From Cyclodextrin Assemblies to Porous Materials by Silica Templating**

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Since the discovery by Beck, Vartuli et al.[1, 2] that ordered mesoporous silicas, such as MCM-41, can be obtained by surfactant templating, the development of new porous materials and porogens as well as the characterization of the resulting structures has become one of the most promising fields in modern materials chemistry.[3–5] Meanwhile, these observations have been extended to a number of techniques by which pore morphology, pore size, and wall material can be varied over a broad range.[6–14]

One of the modifications of the original process relevant here is the "nanocasting" introduced by Attard, Glyde, and Göltner.[15] This is a high-concentration synthesis in which the solidified inorganic compound is a copy of the original phase structure, that is its structure is predetermined by the selection of the template phase. They used lyotropic liquid-crystalline phases, derived from surfactants or—later—block copolymers,[15–17] as templates and obtained the material either as a homogeneous film or as a monolithic object. In addition, this technique also allows the structural characterization of fragile phase structures and transition states of polymers or surfactants by analyzing the well-contrasted solid replica instead of the original soft organic phases.[16, 18]

We extend this approach to supramolecular aggregates of nonpolar cyclodextrins (CDs) in aqueous solution as templates. Our aim is to exploit the use of CDs to generate porous materials, focussing on the fine details of the pore structure and the self-organization of this template. The self-assembly of cyclodextrins has been assumed previously,[19–23] but their organization could—to the best of our knowledge—not be determined in detail.

CDs are cyclic oligosaccharides consisting of covalently linked glucose units (6 units = α-CD, 7 units = β-CD, 8-units = γ-CD); they are characterized by a hydrophilic exterior and a hydrophobic interior[24] the size of which is in the range of 1.5–2 nm. The relatively large number of hydroxy groups per unit area should ideally mediate compatibility with an oxidic inorganic matrix through hydrogen bonding. In fact, this has been proven by three reports in which CDs were employed at low concentrations in a sol–gel process to incorporate functional units such as dyes into a dense and nonporous silica.[25–27]

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So far, CD-containing solutions have been difficult to analyze by standard techniques, thus information about the assembly of CDs in water is still rather limited. We employ nanocasting to investigate the CD assemblies as templates for the silica pore in detail, and we also investigate the driving force for the self-assembly of the cyclodextrin molecules to ordered aggregates.

In a solution of a hydrophilic sugar, such as a cyclodextrin, one would assume that it is moleculary dispersed in the aqueous phase. Nanocasting by a sol–gel process should then result in a porous material in which each pore exhibits the size and shape of a CD molecule, and in which the pores are not mutually ordered. Depending on the concentration, mesoporosity would be achieved by a molecular percolation process at corresponding volume fractions of template to water, but still a disordered pore system would be obtained (as found for instance for polyethyleneglycol solutions[28]).

When a 18 wt% solution of α-CD was templated we observed a different behavior, namely evidence for an ordered aggregation of CDs instead of their molecular dispersion in the silica matrix (see experimental conditions in Table 1 and Supporting Information; all unmodified CDs were templated at a concentration near to their saturation limit in water; the presence of CD in the silica before calcination was verified by IR, thermogravimetric analysis (TGA), and UV/Vis measurements as given in the Supporting Information).[29]

Table 1. Experimental conditions for the preparation of the CD-based silica materials.

Sample name	Amount of CD [g]	Amount of H_2O [g]	Amount of TMOS [g]	Casting temperature [°C]	BET surface [$m^2 g^{-1}$]
α-CD-silica	2	5	4	60	644
β-CD-silica	0.1	5	4	60	2
γ-CD-silica	0.7	5	4	60	–
β-MCD-silica	2	3	4	60	712
β-MCD_*p*-xylene-silica	2.16	3	4	60	596
α-HPCD-silica	2	2	4	60	832
β-HPCD-silica (1)	2	2	4	60	817
β-HPCD-silica (2)	2	3	4	60	873
γ-HPCD-silica	2	2	4	60	763

The CD assembly is expressed in the silica through a bicontinuous "worm-type" pore system with a diameter d of about 1.5 nm (Figure 1). The bicontinuity introduced by the curved and ramified pores, which is apparent in the transmission electron microscopy (TEM) images, is also verified by nitrogen sorption measurements. The material has an internal surface area of 644 $m^2 g^{-1}$, which is too low to be caused by "single CD molecule pores", but is consistent with the observed worm-type pores. A typical N_2 isotherm is given in Figure 2 for a related system (silica obtained with γ-hydroxypropylated CD (γ-HPCD-silica)).

