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Controlling the Length of Cooperative Supramolecular Polymers with Chain Cappers

Gijs M. ter Huurne,^[a] Pongphak Chidchob,^[a] Augustin Long,^[b] Alexandre Martinez,^[b] Anja R. A. Palmans,^{*[a]} and Ghislaine Vantomme^{*[a]}

Abstract: The design and the characterization of supramolecular additives to control the chain length of benzene-1,3,5-tricarboxamide (BTA) cooperative supramolecular polymers under thermodynamic equilibrium is unraveled. These additives act as chain cappers of supramolecular polymers and feature one face as reactive as the BTA discotic to interact strongly with the polymer end, whereas the other face is nonreactive and therefore impedes further polymerization. Such a design requires fine tuning of the conformational preorganization of the amides and the steric hindrance of

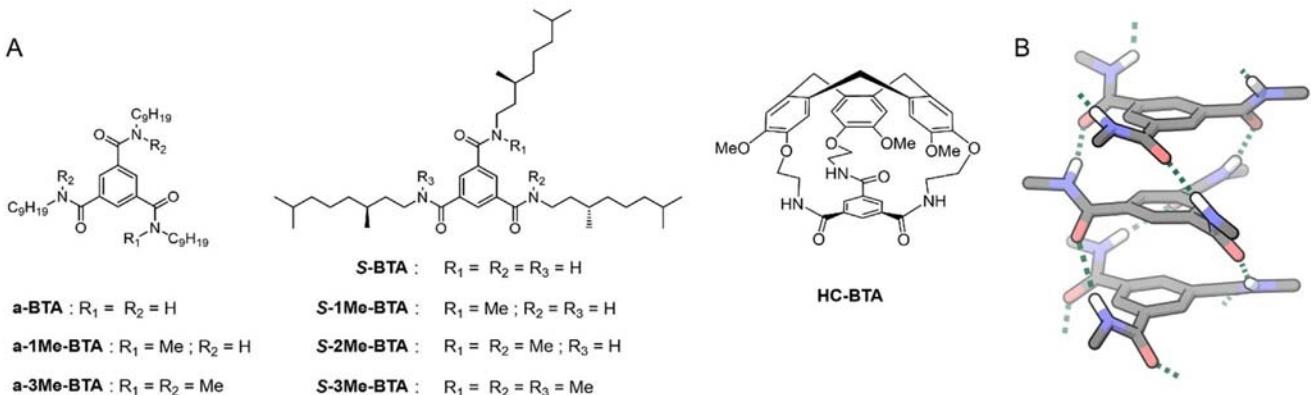
the motif. The chain cappers studied are monotopic derivatives of BTA, modified by partial *N*-methylation of the amides or by positioning of a bulky cyclotrimeratrylene cage on one face of the BTA unit. This study not only clarifies the interplay between structural variations and supramolecular interactions, but it also highlights the necessity to combine orthogonal characterization methods, spectroscopy and light scattering, to elucidate the structures and compositions of supramolecular systems.

Introduction

Control over the nanoscale morphology of multicomponent systems is one of the key parameters to improve the performance of supramolecular polymeric materials.^[1] In fact, fine tuning of the noncovalent interactions connecting the supramolecular motifs is at the core of the material properties.^[2] Although significant progress has been made in controlling the assembly pathway, structure and composition of supramolecular polymers,^[3] major challenges remain to control the chain length and the polymer sequence of supramolecular (co)polymers. The development of kinetically controlled supramolecular polymerization techniques, such as living supramolecular polymerization, has allowed significant progress in that direction.^[3g-i] For systems under thermodynamic equilibrium, we recently reported on the various mechanisms directing the chain length in supramolecular (co)polymerizations.^[4] Next to the addition of good solvent,^[5] supramolecular additives can reduce

the chain length by chain-capping the polymers or by stabilizing the monomers. In the latter, the additive is a competitor which depolymerizes the supramolecular chains without participating in the polymer sequence. The additive forms competitive, stable species that stabilize the monomers.^[6] In the former scenario, the additive is a chain capper, a component that interacts with the chain end, and inhibits further growth of the polymer chain.^[7] This chain-capping strategy has also been used to control dynamic libraries of cyclic and linear oligomers^[6b,8] and to synthesize rotaxanes.^[9]

