Amplification of chirality in benzene tricarboxamide helical supramolecular polymers†

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Received (in Cambridge, UK) 17th July 2006, Accepted 16th August 2006
First published as an Advance Article on the web 13th September 2006
DOI: 10.1039/b610051a

The chirality of benzene tricarboxamides is expressed and amplified into the helicity of self-assembled columnar aggregates according to 'sergeants and soldiers' and 'majority rules' principles; the strength of the amplification is analysed quantitatively and the effect of the number of chiral groups in the sergeants is studied.

A current endeavour in macromolecular science is to reproduce facets of biological expression of chirality during synthesis.[1–3] Self-assembly[4–6] has emerged as an attractive strategy by which this can be achieved, because the use of non-covalent interactions allows the expression of molecular properties of small and easy to synthesise components in a cooperative fashion. Discrete self-organising systems have been shown to elicit so called supramolecular induction of chirality[7,8] *via* 'sergeants and soldiers' effects and supramolecular memory of chirality.[9] The 'sergeants and soldiers' principle describes the disproportionally large effect on optical activity of a small amount of chiral comonomer in a helical polymer of achiral monomers. The related 'majority rules' principle concerns analogous effects of a small excess of one enantiomer of a chiral monomer. These cooperativity effects were first observed in covalent polymers[1] and have also been studied in supramolecular polymeric systems. Theoretical descriptions of both principles in supramolecular systems have been recently reported.[10,11] In recent years, ourselves and others have reported on the self-assembly of C_3 symmetrical tricarboxamides[12–17] into helical columnar aggregates,[7,18–21] and the quantitative analysis of the 'majority rules' principle in aggregates of extended discotics was reported. The smaller and simpler discotics discussed in this paper are particularly attractive motifs with which to study cooperativity effects in supramolecular polymers because of their modular and highly accessible synthesis.

As part of a programme aimed at the covalent fixation[22] of supramolecular chirality by postpolymerisation of monomer **1**,[23] we report here on chiral induction as a function of the fraction of sergeant molecules, and the number of chiral alkyl chains they contain. The data are analysed using a theoretical treatment of the supramolecular 'sergeants and soldiers' experiment and the 'diluted majority rules' experiment.[24] Using this model, the average distance between helix reversals in columns of **1** is estimated, as well as the energetic penalty for a chiral sergeant present in a column with non-preferred helicity.

Benzene tricarboxamides have been shown to form helical columnar assemblies in apolar solution *via* a combination of van der Waals packing of alkyl chains, aromatic stacking and cooperative hydrogen-bonding. The latter interaction was confirmed from IR spectra of **1** in cyclohexane which are concentration independent between 10^{-2} and 10^{-5} M (see Fig. S1 ESI†) and show NH and C=O stretch vibrations at 3240 cm^{-1} and 1645 cm^{-1}.

In order for hydrogen-bonding to take place the amides must distort out of conjugation with the aromatic core of the trimesic amide, resulting in the cooperative formation of a triple helical seam of hydrogen-bonds down the axis of the column as shown in Fig. 1. Previously, we showed that, in the presence of chiral sergeant **2a**, a large negative induced CD is observed that reflects the absorption spectrum of trimesic amide **1**. The CD spectrum increases non-linearly with the quantity of added sergeant **2a** (Fig. 2i). The observation of a Cotton effect in the absorption spectrum of the sorbyl group around 250 nm demonstrates incorporation of chiral molecules into the columns of **1**, while the absence of a CD effect in a solvent mixture containing 0.5% of methanol confirms the importance of hydrogen-bonding in the