To explain these results, we assume that α-CD self-assembles to "worm-type" aggregates because of its hydrophobic interior and the hydrophilic shell. Maximum contact between the hydrophobic domains and between the hydrophilic domains is given when the flat (uncurved) CD sides are

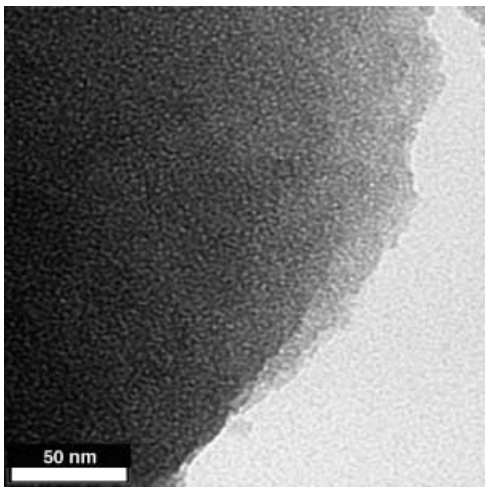

Figure 1. TEM image of α-CD-silica.

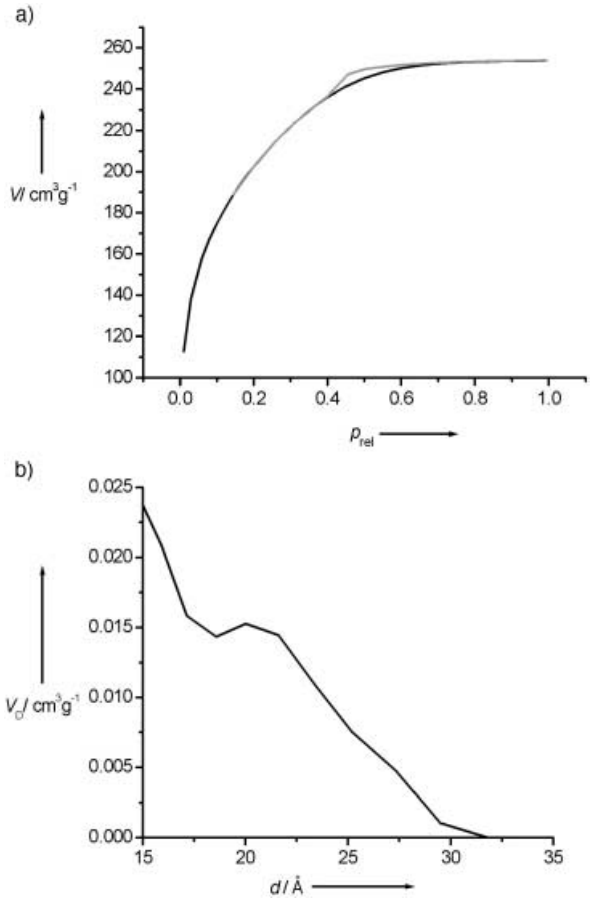

Figure 2. N_2 isotherm of γ-HPCD-silica (a, adsorption printed in black, desorption in gray) and the corresponding DFT pore size distribution (b). V = adsorbed volume, p_{rel} = relative pressure, V_D = differential pore volume, d = diameter.

stacked on top of each other. This situation would be energetically favorable and we assume this to be the driving force for the self-assembly.

This type of amphiphilic organization has little in common with the standard organization of amphiphiles, since the distribution of cohesion energy in CDs has no dipolar or vectorial contributions, but a strong quadrupolar character. Consequently, the aggregation is not seen in surface tension measurements of the concentrated solutions (which behave like classical binary mixtures). Dynamic light scattering, preliminary small-angle X-ray (SAXS) and neutron scattering (SANS) experiments, however, confirm the existence of larger aggregated species already in pure water, that is it is not an artifact of the silica preparation depicted here. The presence of CD assemblies has been proposed by Häusler et al.[19] and Coleman et al.[23] but also mistrusted by Perly et al.[30] Therefore, we conclude that the structures that manifest themselves in the silica pore structure are directly related to the CD organization in pure water and not caused by the presence of silica.