In the field of isodesmic supramolecular polymerization, the noncovalent analogue of covalent step-growth polymerization, the concept of chain capper is well-established and its impact on the molecular weight has been studied in great detail.^[7,10] The design of a chain capper is straightforward because it is a monotopic derivative of the ditopic monomer. However, in cooperative supramolecular polymerization, the noncovalent analogue of covalent chain-growth polymerization, the design of a chain capper is far from trivial and only two examples have been formally reported in organic solvent.^[11,12] The challenge in designing an effective chain capper arises from the same molecular features that make the polymerization cooperative: a correlated reactivity of the two binding sites of the monomer. Hence, the monomer needs to be modified into a mono-functional derivative without affecting its association constant. To unravel the basic principles of chain-capping cooperative supramolecular polymers under thermodynamic control, a benzene-1,3,5-tricarboxamide monomer decorated with alkyl chains (**a-BTA**) is an ideal model system because of the simple design and the extensive knowledge acquired on its assembly properties.^[13] In addition, the assembly of benzene-1,3,5-tricarboxamides with aliphatic side chains is always under thermo-



Scheme 1. (A) Chemical structures of the BTA derivatives studied in this work. (B) Schematic representation of the helical arrangement of the hydrogen bonds in the **a-BTA** supramolecular polymer.

dynamic control, and mixing two derivatives results in almost instantaneous co-assembly.^[14] This self-complementary **a-BTA** motif assembles cooperatively into one-dimensional aggregates stabilized by helically ordered, intermolecular hydrogen-bond networks.

Here, we present our insights into how different designs of chain cappers affect the length of **a-BTA** polymers, and show which prerequisites need to be fulfilled to make the chain capper effective. To this end, a series of BTA-based molecules was synthesized and mixed with **a-BTA** polymers to investigate the influence of the amide conformation and the steric hindrance on the chain-capping effect. In order to gradually vary the structural similarity with the monomer **a-BTA**, we synthesized five monotopic BTA derivatives by *N*-methylation of three,^[15] two and one amides (chiral **S-3Me-BTA**, **S-2Me-BTA** and **S-1Me-BTA** and achiral **a-1Me-BTA** and **a-3Me-BTA**, Scheme 1). We opted for chiral, non-racemic methylated derivatives to permit the use of chiroptical spectroscopic techniques. In addition, one monotopic BTA derivative that comprises a bulky cyclotrimeratrylene cage^[16] was also investigated (**HC-BTA**, Scheme 1). We examine in detail the influence of the chain capper on the structure of the supramolecular polymers using a combination of static light scattering (SLS), infrared (IR), UV and circular dichroism (CD) spectroscopy and density functional theory (DFT) calculations. The co-assembly experiments described here are conceptually similar to experiments reported in other studies.^[11,17]

Results and Discussion

Chemical design

First, we investigate the prerequisites that need to be fulfilled to design the ideal chain capper. Taking inspiration from the design of chain cappers for isodesmic polymerization, a previous attempt to make a chain capper for **a-BTA** polymers was based on the monotopic *N*-methylated **3Me-BTA**.^[15] This monotopic derivative lacks the N–H groups, which were alkylated into N–Me motifs. As a result, **3Me-BTA** cannot act as a hydrogen bond donor but only as a hydrogen-bond acceptor

through the carbonyls. Although **3Me-BTA** was found to decrease the viscosity of **a-BTA** solution, it is not a chain capper of **a-BTA** polymers.^[15] When analyzed by DFT calculations, a different pre-organization of the amides of **3Me-BTA** when compared to **a-BTA** was proposed to explain the unfavorable interaction between **3Me-BTA** and **a-BTA** stacks.^[15] This example showed how the design of supramolecular (co)monomers is challenged by molecular pre-organization and in particular conformational preferences of the reactive groups.^[15,18] Thus, end-capping cooperative supramolecular polymers requires a subtle balance of the reactivity of the two faces of the chain capper, with one face preorganized to be as reactive as the monomer and the other face nonreactive to impede the supramolecular polymerization.

