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Dynamic self-assembled polymer: HCl responsive inversion of supramolecular polymer handedness†

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A series of discotic tricarboxyamides with varied amino acid side arm functionality and their HCl responsive diverse self-assembly behavior and formation of dynamic polymer is studied. Discotic trisamide **1** obtained from Boc protected L-Lys self-assembled into a long fibrillar aggregate-like supramolecular P helical polymer. However, on addition of HCl, the supramolecular helical handedness of the assemblies is completely inverted. Irrespective of the chiral centres configuration, supramolecular chiral bias is arising from molecular conformations. FE-SEM reveals the formation of right handed entangled polymeric fibers. However, left handed entangled fibers have appeared on addition of 0.12 M HCl. The trisamide **2** containing Boc protected L-Trp exhibits disk like morphology both in the presence and absence of 0.12 M HCl and does not show a change of supramolecular handedness. This demonstrates how remarkably distinct morphologies originate from stimuli responsive building blocks assembled in a subtly different manner.

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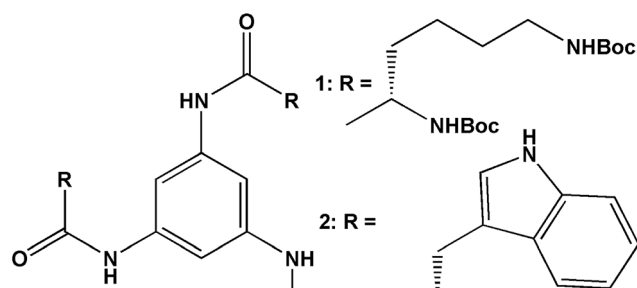
Introduction

Supramolecular polymers are highly interesting for their dynamic character. Tuning the nature, directionality and spatial arrangement of stimuli responsive building blocks in self-assembled systems provides chiral supramolecular polymers with new features compared to the bulk materials.¹ Understanding the chirality of supramolecular systems^{2–4} is highly important for biological sciences as well as material sciences mainly in the fields of chiral recognition and sensing,⁵ optoelectronic materials,⁶ chiroptical switches,^{7,8} asymmetric catalysts^{9,10} and separation processes,¹¹ metal coordination,¹² redox reactions,¹³ host–guest interactions,¹⁴ anions,^{15,16} solvent polarity,¹⁷ concentrations variations,^{18,19} light irradiation,^{20,21} high pressure²² and temperature²³ on large discotic,²⁴ dendritic,^{25,26} and gelator molecules.²⁷ Feringa, van Esch and coworkers have reported the cyclohexane based C₃ symmetric discotic hydrogelator containing three amino acid side groups.^{28–31} Meijer and coworkers have discussed analogous systems with 1,3,5-benzene tricarboxylic acid core.^{32–36} For these compounds, tuning experimental conditions promotes the selection of a predominant assembly.³⁷ Changing the stereochemistry of the building blocks as well as experimental condition can control the supramolecular chiral amplification.³⁸ However, the examples of designer supramolecular assemblies that can adopt diverse well-defined

chiral nanostructures by simply changing the molecular conformation are relatively rare.³⁹

Herein, we report the conformational preferences in the trisamide system over the configuration of the chiral center to determine the helical handedness of supramolecular polymers. We have designed and synthesized a series of trisamides containing Boc protected L-lysine (Lys), L-tryptophan (Trp) and benzene-1,3,5-triamine and investigated their structures and stimuli responsive behavior. Interestingly the trisamide **1** containing (Boc)₂-L-Lys formed one-dimensional supramolecular helical polymer. On protonation, the supramolecular helical handedness of the polymeric assemblies has inverted. However, the analogue **2** containing (Boc)-L-Trp exhibits disk like morphology both in presence and absence of 0.12 M HCl and does not show change of supramolecular handedness.

Starting from commercially available 1,3,5-trinitrophenol (picric acid), 1,3,5-triaminobenzene was synthesized in single step in 86% yield, by refluxing with ammonium formate and Zn dust in methanol at 60 °C for 1 h (Scheme 1, ESI†). The

Scheme 1 The trisamides **1** and **2**.

