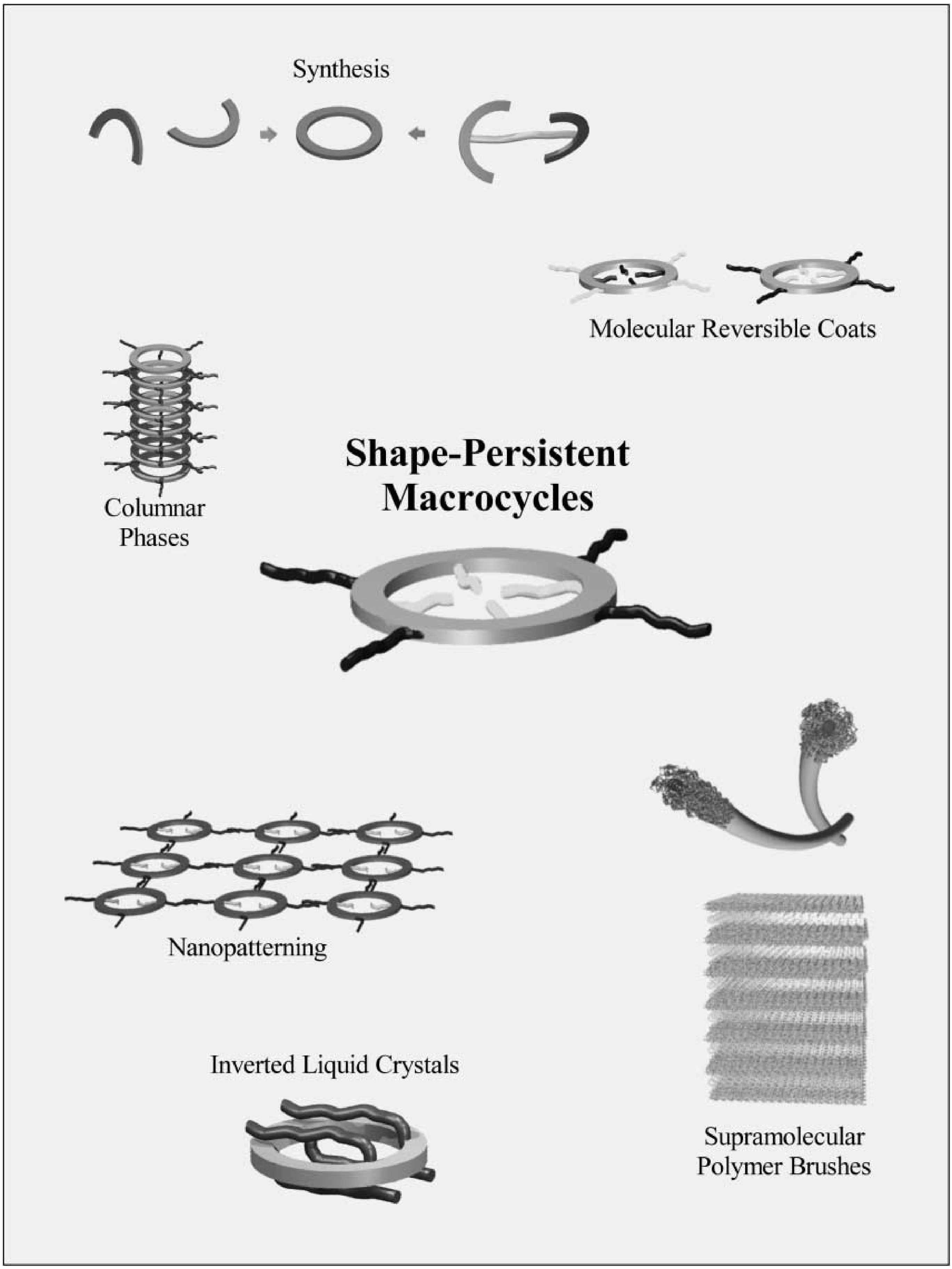

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Shape-Persistent Macrocycles: From Molecules to Materials

Sigurd Höger*[a]

Abstract: Shape-persistent macrocycles with an interior in the nanometer regime allow the attachment of (functional) side groups at defined positions at the ring. These side groups can have either a fixed orientation relative to the molecular backbone or they can adapt their orientation according to an external stimulus. The properties and applications of the compounds depend strongly on the orientation of these side groups. Macrocycles with intraannular or adaptable long alkyl groups display a new design principle for discotic liquid crystals. Macrocycles with extraannular (oligo)alkyl groups can be used for surface patterning in the nanometer regime and rings with extraannular oligostyryl groups are able to aggregate to supramolecular hollow polymer brushes.

Keywords: host–guest systems · liquid crystals · macrocycles · nanostructures · self-assembly

Introduction

The organization of molecular entities into structures with a high level of complexity is one of the great objectives of supramolecular chemistry. Shape-persistent macrocycles with an interior in the nanometer regime are interesting compounds in this sense, because their rigidity allows the defined positioning of (functional) side groups and the study of their influence on the compounds' properties and applications.[1,2] The term shape-persistent macrocycle means that the building blocks of the ring are rather rigid and their connection is performed in such a way that the final structure cannot collapse, in contrast to flexible structures like crown ethers or cycloalkanes.[3] A more precise definition of shape-persistence is not based on the molecular building blocks, but on the flexibility of the final structure: According to rigid rod polymers,[4] shape-persistent macrocycles have an interior (lumen) d that is, on average, equal to the contour length l of their molecular backbone divided by π (Figure 1).