Based on the above results, we hypothesized that an efficient chain capper should have the following structural features: 1) a conformational preorganization of the amides similar to the monomer to ensure a strong binding with the polymer end, and 2) the presence of sterically hindered groups to mask the binding site for another monomer. Based on these design rules, we selected asymmetrically *N*-methylated BTA units (**S-1Me-BTA** and **S-2Me-BTA**) because of their structural similarity with **a-BTA** and the bulkiness of the methyl groups.

Moreover, hemicryptophane-BTA (**HC-BTA**)^[16] previously developed for molecular recognition and catalysis,^[19] was selected for this study because of the preorganization of the amide units and the crowding of one of its faces^[3] with a bulky cyclotrimerateylene cage. The crystal structure of **HC-BTA** was previously solved^[16] and presents a conformational organization of the three amides oriented in the same direction to one another with a tilt angle from 5° to 19° with respect to the benzene ring, comparable to the amide conformations in **a-BTA** monomer (12° tilt).^[13b] Here, we used (–)-M-**HC-BTA** for all experiments.

Synthesis

Chiral **S-1Me-BTA**, **S-2Me-BTA** and **S-3Me-BTA** were synthesized in one step in 14%, 19% and 53% yield, respectively, starting from **S-BTA** (see Supporting Information for details). Whereas chiral **S-BTA** was obtained as a white solid, all **S-nMe-BTAs** (with $n=1, 2$, and 3) were obtained as colorless isotropic liquids. **HC-BTA** was synthesized from a cyclotrimerateylene derivative and benzenetricarbonyl trichloride in 5% yield and was obtained as a white solid.^[16]

Homoaggregation of **S-nMe-BTAs**

S-1Me-BTA, **S-2Me-BTA** and **HC-BTA** exhibit self-complementary hydrogen-bond donor/acceptor units in their structures, so we first investigated their ability to assemble into supramolecular homoaggregates. Previous studies showed that when BTAs polymerize into one-dimensional aggregates stabilized by a helically ordered, intermolecular hydrogen-bond network, IR spectra show an N–H stretch at about $\approx 3240\text{ cm}^{-1}$, the C=O amide I at $\approx 1640\text{ cm}^{-1}$ and the amide II at $\approx 1560\text{ cm}^{-1}$.^[13b] In contrast, vibrations for the NH stretch at $\approx 3306\text{ cm}^{-1}$ and an amide II vibration at $\approx 1539\text{ cm}^{-1}$ are typical for lateral hydrogen-bond networks.^[13b] The IR spectra in the bulk state of **S-1Me-BTA** and **S-2Me-BTA** reveal the N–H stretch at $\approx 3320\text{ cm}^{-1}$, the C=O amide I vibrational mode at $\approx 1635\text{ cm}^{-1}$ and the amide II vibrational mode at $\approx 1539\text{ cm}^{-1}$ (Figure S1). This indicates that these compounds do not form helically-ordered intermolecular hydrogen bonds in the bulk. In dilute solution of nonpolar solvent (methylcyclohexane (MCH), 1 mM), **S-1Me-BTA** and **S-2Me-BTA** exhibit the N–H stretching vibration at $\approx 3300\text{ cm}^{-1}$ and 3450 cm^{-1} , three C=O stretch I vibrations around 1674 cm^{-1} (free C=O), 1627 cm^{-1} and 1650 cm^{-1} (bonded C=O) and the amide II vibration at $\approx 1539\text{ cm}^{-1}$ (Figure 1). These data point to the coexistence of free amides and intermolecular lateral hydrogen-bonded amides. IR measurements of **HC-BTA** show the characteristics of the monomeric state both in bulk and in toluene, with vibrations of the N–H stretch at 3440 cm^{-1} (free N–H), the C=O stretch at about 1665 cm^{-1} and 1520 cm^{-1} (Figure 1). These IR signals are similar to **S-BTA** in tetrachloromethane.^[20] Toluene was chosen here because of the poor solubility of **HC-BTA** in millimolar concentration in MCH. In addition, the chiroptical properties of these solutions were investigated by CD and UV/Vis spectroscopy. The diluted solutions of **S-nMe-BTA** in MCH

