Supramolecular Polymers

Nanopatterned Superlattices in Self-Assembled C₂-Symmetric Oligodimethylsiloxane-Based Benzene-1,3,5-Tricarboxamides

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Abstract: The synthesis of C₁ and C₂-symmetric benzene-1,3,5-tricarboxamides (BTAs) containing well-defined oligodimethylsiloxane (oDMS) and/or alkyl side chains has been carried out. The influence of the bulkiness of the oDMS chains in the aggregation behavior of dilute solutions of the oDMS-BTAs in methylcyclohexane was studied by temperature-dependent UV spectroscopy. The formation of hierarchically self-assembled aggregates was observed at different BTA concentrations, the tendency of aggregation increases by shortening or removing oDMS chains. Chiral BTAs were investigated with circular dichroism (CD) spectroscopy, showing a stronger tendency to aggregate than the achiral ones. Majority rules experiments show a linear behavior consistent with the existence of a high mismatch penalty energy. The most efficient oDMS-BTAs organogelators have the ability to form stable organogels at 5 mg mL⁻¹ (0.75 wt %) in hexane. Solid-state characterization techniques indicate the formation of an intermolecular threefold hydrogen bonding between adjacent molecules forming thermotropic liquid crystals, exhibiting a hexagonal columnar organization from room temperature to above 150 °C. A decrease of the clearing temperatures was observed when increasing the number and length of the oligodimethylsiloxane chains. In addition to the three-fold hydrogen bonding that leads to columnar liquid crystalline phase, segregation between the oDMS and aliphatic chains takes place in the BTA functionalized with two alkyl and one oDMS chain leading to a superlattice within the hexagonal structure with potential applications in lithography.

Introduction

Polydimethylsiloxane (PDMS) is biocompatible and hydrophobic, stable to thermal and oxidative conditions, transparent, electrically insulating, and gas permeable. Due to its excellent properties, PDMS has multiple applications in our daily lives including wire coatings, motor insulators, food processing, cosmetics, and lubricants, to name a few. [1] Currently, industrial and academic research focuses on applications in biomedical uses,[2] microfluidic devices,[3] and the fabrication of topographically nanopatterned surfaces through self-assembly of PDMS block copolymers.[4] In addition, PDMS has been explored as a precursor polymer for supramolecular polymers to obtain dynamic systems and nanostructured functional materials that are often difficult to access using covalent chemistry. This combination has been studied in the solid state using polydimethylsiloxane end-functionalized with different supramolecular moieties such as bisurea,[5] ureidopyrimidinone (UPy),[6] and pyrene[7] in order to achieve supramolecular thermoplastic elastomers or self-healing properties based on the low glass transition temperature of the PDMS. Moreover, the supramolecular attachment of PDMS to polymers of various chemical natures leads to the formation of supramolecular block copolymers. Due to the incompatibility and large surface tension mismatch of PDMS with most other polymers, nanophase segregation takes place, leading to gel formation[8] or materials with well-organized morphologies that have potential applications in lithography.[9]

Our group studied in detail the self-assembly properties of benzene-1,3,5-tricarboxamides (BTAs) in solution and in the bulk phase. Driven by the formation of three hydrogen bonds between the amide groups of adjacent units, BTAs form well-defined, helical, rodlike supramolecular polymers.[10] The helicity in the aggregates has been unequivocally observed in crystal structures[11] and in solution by CD spectroscopy when stereochemical centers are introduced at the periphery. This versatile discotic motif has been decorated with a variety of functional groups and side chains such as alkyl,[12] pyridyl,[13] triphenyl[14] oligo(p-phenylenevinylene),[15] peptides,[16] oligo(ethylene-oxide),[17] perfluorinated chains,[18] and macromolecules [19] Accordingly, depending on the side chain used, BTAs have been explored for multiple applications, such as organogelators with self-healing properties,[20] nucleating agents for isotactic polypropylene,[21] folding polymers into catalytically active nanoparticles,[22] multivalent scaffolds for biomedical applications,[23]...
nanostructured materials,\textsuperscript{24} and thermotropic liquid crystals which can be homeotropically aligned.\textsuperscript{25}

To address challenges in bottom-up lithography, we here explore the functionalization of BTAs with small and well-defined oligodimethylsiloxane (oDMS) chains. The proposed combination affords unique materials with the dynamic nature of supramolecular polymers but, at the same time, possessing the intrinsic properties from flexible PDMS chains. Furthermore, the use of two chemically different substituents in the same structure, such as siloxanes and aliphatic chains, can result in the formation of phase-separated nanostructures within the liquid crystal caused by their incompatibility. These phase-separation phenomena have been observed before for the combination of PDMS with \( \pi \)-conjugated disc-shape mesogens.\textsuperscript{26}