To compare the systems on the basis of equal overall porosities, the more water-soluble statistically hydroxypropylated cyclodextrins (HPCDs; 1.6 hydroxypropyl (HP) groups per CD) were employed, here with 25 wt % of the template in the casting solution. For α-, β-, and γ-HPCD a more disordered pore structure was found (Figure 3 a). The statistical evaluation of the TEM images and SAXS data reveals that the pore size correlates nicely with the molecular diameter of the CDs. The obtained values for the pore size are 1.4($\pm$0.3) nm for α-HPCD as a template, 1.6($\pm$0.3) nm for β-HPCD, and 1.8($\pm$0.3) nm for γ-HPCD (molecular diame-

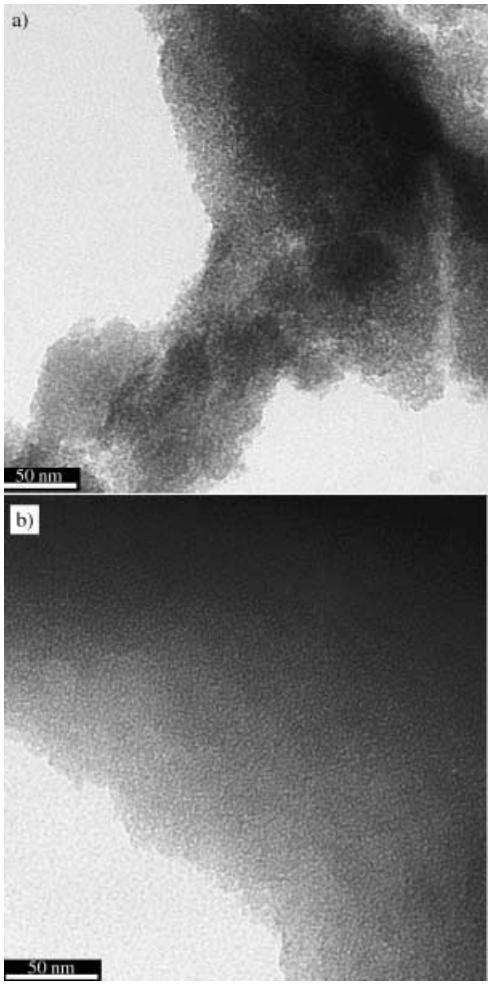

Figure 3. TEM micrographs of β-HPCD-silica (a) and β-MCD_p-xylene-silica (b).

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ters for underivatized CDs[31]: 1.37 nm for α-CD, 1.53 nm for β-CD and 1.69 nm for γ-CD).

These values are supported by nitrogen sorption measurements which show characteristics of type I and type IV isotherms (Figure 2; between micro- and mesopores)[32] and pore size distributions (density functional theory (DFT) calculations)[33, 34] with a small maximum at about 2($\pm$0.2) nm. The surface areas of the silica materials prepared with the more soluble and disordered HPCDs are in the range of 800 – 900 $m^2 g^{-1}$ with a porosity of 0.32 $cm^3 g^{-1}$ for all three samples.

β-methylcyclodextrin (β-MCD; also statistically methylated) as a CD of intermediate solubility showed again the wormlike structure typical for unsubstituted CDs, and its BET surface area was lower than the one of the corresponding β-HPCD due to the smoother pore walls. This underlines the influence of the CD substitution pattern on the intermolecular organization of the CD molecules.

To verify the assumption that the quadrupolar amphiphilic character of the CDs is responsible for the alignment to wormlike aggregates, the inclusion compounds of β-MCD with *p*-xylene and naphthalene were prepared, silica-casted, and compared to the structures of the pure β-MCD- and β-HPCD-based silicas. The inclusion leads to a hydrophobized CD pocket. Analytical details about the inclusion compounds are given in the Supporting Information. The resulting silicas were initially investigated by TEM. Figure 3a and b show the TEM results for two extreme cases from the series (β-HPCD (most hydrophilic), β-MCD_*p*-xylene (most quadrupolar amphiphilic)).

In all cases, worm-type pores are observed. A more careful visual inspection, however, reveals that structure, definition, and shape persistence increase with increasing polarity difference within the template (compare Figure 3a and b). Although the TEM images give some indications for the differences in the order of the supramolecular structure, the differences are hard to quantify by electron microscopy solely. The pore structure was additionally characterized by SAXS, which is the appropriate technique to investigate the degree of order of the pore system and to determine the average pore size.