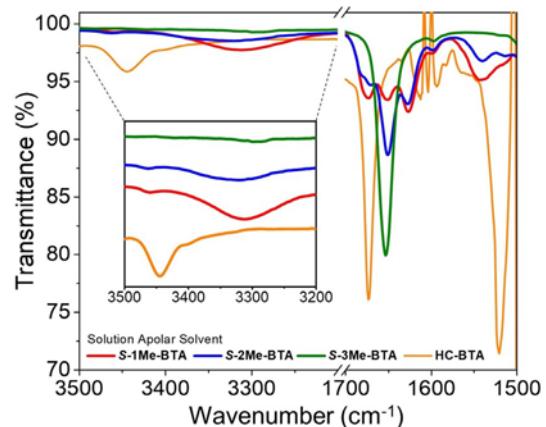


Figure 1. FTIR spectra of **S-nMe-BTA** ($n=1, 2$ or 3) in MCH ($T=20^\circ\text{C}$, $c=1\text{ mM}$) and **HC-BTA** in toluene ($T=20^\circ\text{C}$, $c=1\text{ mM}$).

are CD silent (Figure S2), which corroborate the IR data that no C_3 -symmetrical helical aggregates are formed. For **HC-BTA**, a $10\text{ }\mu\text{M}$ solution in MCH displays a CD pattern that is similar to the spectrum previously reported in acetonitrile.^[16] However, the CD intensity does not change over temperature (Figure S3). These results also confirm that **HC-BTA** does not aggregate in diluted solution.

Co-assembly studied by spectroscopy

We then performed mixing experiments between **a-BTA** and **S-nMe-BTA** ($n=1, 2$ or 3) or **HC-BTA** at different concentrations in nonpolar solvent, and analyzed the solutions by IR, UV and CD spectroscopy. The concentration of **a-BTA** was fixed and the quantity of additives **S-nMe-BTA** was gradually increased in the mixtures from 0 to 25 mol %. Surprisingly, in CD spectroscopy, only a weak chiroptical signal was detected in the various mixtures of $50\text{ }\mu\text{M}$ **a-BTA** containing **S-nMe-BTA** in MCH (Figure S4). This result indicates that the chiral additive **S-nMe-BTA** is not able to bias the helical preference of the polymers formed by achiral **a-BTA** monomers. This is in sharp contrast to the full bias of helicity observed when mixing 5 mol % of the chiral **S-BTA** with **a-BTA** stacks.^[14] Variable-temperature UV experiments were carried out on these **a-BTA/S-nMe-BTA** mixtures (Figure 2). All UV cooling curves overlap and have a non-sigmoidal shape indicating an assembly via a cooperative mechanism as observed for **a-BTA** homopolymers. Moreover, we observed no change in the temperature at which aggregation starts (the elongation temperature, T_e) upon the addition of **S-nMe-BTA**. This suggests that the thermal stability of the **a-BTA** polymers is not affected by the presence of **S-nMe-BTA**. These results point to either an absence of interactions between **a-BTA** polymers and **S-nMe-BTA** (self-sorting) or to a chain-capper role of **S-nMe-BTA** for **a-BTA** stacks.^[4] This is in contrast to two other scenarios: 1) an increase in T_e is expected if **S-nMe-BTA** intercalates into **a-BTA** stacks because the total concentration of BTAs present in supramolecular polymers increases,^[21] or 2) a decrease of T_e is expected when **S-nMe-BTA** interacts with **a-BTA** monomers by forming short stable side

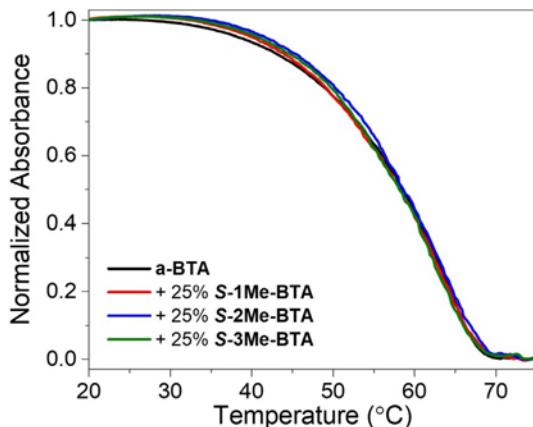


Figure 2. Temperature-dependent UV spectra of solutions of 50 μM a-BTA with addition of 25 mol% of S-nMe-BTA probed at 217 nm in MCH (cooling rate = 2 $^{\circ}\text{C min}^{-1}$).

species in a competitive pathway, which effectively decreases the concentration of BTAs present in the supramolecular polymers.^[6c] For the analysis of HC-BTA, UV/CD spectroscopy could not be performed for a-BTA/HC-BTA solutions in toluene because of the overlap between the solvent absorption and the maximum absorption of BTA monomers.