In order to investigate the potential of oDMS/alkyl hybrid BTAs, we prepared a library of compounds in which the length and the number of the PDMS chains attached to the BTA scaffold, as well as the chirality, was varied (Scheme 1). The synthesis and characterization of \( C_3 \)- and \( C_2 \)-symmetric BTAs containing well-defined oligodimethylsiloxane and alkyl side chains is presented, as well as a detailed characterization of their behavior in solution and in the solid state. The self-assembly behavior of BTAs in solution and their tendency to form organogels was assessed in dilute and concentrated alkane solutions by UV spectroscopy and circular dichroism spectroscopy (CD). Finally, temperature-dependent UV and CD measurements were performed to investigate the stability of the aggregates. In addition, characterization in the solid state was conducted with infrared (IR) spectroscopy, differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction. The results show that the helical aggregation of the BTAs is retained in these structures, and the tendency of aggregation increases by shortening or removing oDMS chains. Importantly, segregation between the oDMS and aliphatic chains takes place in the liquid crystalline phase of the \( C_2 \)-symmetric BTAs, leading to a superlattice within the hexagonal structure, which is highly promising for applications in lithography.

Results and Discussion

Synthesis of BTAs

The synthesis of oDMS-substituted BTAs (oDMS-BTAs) was carried out using oligodimethylsiloxane hydrides 1a and 1b as starting materials. Since well-defined dimethylsiloxane hydrides are not commercially available, 1a and 1b were isolated by distillation under vacuum from a commercially available liquid mixture of differently sized oligomers with an average molecular weight of 800–900 g mol\(^{-1}\). \( C_2 \)-symmetric BTAs 2, (R)-5, and (S)-5 were synthesized from benzene-1,3,5-tricarbonyl trichloride and the corresponding commercially available vinylamines in dry chloroform, in the presence of triethylamine. \( C_3 \)-symmetric BTAs 3 and 4 were obtained after statistical reaction of vinyl amine and decylamine with benzene-1,3,5-tricarbonyl trichloride after column chromatography using the above-mentioned conditions, in yields of 31 and 29\%, respectively. Finally, the coupling between oligodimethylsiloxane hydrides 1a and 1b, and vinyl-substituted BTAs (2–5) was performed by hydrosilylation of the olefins using (the well-known) Karstedt’s catalyst \([\text{Pt}_{3}(\text{sym-tetramethyldivinylsiloxane})]^{27}\) (Scheme 1). BTAs 6–10 were obtained with good yields (83–93\%) and excellent purities as evidenced by NMR and MALDI-TOF-MS (see Supporting Information).

Formation and stability of oDMS-BTAs supramolecular polymers in MCH solution

The self-assembly of oDMS-BTAs 6–9 into supramolecular polymers was investigated by UV/Vis spectroscopy measurements in methycyclohexane (MCH) solutions. When H-aggregates stabilized by threefold hydrogen bonding are formed, a hypsochromic shift of the absorption maximum from 207 nm (molecularly dissolved BTAs) to around 194 nm is observed.\textsuperscript{10,29} In contrast to the alkyl-substituted BTAs, which are fully aggregated at \( \mu \)M concentrations, the presence of the oDMS chains increases the concentration at which aggregation starts 10 to 100 times (Figure 1 and Figure S1 in the Supporting Information). In fact, the initial formation of columnar aggregates is observed at different concentrations for each BTA; the aggregation concentration increased with the number and length of the oDMS chains in the case of the achiral oDMS-BTAs 6, 7, and 8. This observation can be re-
Methylcyclohexane. a) 6 steps and d) 9 steps.

Figure 1. Changes in the absorption spectra of oDMS-BTAs 6, 7, 8 and 9 in methylcyclohexane. a) 6 (1.3 × 10⁻⁵ M) at temperatures between 0 and 90 °C by 10 °C steps, b) 7 (1 × 10⁻⁵ M) at temperatures between 0 and 90 °C by 10 °C steps, c) 8 (5 × 10⁻⁵ M) at temperatures between 0 and 90 °C by 10 °C steps and d) 9 (7 × 10⁻⁵ M) with the addition of increasing amounts of 2-isopropanol (up to 23 equiv). Arrows indicate the depolymerization upon increasing temperature or amount of isopropanol.

Figure 2. a) UV/Vis and b) CD spectra of oDMS-BTAs (R)-10 and (S)-10 show mirror image CD spectra in MCH, resulting from the aggregation of the two enantiomers into supramolecular polymers with the opposite helicity (Figure S3 in the Supporting Information). (R)-10 and (S)-10 show positive and negative values, respectively, at 223 nm with a |Δε| around 35 L mol⁻¹ cm⁻¹, indicative for P and M helical aggregates, respectively. The molar ellipticity Δε for oDMS-BTAs (R)-10 and (S)-10 is in good agreement with those reported for chiral aliphatic BTAs in MCH and in water. Finally, the UV shifts and the reduction of the Cotton effect upon increasing the temperature are consistent with evolution from the aggregated state to the molecularly dissolved state (Figure 2a,b).