Figure 1. Shape-persistent macrocycles have an interior d that is, on average, equal to the contour length l of their molecular backbone divided by π.

In order to keep these rigid structures tractable, side groups have to be attached to the backbone. The orientation of the side groups relative to the molecular backbone has a strong influence on the materials properties. For example, macrocycles with an orthogonal arrangement (orthogonal substituents, Figure 2, left) of polar functional groups are able to form tubular superstructures in the solid state.[5] If the polar functional groups point to the outside of the macrocycle (extraannular substituents, Figure 2, middle) this may lead to the formation of a 2D network in the solid state.[6] Shape-persistent macrocycles with polar groups pointing to the inside (intraannular substituents, Figure 2, right) play a special role in supramolecular chemistry.[7] The

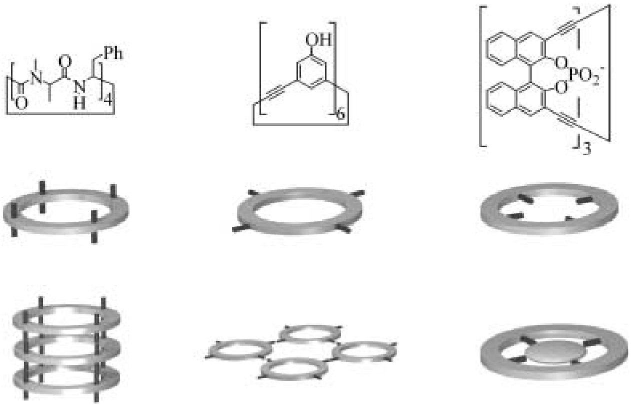

Figure 2. Possible orientations of polar side groups (dark gray) in shape-persistent macrocycles and their respective properties or functions.

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convergent preorganization of the binding sides allows them to act as host molecules for the recognition of appropriate guest molecules according to the *lock and key principle*.[8]

Shape-Persistent Macrocycles with Adaptable Substituents

All macrocycles described above have a fixed side chain orientation, given by the building blocks and the synthesis. However, if the building blocks of the macrocycle carrying the functional groups can rotate freely, the side group orientation is not determined by the synthesis, but by an external parameter (adaptable substituents). Moreover, if the macrocycle contains adaptable substituents of different polarity, it might be possible that the solvent influences the actual conformation in such a way that in a polar solvent the polar substituents point to the outside and a less polar interior is formed, and vice versa (Figure 3).

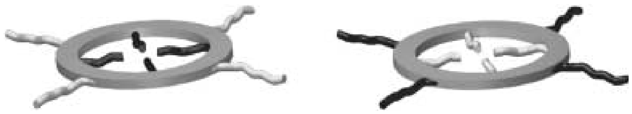


Figure 3. An adaptable amphiphilic macrocycle might change the orientation of the polar and nonpolar side groups according to an external stimuli. In a nonpolar solvent (left) the nonpolar side chains (light gray) point to the outside and the polar side chains (dark gray) point to the inside, and vice versa (right).

The macrocycles might also act as host molecules for appropriate guest molecules. However, opposite to the case described in the previous section, the conformation of the host is influenced by the guest molecule and therefore the binding process resembles the *induced fit mechanism*. The combination of a low rotational barrier for parts of the macrocycle together with an overall structural rigidity is found in phenylene–ethynylene macrocycles.[9]

Figure 4 displays the general structure of the compounds described in this article. The sides of the macrocycle are formed by the adaptable units and the corner pieces. Depending on the position at which the side groups (which can also contain functional groups) are attached to the ring, they have either a fixed intraannular (I, I′), fixed extraannular (E, E′), or adaptable orientation (A, A′). A proof of the last hypothesis will be given in the next chapter. Of course, it is also possible to prepare macrocycles that contain (different) functional groups attached to the ring at more than one position.

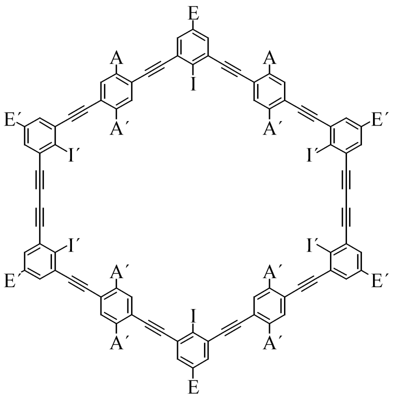
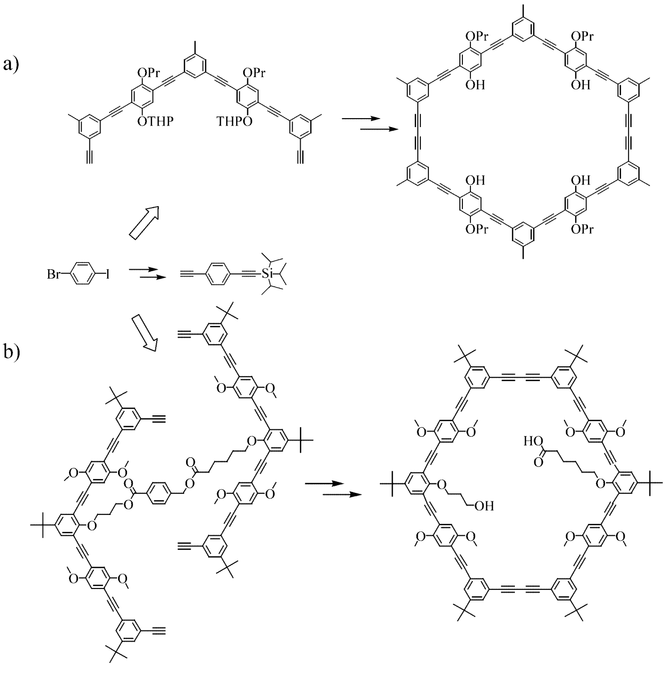