The IR spectroscopy analyses were performed on 1 mm a-BTA solutions in MCH, with the addition of 100 mol% and 25 mol% of S-nMe-BTA (Figure 3A and Figure S5). For the mixtures of S-3Me-BTA and a-BTA, no clear proof of interaction is visible because of the overlap between the stretching vibrations of free C=O of the tertiary amide in S-3Me-BTA and bonded C=O in a-BTA. In contrast, the mixtures of S-1Me-BTA/a-BTA and S-2Me-BTA/a-BTA show a shift in the ratio between free and bonded C=O stretch vibrations (at 1647 cm^{-1} /1630 cm^{-1}), indicating the preference of bonded C=O, which characterizes the presence of helical polymers. These changes are, however, rather small so that unambiguous conclusions on the nature of the co-assembly in mixtures of S-1Me-BTA/a-BTA and S-2Me-BTA/a-BTA cannot be drawn. When 10 mol% of HC-BTA was added into 5 mm toluene solution of a-BTA, the IR spectrum obtained for the mixtures of the solutions is very close to the linear combinations of the separate components (Figure 3B). Therefore, we cannot conclude whether the mixtures of HC-BTA and a-BTA assemble into a-BTA homopolymers with free HC-BTA or if an interaction between the two is present. And further analysis with light scattering techniques was conducted.

Coassembly studied by light scattering

To further understand the interactions between the different additives and a-BTA, the weight-average length of the supramolecular polymers as a function of the addition of S-nMe-BTA and HC-BTA was measured by static light scattering (SLS) experiments (Figure 4 and Figure S6). The scattering curves were fitted to a cylinder model with a fixed radius of 6 nm (radius obtained from SAXS measurements).^[6c] Upon addition of S-3Me-BTA to a-BTA, the changes in a-BTA polymer length

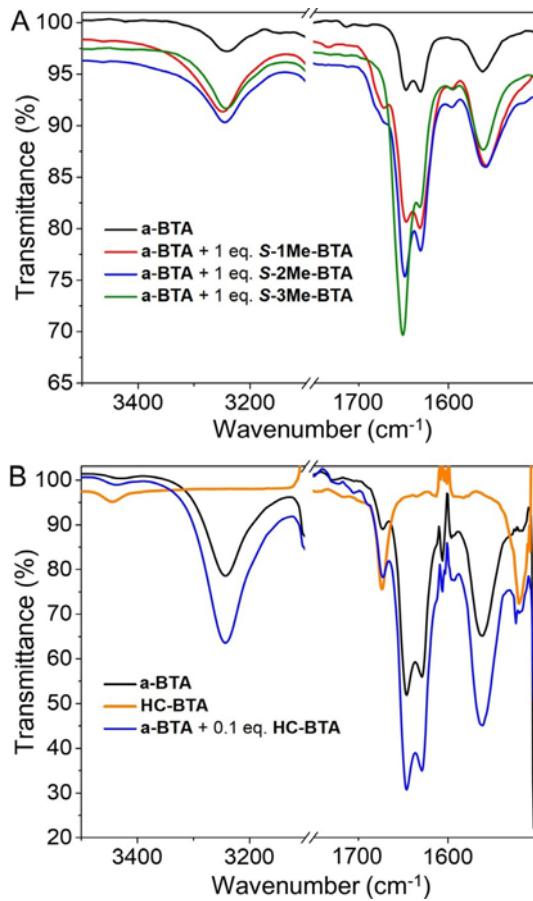


Figure 3. A) FTIR spectra of 1 mm MCH solutions of a-BTA containing an additional 100 mol% (1 equiv.) of S-nMe-BTA ($n=1, 2$ and 3) at 20 $^{\circ}\text{C}$. B) FTIR spectra of 5 mm toluene solutions of a-BTA, HC-BTA and a-BTA with addition of 10 mol% (0.1 equiv.) of HC-BTA at 20 $^{\circ}\text{C}$.