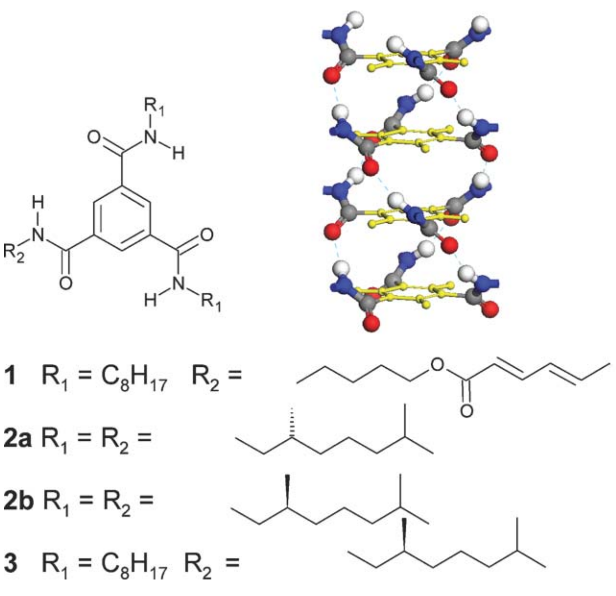

Fig. 1 Trimesic amides **1–3** and a cartoon of the proposed assembly motif based on a crystal structure.[16]

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† Electronic supplementary information (ESI) available: Synthetic procedures, spectroscopic studies and extended discussion of the curve fitting process. See DOI: 10.1039/b610051a

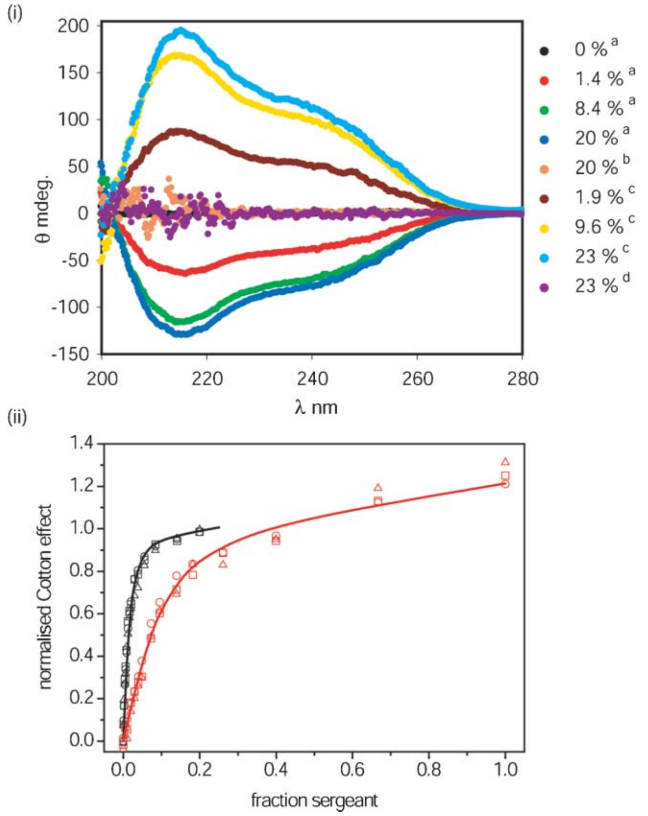

Fig. 2 (i) CD spectra of **1** in the presence of different amounts of sergeants **2a** (negative CD) or **2b** (positive CD) ([a][**1**] = 8.1 × 10^{-4} M in cyclohexane, [b][**1**] = 8.1 × 10^{-4} M in 95 : 4.5 : 0.5 C_6H_{12} : $CHCl_3$: CH_3OH, [c][**1**] = 9.3 × 10^{-4} M in cyclohexane, [d][**1**] = 9.3 × 10^{-4} M in 95 : 4.5 : 0.5 C_6H_{12} : $CHCl_3$: CH_3OH). (ii) Normalised Cotton effect as a function of the fraction of sergeant **2a** (black) or **3** (red) in mixtures with **1**. The lines are fitted using the theoretical model described in the text. The different symbols denote normalised Cotton effects at (○) 240, (□) 251 and (△) 261 nm (see also Fig. S2 ESI†).

formation of the helical aggregates. Fitting of the data (Fig. 2ii), using the model outlined by van Gestel,[24] resulted in excellent agreement between theory and experiment, with a value of 13.5 kJ mol^{-1} for the helix reversal energy and a mismatch penalty of 1.2 kJ mol^{-1}.‡ The former parameter corresponds to the penalty of introducing a helix inversion between columnar sections, and allows us to estimate a mean correlation length between helix reversals of 225 monomeric units. The mismatch penalty corresponds to the energetic cost of incorporation of the chiral monomer in columns with non-preferred helicity, and its value in the present system is significantly lower than the helix reversal energy, as was also observed in previously analysed columnar stacks of C_3-symmetrical molecules.[21] The fitting procedure also accounts for the fact that the Cotton effect continues to grow beyond the point where the induction of helicity has become complete.