Figure 4. Shape-persistent macrocycle with intraannular (I, I′), extraannular (E, E′) and adaptable (A, A′) substituents.

The synthesis of these macrocycles becomes evident by looking at their structure: the cyclization step is the oxidative acetylene coupling of rather rigid phenylene–ethynylene oligomers ("half rings") performed under pseudo-high-dilution conditions in order to suppress extended polymer formation.[10] The cyclization can be performed by two different approaches: either by a statistical reaction giving isolated product yields of about 40–50 % (Scheme 1 a), or by a template-supported cyclization giving the macrocycles often in over 90 % yield (Scheme 1 b).



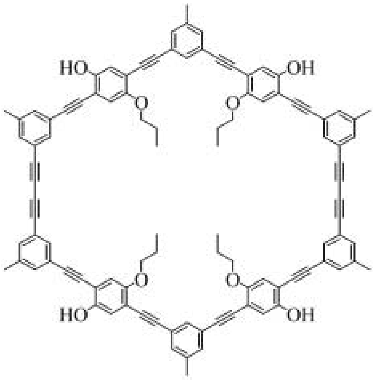
Scheme 1. Macrocycle formation by the a) statistical and b) template-supported oxidative acetylene coupling.

Moreover, the use of a covalent template allows also the formation of nonsymmetrical macrocycles by simply using a nonsymmetrical template.[11] In any case it is necessary to form the required half rings by a repetitive synthesis by using monoprotected bisacetylenes as key compounds. Their preparation is based on the combination of the bromo–iodo selectivity of the Pd-catalyzed Hagihara–Sonogashira coupling and the possibility to deprotect bisacetylenes with two different silyl protecting groups stepwise.[12–14] It cannot be overemphasized enough that a properly designed synthesis with orthogonal protective groups is the prerequisite to prepare functional macrocycles in amounts such that not only their molecular properties but also their material properties can be investigated in detail.[1d]

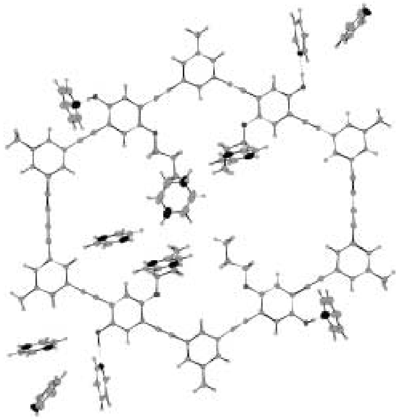
Molecular Reversible Coats

Although the arene moieties carrying the adaptable substituents should be able to rotate freely, it has not been proven before that the macrocycle conformation can indeed be influenced by an external parameter.

Recrystallization of **1** from pyridine gave single crystals suitable for X-ray analysis (Figure 5).[14] For each macrocycle eight molecules of pyridine were localized. Four of them form hydrogen bonds to the phenol-OH groups of the ring, the remaining pyridines pack within the crystal lattice without specific interaction. Most interesting is the observation that the macrocycle adopts, through recrystallization from a polar solvent, a conformation in which the polar phenol-OH groups point to the outside and the nonpolar groups point to the inside, as proposed in Figure 3. The question whether an opposite conformation could also be identified in this class of macrocyclic amphiphiles was answered with the help of host–guest chemistry.[15] Based on computer models, the rigid tetraamines **2a** and **2b**were identified as fitting nearly perfect into the cavities of the macrocyclic tetraphenols **3a** and **3b** if the phenol-OH groups of the macrocycle point to the inside. NMR spectroscopic determination of the binding constants for **2a**···**3a** (160 M^{-1}), **2a**···**3b** (170 M^{-1}), and **2b**···**3b** (10 M^{-1}) in $C_2D_2Cl_4$ indicates that in the host–guest complex the tetraamine is located in the interior of the macrocycles.

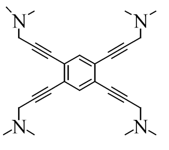


1

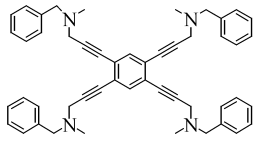


1 · 8 py

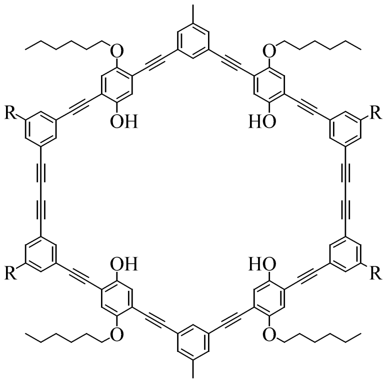
Figure 5. Molecular structure of **1** and X-ray structure of **1**·8py.



