Porphyrin-Based Bola-Amphiphiles as Structure-Directing Agents for the Synthesis of Mesostructured Silica

Peter Behrens[*] and **Andreas M. Glaue**

Institut für Anorganische Chemie, Universität Hannover,
D-30167 Hannover, Germany

Summary. Amphiphilic porphyrins with a bola-type arrangement of trimethylammonium headgroups can be used to generate M41S-type silica mesostructures with a lamellar topology and alternating organic–inorganic layers. Within the organic layers, the porphyrin entities are aggregated as shown by UV-Vis spectroscopy. The use of a bola amphiphile as structure-directing agent extends the possibilities of surfactant-controlled assembly of inorganic structures. In addition, the direct functionalization of the organic part of organic–inorganic hybrid nanostructures is possible due to the combination of the amphiphilic function with that of a chromophore.

Keywords. Chromophores; Mesostructures; Nanostructures; Silica; Surfactants.

Introduction

The synthesis of hybrid organic–inorganic materials based on aqueous inorganic sol–gel processes performed in the presence of surfactants has been an important theme of research during the last years [1–9]. In the initial work, the formation of hexagonal, cubic and lamellar silica mesostructures in the presence of alkyltrimethylammonium ions was described [1, 2]. The preparative chemistry has since then focussed mainly on the chemistry at the interface between organic and inorganic matter and on the variation of the inorganic component, with only few efforts directed to variations of the hydrophobic part of the structure-directing amphiphiles. *Zhou* and co-workers have shown that hexagonal silica mesostructures can be formed with an 11-ferrocenylundecyltrimethylammonium surfactant [10, 11]. However, this amphiphile behaved largely like a normal alkyltrimethylammonium surfactant and no special effects in the synthesis caused by the ferrocenyl units were observed. In a work related to that presented here, we have used amphiphilic

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[*] Corresponding author. E-mail: peter.behrens@mbox.acb.uni-hannover.de

azo-dyes, i.e. azobenzene chromophores equipped with hydrophilic headgroups. Here, the presence of the azobenzene group within the hydrophobic part of these amphiphiles causes additional structure-directing effects [12, 13].

The supramolecular and materials chemistry of porphyrins [14–21] has been investigated intensively during the last decades. Their supramolecular aggregates often possess valuable photophysical and photochemical, conducting (semiconductivity, metallic conductivity, photoconductivity) and other interesting properties. Amphiphiles based on porphyrin moities equipped with hydrophilic headgroups have been shown to form aggregates and mesophases in aqueous solutions [14–18, 20, 21]. Of special interest are the so-called bola or tentacle amphiphiles containing more than one hydrophilic headgroup attached to the hydrophobic porphyrin core.

It has been shown that the presence of silica can strongly enhance the tendency of amphiphilic molecules to form mesostructures [4, 22]. Organic–inorganic composite mesostructures are mechanically more stable than aqueous lyotropic phases or *Langmuir-Blodgett*-type aggregates and chromophores embedded in inorganic matrices are protected by their surrounding, a fact which can be of special importance when photochemical applications are envisaged [23–28]. These facts make the exploration of the supramolecular chemistry of functional organic mesogenes with silica, exemplified by the use of amphiphilic dyes [10–13], worthwhile.

The advantages related to the incorporation of chromophores in zeolites have been exemplified by a large number of reports (as reviewed in [23, 27, 28]). Recently, M41S materials have been discovered as new host materials for chromophores [10–13, 28–35], yielding interesting properties for the composites as lasing [32, 33] and sensing [34, 35].

Usually, the chromophore functionality is introduced in an unspecific way, either by co-inclusion within the micellar environment during synthesis or by post-synthetic loading of the mesoporous host [28]. This method is often satisfactory when the properties of individual, non-interacting chromophore molecules are to be exploited. Access to the properties of chromophore aggregates, however, can be obtained when the functional chromophore molecules also acted as a structure-directing agent (SDA) during the synthesis. This path has been investigated only rarely [10–13], although such a direct synthesis of functional composites has several advantages: It leads to homogeneous and full occupation of the voids of the porous host and to well-defined environments of the chromophore.