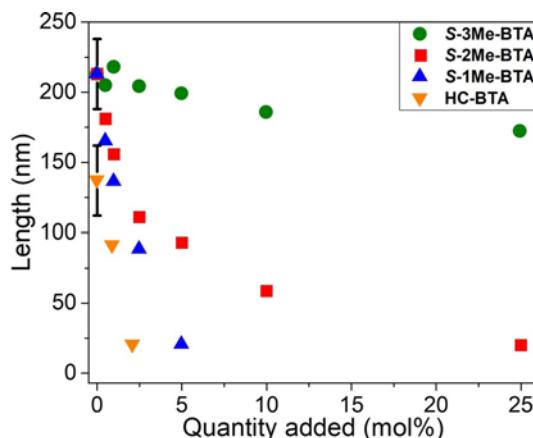


Figure 4. Measured weight-average length of the supramolecular polymer as function of S-nMe-BTA ($n=1, 2$ and 3) added (blue, red, and green traces, respectively) determined by SLS at $c_{\text{a-BTA}}=0.5$ mm in MCH and of HC-BTA added (orange trace) at $c_{\text{a-BTA}}=5$ mm in toluene at 20 $^{\circ}\text{C}$.

are negligible. This result confirms that S-3Me-BTA does not have a high affinity for the polymer-ends (Figure 4, green dots).^[15] However, when small amounts of S-1Me-BTA, S-2Me-BTA or HC-BTA are added to the solutions of a-BTA stacks, a

strong decrease in polymer length is observed (Figure 4, blue, red and orange dots, respectively). Recent theoretical modelling developed to elucidate the role of an additive on the length of supramolecular polymers reveals that this sharp decrease of the polymer length with small amount of additive is indicative for a chain-capping effect.^[4] Therefore, we conclude that **S-1Me-BTA**, **S-2Me-BTA** and **HC-BTA** act as chain cappers of **a-BTA** stacks. The sharpest reduction in chain length is obtained with the addition of **HC-BTA**. However, no comparison can be drawn with the efficiency of **S-nMe-BTA** because the measurements are performed in a more polar solvent at higher concentration, which has a strong impact on the polymer length.^[4] Overall, this result shows that the chain capping is more efficient when the molecular structures of the chain capper and the monomer are similar.

Computational characterization of **S-nMe-BTA**

The question remains why **S-3Me-BTA** does not act as a chain capper while **S-1Me-BTA** does. To understand the origin of this result, density functional theory (DFT) calculations were performed on **nMe-BTA** bearing short methyl side chains to reduce computational costs. For **3Me-BTA**, it was previously reported that the equilibrium geometry is characterized by an antiparallel arrangement of the amide moieties with an average torsion angle of 41°.^[15] Similarly, the equilibrium geometries obtained for **1Me-BTA** and **2Me-BTA** also display an anti-parallel arrangement of the amide moieties with a torsion angle of about 20° for the NH amides and about 40° for the NMe amides (Figure 5 and Figures S7 and S8). For **nMe-BTA** to interact with **a-BTA** stacks, a similar organization of the amides is necessary. We hypothesized that the difference in the energy

barrier for the conformational inversion of amides NH and NMe would explain the difference in chain-capping properties between **S-1Me-BTA** and **S-3Me-BTA**. The energies profiles were obtained by scanning the torsional potential surface in 10° increments for the C_{arom}-C_{arom}-C_{CO}-O dihedral angle of **nMe-BTA** and optimizing the equilibrium geometries (Figure 5). The results show that the energy barrier to rotate the C_{arom}-C_{arom}-C_{CO}-O dihedral angle of a NH amide of **1Me-BTA** is about 0.2 kcal mol⁻¹ (Figure 5, top panel), in agreement with previously reported values for BTA.^[13b] In contrast, for **3Me-BTA**, the rotation of the NMe amide goes through an energy barrier of 4.2 kcal mol⁻¹ (Figure 5, bottom panel). This energy difference is attributed to the steric repulsion generated by the N-methyl group coming into the plane of the benzene ring. Thus, the difference in binding affinity between **S-1Me-BTA** and **S-3Me-BTA** with **a-BTA** stacks can be attributed to the less energetically demanding pre-organization of the amide moieties for **S-1Me-BTA** compared to **S-3Me-BTA**.