Amplification of chirality

Since the self-assembly behavior of BTAs is very similar to that previously observed for alkyl-substituted BTAs, we investigated if amplification of chirality is also operative in these systems. Thus, we performed “Sergeants and Soldiers” [31] and “Majority Rules” [32] experiments on mixtures of 6 and (S)-10, and (S)-10 and (R)-10, respectively (Figure 3a and Figure S3). In the “Sergeants and Soldiers” (SaS) experiment, a small amount of a chiral sergeant (S)-10 biases the helical preference of a large excess of achiral BTA soldiers 6 (normally forming racemic mixtures of P and M helices). Therefore, solutions of sergeant (S)-10 and soldier 6 were mixed keeping the total BTA concentration constant (6 × 10⁻⁴ M). The solutions where heated to 85 °C

Figure 3. a) Sergeants and soldiers experiment at 20 °C (6 × 10⁻⁴ M), Δε at 225 nm extracted from CD spectra of mixtures of 6 (6 × 10⁻⁴ M) in MCH as a function of (S)-10 percentage. b) Majority rules experiment at 20 °C (6 × 10⁻⁴ M) in MCH. Δε at 225 extracted from CD spectra of enantiomeric mixtures of (R)-10 and (S)-10 as a function of ee. The lines are to guide the eye.
in order to obtain the molecularly dissolved state, and after slow cooling to 20 °C, the Cotton effect was monitored as a function of the fraction of chiral (S)-10 added (Figure 3a). Full expression of one helical sense is obtained when adding around 15% of sergeant. Thus, the system shows a pronounced nonlinear amplification of the supramolecular aggregates chirality, similar in size to that previously observed in methyl-substituted alkyl BTAs.[33] The majority rules (MR) experiment, in contrast, shows a completely different trend. The CD effect at 225 nm of the scalemic mixtures of enantiomers, represented as a function of the enantiomeric excess (ee), surprisingly reveals linear behavior (Figure 3b).

In the previously reported alkyl-substituted BTAs, both the SaS as well as the MR effect are strongly nonlinear, which indicates that the different BTAs are randomly incorporated in the different stacks.[28,32] However, bulky L-phenylalanine substituted BTAs showed nonlinearity in the SaS experiments but a linear behavior in the MR experiment. The latter was attributed to the fact that the bulky enantiomers did not mix with each other, while the achiral, sterically less demanding soldier BTA in the SaS experiment did mix with a bulky enantiomer.[34] In the oDMS substituted BTAs, the SaS experiment indicates that (S)-10 (the sergeant) is incorporated into the stacks of achiral 6, biasing their helicity, whereas the MR experiment suggests a lack of mixing between the two enantiomers. This behavior presumably originates from the three branching methyl groups close to the amide in the enantiomers (S)-10 and (R)-10.

**Table 1. Critical gelation concentration (CGC) of oDMS-BTAs in hexane.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>[mg mL⁻¹]</th>
<th>[wt %]</th>
<th>[mM]</th>
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<tbody>
<tr>
<td>6</td>
<td>7.0</td>
<td>1.05</td>
<td>4.4</td>
</tr>
<tr>
<td>7</td>
<td>10.0</td>
<td>1.50</td>
<td>4.0</td>
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<td>8</td>
<td>15.0</td>
<td>2.24</td>
<td>11.9</td>
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<tr>
<td>9</td>
<td>30.0</td>
<td>4.38</td>
<td>31.9</td>
</tr>
<tr>
<td>10</td>
<td>5.0</td>
<td>0.758</td>
<td>3.1</td>
</tr>
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</table>

Oligodimethylsiloxane BTA-based supramolecular organogels

At higher concentrations in hexane, we observed that compounds 6, 7, 8, 9, (R)-10, and (S)-10 formed highly viscous solutions, as can be expected for supramolecular polymers in concentrated solution. To qualitatively assess if oDMS-BTAs are capable of forming organogels in hexane, the critical gelation concentration (CGC) was evaluated by vial inversion tests (minimal concentration of BTA in the solution so that it does not flow down upon inverting the vial). The samples were prepared by cooling a solution from 60 °C to room temperature in a small vial (Figure 4a). A significant influence of the length and number of oDMS chains was observed in the CGCs (Table 1). A lower CGC was detected when increasing the dimethylsiloxane percentage per molecule (Table 1). This fact can be attributed to the higher tendency of dimethylsiloxanes to form entanglements. Compound 10 showed the lowest CGC, an observation that correlates nicely to its high stability observed in UV and CD experiments (vide supra) and a high clearing temperature (vide infra).