2a



2b



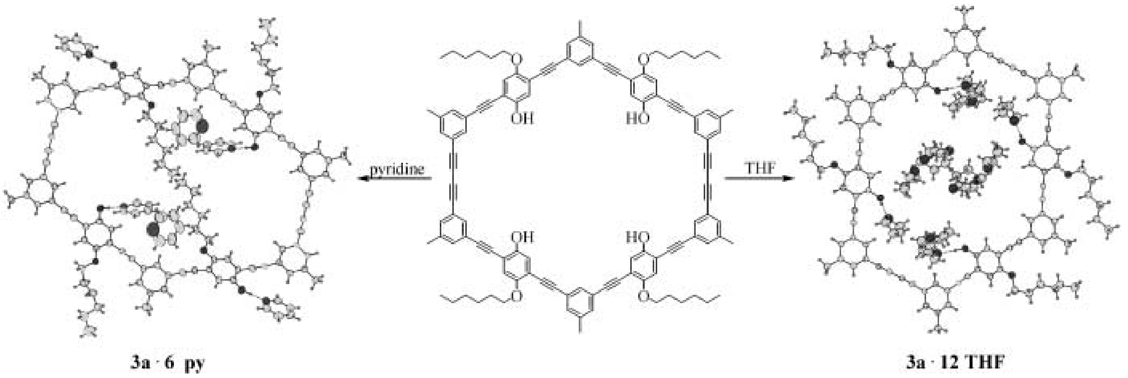
3a: R = Me
3b: R = *t*-Bu

Since in that case a binding is only possible if the orientation of the polar phenol-OH groups is opposite to that found in the pyridine solvate of **1**, these macrocycles were given the name "*molecular reversible coats*". Schematically, the structure of the host–guest complex is the same as in Figure 2 (bottom, right). However, the binding here resembles the *induced fit mechanism*.

Moreover, recent experiments have shown that even the solvent influence alone can change the macrocycles' conformation (Scheme 2).[16] Recrystallization of **3a** from pyridine leads to half of the nonpolar alkyl groups point to the outside and half of them to the inside, whereas recrystallization from the less polar solvent THF leads to the macrocycle adopting a conformation in which all nonpolar alkyl groups point to the outside. The different conformations lead also to a different supramolecular organization of the rings in the crystal lattice: **3a**···12THF forms a supramolecular tube consisting of channels with pore sizes (ca. 8 × 12 Å) larger than those found in cyclodextrines (Figure 6).[17] In addition, these channels contain polar functional groups.

Shape-Persistent Macrocycles as Elements of Complex Molecular Architectures

Liquid crystals with an inverted conformation: The synthetic tool box and the observed behavior of the macrocycles were the basis for the investigation of these structural motifs as parts of more complex structures. One of the obvious questions is whether these rings with their large internal cavity can exhibit liquid crystallinity. Liquid crystals based on disklike or cyclic molecules were first described by Chandrasekhar more than 25 years ago.[18] In the meantime macrocyclic and even shape-persistent macrocyclic compounds have



Scheme 2. Solvent triggering between conformational states in **3a**.

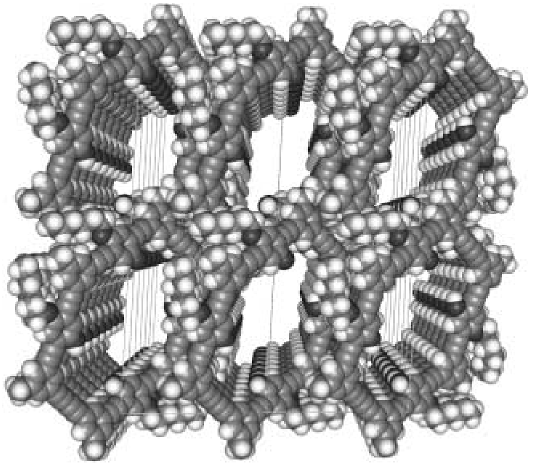
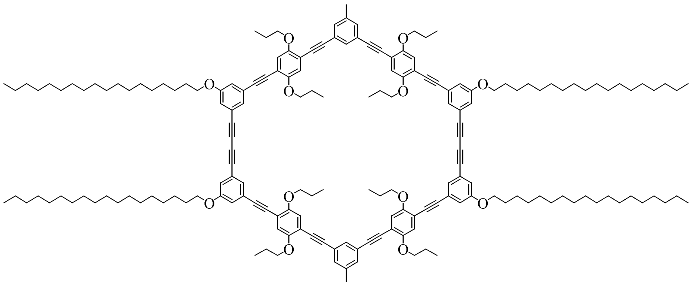


Figure 6. View down the crystallographic *b* axis of **3a**·12 THF (solvent molecules are removed).

been found to be liquid crystalline.[19,20] All these discotic liquid crystals follow the same design principle: a rigid core structure is surrounded by a flexible periphery (Figure 7).

