, by utilizing several different surfactants as reaction media, our group synthesized many crystalline MOFs with diverse structures and interesting properties. Poly(ethylene glycol) (PEG) is a neutral surfactant, and also a promising reaction medium for the crystal growth of MOFs because 1) PEG is nontoxic and biodegradable and therefore an environmentally friendly solvent; 2) PEG chains contain many oxygen atoms that can bond with metal ions to control the crystal growth of MOFs; and 3) PEG has wide liquid temperature range owing to the variable melting points corresponding to molecular weight. In our primary study, we used PEG-200 as a solvent and 1,4-benzenedicarboxylic acid (BDC) or isophthalic acid (IPA) as the ligand to coordinate with various transition-metal ions (Fe^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}). Eight new two-dimensional and three-dimensional MOFs were prepared.[74] Interestingly, when organic solvents (such as methanol, ethylene glycol, and DMF) were used instead of PEG-200 in these reaction systems, no crystals were obtained, which suggested that the surfactant environments were quite different from the solvothermal conditions. Following this study, we synthesized four new three-dimensional heterometal–organic frameworks (HMOFs) by the reaction of copper nitrate, a transition-metal acetate, trimesic acid (BTC), and pyridine (py) in PEG-400.[32] These four HMOFs were isostructural with the general formula $M(BTC)Cu(py)_2$ (M = Co for NTU-Z7a, Mn for NTU-Z7b, Ni for NTU-Z7c, and Zn for NTU-Z7d). Clearly, the surfactant PEG-400 was very important for the formation of these crystalline HMOFs, since no crystals were produced when PEG-400 was replaced with organic solvents (such as methanol and DMF) in these reaction systems.

Surfactants provide many possibilities for reaction systems because of their multifunctional (neutral, cationic, anionic, zwitterionic, basic, and acidic) properties. In our continuing research, we have used different functionalized surfactants as reaction media to prepare new crystalline MOFs. For the synthesis of MOFs based on zinc 1,3,5-benzenetricarboxylate (BTC), three different surfactants with neutral, acidic, and cationic characteristics were used as reaction media: PEG-400, octanoic acid, and tributyl(hexadecyl)phosphonium bromide.[75] Six novel zinc BTC MOFs with 1D or 3D structures were successfully synthesized by altering the surfactant and zinc-salt source. By using the surfactant nonanoic acid as the reaction medium, we prepared three new cobalt BTC MOFs with 3D structures, namely, $[Co_3(\mu_3\text{-}OH)(HBTC)(BTC)_2Co(HBTC)]\cdot(HTEA)_3\cdot H_2O$ (NTU-Z30), $[Co(BTC)]\cdot HTEA\cdot H_2O$ (NTU-Z31), and $[Co_3(BTC)_4]\cdot(HTEA)_4$ (NTU-Z32; TEA = triethylamine).[76] NTU-Z30 and NTU-Z32 feature two new topologies, 3,3,6,7-c net and 2,8-c net, respectively, whereas NTU-Z31 exhibits a known topology of the **rtl** type (3,6-c net). Moreover, NTU-Z30 showed excellent catalytic activity for the aerobic epoxidation of alkenes. Very recently, we found that two mixed MOF phases ($[Ni_2(H_2L_2)(bpy)_2]\cdot 2\,H_2O$ (yellow-green block crystals) and $Ni_2L(bpy)_{1.5}$ (bright-green cluster crystals; L = pyridyl tetracarboxylate, bpy = 2,2′-bipyridine), obtained with water as the solvent, could be completely separated by adding different surfactants to the reaction systems.[77] More research is still required for further understanding of these factors. Thus, it is clear that surfactants with different characteristics do have strong effects on the construction of crystalline MOFs.

4. Zeolite Analogues

Zeolites are generally crystalline aluminosilicate materials that contain pores and cavities with molecular dimensions of 1.5 nm or less. These microporous materials are of interest owing to their rich structural chemistry and applications as molecular shape-selective absorbents, catalysts, and ion-exchange materials.[78,79] Hydrothermal syntheses of these typical crystalline microporous materials have been investigated extensively, whereby inorganic cations or organic ammonium cations (especially quaternary ammonium salts) have been used as structure-directing agents or charge-balancing cations.[80] Nevertheless, small inorganic or organic cationic species normally promote the formation of pores with narrow sizes through steric matching and thus limit molecular diffusion in catalysis and absorption applications of the resulting materials. Surfactants with a polar hydrophilic head and a hydrophobic hydrocarbon chain can form various aggregates in solution. These aggregates are good candidates as structure-directing agents for the construction of mesoporous molecular sieves with much larger pores (pore diameters in the range of 2–50 nm). On the basis of this surfactant-templated synthetic strategy, numerous mesoporous molecular sieves were synthesized by the use of diverse surfactants in the past two decades. For example, the most well known mesoporous materials, MCM-41 and SBA-15, which contain ordered mesopores, were prepared in the presence of long-chain alkyl quaternary ammonium surfactants and amphiphilic triblock copolymers, respectively.[9,10] However, the mesopore walls of MCM-41 and SBA-15 are built up by noncrystalline frameworks with low acidity and consequently exhibit low catalytic activity. Therefore, hierarchically meso-/microporous zeolites with mesopore walls built up by crystalline zeolite frameworks are highly desirable for application in catalysis. By using amphiphilic organosilanes and multiquaternary ammonium surfactants as bifunctional templates, Ryoo and co-workers prepared a series of hexagonal mesostructured molecular sieves and two-dimensional MFI zeolite nanosheets that contained crystalline microporous zeolite frameworks.[12–14,81–85] Through the use of single-headed quaternary ammonium surfactants with aromatic tails as templates, Che and co-workers synthesized single-crystalline MFI zeolite nanosheets with lamellar structures.[15,86]