The supramolecular structure of the BTA organogels was investigated by IR spectroscopy, and organogel 10 was also analyzed by CD and UV spectroscopy. BTA organogels show N–H vibrations around 3249 cm⁻¹ and C=O vibrations at 1641 cm⁻¹, which confirm the formation of columnar aggregates by means of threefold hydrogen bonding (Figure S4 in the Supporting Information). UV and CD spectra corroborate the formation of helical columnar aggregates (Figure 4b,c). The CD spectrum of the organogel formed by (S)-10 shows a |δR| of around 10 L mol⁻¹ cm⁻¹, a value that is significantly lower than that of the solutions (vide supra), indicating a lower degree of order within the stack.[35] The shape of the UV spectrum and the Cotton effect also changes slightly, possibly as a consequence of a different or less defined packing within the aggregates.

**Figure 4.** Organogel formed by (S)-10 in hexane, c = 3.1 × 10⁻⁴ M. a) Image of organogel, b) UV spectrum and c) CD spectrum.

**Self-assembly of BTAs in the solid state**

Infrared spectroscopy (IR) is a sensitive technique to investigate the presence of hydrogen-bonding interactions in the solid state. It has been reported that threefold intermolecular hydrogen bonding of the BTA amides can be identified unambiguously in the solid state and in the liquid-crystalline (LC) state by the presence of peaks at around 3240 (NH stretch), 1640 (amide I), and 1564 cm⁻¹ (amide II).[28a,29] The oDMS-BTAs functionalized with siloxanes (6–9) show N–H vibrations around 3249 cm⁻¹ and amide vibrations at 1641 and 1564 cm⁻¹ in the solid state, confirming the formation of columnar aggregates by means of intermolecular hydrogen bonding (Figure 5a). Interestingly, BTAs (R)-10 and (S)-10 exhibit slightly lower values for the N–H stretch, around 3229 cm⁻¹, which could be indicative of a tighter packing between the BTAs due to the presence of the branched methyl group.[12a,29] These results imply that the presence of bulky oDMS sidechains next to the amide core does not significantly affect the H-bonding pattern of BTAs in the solid state. The IR spectra also showed two absorption peaks located at 1092 and 1017 cm⁻¹, which were assigned to the antisymmetric stretching bands of Si–O–Si bonds.[28a]

The thermal stability of the oDMS-BTAs aggregates was investigated by performing variable-temperature IR measurements. The loss of hydrogen bonding between the BTAs was observed at different temperatures for each BTA (Figure S5 in the Supporting Information), observing significant changes in

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the NH stretch ($\tilde{\nu} = 3400–3500$ cm$^{-1}$), amide I ($\tilde{\nu} = 1700–1620$ cm$^{-1}$), and amide II ($\tilde{\nu} = 1600–1470$ cm$^{-1}$) bands upon increasing the temperature (Figure 5b). The loss of intermolecular hydrogen bonds appears to be connected with the phase transitions observed by DSC, the isotropization temperature increases going from $6 < 7 < 8 < 9 < (R)-10$ and $(S)-10$ (vide infra), indicating that the chiral compounds show the highest stability in the solid state.

Characterization of the mesophase of the BTAs

The thermal behavior of the synthesized BTAs was investigated using polarized optical microscopy (POM) and dynamic scanning calorimetry (DSC). Under crossed polarizers, compounds 6–9 are slightly birefringent at room temperature, indicating the presence of a mesophase. In contrast, compounds $(R)-10$ and $(S)-10$ are amorphous solids at room temperature. Slow cooling from the clearing temperature at a rate of 2 K min$^{-1}$ induces the growth of larger, birefringent features. Pseudo-focal conic patterns, typical for a columnar mesophase, were observed. Compound 9 showed different textures (Figure S6 in the Supporting Information), probably due to the formation of different columnar packing as observed by XRD (vide infra).