Figure 4a shows the comparison of the SAXS curves of β-HPCD-, β-MCD-, and β-MCD_xylene-silica. To have comparable conditions samples with identical template concentrations were prepared (see Table 1). β-HPCD-silica was therefore analyzed near to its saturation limit (1) and at a standard concentration (2). Already the bare scattering curves indicate a clear difference between the pore systems. For β-$HPCD_{(2)}$, the curve is typical for pores of the size of single CD molecules which are randomly distributed in the silica matrix. Compared to those of β-$HPCD_{(2)}$-silica, the other scattering curves are caused by larger structures than single CD units, since the s^{-4} Porod behavior begins at significantly smaller *s* values.

The SAXS curves were evaluated by using the concept of "chord length distribution" (CLD), which was previously established to investigate the structure of two-phase systems and, in particular, porous materials.[35, 36] The CLD (which is similar to a pore size distribution) for β-$HPCD_{(2)}$ (Figure 4b)

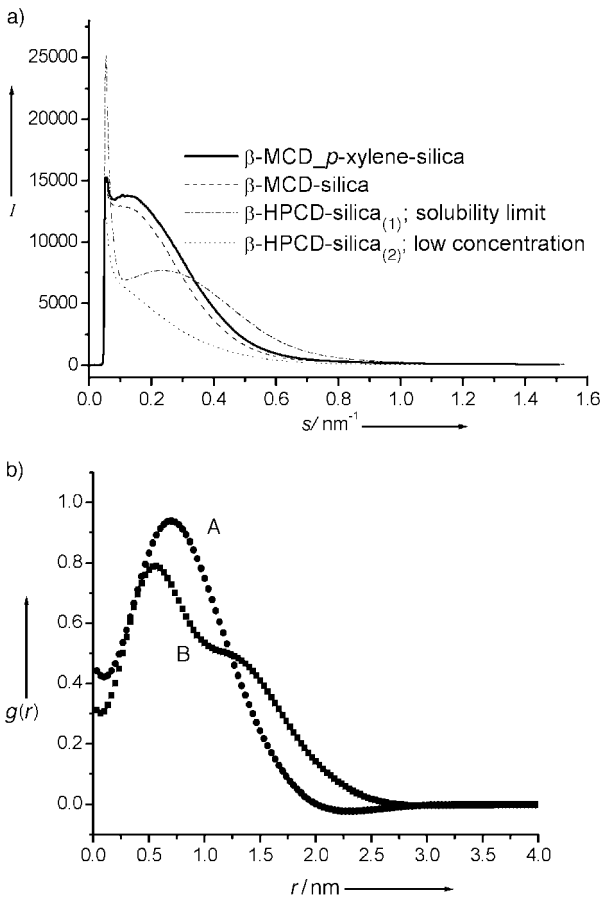

Figure 4. a) SAXS diffractograms of β-HPCD-, β-MCD-, and β-MCD_*p*-xylene-silica, b) corresponding chord length distributions for the two extreme cases β-$HPCD_{(2)}$ (A) and β-MCD_*p*-xylene (B). I = scattering intensity; s = scattering vector; $g(r)$ = chord length distribution function; r = radius.

shows a marked maximum at $r \approx 0.7$ nm and nearly vanishes at $r \approx 2$ nm, related to the cross section and the diameter of the single CD unit. The average chord length of the pores (l_{pore}), which can be regarded as an average pore size *D*, can be calculated from the Porod length l_p, the first moment of the CLD, through the relation $l_{pore} = l_p/(1-\phi)$, where ϕ is the porosity. Using this approach, for β-HPCD-silica a mean pore size of $D \approx l_{pore} \approx 1.5$ nm is obtained which is in reasonable agreement with the size of a single β-HPCD molecule. Moreover, the CLD starts with a value only slightly above zero which is indicative of a smooth pore/wall interface without angularity and free of very small micropores below 0.5 nm, that is the walls are not porous themselves.[37] Similar results were obtained for the other CD-derived silicas. This differentiates the CD-born silicas from similar structures synthesized with nonionic surfactants and amphiphilic block copolymers.[14, 38, 39] CD-casted porous materials can therefore be regarded as more defined in the monodispersity of their pores. SAXS shows that the more water-soluble HPCDs form essentially disordered molecular pores of the size of the CD, and smooth walls with no disturbing microporosity.