Here, we report on the formation and properties of well-defined chromophore–silica mesostructures which were obtained by direct synthesis with a quadruple bola-porphyrin amphiphile. We have used *meso*-tetrakis (4-(6-trimethylammonio)-hexyloxy)phenyl-porphyrin (H$_2$TAHPP, free base, Fig. 1a) or its copper complex (Cu-TAHPP, Fig. 1b), respectively, as SDA in synthesis protocols which are typical for the formation of silica M41S materials. Before this work, porphyrins have been introduced into M41S materials via the co-inclusion method (using dodecyltrimethylammonium bromide as the SDA) [30], via post-synthetic ion exchange of as-synthesized MCM-41 [30] or via physisorption on template-free MCM-41 [31]. In contrast, in the work presented here, the amphiphilic porphyrins were not mixed with other surfactants but were present as the sole amphiphilic SDAs in the synthesis solution. Before our application of these bola amphiphiles, *Bagshaw* and *Hayman* had introduced another family of bola amphiphiles as SDAs in M41S-type
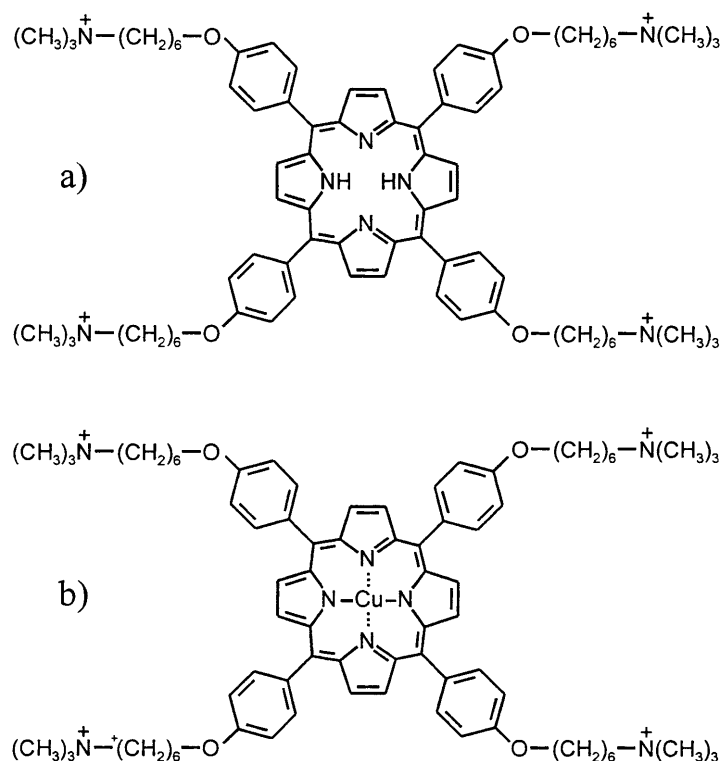
Fig. 1. The two porphyrin-based bola-amphiphiles used in this study: a) H$_2$TAHPP, b) Cu-TAHPP

syntheses, which yielded supermicroporous samples. The bola amphiphiles they used had two headgroups per amphiphile molecule (ω-hydroxyalkyl triethylammonium bromides) [36, 37]. Another type of bola amphiphile, also with two headgroups, was used by *Zhao* et al., to prepare the mesostructure SBA-8 [38].

Results and Discussion

Organic-silica composites obtained from the reaction between TEOS (tetraethoxysilane) and the porphyrin bola-amphiphiles in aqueous KOH exhibited the X-ray diffraction patterns in Fig. 2. These show two or three reflections below 10° 2Θ for the H$_2$TAHPP and the Cu-TAHPP composite, respectively. Their *d* values have ratios of 1:2 and 1:2:3, respectively. Upon calcination, which is accompanied by a mass loss of 65% for the H$_2$TAHPP composite and 63% for the Cu-TAHPP composite, these reflections disappear; amorphous silica is produced. These observations are in line with a lamellar composite structure, similar to corresponding lamellar M41S phases, with alternating organic and inorganic layers.