DSC experiments were carried out to determine the phase transition temperatures of the oDMS-BTAs. Only one transition, corresponding to isotropization, was observed for oDMS-BTAs. Presumably, the presence of the flexible and bulky oDMS chains prevents crystallization of these BTAs. When comparing the different BTAs, a decrease of the transition temperatures and enthalpies was observed when increasing the number and length of the oligodimethylsiloxane chains (Table 2). This fact is related to the steric hindrance of the oDMS side chains, given that the lowest isotropization temperature is observed for BTA 7 that contains three octadimethyl siloxane chains. Chiral BTAs $(R)-10$ and $(S)-10$ exhibited the transition to the isotropic melt at higher temperatures than the corresponding symmetric achiral BTA 7, in good agreement with previously reported transition temperatures for alkyl-BTAs.$^{[12b]}

The nature of the liquid crystals of oDMS-substituted BTAs was elucidated by XRD. All compounds showed three reflections in the low-$q$ portion of the graph, corresponding to a reciprocal ratio of 1: $\sqrt{3}$: 2: $\sqrt{7}$, consistent with a hexagonal packing of the columnar structures (Figure 6 and Table 3). In addition, three more reflections were observed for all the oDMS-BTAs in the higher-$q$ part of the graph, two diffuse reflections around 0.75 and 0.46 nm and a sharper halo at 0.35 nm. The first reflection ($d \approx 0.75$ nm) can be attributed to the short range order of the oDMS chains and increases in intensity upon increase of the length and the number of oDMS chains. The second halo ($d \approx 0.46$ nm) is typically assigned to the aliphatic side chains. The last reflection ($d \approx 0.35$ nm) indicates the interdisc distance of the BTAs, confirming the presence of ordered columnar structures. Interestingly, the disc-disc distance decreases slightly for compound 9, probably due to the lower steric hindrance of the aliphatic chains compared to the oDMS chains.

Table 2. Isotropization temperatures [°C] and corresponding enthalpies [kJ mol$^{-1}$] of oDMS-BTAs obtained by DSC measurements.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T$ [°C]</th>
<th>$\Delta H$ [kJ mol$^{-1}$]</th>
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<tbody>
<tr>
<td>6</td>
<td>171</td>
<td>20.3</td>
</tr>
<tr>
<td>7</td>
<td>166</td>
<td>17.3</td>
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<td>8</td>
<td>198</td>
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<tr>
<td>9</td>
<td>200</td>
<td>21.9</td>
</tr>
<tr>
<td>10</td>
<td>253</td>
<td>35.5</td>
</tr>
</tbody>
</table>

Figure 5. IR spectra of BTA 7. a) Full spectrum at room temperature. b) IR spectra upon heating from 20 to 200 °C by 20 °C steps. Arrows indicate the depolymerization upon increasing temperature.

Figure 6. Radially averaged scattering patterns of oDMS-BTAs 6–10.
Importantly, the XRD pattern of BTA 9 contains an intense extra reflection compared to the other DMS-BTAs at a q value of 0.15 Å⁻¹. This feature demonstrates the presence of a periodic repeating structure within the columnar hexagonal packing. The reflection corresponds to a d spacing of 4.2 nm, nearly twice as large as the (100) distance for the hexagonal packing. This is likely to be caused by the two different substituents: dimethylsiloxanes and aliphatic chains in the same supramolecular motif induce the formation of phase-separated nanostructures within the liquid crystal. Thus, segregation between the DMS and aliphatic chains is likely responsible for an additional periodic structure within the LC phase. One possible model for the superstructure is presented in Figure 7, in which three siloxane groups point to each other within the hexagonal lattice, hereby forming a hexagonal superlattice with a unit cell almost twice as large as the lattice corresponding to the spacing of the BTAs. Homeotropically alignment of this superlattice would give access to ordered patterned surfaces with features smaller than 5 nm, which have tremendous potential for future applications in lithography.

**Conclusion**

_C_₅ and _C_₇-symmetric benzene-1,3,5-tricarboxamides substituted with well-defined DMS side chains have been synthesized and characterized in the bulk and in solution. The presence of the bulky DMS side chains has a significant influence on the aggregation behavior of the DMS BTAs, but at the same time such bulky substituents allow the formation of threefold helical hydrogen bonding in solution and in the solid state. When increasing the length and the number of the DMS chains per BTA, the aggregation tendency of DMS-BTA diminishes in solution and in the solid state, while their organogelating ability improves. Chiral DMS-BTAs have a higher tendency of aggregation, presumably due to a tighter packing within the stacks. Chiral amplification experiments show that while chiral BTAs can be randomly introduced into achiral columnar aggregates biasing their helicity, a self-sorting phenomenon takes place when mixing chiral BTA enantiomers. The DMS-BTAs form liquid crystalline mesophases with a hexagonal packing within the columnar structures.

Intriguingly, a careful balance between alkyl and DMS side chains attached to the BTAs allows the introduction of additional phase separation. For BTA 9, substituted at the periphery with one DMS chain and two aliphatic chains, a different packing was observed both in solution and in the solid state. In the solid state, we observe the formation of a superlattice within the hexagonal lattice due to the phase separation between alkyl chains and DMS. Since alkyl-BTA liquid crystals can be homeotropically aligned by applying an electrical field, the preparation of perfectly patterned surfaces with extraordinary small features, at the scale of 1–5 nm could be feasible. Furthermore, the inherently dynamic nature of one-dimensional stacks and supramolecular interactions in conjunction with chemically patterned surfaces facilitates access to smaller and more complex patterns than the currently used covalent block copolymers.