Figure 7. Design principle of disklike (left) and cyclic molecules (right) capable of forming thermotropic mesophases.



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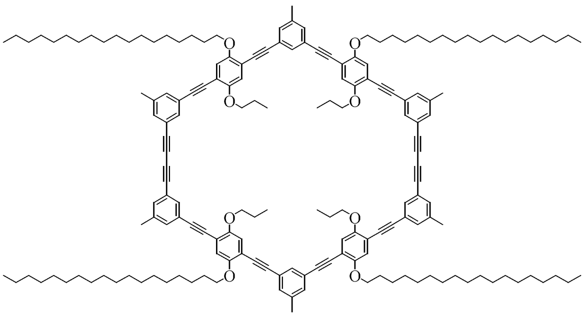


5

Therefore, macrocycles **4** and **5** were prepared and investigated in terms of their thermotropic behavior.[21]

Although both compounds correlate at first glance with the design principle of discotic liquid crystals, only the latter exhibits a stable thermotropic mesophase (C 185 N_D 207 I) (Figure 8, top). It can be speculated that the large internal void inside the shape-persistent macrocycles avoids the formation of a stable LC phase. Since an intramolecular alkyl-chain back-folding is rather improbable for **4**, alkyl groups of neighboring rings have to fill the macrocycles interior, leading to geometric constrains that prevent the formation of a stable LC phase. The new riddle, namely why **5** exhibits a stable LC phase, could be solved by single-crystal X-ray analysis showing that **5** fills the interior with its own alkyl chains (Figure 8, bottom). This is possible because the long alkyl chains are located at the adaptable positions of the ring, thus allowing an intraannular orientation of the alkyl chains without paying an energetically and entropically high price. Even more interesting is the finding that the topology of the macrocycle in **5** is opposite to all discotics described before: a rigid periphery acts as a framework for flexible side groups located intraannular (Figure 9).

However, at this point one important question was yet not answered. In order to explain the stable LC phase of **5**, its conformation in the LC phase was derived from the X-ray data, not knowing if the adaptable alkyl chains point in the LC phase inside the macrocycle. Since there is no simple experiment that gives an answer to the question of whether **5** is really a discotic liquid crystal with inverted topology, the missing isomer in this series of macrocycles was prepared. In **6** the long intraannular alkyl chains are now attached at the corner pieces of the ring and can not rotate outwards. Compound **6** also exhibits a stable nematic LC phase (C 134 N_D 159 I), and, therefore, the question wheth-

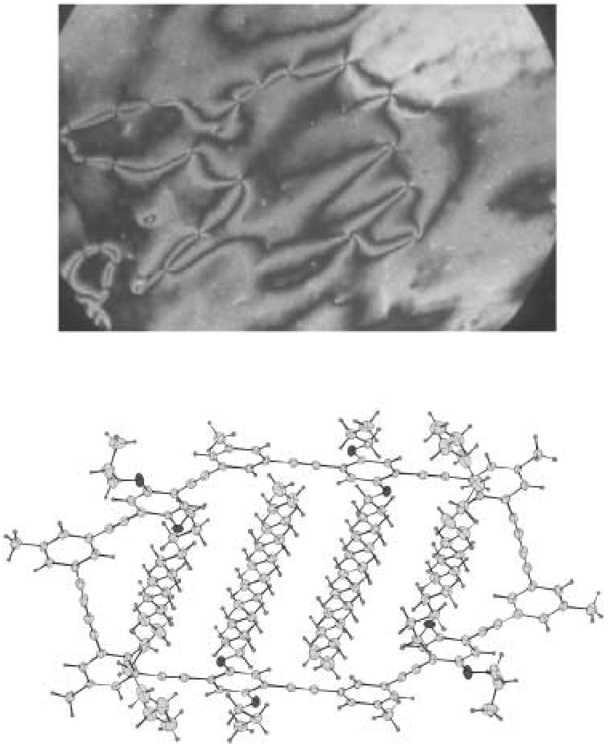


Figure 8. Texture of **5** at 200 °C viewed between crossed polaizers (top); structure of **5** in the crystal (bottom).

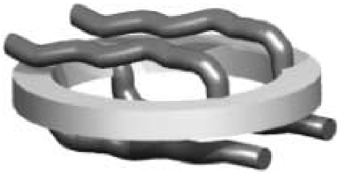
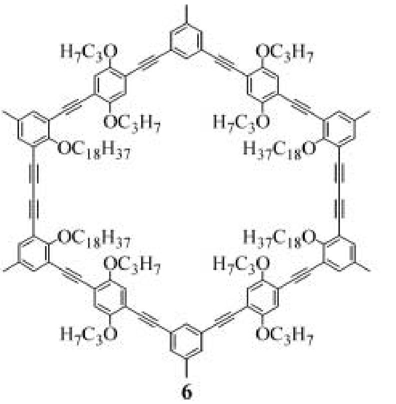


Figure 9. Schematic representation of the arrangement of the alkyl chains in **5**.

er liquid crystalline macrocycles with an inverted topology really exist can be positively answered (Figure 10).[22]



