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## COMMUNICATION

## Twists and turns in the hierarchical self-assembly pathways of a non-amphiphilic chiral supramolecular material†

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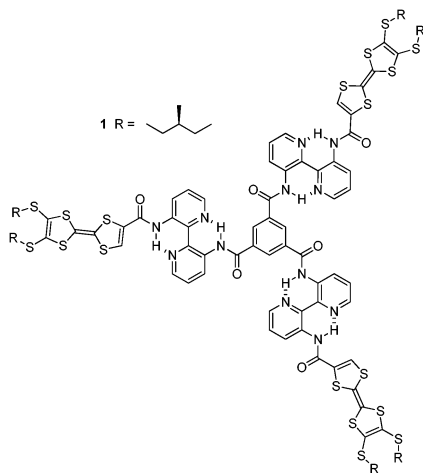
The formation of helical self-assembled fibres by a  $C_3$  symmetric molecule incorporating three tetrathiafulvalene units is shown to be influenced dramatically by the processing conditions, leading to a variety of different chiral forms, including unprecedented croissants.

The emergence of macroscopic helical morphology in fibres built up from chiral molecular and macromolecular components is a familiar yet poorly understood phenomenon.<sup>1</sup> Surfactant-like molecules frequently show helical structures based on twisted or folded ribbons<sup>2</sup> with the explanations of their structure usually implying the formation of bilayers where twists arise because of interfacial tension caused by the presence of the stereogenic centres.<sup>3</sup> Yet the reason for the absence of emergence of chiral morphology is still unknown. Chiral fibres of symmetric discotic-like molecules are relatively common,<sup>4</sup> yet although they show optical activity as a result of single stacks<sup>5</sup> the observations of more macroscopic asymmetry are very rare. Although chiral morphologies are evident in

tapes of porphyrin derivatives<sup>6</sup> chiral hydrophobic systems do not show visually chiral fibres.<sup>7</sup>

We have shown<sup>8</sup> that the non-amphiphilic  $C_3$  symmetric molecule **1**, self-assembles in dioxane at an approximate concentration of  $10^{-5}$  M to give solubilised helical stacks.<sup>9</sup> When the compound was dissolved in hot dioxane at  $10^{-3}$  M and the resulting solution was allowed to cool on the bench, long macroscopic and obviously chiral fibres were formed, whose helicity was directly related with the stereochemistry of the molecules of which they were comprised. However, the path which is followed to these fibres is far from clear. Molecular modelling suggested that three unimolecular wide strands can unite to give a superhelical structure, yet a gap in the hierarchy of the self-assembly lies before us. In this communication, we report new and remarkable findings concerning the pathway to the fibres, and how this path can be altered by controlling the conditions for the growth of the assemblies.

In an effort to identify the morphology of the fibres that are formed prior to the macroscopic twists we deposited a drop of a solution of **1** (we refer to the all *S* enantiomer throughout) when completely dissolved. Firstly, a drop of a room temperature solution of **1** in dioxane at a concentration of  $10^{-6}$  M was deposited onto different surfaces. On gold, scanning electron microscope (SEM) images (Fig. 1) show the presence of long and interconnected fibres. Here, the gold is advantageous for imaging, as no coating of the organic sample is necessary to dissipate charge in the SEM experiment. The width of the individual fibres is less than 100 nm in all cases, and is often less than 30 nm. These fibres cross and fuse into larger ones on the surface, yet no chiral morphology being evident. When the same solution was deposited on mica and the morphology was investigated by atomic force microscopy (AFM) individual fibres are clearly imaged. These fibres are mainly 4.8 nm in height from the surface (the width is approximately 100 nm, which includes convolution of the AFM tip). In certain locations (Fig. 2) less thick fibres are observed which on occasions seem to peel away from the main fibre, and in some places a thin fibre has areas where the thickness apparently doubles. The thin fibres must contain molecules which are tilted to the normal to the surface, yet which are not coplanar (the thickness of the molecule with the sidearms in their twisted conformation is approximately 0.7 nm) as in other aggregates on surfaces,<sup>10</sup> except that in the case of **1** the fibres are extremely well defined, pointing to the strong interaction between the molecules in the fibre and a slight influence of the surface on the thickness of the fibre. On graphite,