Alkyl trimethylammonium surfactants with the formula $C_nH_{2n+1}(CH_3)_3NBr$ have been widely used as structure-directing agents in the synthesis of mesoporous molecular sieves. When this type of surfactant is used as a template for the preparation of crystalline microporous zeolites, such as ZSM-5 and ZSM-35,[26,87,88] various synthetic parameters can influence the formation of these crystalline zeolites, including the length of the surfactant alkyl chain, the surfactant concentration, the Si/Al ratio, and the reaction temperature. However, these crystalline zeolites are known frameworks templated by alkyl trimethylammonium surfactants, and because of the absence of single crystals, the existence of surfactants in the structure needs to be confirmed by multiple characterization techniques, such as elemental analysis, solid-state ^{13}C NMR spectroscopy, and IR spectroscopy. Recently, Lii and co-workers reported the single-crystal growth of a new nanostructured zinc phosphite, $(CTA)ZnBr(HPO_3)$, under hydro(solvo)thermal conditions by the reaction of $Zn(NO_3)_2{\cdot}6\,H_2O$, H_3PO_3, cetyltrimethylammonium bromide (CTAB), HF, H_2O, and tri(ethylene glycol) at 150 °C for 2 days.[28] Single-crystal XRD revealed that the compound features a two-dimensional anionic layer composed of $[ZnBr(HPO_3)]^-$, which is constructed by the combination of ZnO_3Br and HPO_3 tetrahedra. The CTA^+ surfactant molecules are located between the inorganic layers in the form of a largely lamellar liquid-crystalline structure. This nanostructured zinc phosphite exhibited the ability to adsorb the pollutant 1-naphthol from wastewater. By using alkyl monoamine surfactants ($C_nH_{2n+1}NH_2$; $n = 4, 6, 8, 12, 14, 16, 18$) as structure-directing agents, Wang and co-workers synthesized a family of crystalline gallium zincophosphites with systematically tunable channels from 24-membered rings (24R) to 28R, 40R, 48R, 56R, 64R, and 72R, in which pore sizes were as large as 3.5 nm (Figure 3).[27] The channel walls of these compounds were built up by the condensation of three building blocks: anionic chains of $[GaF(HPO_3)_2]_n^{2n-}$, neutral chains of $[Zn(HPO_3)]_n$, and anionic clusters of $[Zn(HPO_3)_2(H_2O)_4]^{2-}$. These studies indicated that the surfactant-templating strategy can also be applied to the preparation of novel crystalline mesostructured zeolite analogues.

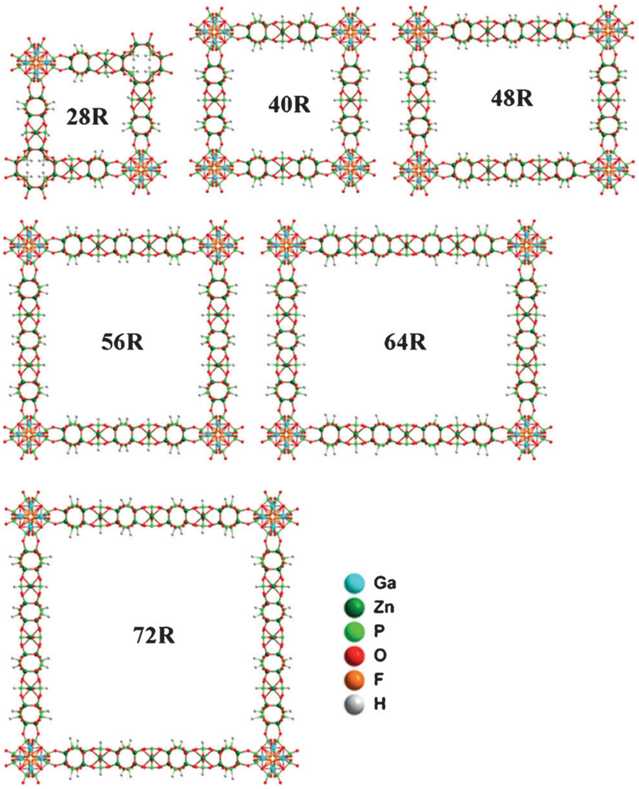


Figure 3. Crystal structures of a series of crystalline gallium zincophosphites with systematically tunable channels from a 28-membered ring (28R) to 40R, 48R, 56R, 64R, and 72R.

5. Summary and Outlook

In this Minireview, progress in the application of surfactants in the synthesis of crystalline inorganic materials, including chalcogenides, metal–organic frameworks, and zeolite analogues, has been summarized. It can be concluded that surfactants not only act as templates in the construction of crystalline inorganic frameworks, but can also be used as reaction media to control the crystal growth of inorganic materials. Various crystalline inorganic materials with diverse structures and interesting properties can be synthesized by altering the shape and properties of surfactants, as well as the reaction conditions, such as the reaction temperature and time. Although surfactants have been demonstrated to be promising media for the synthesis of new crystalline inorganic materials, studies in this field are still at an early stage, and more effort must be devoted to the investigation of: 1) how surfactants interact with inorganic species in the reaction systems; 2) when two or more surfactants with different functions are used in the reaction system, how the surfactants interact with each other to control the crystal growth of inorganic materials; 3) how the reaction conditions (such as reaction temperature and time, pH value, auxiliary solvents, and other small-molecule directing agents) affect the nucleation of inorganic species in surfactant-based reaction media; and 4) the possibility of approaching the synthesis of crystalline mesoporous materials or crystalline inorganic functional polymer composites by the use of surfactant media.

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