6

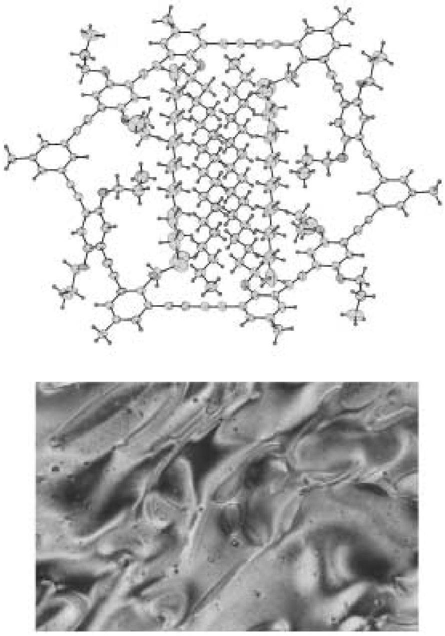


Figure 10. Crystal structure of **6** and texture of **6** at 150 °C viewed between crossed polarizers.

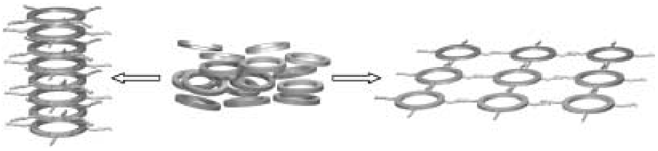
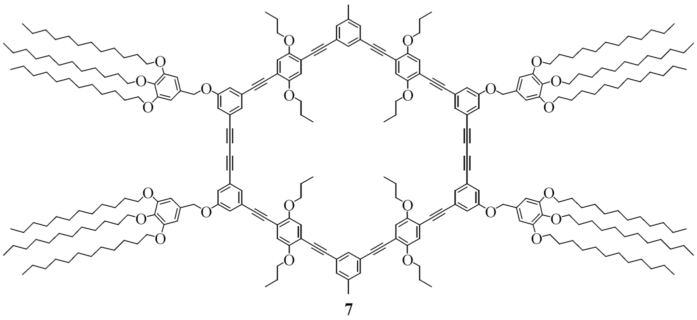


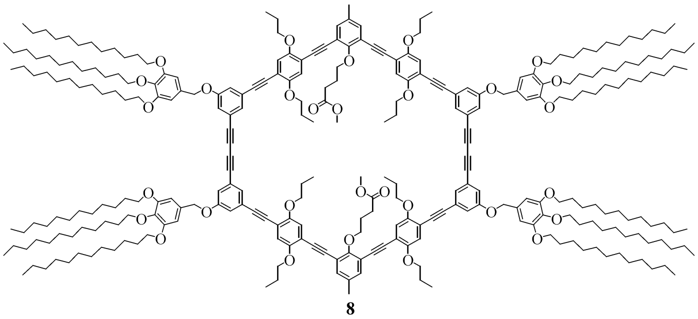
Figure 11. Schematic representation of the macrocycle arrangement in the nematic discotic phase (middle), in a tubular superstructure (left) and in a two-dimensional crystal (right).

Aggregates with a higher level of organization: In the nematic discotic LC phase, the macrocycles have only orientational correlation and no positional correlation. This can be obtained by the one- or two-dimensional organization of the rings, as schematically shown in Figure 11. However, in contrast to the macrocycle organization shown in Figure 2, the driving forces for the superstructure formation should be purely nonspecific for the following reason. If the basic principles for the self-organization by nonspecific interactions in these systems are understood, additional polar functional groups can be added, thus forming functionalized superstructures. In other words, the functional groups will not be used for the superstructure formation, but the superstructure formation will be used for the organization of the functional groups. In the ideal case, the functional groups are not influenced by the superstructure formation, thus remain "free" and should be able to recognize additional guest molecules. The driving force for the two-dimensional pattern formation is the interaction with an appropriate substrate, and for the one-dimensional organization the incompatibility of the rigid core and the flexible corona of the macrocycles.

Two-dimensional organization: The first example of our investigations was the macrocycle **7** with oligo–alkyl substituents at the periphery. The organization in two dimensions is possible in the presence of an appropriate substrate, in this case highly oriented pyrolytic graphite (HOPG) was used.[23,24] High-resolution scanning tunneling microscopy



7



8

(STM) images measured under liquid show the arrangement of **7** in a two-dimensional array with lattice constants $A=3.6$ nm, $B=5.7$ nm, and $\Gamma=74°$ (Figure 12, top). In addition to most other molecules able to form self-assembled-monolayers (SAMs), macrocycles like **7** offer the possibility to incorporate functional groups in its interior and thus leading not only the creation of *nano-patterned surfaces*, but also the formation of *functionalized nano-patterned surfaces.* Subsequently, macrocycle **8** was prepared and adsorbed on the HOPG surface (Figure 12, bottom).[25] Although locally ordered, **8** does not form a two-dimensional crystal, probably due to an unfavorable solute–solvent interaction.[26] Nevertheless, the data allow the extrapolation of the lattice constants of a unit cell of oblique symmetry to be in the order of $A=3.4$ nm, $B=5.2$ nm, and $\Gamma=87°$. These data show a similar molecular size of **7** and **8** at the graphite surface. Ultimately, these two-dimensional structures could be used as a platform for the growth of supramolecular three-dimensional structures.[27]

