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Gels of shape-persistent macrocycles: the role of the interior†

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The aggregation of shape-persistent macrocycles with an empty cavity, an undecyldiether strand and a tetraethylene glycol strand leads in all cases to a macroscopic gelation of the solvent. However, the gelation temperatures are fine-tuned by the intraannular substituents.

Self-assembly of molecular building blocks towards complex predictable architectures has become manifested as an established concept in chemistry.[1] Among the manifoldness of supramolecular structures, rod-shaped and tubular aggregates have received increased attention.[2] More particularly, they were recently discussed as sensor materials,[3] electrically conductive molecular wires,[4] and ion channels.[5] An approved design principle of molecular building blocks forming the designated highly anisotropic structures in solution is based on oblate shape-persistent backbones, surrounded by a flexible periphery, which—due to different solubility—aggregate by non-specific interactions (that is without the help of adjunct functional groups).[6–8] Association of tubular aggregates may also lead to the formation of ribbon-like or vesicular structures.[7c,9] Beyond polycyclic aromatic hydrocarbons,[10] comparably large arylene–alkynylene-macrocycles[11] allow—beside the tailorable design of the rigid core dimensions and shapes—the implementation of central cavities and the intraannular attachment of functional units. This should nominally facilitate an independent host–guest chemistry within the tubular channels, ideally without influencing the aggregate structure.[6a] Whereas the influence of the electronic structure of the shape-persistent macrocyclic backbones on the aggregation behavior has been intensively investigated,[8d–f] the cavity filling has largely been unexplored.

Recently, we demonstrated that shape-persistent macrocycles carrying extraannular bulky oligostyrene or oligoalkyl side chains form nanoscale tubular aggregates under specific solvent conditions.[6,12] In some cases, due to interactions between individual tubes, there are formed bundles and/or ribbons and even networks. The latter leads to a macroscopically observable gelation.[13] During our studies on the template directed macrocycle synthesis we observed that macrocycle **1**, with an intraannular ring-crossing aliphatic bridge and extraannular octadecyloxy side chains, is capable of forming gels in selected non-polar solvents (Fig. 1). To evaluate the effect of the interior filling on gelation, we additionally synthesized two derivatives of **1** comprising an empty cavity (**2**) and a tetraethylene glycol strand (**3**).[14] Both of them are also gel-forming.

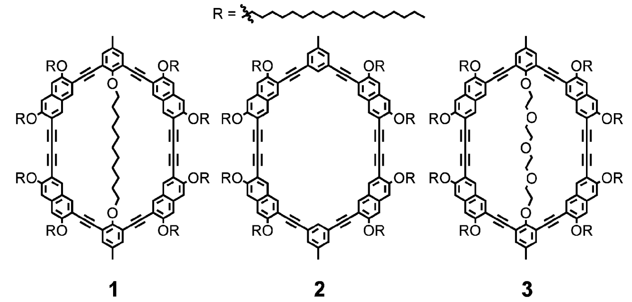

Fig. 1 Structures of the gel forming macrocycles.

The gels are obtained after dissolving the macrocycles in hot cyclohexane (CHX), methylcyclohexane (MCH), or decaline, and subsequent cooling to room temperature. Within 1 min (**2** and **3**) or 10 min (**1**) slightly yellow, translucent gels are formed. The critical gelation concentration (cgc) in CHX is 0.5 wt% for all three compounds, as determined by stable-to-inversion tests. Below cgc—stored at room temperature or below—a gel phase separates from a solution of **1**. Under identical conditions, **2** or **3** form a cloudy (not gel-like) precipitate. Gels of **1** and **3** (1 wt% in CHX) maintain unaltered consistence for days and weeks, respectively, while the corresponding gel of **2** significantly loses stiffness overnight.

The atomic force microscopy (AFM) investigations of solution and gel samples cast on mica allow a detailed characterization of the aggregate morphology. All compounds (**1**, **2**, and **3**) form self-assembled networks, consisting of randomly oriented ribbons (Fig. 2a and b and ESI†) with a minimum height of 4.0 ± 0.5 nm (AFM height measurements, Fig. 2d). At crossing points a height addition (to 7.5 ± 0.5 nm; 11.0 ± 0.5 nm) is observed.