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† Electronic supplementary information (ESI) available: Synthesis and characterization of compounds, ¹H NMR, ¹³C NMR, solid state FTIR spectra, Fig. S1–S17. See DOI: 10.1039/c7ra08035b

trisamides **1** and **2** (Scheme 1) were synthesized by conventional solution phase DCC (dicyclohexylcarbodiimide) mediated coupling of 1,3,5-triaminobenzene with the (Boc)₂-L-Lys and (Boc)-L-Trp following a high purity, as confirmed by ¹H-NMR (nuclear magnetic resonance), ¹³C-NMR, FT-IR (Fourier-transform infrared) and mass spectrometry (MS) analysis (ESI†). For C₃-symmetric trisamides **1** and **2** the design principle explored was to incorporate chiral amino acid side chains that are responsive to external stimuli like protonation. The bulky Boc protective groups at side chains may force the amides groups out of the plane of the central aromatic core and facilitates the formation of three intermolecular hydrogen bonds for stack or dimer structure.

For trisamide, the hydrogen-bonded self-assembly promotes mainly dimers or stacks, which can be controlled by the nature of the substituent or experimental conditions (concentration) or external stimuli such as temperature, magnetic field, metal ions.³⁹ Depending on the ratio of the number of pairs of hydrogen bond dipole vectors which are parallel or antiparallel to each other, the hydrogen-bonded stack of trisamide can exist in two conformations, 3 : 0 and 2 : 1.³⁹ In 3 : 0 stacking, all the amide oxygens attached to central core are oriented in the same direction with respect to the central benzene plane (Fig. S1, ESI†). However, in 2 : 1 stacking, two amide oxygens attached to central core are on one side and the third one is on other side of the central benzene plane (Fig. S2, ESI†).³⁹ From our previous reports, by X-ray crystallography it has proved that 3 : 0 conformation stack in right handed helical manner (P helix) and the 2 : 1 conformation stack in left handed helical manner (M helix) (Fig. 1). This is irrespective on the chirality of the side chains. A trisamide containing achiral β-alanine adopts

2 : 1 conformations and formed M helix (Fig. 1a).⁴⁰ However, trisamide containing achiral γ-aminobutyric acid (Fig. 1b) or chiral methionine (Fig. 1c) adopts 3 : 0 conformations and formed P helix.⁴¹

Results and discussion

The supramolecular propensities of the reported trisamides **1** and **2** containing chiral (Boc)₂-L-Lys and (Boc)-L-Trp have been studied using a wide variety of different spectroscopic techniques in methanol solution. The typical UV-Vis absorption spectra of trisamide **1** in methanol (0.13232 mM) show an absorption band at 208 nm, responsible for π to π* transition (Fig. S3, ESI†). However, the 10 nm bathochromic shift of the absorption band with increasing concentration indicates J-type stacking between the trisamide **1** molecules.² There is also another band at 360 nm. Comparing with studies, we conclude that trisamide **1** formed one-dimensional supramolecular columnar stacks. The absorption spectra of trisamide **2** in methanol (0.06788 mM) also show an absorption bands at 208 nm and 280 nm but only intensity increase with increasing concentration (Fig. S4, ESI†). Hence the trisamides **1** and **2** have different aggregation propensities.

The methanol solution of trisamide **1** is light green in colour. With increasing trisamide **1** concentration in methanol solution the intensity of the colour increases. But we observed that on addition of 0.12 M HCl the solution become colourless (inset of Fig. 2a). There is a possibility of Boc-NH groups deprotection in presence of acid. But in the solution phase synthesis procedure we have work up the trisamides with 2 M HCl and there is no Boc-NH groups de protection as it was confirmed by ¹H-NMR, ¹³C-NMR, FT-IR and mass spectrometry analysis. So, the self-assembly of the trisamide **1** is responsive towards HCl. We have further explore this phenomenon using a wide variety of different spectroscopic techniques. The UV-Vis titration of trisamide **1** methanol solution (1.984×10^{-4} M) with gradual addition of 0.12 M HCl shows the gradual increase of the absorption band intensity at 208 nm (Fig. 2a). However, the absorption band at 360 nm disappeared (Fig. 2a). On the other hand, very light green colour of trisamide **2** in methanol solution become intense green colour by addition of 0.12 M HCl (inset of Fig. 2b). The UV-Vis titration of trisamide **2** methanol solution (3.451×10^{-5} M) with gradual addition of HCl shows the gradual increase of the absorption bands intensities at 208 nm and 280 nm (Fig. 2b). So, protonation can tuned self-assembly of the trisamides.