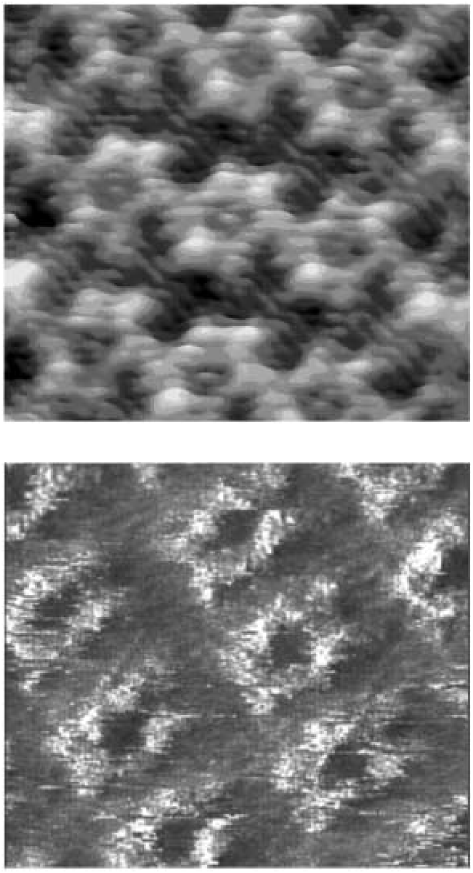
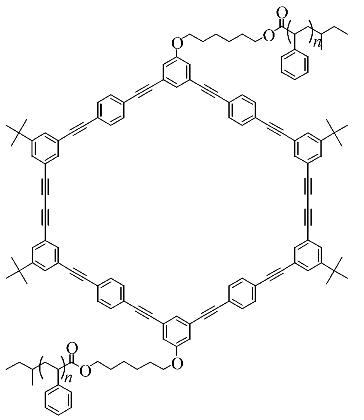


Figure 12. STM images of shape-persistent macrocycles adsorbed from solution onto HOPG: **7** from trichlorobenzene (top); **8** from phenyloctane (bottom).

It is worth noting that **8** exhibits, in contrast to **7**, a stable LC phase, most probable due to the intraannular filling of the cavity.[28] Moreover, the intraannular polar groups stabilize a columnar packing motive in the mesophase by preventing the molecules from sliding relative to each other.

One-dimensional superstructures: One possibility to force the macrocycles into tubular superstructures by means of dissipative forces only is to use the incompatibility of the rigid core and the flexible corona.[29,30] Macrocycles like **7** with oligo–alkyl side groups have only limited solubility in solvents with a preference for the corona; therefore, extended tubular structures are not observed in solution.[31,32] A simple way to overcome the solubility problem is the attachment of anionically prepared, narrowly distributed (PD (M_w/M_n) <1.1) polystyrene carboxylic acid oligomers (PS-COOH) of different molecular weight (M_w(PS): 1000–5000 g mol^{-1}; Figure 13).[33,34]

The structures **9a–e** can be described as coil–ring–coil block copolymers, a subclass of rod–coil block copolymers, which are known to separate in microphases to form well-ordered superstructures even at relatively small block sizes.[35] All block copolymers are well soluble in THF, toluene, or halogenated solvents at room temperature.[36] However, the solubility of the block copolymers in aliphatic solvents strongly depends on the size of the coiled block. While **9a** only a suspension forms even in warm cyclohexane, **9b–e** are very soluble in cyclohexane at elevated temperatures. Upon cooling, **9b** forms a gel at concentrations above 0.5 wt%. Under the same conditions **9c** rapidly forms a very viscous solution, as does **9d** after several days. These solutions are also strongly birefringent with the exception of solutions of **9e**, which exhibit neither unusual viscosity nor birefringence. These observations can be explained by the different solubility of the rigid and the flexible parts of the molecule, bearing in mind that cyclohexane is a Θ-solvent for PS, but in contrast to THF or toluene, a nonsolvent for the rigid core. Solutions of **9c** in cyclohexane were investigated in more detail. Dynamic light scattering (DLS) was performed on solutions of **9c** in toluene and cyclohexane



9a, M_w (PS) = 1000 g mol^{-1}
9b, M_w (PS) = 1500 g mol^{-1}
9c, M_w (PS)= 2500 g mol^{-1}
9d, M_w (PS)= 3500 g mol^{-1}
9e, M_w (PS)= 5000 g mol^{-1}

Figure 13. Structure of the ring-coil block copolymers **9** with oligostyrene side chains of different size (average molecular weight for each PS block is given).

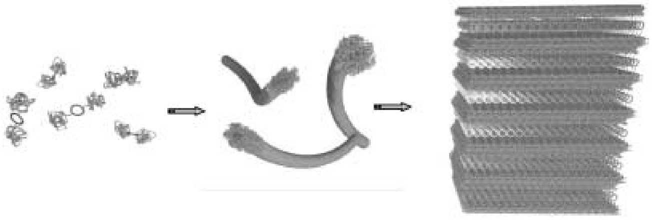


Figure 15. Schematic representation of the aggregation of the block copolymers into hollow cylindrical brushes (middle) and formation of a layerd structure in the solid state (under equilibrium conditions) (right).