The approach presented here has enormous potential in bottom-up lithography. Small changes in the BTA structure could give access to different secondary architectures (e.g., hexagonally packed cylinders, spheres) that can be easily manipulated by using a single component, as opposed to the tedious requirement of remaking a multicomponent block copolymer each time one wishes to alter composition. Furthermore, it is known that PDMS can be easily converted to silica by oxygen plasma treatment or calcination, thus producing topographically patterned silica. Therefore, this technique would reduce the current size limits of conventional lithography of new complex patterns.

**Experimental Section**

**Materials**

(2S)-3-Buten-2-amine hydrochloride and (2R)-3-buten-2-amine hydrochloride were obtained from NetChem, (ee = 97.4 and 98.0%, respectively). The polydimethylsiloxane monohydride terminal mixture was purchased from ABCR (MW average = 800–900 g mol⁻¹, 95 %). All other chemicals were obtained from either Acros or Aldrich at the highest purity available and used without further purification. All solvents were of AR quality and purchased from Biosolve. Dry THF was tapped off a distillation setup which contained molecular sieves, deuterated chloroform was dried over molecular sieves and triethylamine was stored on KOH pellets. Flash chromatography was performed on a Biotage flash chromatography system using 200–425 mesh silica gel (Type 60A Grade 633). Water...
was purified on an EMD Millipore Milli-Q Integral Water Purification System. Reactions were followed by thin-layer chromatography (precoated 10×25 mm, 60-F254 silica gel plates from Merck). All reactions were performed under an atmosphere of dry argon unless stated otherwise.

Methods

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Varian Mercury Vx 400 MHz (100 MHz for $^{13}$CNMR) spectrometer. Chemical shifts are given in ppm (δ) values relative to residual solvent or tetramethysilane (TMS). Splitting patterns are labelled as s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; quin, quintet; m, multiplet and b stands for broad. Matrix-assisted laser desorption/ ionization mass spectra were obtained on a PerSeptive Biosystems Voyager DE-PRO spectrometer or a Bruker autoflex speed spectrometer using a Pilatus 300 K silicon pixel detector with a 487 μm/pixel dimension and with 172 μm/pixel size at 113 and 1513 mm pixel size. Scattering patterns were collected with a Linkam THMS 600 heating device, with crossed polarizers. The solutions were done using a Jenaval polarization microscope equipped with an oscillation bath at 40 °C, 8 Hz.

Synthetic procedures

Oligodimethylsiloxanes (1a) and (1b) were obtained by separation of a commercial available mixture of polydimethylsiloxane monohydrides (10 g) by triply distillation on a Kugelrohr, giving (a) (2.8 g, 160 °C, 1 mmHg) and (b) (1.9 g, 195 °C, 1 mmHg) as transparent oils.

1-Butyl-1,3,3,5,5,7,9,9-decamethylpentasiloxane (1a): $^1$H NMR (400 MHz, CDCl$_3$ δ): 4.70 (d, J = 5.6, 2.8 Hz, 1H, Me$_2$Si-H), 1.31 (tt, J = 8.9, 4.5 Hz, 4H, Me$_3$Si-CH$_2$-CH$_2$-CH$_3$), 0.89 (t, J = 6.7 Hz, 3H, -CH$_2$-CH$_3$), 0.66–0.40 (m, 2H, Me$_3$Si-CH$_2$-CH$_2$-CH$_3$), 0.19 (d, J = 2.8 Hz, 6H, Me$_2$Si-H), 0.12–0.03 ppm (m, 24H, O-SiMe$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$ δ): 26.54, 25.62, 18.13, 13.97, 13.0, 1.18, 1.03, 0.86, 0.34 ppm; FT-IR (ATR) ν (cm$^{-1}$): 2963, 2858, 2124 (Si-H), 1469, 1258, 1192, 1040, 1036, 908, 838, 937, 827, 798, 769, 689.

1-Butyl-1,3,3,5,5,7,9,9,11,13,15,17,17-octadecamethylhexasiloxane (1b): $^1$H NMR (400 MHz, CDCl$_3$ δ): 4.71 (d, J = 5.4, 2.8 Hz, 1H, Me$_2$Si-H), 1.32 (tt, J = 6.9, 4.5 Hz, 4H, Me$_3$Si-CH$_2$-CH$_2$-CH$_3$), 0.88 (t, J = 6.6 Hz, 3H, -CH$_2$-CH$_3$), 0.54 (dd, J = 10.3, 5.7 Hz, 2H, Me$_3$Si-CH$_2$-CH$_2$-CH$_3$), 0.19 (d, J = 2.8 Hz, 6H, Me$_2$Si-H), 0.13–0.02 ppm (m, 48H, O-SiMe$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$ δ): 26.52, 25.60, 18.11, 13.96, 13.1, 1.21, 1.19, 1.01, 0.85, 0.34 ppm; FT-IR (ATR) ν (cm$^{-1}$): 2963, 2858, 2124 (Si-H), 1469, 1258, 1192, 1040, 1036, 908, 838, 937, 827, 798, 769, 689.