Fusing and splitting of individual ribbons along their direction occurs frequently (*e.g.* arrows in Fig. 2b). Transmission electron microscopy (TEM) investigations of a dried gel of **1** (from a diluted 1 wt% CHX-gel) on a holey carbon film confirm the

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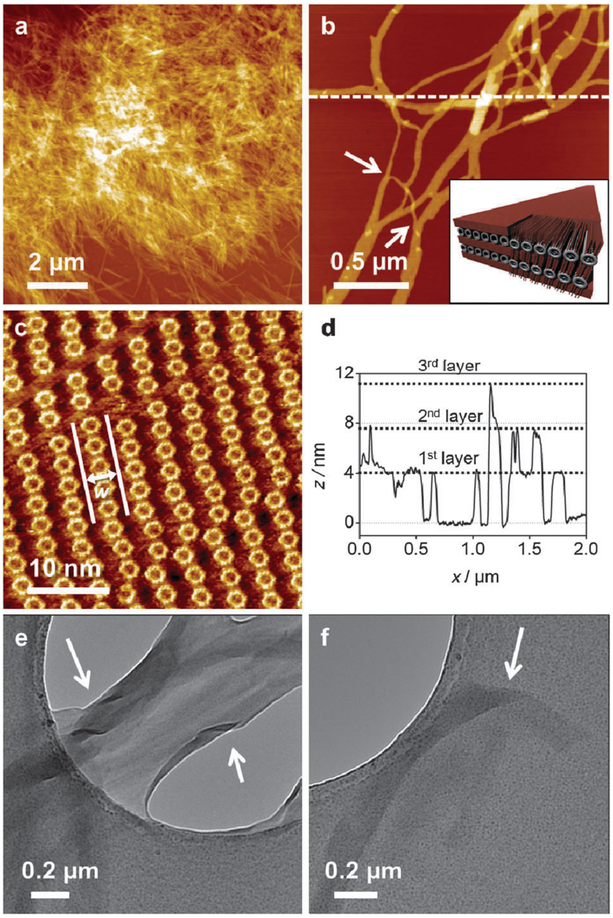

Fig. 2 (a) and (b) Atomic force microscopy (AFM) images of aggregates of **1** on mica. (a) A dense fibrous network is observed near the edge of a gel film of **1** (2.5×10^{-3} M, 1.0 wt%, CHX), slightly spread by spinning. (b) Several ribbons with varying widths are cast from a dilute solution (1.5×10^{-4} M, 0.06 wt%, MCH), which randomly fuse/split (arrows) and cross. Inset: proposed aggregate model. (c) Scanning tunneling microscopy (STM) image of **1** at the TCB–HOPG interface ($c = 10^{-5}$ M, $V_S = -1.2$ V, $I_t = 30$ pA). The distance w between two rows is 4.2 ± 0.2 nm, which is closely related to the height of the ribbons measured by AFM along the white dotted line in (b) (see topography cross section in (d)). (e) and (f) Transmission electron microscopy (TEM) images of aggregates obtained from a gel of **1** in CHX (2.5×10^{-3} M, 1.0 wt%, diluted with CHX) on holey carbon. Folding of the aggregates is observed (arrows), which confirms their ribbon-like structure.

ribbon-like aggregate structure (Fig. 2e and f) with a variable width of about 50 to 200 nm (see ESI†).

Based on previous results[2b,9,15] we also assume here the phase separation of rigid and flexible parts of the molecules. The macrocycles aggregate and stack on top of each other to form columns that assemble tightly. As a consequence, a sheet-like structure is formed, in which adjacent stacks of rigid backbones arrange as a layer embedded between the flexible side chain layers.[16] Scanning tunneling microscopic (STM) investigations of **1** at the interface of 1,2,4-trichlorobenzene (TCB) and highly oriented pyrolytic graphite (HOPG) show self-assembled monolayers. The rows of adjacent, densely packed backbones are separated by interdigitating alkoxy side chains (Fig. 2c). They are 4.2 ± 0.2 nm apart, a value similar to the ribbon height (Fig. 2d). Therefore, the monolayer pattern resembles a cross section through a multilayer of several ribbons of the gel. UV/Vis spectroscopy of MCH-solutions of **1–3** at different temperatures supports this hypothesis. At low temperatures, the absorption spectra are red-shifted compared to the spectra at higher temperatures, indicating π–π-interaction of the aromatic macrocyclic backbones upon aggregate formation (see ESI†).[17]