FT-IR spectroscopy is an excellent technique to investigate the HCl responsive self-assembly of trisamide **1**. The region 3500–3200 cm⁻¹ is important for the N–H stretching vibrations and 1800–1500 cm⁻¹ corresponding to C=O stretching vibration. The intense band at 3382 cm⁻¹ is for six Boc-NH groups which are hydrogen bonded (Fig. 3a). The band at 3201 cm⁻¹ is responsible for three core amide NH groups which are hydrogen bonded to form the columnar stack (Fig. 3a). The trisamide **1** shows the amide I band at 1682 cm⁻¹ and amide II band at 1523 cm⁻¹. On addition of HCl the N–H stretching vibrations appears at 3406 cm⁻¹ (Fig. 3a). The 3201 cm⁻¹ band is now very

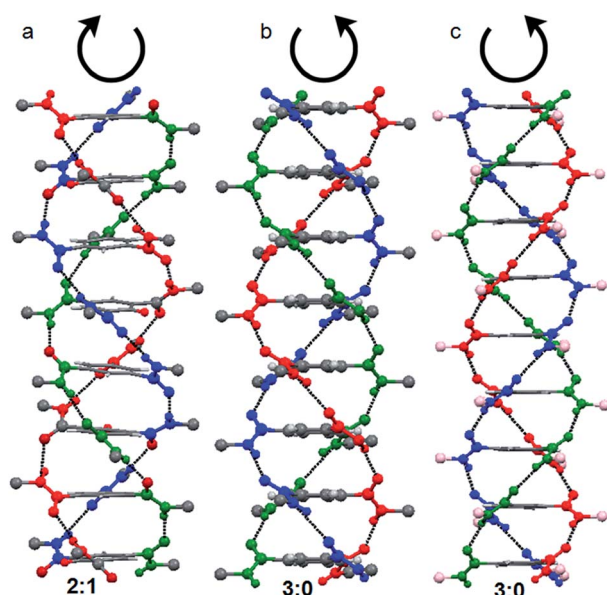


Fig. 1 (a) M helix from a trisamide with 2 : 1 conformations containing achiral β-alanine. (b) P helix by a trisamide with 3 : 0 conformations containing achiral γ-aminobutyric acid. (c) The trisamide containing chiral methionine (pink balls) adopts 3 : 0 conformations and formed P helix. Amino acids side chains are omitted for clarity.





Fig. 2 The UV-Vis titration of (a) trisamide 1 and (b) trisamide 2 methanol solution (1.984×10^{-4} M) and (3.451×10^{-5} M) respectively with gradual addition of 0.12 M HCl. Inset: colour change by addition of HCl.

broad. The amide I bands are now split in 1 : 2 ratio and appear at 1689 and 1640 cm^{-1} (Fig. 3a). The intensity of amide II band at 1523 cm^{-1} is very low (Fig. 3a). Fig. S5, ESI[†] shows the FT-IR spectra of 2.

Moreover, to investigate the effect of HCl on trisamide 1, the NMR titration experiments were performed. To a solution of compound 1 1.082×10^{-2} (M) in CD_3OD the 0.57 (M) HCl solution was gradually added by an amount of 10 μL at room temperature and the NMR spectra were recorded. The results of the NMR titrations of trisamide 1 have been shown in the Fig. 3b. The NMR titrations data show that the NH protons get exposed to the acid and there are significant shift of NH protons for the trisamide 1 with gradually increase in HCl concentration. From the stack plot, the core amide NH exhibits upfield shift suggest the strong hydrogen bond formation. Whereas the protons of central aromatic core show no shift *i.e.* the stacking structure is not changing. The Boc protected NHs of Lys exhibits downfield shift as well as broadening suggest that these NHs are open to acid. Fig. S6, ESI[†] shows the acid dependence NH chemical shifts of 2.

In order to gain more information on the structural changes of these trisamides in presence of acid, we performed circular dichroism (CD) measurements. The positive cotton effect observed (185 nm) in the CD spectra of trisamide 1 in methanol



Fig. 3 (a) FT-IR spectra of trisamide 1 in absence of HCl (black) and in presence of HCl (red). (b) The acid dependence of NH chemical shifts of trisamide 1 at varying concentrations of HCl. Star: core CONH, circle: core aromatic Hs, square: Lys side chain NHs, triangle: Lys NHs.