The periodicities perpendicular to the layers are 35.4 Å and 36.3 Å for the H$_2$TAHPP and the Cu-TAHPP composite, respectively. Taking 5 to 8 Å as the typical thickness of silica walls or layers in M41S materials, the organic layers have a thickness of *ca.* 30 Å. The cross diameter of a tetraphenylporphyrin unit from one *para*-phenyl C atom to the other is *ca.* 15 Å [39]. In accordance with the structures of M41S-type materials formed from alkyltrimethylammonium ions, the trimethylammonium headgroups of the bola amphiphiles should be in contact with
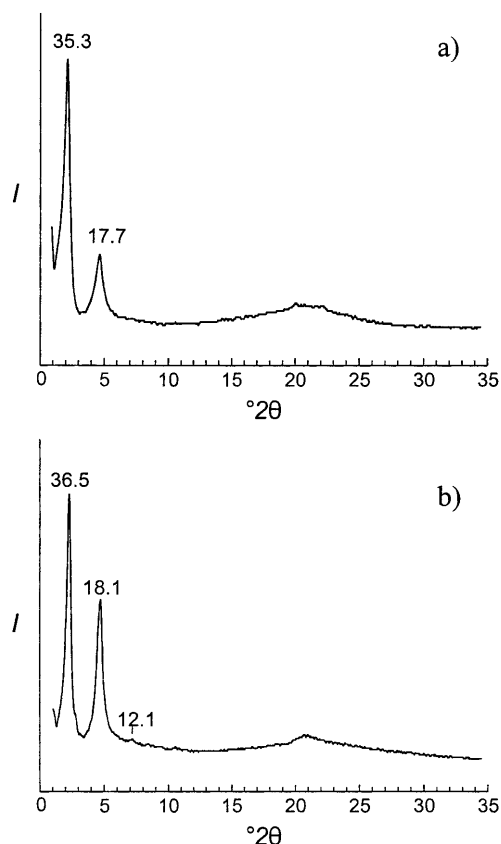
Fig. 2. X-ray diffraction patterns of mesolamellar composites of silica with a) H$_2$TAHPP and b) Cu-TAHPP; the d values of the reflections are given in Å

the silica layers. Based on this requirement, the large interlayer space can only be propped up by an arrangement where the hexamethylene spacers between the porphyrin unit and the headgroups are in extended conformation and where the porphyrin plane is oriented nearly perpendicular to the layers.

The UV-Vis spectra of H$_2$TAHPP and Cu-TAHPP in methanolic solution (where the dye molecules are isolated from each other) and in their composites are presented in Fig. 3. The general appearance of the spectra is in line with the known spectroscopic properties of porphyrin free bases and porphyrin metal complexes. Free bases as H$_2$TAHPP exhibit a strong band at around $400 \, cm^{-1}$ (the B or *Soret* band) and four weak signals between $500–700 \, cm^{-1}$ (the Q band). Due to the higher symmetry of metal complexes as Cu-TAHPP, these give only two signals in the Q band [40]. The UV-Vis spectra thus support the presence of intact porphyrin molecules in the silica composites.

For the porphyrins in the composites, a drastical shift in intensities is observed between the *Soret* and the Q bands as compared to the corresponding molecules in solution. Furthermore, all bands experience red shifts upon occlusion in the silica composite, and the *Soret* band becomes much broader. The shifts and the broadening can be ascribed to aggregation of the molecules [18] pointing to a relatively tight-packed arrangement of the porphyrin molecules between the silica layers.
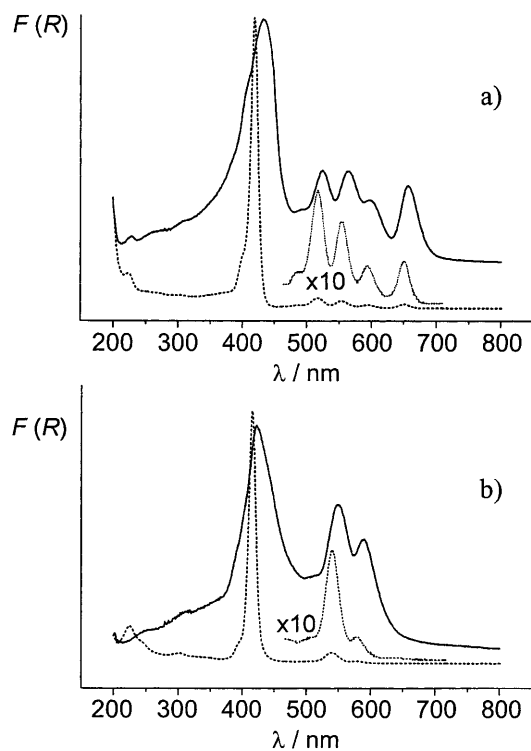
Fig. 3. UV-Vis spectra of a) H_2TAHPP and b) Cu-TAHPP in their silica composites (full lines) and in methanol solutions (dotted lines). The Q band regions of the porphyrins in solution are enlarged by a factor of 10

The elucidation of the type of arrangement within the porphyrin layers needs further analysis before a more definite structural picture can be given, based for example on a quantitative interpretation of the red shifts using molecular exciton theory [41].