The SAXS curve of β-MCD_*p*-xylene-silica (Figure 4a) differs significantly from that of β-$HPCD_{(2)}$-silica and shows a broad, but significant peak at $s \approx 0.12$ nm^{-1} and a downturn at

still smaller s values due to an intermolecular correlation hole which can be interpreted as the ordered packing of large pores. The position of the correlation hole "peak" corresponds to a length scale of about 8 nm, the averaged pore-to-pore distance. From the SAXS curve, no information about the length of the worm-type holes can be obtained, since the packing effect truncates the structure factor towards smaller s values. Furthermore, the CLD for β-MCD_p-xylene-silica (Figure 4b) is typical for cylindrical objects for which the first maximum corresponds to the cross section, whereas the tail towards longer distances describes the (here truncated) averaged length of the cylinder. SAXS therefore implies that the pore organization for this silica is given by the copy of a columnar stacking of the CDs where the stacks are mutually correlated, but not long-range ordered. A more detailed κ,ι-analysis of the SAXS data confirmed this conclusion (see Supporting Information).[40–42]

The SAXS curve of β-MCD-silica lies between the two extreme cases (Figure 4a), but is very close to that of the xylene inclusion compound. The latter comparison reveals the influence of a hydrophobic guest in the cavity on the intermolecular order. The difference lies mainly in the region ahead of the peak at $s = 0.12\ \mathrm{nm}^{-1}$ where a stronger downturn is found for the inclusion complex based silica. This behavior is attributed to a higher intercolumnar ordering of the β-MCD_p-xylene aggregates compared to β-MCD.

With the SAXS measurements in mind, it is possible to reanalyze the surface area measured by N_2 sorption for the three silicas under consideration (with identical preparation conditions and CD concentrations). β-MCD_p-xylene-silica has a surface area of 596 $\mathrm{m^2\,g^{-1}}$ and a porosity of 0.28 $\mathrm{cm^3\,g^{-1}}$, the values for β-MCD- and β-HPCD$_{(2)}$-silica are 712 $\mathrm{m^2\,g^{-1}}$/0.33 $\mathrm{cm^3\,g^{-1}}$ and 873 $\mathrm{m^2\,g^{-1}}$/0.40 $\mathrm{cm^3\,g^{-1}}$, respectively. This tendency is consistent with the trend towards less order and increasing dispersity as the quadrupolar amphiphilicity decreases, as already observed with TEM and SAXS (more disordered pores create higher surface areas due to the higher fraction of moleculary imprinted pores).

β-MCD_naphthalene-silica showed similar features in the TEM images, N_2 sorption, and SAXS as the xylene compound, and no further analytical details for this material are given here.

For a better understanding of the unusual assembly of CD molecules we also performed molecular modeling calculations. First, the structure of a β-CD inclusion complex was calculated with force field (MM2) methods. Our data were in good agreement with those of other calculations.[43] From this starting geometry we calculated the electrostatic potential with the ab initio Hartree–Fock method and a 3-21G basis set. This allowed verification of the proposed quadrupolar gradients in the cyclodextrins. Indeed, a cyclodextrin inclusion complex can be regarded as a cylindrical unit with a hydrophobic core and a hydrophilic exterior (Figure 5a). Then, we investigated the interaction potentials between two CD inclusion units with the semiempirical CNDO method. Three geometries were evaluated with regard to the inter-ring distance (Figure 5b): 1) ideally parallel, 2) staggered parallel, 3) perpendicular orientation of the rings. The interaction of CDs perpendicular to each other is purely repulsive. An