(1.474×10^{-5} M) is suggesting a supramolecular right handed helix (Fig. 4a) which is consistent with the handedness of the helices formed by the tricarboxamide containing L-methionine methyl ester with 3 : 0 conformation in the crystalline state.⁴¹ On addition of HCl, (4×10^{-5} M) the helical handedness of the supramolecular polymer reverses to negative cotton effect (Fig. 4a). The CD spectra is suggesting a left handed supramolecular polymer which is consistent with the handedness of the helices formed by the tricarboxamide containing β -alanine methyl ester with 2 : 1 conformation in crystal.⁴⁰ This suggest that only 2.713 equivalent HCl is enough for the chirality change of tricarboxamide 1. However the trisamide 2 in methanol (1.474×10^{-5} M) has a positive band at 185 nm which does not change after addition of HCl (4×10^{-5} M) (Fig. 4b). There also a negative band at 200 nm and 217 nm which does not shift in presence of acid (Fig. 4b). The CD experiments also performed with trisamide containing achiral β -alanine and γ -aminobutyric acid in absence and presence of HCl. The γ -aminobutyric acid containing trisamide shows a positive band at 210 nm which does not shift in presence of acid (Fig. S7, ESI[†]). Another trisamide containing β -alanine shows a negative band at 200 nm and after addition of HCl it remain in the same conformation (Fig. S8, ESI[†]). To examine the supramolecular



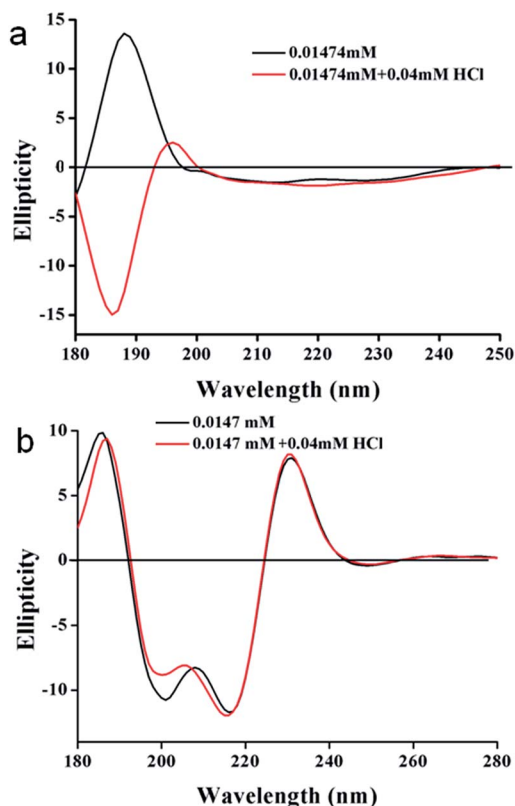


Fig. 4 (a) CD spectra of trisamide 1 in methanol without HCl (black) and in presence of HCl (red). (b) CD spectra of trisamide 2 in methanol without HCl (black) and in presence of HCl (red).

polymer formation, we have performed the DOSY NMR experiment with trisamide 1. From DOSY experiment, trisamide 1 have viscosity coefficient $3.047 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$, however after addition of HCl it shows viscosity coefficient $2.416 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$. This is due to the supramolecular polymer formation (Fig. S9, ESI†).



Fig. 5 FE-SEM images of trisamide 1 (a) without acid, (b) after addition of HCl. (c) and (d) FE-SEM images of trisamide 2 without HCl and with 0.12 M HCl respectively.

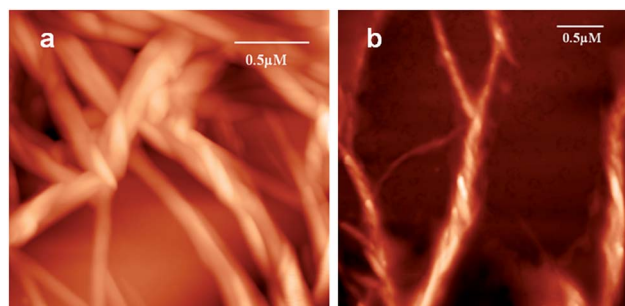


Fig. 6 AFM images of helical supramolecular polymer of trisamide 1 (a) without acid, (b) after addition of 0.12 M HCl.