General procedure for symmetric vinyl-BTAs 2, (5)-5, (R)-5: To a solution of allylamine, (2-buten-2-amine hydrochloride or 2R,3R-but-2-amine hydrochloride (17.1 mmol) and triethylamine (21.3 mmol) in 2 mL of dry CH$_2$Cl$_2$, a solution of benzene 1,3,5-tricarboxylic acid (3.62 mmol) in 10 mL CH$_2$Cl$_2$ was added dropwise at 0 °C under argon atmosphere. The reaction was stirred for 45 min when it was monitored by TLC. The reaction mixture was then concentrated on a rotary evaporator and the crude was dissolved in THF (50 mL) and washed with 1 M HCl (50 mL), 100 mL of saturated sodium bicarbonate (aq) and 100 mL of brine. The THF solution was dried over MgSO$_4$. After removal of the solvents by vacuo, the products were obtained as white solids: (2) (89%) (S)-5 (93%) and (R)-5 (90%).

N,N,N′,N′-Triallylbenzene-1,3,5-tricarboxamide (2): $^1$H NMR (400 MHz, CDCl$_3$ + MeOH δ): 8.35 (s, 3H, Ar), 7.79 (t, J = 5.8 Hz, 3H, C=ONHCH$_2$), 5.88 (ddt, J = 17.2, 10.2, 5.6 Hz, 3H, -CH$_2$-CH$_2$-CH$_3$), 5.48–4.97 (m, 6H, -CH$_2$-CH$_2$-CH$_3$), 4.02 ppm (t, J = 5.8, 1.6 Hz, 6H, C=ONHCH$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$ δ): 166.56, 135.02, 133.68, 128.73, 116.79, 70.59, 42.80 ppm; MALDI-TOF-MS: elemental analysis calc (%) for C$_{24}$H$_{30}$NO$_3$: M$_w$ = 375.17 g/mol $^1$, found m/z = 328.19 [M-H$^+$], m/z = 350.17 [M+Na$^+$]; FT-IR (ATR) ν (cm$^{-1}$): 3292, 3076, 1663, 1632, 1528, 1419, 1341, 1279, 1259, 1403, 1064, 986, 918, 744, 710, 640, 538.

N,N,N′,N′-Triallylbenzene-1,3,5-tricarboxamide (S)-5, (R)-5: $^1$H NMR (400 MHz, CDCl$_3$ + MeOH δ): 8.32 (s, 3H, Ar), 7.47 (d, J = 8.1 Hz, 3H, C=ONHCH$_2$), 5.88 (dd, J = 17.1, 10.5, 5.3 Hz, 3H, -CH$_2$-CH$_2$-CH$_3$), 4.70 (dd, J = 7.0, 5.2 Hz, 3H, CH$_2$-CH$_2$-CH$_3$), 1.32 ppm (t, J = 6.8 Hz, 9H, -CH$_2$-CH$_2$-CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$ + MeOH δ): 166.07, 139.03, 135.19, 128.64, 114.62, 47.88, 20.80 ppm; MALDI-TOF-MS: elemental analysis calc (%) for C$_{24}$H$_{30}$O$_3$ M$_w$ = 375.17 g/mol $^1$, found m/z = 328.19 [M-H$^+$], m/z = 350.17 [M+Na$^+$]; FT-IR (ATR) ν (cm$^{-1}$): 3292, 3027, 2974, 2933, 1630, 1555, 1454, 1383, 1307, 1292, 1275, 1182, 1120, 1049, 1017, 990, 914, 723, 691, 586.

General procedure for vinyl-BTAs 3 and 4: A 25 mL round bottom flask was charged with a solution of allylamine (0.17 g, 3.0 mmol), triethylamine (0.70 g, 6.9 mmol) and decylamine (0.71 g, 3.0 mmol) in 5 mL dry CH$_2$Cl$_2$ and stirred under argon atmosphere. The mixture was cooled in an ice bath and a solution of benzene 1,3,5-tricarboxylic acid (0.50 g, 1.88 mmol) in 5 mL of dry CH$_2$Cl$_2$
was added dropwise. After the addition the reaction was stirred overnight at room temperature under inert atmosphere. The solvent was evaporated and the crude mixture was purified by column chromatography (silica gel, CHCl₃-MeOH, 50/1 v/v). The fractions containing the desired products were collected and evaporated in vacuo yielding white and sticky solids: 3 (168 mg, 21 %) and 4 (227 mg, 23%).