We have shown that M41S-type lamellar structures can be generated using amphiphilic SDAs with a bola-type arrangements of surfactant headgroups. The porphyrins H_2TAHPP and Cu-TAHPP are the most complex surfactants used so far for the production of M41S-type materials and their ability to induce silica meso-structures enlarges the meaning of the term SDA (or template) for this class of materials from simple linear surfactants to quadruple bola-type amphiphiles with radially distributed hydrophilic headgroups. In contrast, the dual bola amphiphiles used in the work of *Bagshaw* and *Hayman* [36, 37] and of *Zhao* et al. [38] were linear as are the surfactants normally used for the synthesis of M41S-type materials, and for another porphyrin-based bola amphiphile used in the synthesis of M41S-type materials, namely *meso*-tetrakis (5-trimethylammoniopentyl)-porphyrin, no evidence was given that this surfactant molecule alone could induce the formation of silica mesostructures [30].

In addition to being able to act as a true SDA for the formation of mesostructures, the porphyrin bola amphiphile used here bears the functionality of a chromophore, allowing on the one hand to obtain further information on the structural arrangements inside the organic part and promising on the other hand possible

applications of these novel ordered organic-inorganic hybrid nanostructures. Thus, a direct functionalization of the organic part of mesostructured composites is possible without additional modifications (as template removal and subsequent insertion of functional molecules). The occlusion of the porphyrin chromophores within the composite should offer these molecules stabilization and protection [23, 28].

Experimental

The free base H_2TAHPP of the bola amphiphile was synthesized as the bromide salt by varying the literature procedure [18] described for the preparation of *meso*-tetrakis (4-(6-trimethylammonio)propyloxy)phenyl-porphyrin. Following the literature, *meso*-tetrakis (4-hydroxyphenyl)-porphyrin is obtained from *para*-hydroxybenzaldehyde and pyrrol. Then, ether functions are formed from the phenol groups using a twelvefold excess of 1,6-dibromohexane (in boiling ethanol, four equivalents of KOH added in small portions within three hours). Afterwards, the solution is given on ice. The violet precipitate with a metallic luster is isolated and washed with methanol. The intermediate product is purified by column chromatography (Merck, Kieselgel 60, CH_2Cl_2). Finally, quarternized amino functions are formed by treatment with trimethylamine in dimethylformamide (3 d at 60°C). The solvent and excess trimethylamine are removed by destillation. The crude product is dissolved in water and extracted with CH_2Cl_2. The aqueous phase is then reduced; upon addition of acetone, a red-violet solid precipitates, which is twice re-crystallized from an ethanol-hexane mixture to give a violet solid with a yield of 54% referred to the *meso*-tetrakis (4-hydroxyphenyl)-porphyrin. ^{1}H NMR (d_4-methanol, 400 MHz) $\delta = 1.4 - 1.8$ (m, 32H), 3.30 (s, 36H), 4.02 (t, $J = 6.02$ Hz, 8H), 4.12 (t, $J = 6.05$ Hz, 8 Hz), 7.15 (d, $J = 8.31$ Hz, 8H), 7.94 (d, $J = 8.30$ Hz, 8H), 8.80 (s, 8H).

The copper complex Cu-TAHPP was obtained by heating a water/ethanol solution of H_2TAHPP and $CuCl_2$ (in 10% excess) to reflux for 24 h [42, 43]. The colour of the solution changed from violet to red. The complex was precipitated by addition of a saturated KI solution and recrystallized twice from acetone/ethanol. Using an ion exchange column (amberlite IRA 400, Cl^- form), the tetraiodide was transformed to the tetrachloride salt, which has a better solubility in water. The red product was obtained with a (non-optimized) yield of 5%. Methanolic solutions of the two compounds gave UV-vis spectra (shown in Fig. 3 as dotted lines) typical of porphyrin free bases and metal complexes, respectively.

Mesostructured composites of silica and of one of the porphyrins H_2TAHPP or Cu-TAHPP were obtained using synthesis protocols typical of M41S materials. H_2TAHPP or Cu-TAHPP (as the tetra-bromide or the tetrachloride salt, respectively) were mixed with TEOS in aqueous KOH (molar ratios of SiO_2:porphyrin:H_2O:KOH = 1:0.07:0.825:139). After mixing, the reaction mixtures were stirred for two hours, transferred into Teflon-lined steel autoclaves and afterwards heated to 110°C for 3 days. After the reaction, the reddish-brown products were washed with hot water, filtered and dried under ambient conditions. Calcination of the composites was performed by heating to 600°C for 2 h.

X-ray diffraction patterns were obtained on a Seifert ISO-Debyeflex 1001 diffractometer employing *Bragg-Brentano* geometry. UV-Vis spectra were taken on a Cary-5E spectrometer from Varian. Solid samples were ground together with barium sulfate and measured in diffuse reflectance using a *Praying Mantis* device from *Harrick* for diffuse reflection measurements. The absorbance was calculated according to the *Kubelka-Munk* theory.

Acknowledgements

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