The morphology of trisamide 1 was observed by field emission scanning electron microscopy (FE-SEM). The analysis of the morphology of trisamide 1 by FE-SEM reveals the formation of right handed entangled polymeric fibers (Fig. 5b). After addition of 0.12 M HCl, left handed entangled fibers have appeared. The trisamide 2 exhibits disk like morphology (Fig. 5c) which is consistent with the morphology of the tri-carboxyamides that formed dimer in crystal.⁴² On addition of 0.12 M HCl, the trisamide 2 does not exhibit significant change, only the disks are talking to each other (Fig. 5d).

To investigate the topology of the supramolecular polymer, atomic force microscopic (AFM) studies were performed. The trisamide 1 solutions in methanol were drop-casted on a microscopic glass cover slip and investigated by AFM. The trisamide 1 shows right handed helical supramolecular polymer fibers (Fig. 6a). However, after addition of 0.12 M HCl, it shows left handed helical fibers (Fig. 6b).

Experimental

General methods and materials

All L-amino acids (L-lysine, L-tryptophan, and trinitrophenol) were purchased from Sigma chemicals. HOBT (1-hydroxybenzotriazole) and DCC (dicyclohexylcarbodiimide) were purchased from SRL. Synthesis. The peptides were synthesized by conventional solution-phase methodology by using a racemization free fragment condensation strategy. The Boc group was used for N-terminal protection and. Couplings were mediated by dicyclohexylcarbodiimide/1-hydroxybenzotriazole (DCC/HOBT). The products were purified by column chromatography using silica gel (100–200 mesh) as the stationary phase and *n*-hexane–ethyl acetate mixture as eluent. All the intermediates were characterized by 500 MHz and 400 MHz ^1H NMR and mass spectrometry. The final compound was fully characterized by 500 MHz and 400 MHz ^1H NMR spectroscopy, ^{13}C NMR spectroscopy (125 MHz, 100 MHz), mass spectrometry, and IR spectroscopy.

(a) **Boc₂-Lys-OH.** A solution of L-lysine (1.46 g, 10 mmol) in a mixture of dioxane (20 mL), water (10 mL) and 1 M NaOH (10 mL) was stirred and cooled in an ice-water bath. Di-*tert*-butylpyrocarbonate (4.8 g, 22 mmol) was added and stirring was continued at room temperature for 6 h. Then the solution was



Field emission scanning electron microscopy

Morphologies of all reported compounds were investigated using field emission-scanning electron microscopy (FE-SEM). A small amount of solution of the corresponding compound was placed on a clean silicon wafer and then dried by slow evaporation. The material was then allowed to dry under vacuum at 30 °C for two days. The materials were gold-coated, and the micrographs were taken in an FE-SEM apparatus (Jeol Scanning Microscope-JSM-6700F).

Atomic force microscopy

The morphology of the reported compound was investigated by atomic force microscopy (AFM). A drop of the sample solution in methanol were placed on a clean microscope cover glass and then dried by slow evaporation. The material was then allowed to dry under vacuum at 30 °C for two days. Images were taken with an NTMDT instrument, model no. AP-0100 by semicontact-mode.

Conclusions

In summary, we have shown the addition of HCl reverses the helical handedness of the supramolecular polymer obtained from the self-assembly of chiral amino acid modified C₃-symmetric trisamide. The intermolecular three fold hydrogen bonds break and amide functional groups re-organized in the opposite side of central aromatic core by virtue of interaction with HCl. Irrespective of chiral centres configuration, supramolecular chiral bias is arising from molecular conformations. FE-SEM reveals the formation of right handed entangled polymeric fibers. However, left handed entangled fibers have appeared on addition of 0.12 M HCl. The trisamide 2 containing Boc protected L-Trp exhibits disk like morphology both in presence and absence of 0.12 M HCl and does not show change of supramolecular handedness. The acid responsive supramolecular chirality inversion strategy has potential for other building blocks that form multiple competing chiral supramolecular structures.

Conflicts of interest

Authors do not have any conflict of interest.

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