(Figure 14, top), revealing that in toluene only one species, with a hydrodynamic radius of approximately 2 nm, is present; this corresponds to the size of a simple block copolymer molecule **9c** (Figure 15, left).

In contrast, the light scattering data in cyclohexane indicate additionally the presence of species with a broad distribution of hydrodynamic radii around 60 nm, corresponding to a total length of the objects between 250 and 1300 nm. The angle dependence of the scattered light intensity of the larger objects suggests the presence of rod-shaped objects with a high "virtual" persistent length of more than 100 nm. Additional X-ray scattering measurements indicate that the coil–ring–coil block copolymers aggregate in solution into *hollow* cylinder-shaped objects (Figure 15, middle). Additional support of the proposed aggregation came from the investigation of solid samples of **9c** prepared under "non-equilibrium conditions" (i.e., by fast solvent evaporation). The transmission electron micrograph (TEM) of a sample obtained by freeze-drying a cyclohexane solution (Pt/C-shadowed film) shows ribbons of different width at the sample surface, the narrowest in the range of approximately 15 nm (Figure 14, middle). Atomic force microscopy (AFM) images of a polymer film on mica show long bundles of two or three cylindrical aggregates, together with individual aggregates (Figure 14, bottom), these last having a diameter of approximately 10–15 nm. The dimensions obtained by TEM and AFM correspond well with the molecular dimensions obtained by scattering methods and are in accordance with the molecular dimensions of the molecular building blocks. Moreover, surveying the most curved cylindrical object found in the AFM (Figure 14, bottom, black arrow) and treating it as wormlike chain results in a persistent length of approximately 350 nm of the cylindrical aggregate.

In contrast to the superstructure formation of **9c** in cyclohexane, we were unable to observe the formation of any superstructure by thermal treatment of this material (i.e., slow or fast cooling from the melt). However, if solid samples of **9c** were prepared by slow evaporation of a cyclohexane solution (i.e., under "equilibrium conditions"), superstructure formation could be observed on different length scales.[37] Detailed X-ray and electron diffraction studies were performed on these samples. It became evident that the coil–ring–coil block copolymers adopt a morphology in the solid state in which columns of macrocycles are aggregated into layers that are separated by the polystyrene, and that the initially in solution formed supramolecular cylindrical brushes do not form isolated channels within the amorphous PS matrix (Figure 15, right). This morphology is a result of the attachment of the PS side chain at only two positions of the ring. Ongoing investigations will also deal with the question how the number of grafting positions influence the superstructure formation in solution and in the solid state.

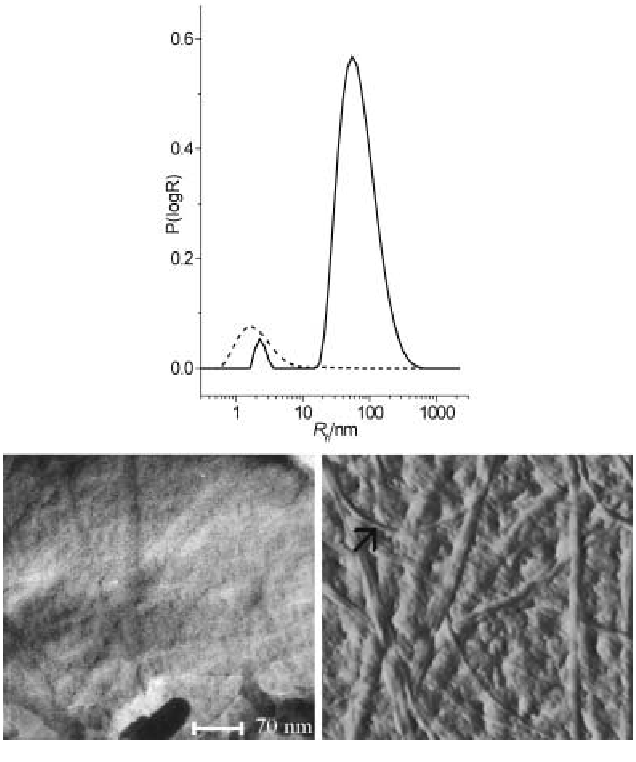


Figure 14. Top: CONTIN-fit: rate distribution of **9c** in toluene (-----) and in cyclohexane (——) at a concentration of 0.11 wt%. Bottom left: TEM: C/Pt shadowed film obtained by freeze drying a 0.15 wt% cyclohexane solution of **9c**. Bottom right: AFM (amplitude picture, 1.5×1.5 μm^2): Film obtained by dipping mica into a 0.15 wt% cyclohexane solution of **9c**.

Future Outlook

Modern synthetic methods allow the preparation of functionalized shape-persistent macrocycles on the hundred milligram scale under mild conditions. The attachment of functional side groups with a defined orientation relative to the molecular backbone allows the construction of new highly functionalized building blocks for complex supramolecular architectures. Strategies for the supramolecular organization by means of dissipative forces only create the possibility to form functionalized superstructures for the recognition of appropriate guest molecules. In addition, strategies for the size control of the superstructure need to be explored. Ultimately, these superstructures shall be used as platform for the one- and two-dimensional organization of guest molecules.

Acknowledgement

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