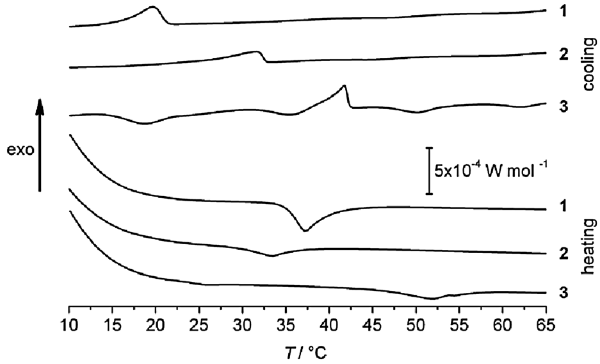

Fig. 3 DSC cooling (1st scan) and heating curves (2nd scan) of gels of **1** (9.2 wt%), **2** (9.6 wt%) and **3** (8.7 wt%) in CHX (heating/cooling rates 5 K min^{-1}).[20]

Differential scanning calorimetry (DSC) investigations of gels of **1–3** (9 to 10 wt% in cyclohexane) allow the determination of the gel–sol- and sol–gel-transition temperatures and enthalpies.[18] Fig. 3 shows the DSC heat flux curves of the gel samples. The gel–sol transition temperatures (T_{gs}), identified by endothermic peaks during heating the sample, are 37 °C, 34 °C, and 52 °C for **1**, **2**, and **3**, respectively (Table 1). Hence, the intraannular substitution pattern has a significant influence on the thermal stability of the gels. The gel formed by the macrocycle with an empty internal cavity (**2**) has a lower melting point compared to the respective gel of **1**, which contains the inner linear alkyl chain. This is attributed to additional van der Waals contacts between the intraannular substituents. The polar inner chain in **3** further increases the gel melting point, most probably due to even enhanced dipole–dipole interactions as well as solvophobic interactions between the polar interior and the nonpolar solvent.[19] Upon cooling, the sol–gel-transition (T_{sg}) shows in the case of **1** in CHX a hysteresis of 17 K with respect to the gel–sol-transition. Similarly, the gelation point of **3** in CHX is about 10 K below T_{gs}, whereas **2** immediately gelates CHX when approaching T_{gs}.

The results obtained by DSC are consistent with the visual observations of the macroscopic gel samples. Conclusively, the combination of microscopic and thermal investigations of the gels has shown that the ring interiors of the macrocycles

Table 1 Transition temperatures and enthalpies determined by DSC measurements of CHX gels of **1**, **2**, and **3**

CHX-gel	Heating T_{gs}/°C (ΔH_{trs}/kJ mol^{-1})	Cooling[21] T_{sg}/°C	Hysteresis $T_{gs} - T_{sg}$/°C
1 (9.6 wt%)	37.3 (−133)	19.9	−17.4
2 (9.2 wt%)	33.5 (−42)	31.6	−1.9
3 (8.7 wt%)	51.8 (−75)	41.6	−10.2

interact intermolecularly in the stacked one-dimensional aggregates and therefore influence the gel properties.

In summary, we synthesized shape-persistent macrocycles with extraannular octadecyloxy chains which are gel forming in apolar solvents due to non-specific interactions. A functionalized cavity is not crucial for gel formation, and the aggregate structure is similar for all compounds, but the intraannular filling influences the gel melting points and aggregation dynamics. The ring interior is therefore clearly a powerful handle to fine-tune the gel properties. Future investigations will include the role of size and flexibility of the intramolecular strands on the supramolecular assembly in one dimension as well as possible guest molecule organization.

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16 The observation of ribbon-like structures gives a hint on the hierarchical nature of the aggregation process of these macrocycles.

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20 The slight oscillation of the cooling curve of **3** is caused by the cooling system of the calorimeter and sometimes cannot be eliminated. The transition temperatures do not change when the scans are repeated.

21 The transition enthalpies could not be determined correctly for the cooling scan.