These results prompted us to investigate the cooperativity of the self-assembly process using a mixture of the enantiomers **2a** and **2b** in a 'diluted majority rules' experiment.

In a solution of **1** (cyclohexane, 6.4 × 10^{-4} M) with 20% of a mixture of **2a** and **2b**, a sigmoidal variation in the magnitude of the CD signal was observed when the ratio of the enantiomeric sergeants was varied (Fig. 3). This indicates that mixed columns composed of **2a**, **2b** and **1** are formed rather than separate columns of **2a** with **1** and **2b** with **1**, which would lead to a linear variation in the magnitude of the Cotton effect. This non-linearity demonstrates that hydrogen-bonding and π–π stacking interactions dominate the composition of the columns but that cooperative packing effects of alkyl chains control their overall helicity. Since essentially the same molecules were used in the 'sergeants and soldiers' and 'diluted majority rules' experiments, we expected that the same parameters would govern the helicity of both systems. It was therefore gratifying to see that both experiments can be well described with the same theoretical model, and indeed with the same parameter values.§

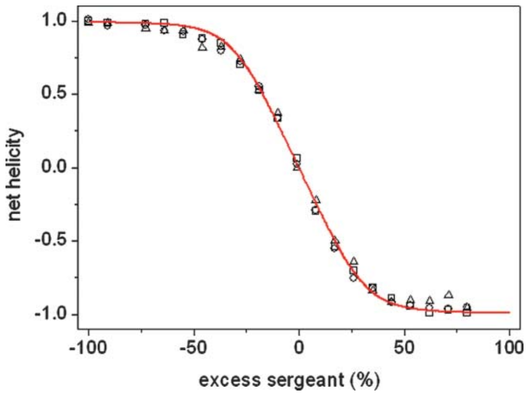

Fig. 3 Net helicity of cyclohexane solutions (total concentration 6.4 × 10^{-4} M of trimesic amides) containing 80% of **1**, and 20% of a mixture of **2a** and **2b**, given as a function of the relative excess of **2a** or **2b**. Symbols indicate experimental data at (○) 240, (□) 251 and (△) 261 nm, while the line indicates the fit of the theory to these points.

In order to study the effect of reducing the strength of helicity-directing interactions, we also probed the effectivity of sergeant **3**, having just a single chiral side chain per molecule. A marked Cotton effect was observed upon adding **3** to **1** (Fig. 2ii), although the non-linearity is not as strong. Thus, **3** is an effective sergeant, but is not as proficient as **2a** at biasing the helicity of columns of **1**. This is reflected by the 6 times lower value of the mismatch penalty (0.2 kJ mol^{-1}).

The value of the helix reversal energy (13.0 kJ mol^{-1}) is similar to that of the system **1** + **2a**, indicating that in both systems this value is mainly determined by the soldiers, which make up the majority of molecules.

In summary, we have shown that in stacks of benzene tricarboxamides with pseudo-C_3 symmetry, 'sergeants and soldiers' and 'dilute majority rules' experiments are described by the same energetic parameters. Moreover, the 'sergeants and soldiers' principle is operative even when only one out of three side chains is chiral. Current research is directed towards the use of 'majority rules' experiments to gain detailed insight into the packing and solvation of alkyl side chains in the helical columns.

Notes and references

‡ A description of the fitting procedure is beyond the scope of this communication, and can be found in the ESI†.

§ Since the 'sergeants and soldiers' and the 'majority rules' experiments were performed at different concentrations, the good fits with identical values of the energetic parameters also justifies the use of the long-chain limit approximation (see ESI†).

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