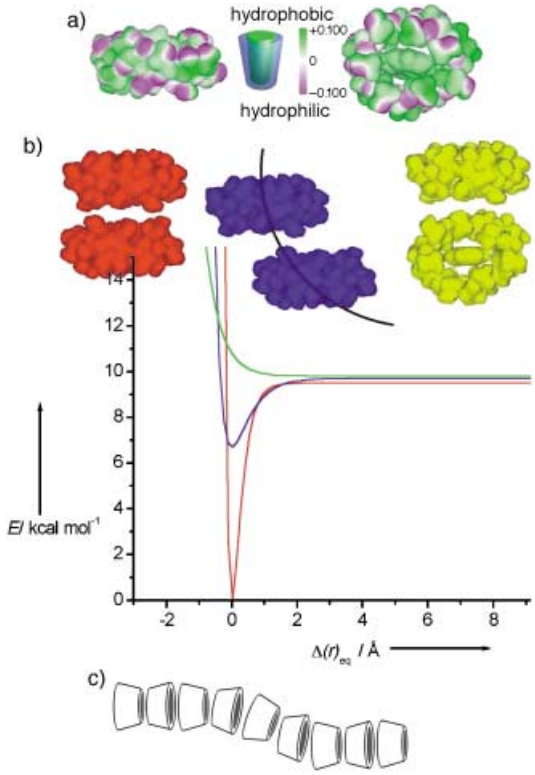

Figure 5. a) MM2-calculated structure of a cyclodextrin inclusion complex and its electrostatic potential distribution from an ab initio Hartree–Fock calculation. b) Calculated energy surfaces as a function of the inter-ring distance for the schematically shown ideally parallel (red), staggered (blue), and perpendicular (yellow) approach. c) Schematic representation of the aggregate structure of α-CD, as revealed by silica nanocasting, dynamic light scattering, and SAXS in solution. Bright: hydrophilic domains; dark: hydrophobic domains. E = energy; $\Delta(r)_{eq}$ = deviance from equilibrium distance.

attractive energy surface is found for the ideally parallel and the staggered parallel arrangement; the minimum of the Morse-type potential is deeper for the ideally parallel orientation.

The energies of the interactions are "soft" and in the range of those of supramolecular organization in agreement with the experimentally found alignment effects. It is energetically favorable for the CD complexes to line up, but slightly bent or staggered geometries (Figure 5c) are also energetically possible, thus resulting in the wormlike structure. A more precise calculational study would need to take into account the solvent and possible entropic effects as well as the influence of hydration and water matrix.

To conclude, cyclodextrins are an alternative to classical amphiphiles as templates for the synthesis of porous materials, for which the pore diameter corresponds exactly to the cyclodextrin size and is in the technically interesting range of 1.5–2.0 nm.

In contrast to all nonionic ethyleneoxide-based surfactants, CDs do not penetrate or mix with the silica walls, that is they create no additional microporosity that would weaken the wall material; such microporosity is one major drawback of previous block copolymer based porous silicas. Only one type of pores is created by the CD route.

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Unexpectedly, unsubstituted and partially methylated CDs self-assemble to larger aggregates, mostly of the "wormlike" type. It is argued that the CDs aggregate because of a special distribution of polar and nonpolar sites, which is, however, not dipolar or vectorial as for classical amphiphiles, but rather quadrupolar or discotic in character (a difference between the inside and the outside of the disks). Minimization of the mutual contact areas of hydrophilic and hydrophobic leads to columnar aggregates of CDs and their inclusion complexes (their structures have so far only been studied in the solid state[44]). This model was supported by modeling calculations. When hydrophobic guests are used in inclusion complexes the quadrupolar amphiphilicity changes, and the order formation is enhanced. This results in the interesting situation that the order of the aggregate can be triggered by inclusion of different guest molecules.

In the case of a true casting or a 1:1 copy of a preexisting template structure in water, the silica nanocasting can be seen as a new technique to investigate the solution organization of CDs and possibly other compounds. We will undertake further investigations to elucidate the structure of CDs in pure water and to prove that the organization revealed by the silica pores is a copy of the original state. The use of CDs as templates significantly extends the possibilities of nanocasting, since it enables not only the construction of new porous materials with the help of "quadrupolarly organized" template structures, but also the functionalization or loading of the porous inorganic materials through inclusion complexes.

Experimental Section

All CDs were obtained from Wacker, all other chemicals from Aldrich and used without further purification. The MCD and HPCD were only partially derivatized; statistically 1.6 OH groups per CD molecule were modified.

Preparation of cyclodextrin inclusion compounds: An equimolar amount of *p*-xylene was dispersed in a solution of the CD in water. The mixture was stirred at 50 °C for 24 h in a closed vessel. A sample was isolated for analysis (^{1}H NMR) from the resulting homogeneous phase. The residue was directly used for templating. The naphthalene inclusion complex was prepared according to ref. [45].

General method for the preparation of CD-based silica materials (for the exact amounts and reaction conditions see Table 1): The CD was dissolved in water. Under vigorous magnetic stirring concentrated hydrochloric acid (to adjust pH to 1.7 – 2) and then tetramethylorthosilane were added. After homogenization at room temperature the formed methanol was removed under vacuum at 40 °C. The gels were aged for 24 h at 60 °C, and the resulting silica materials were calcined at 500 °C under oxygen for 15 h.

Details about the characterization methods are given in the Supporting Information.

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