Coadssembly studied by sergeant and soldiers experiments

To corroborate the chain-capping effect, a final experiment was performed by using the well-known sergeant and soldiers principle.^[22] Herein, a small amount of chiral **S-BTA** biases the helical preference of **a-BTA** supramolecular polymers. In this case, we add the achiral chain capper **a-1Me-BTA** to investigate its effect on the chiroptical properties of the sergeants/soldiers **S-BTA/a-BTA** mixture (Scheme 1).

A 5/95 mixture of chiral **S-BTA** sergeant and achiral **a-BTA** soldiers was prepared at a total concentration of 50 μM in MCH. The sergeant **S-BTA** intercalates into **a-BTA** stacks and successfully biases the helical preference of **a-BTA** stacks,

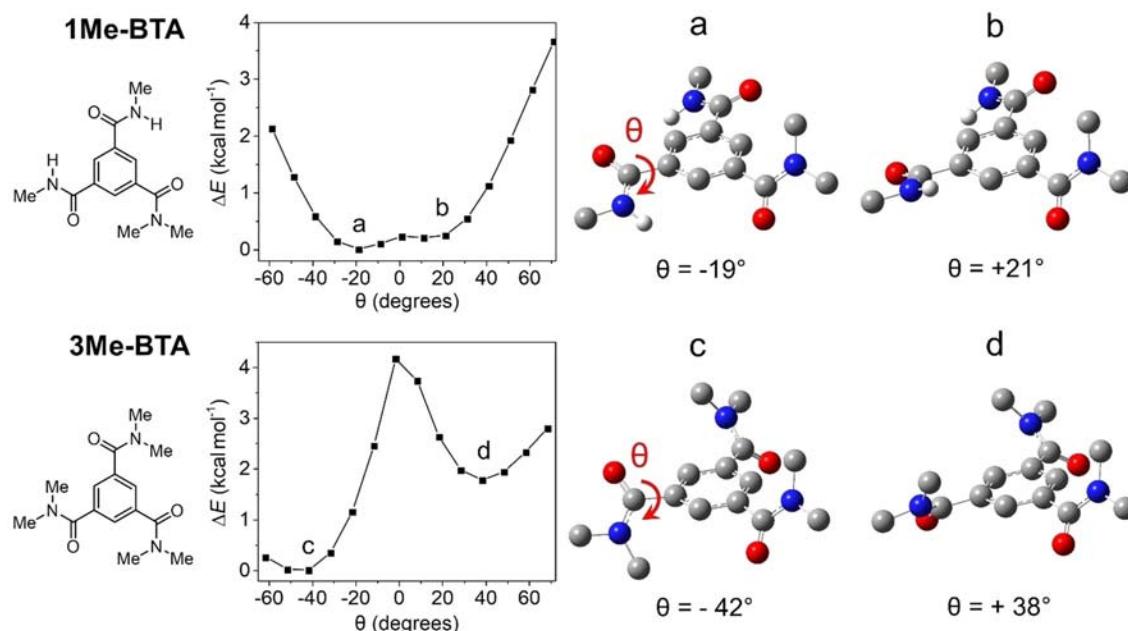


Figure 5. (Left) Potential energy profiles of **1Me-BTA** and **3Me-BTA** as a function of the C_{arom}-C_{arom}-C_{CO}-O dihedral angle θ obtained by single point calculations determined by DFT calculations at the PBE/6-311G+(d,p) level of theory. (Right) Optimized structures of **1Me-BTA** (a and b) and **3Me-BTA** (c and d) highlighted in the energy profiles. The hydrogen atoms of the carbons were omitted for clarity.

giving a maximum CD signal of about $-50 \text{ L mol}^{-1} \text{ cm}^{-1}$. Upon addition of achiral chain capper **a-1Me-BTA** to the sergeant/soldiers mixtures, a pronounced decrease of the CD signal is observed (Figure 6A, Figure S9). Half of the original CD intensity was reached at about 20 mol % (0.2 equiv.) of **a-1Me-BTA** added. This decrease was not observed when **a-3Me-BTA** was added to the sergeant/soldiers mixtures,^[15] indicating that there is a definite interaction between **a-1Me-BTA** and BTA-based aggregates.