N₈,N₉-Diallyl-4’-decylbenzene-1,3,5-tricarboxamide (3): H NMR (400 MHz, CDCl₃, δ): 8.31 (s, 1 H, Ar), 8.29 (s, 2 H, Ar), 6.91 (t, J = 5.9 Hz, 2H, C-ONH-aryl), 6.74 (t, J = 5.9 Hz, 1H, C-ONH-Decyl), 5.89 (ddt, J = 16.3, 11.3, 5.6 Hz, 2H, -CH₂-C₆H₅), 5.42–5.07 (m, 4H, -CH=CH₂), 4.06 (t, J = 5.9 Hz, 4H, -NHCH₂-CH₂-), 3.42 (q, J = 6.8 Hz, 2H, -NH-alkyl), 1.59 (p, J = 7.2 Hz, 2H, -NH-CH₂-alkyl), 1.42–1.10 (m, 14H, alkyl), 0.87 ppm (t, J = 6.6 Hz, 3H, -CH₃). 13C NMR (100 MHz, CDCl₃, δ): 167.34, 135.78, 135.40, 133.80, 127.48, 125.63, 116.62, 42.58, 40.39, 30.45, 29.78, 29.49, 27.22, 22.82, 14.25 ppm; MALDI-TOF-MS: elemental analysis calcd (%) for C₃₂H₅₃N₃O₃: M₊ = 527.41 g mol⁻¹, found m/z = 527.40 [M+H]+; 1H NMR (400 MHz, CDCl₃, δ): 8.35 (s, 3 H, Ar), 6.44 (t, J = 5.8 Hz, 3H, C-ONH-Decyl), 3.46 (p, J = 6.8 Hz, 6H, NHCH₂-CH₂-), 1.44–1.22 (m, 12H, Me₂Si-CH₂-CH₂-CH₂-), 0.88 (t, J = 6.94 Hz, 9H, -CH₃), 0.65–0.56 (m, 6H, Me₂Si-CH₂-), 0.56–0.50 (m, 6H, Me₂Si-CH₃), 0.10–0.02 ppm (m, 90H, -SiMe₃). 13C NMR (100 MHz, CDCl₃, δ): 165.61, 135.44, 128.01, 42.44, 26.51, 25.59, 23.73, 18.10, 15.67, 13.97, 1.36, 1.12, 0.18, 0.36, 0.29 ppm; MALDI-TOF-MS: elemental analysis calcd (%) for C₂₃H₄₇N₅O₁₁Si₁₀: M₊ = 1589.05 g mol⁻¹ [M+Na]+, found m/z = 1588.68 [M+Na]+; FT-IR (ATR) ν (cm⁻¹): 3241, 3071, 2958, 2923, 2872, 1642, 1506, 1412, 1257, 1080, 1022, 839, 787, 683.

N₉,N₉′,N₉″,N₉‴-Tris-(3-(9-butyl-1,1,3,3,5,5,7,7,9-octadecamethyleneoxa-2-yl)benzene-1,3,5-tricarboxamide) (8): H NMR (400 MHz, CDCl₃, δ): 8.35 (s, 3H, Ar), 6.44 (t, J = 5.8 Hz, 3H, C-ONH-Decyl), 3.46 (p, J = 6.4 Hz, 6H, NHCH₂-CH₂-), 1.65 (dd, J = 12.7, 9.9, 5.6 Hz, 6H, NHCH₂-CH₂-), 1.30 (tt, J = 9.1, 4.3 Hz 12H, Me₂Si-CH₂-CH₂-CH₂-), 0.88 (t, J = 6.3 Hz, 9H, -CH₃), 0.65–0.57 (m, 6H, Me₂Si-CH₂-), 0.57–0.47 (m, 6H, Me₂Si-CH₃), 0.01–0.03 ppm (m, 12H, -SiMe₂). 11C NMR (100 MHz, CDCl₃, δ): 165.60, 135.43, 128.01, 43.45, 26.51, 25.59, 23.73, 18.10, 15.67, 13.97, 1.36, 1.12, 0.34, 0.29, 0.15 ppm; MALDI-TOF-MS: elemental analysis calcd (%) for C₉₀H₁₉₁N₅O₇Si₁₀: M₊ = 2476.90 g mol⁻¹ [M+Na]+, found m/z = 2477.90 [M+Na]+; FT-IR (ATR) ν (cm⁻¹): 3241, 3068, 2959, 2923, 2879, 1642, 1560, 1413, 1258, 1084, 1018, 839, 791, 688.

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