An explanation of the observed reduction in the CD effect when adding **a-1Me-BTA** is as follows: when **a-1Me-BTA** acts as a chain capper in the sergeant/soldiers mixtures, the stack length decreases and as a result the number of polymer stacks increases. In this situation, new **a-BTA** stacks can form in both *P* and *M* helical sense, leading to a decrease in the net *M* helicity (Figure 6B). During this experiment, the fraction of monomers aggregated stays approximately the same, as can be seen by the similar T_e of the UV melting curves over addition of chain capper (Figure S10). Interestingly, although **a-1Me-BTA** acts as a chain capper for **a-BTA** polymers, **S-1Me-BTA** is not capable of biasing the helical sense of **a-BTA** polymers (see above). We speculate that **S-1Me-BTA** chain capper is a weak sergeant and that the ditopic intercalation of a sergeant into a polymer chain is necessary to effectively bias the helicity of a polymer.

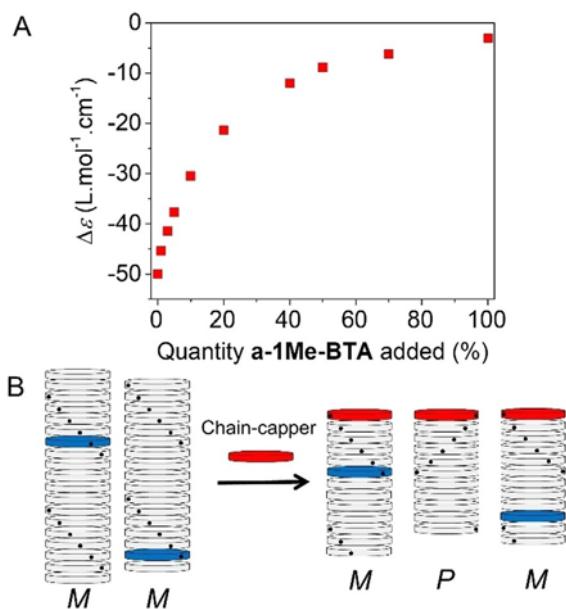


Figure 6. A) Maximum CD intensity of $50 \mu\text{M}$ **a-BTA/S-BTA** 95/5 solution over addition of 1 mM achiral **a-1Me-BTA** (mol %) in MCH at 20°C . B) Scheme of the sergeant (blue disks) and soldiers (grey disks) experiments with addition of chain capper (red disks).

Conclusions

In conclusion, we reported the synthesis and characterization of supramolecular additives designed to end-cap BTA cooperative supramolecular polymers under thermodynamic control. These supramolecular additives are monotopic derivatives of

a-BTA, modified by *N*-methylation of two or one amides or decorated with a hemicryptophane unit to crowd one face of the monomer. The supramolecular copolymerization between **a-BTA** monomers and the chain cappers **S-nMe-BTA** ($n=1$ and 2) or **HC-BTA** were analyzed by IR, UV, and CD spectroscopy as well as static light scattering in nonpolar solvent. The results show that the design of a discotic chain capper requires a fine balance between reactivity, to get one face of the chain capper as reactive as the monomer, and steric hindrance, so the other face hampers the polymerization. These findings also prove that the use of several characterization methods in concert is crucial to understand supramolecular systems. These results contribute to the general understanding of the interactions driving the structures of supramolecular polymers.

Experimental Section

Methods

The solutions for the experiments of CD, UV/Vis, FTIR and SLS were prepared as followed. The desired amount of compounds was weighed into an aluminium pan by using a microbalance and transferred into a 25 mL volumetric flask. Then the flask was filled 3/4 full with MCH and sonicated at 40°C for 1 h. After cooling the flask to 20°C , the liquid meniscus was adjusted to the graduation line of the volumetric flask with MCH. Solutions were stored in the dark at room temperature and used within two weeks after preparation.

For the "Sergeant-and-Soldiers" experiments, stocks solution of **a-BTA**, **S-BTA** and **a-1Me-BTA** were prepared as described above. The 50 μM stock solutions of **a-BTA** and **S-BTA** were mixed in a volume ratio 0.95/0.05 for soldier/sergeant **a-BTA/S-BTA**. Then, a 1 mM stock solution of **a-1Me-BTA** was gradually added to the soldier/sergeant solution.

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