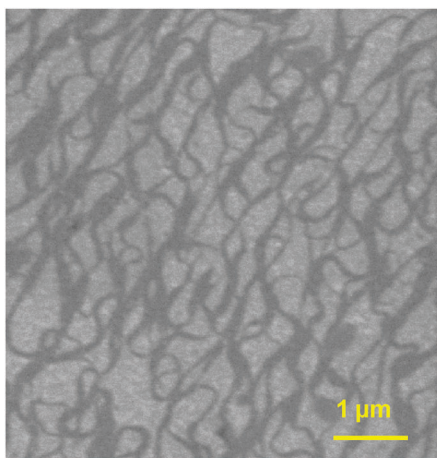


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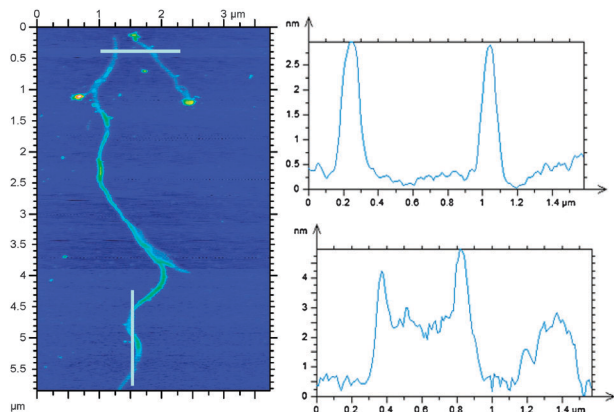
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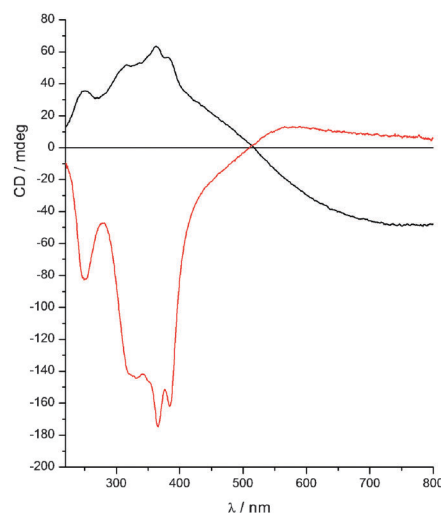
**Fig. 1** A SEM image of homochiral **1** deposited onto gold from a  $10^{-6}$  M solution in dioxane.



**Fig. 2** Dynamic mode AFM topographic image of fibres of **1** formed by casting a dioxane solution onto mica. The profiles on the right correspond to the lines on the AFM image.

layered structures are formed with a wetting type pattern where the thickness corresponds approximately to the thickness of the molecule and subsequent layers on top of it, presumably because of the strong interaction of the TTF units with the surface.<sup>11</sup>

To probe the optical activity of the aggregates as they grow in dimensions, circular dichroism (CD) spectroscopy was used in solution and in the solid state in the fibre form on a quartz surface. The spectra of the enantiomers of **1** at a concentration of  $10^{-5}$  M show mirror image spectra with significant optical activity at approximately 350 nm,<sup>8</sup> as shown for the all *S* compound in Fig. 3 where the bands are negative. However, when a solution of this compound was deposited onto a quartz plate and allowed to dry, the resulting CD spectrum of the solid revealed positive bands with the same features at the same position as the dissolved columns. The CD spectrum of the solid was confirmed by repeating the spectrum on the same sample at different angles with respect to the light beam and by repeating the experiment with different samples. This observation indicates that the type of aggregate is similar to the initially formed fibres in solution, yet during the hierarchical process of larger fibre formation the helicity is inverted, as it is in the macroscopic fibres.<sup>8</sup> This phenomenon was seen upon temperature variation in  $C_3$  symmetric dendrimers and was associated to the rotation of the lateral groups,<sup>12</sup>



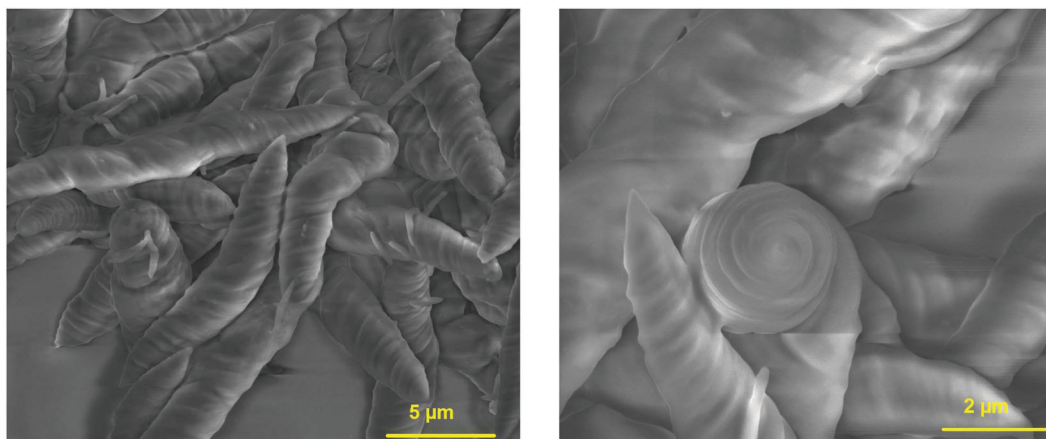
**Fig. 3** CD spectra of a film of all *S* **1** on quartz from  $10^{-4}$  M solution in dioxane (positive bands at 350 nm) and the solution state at concentration  $5 \times 10^{-5}$  M in dioxane in a rectangular cell with a 2 mm path length (negative band at 350 nm).

and a similar situation could be envisaged here upon aggregation of the single stacks which could cause a supramolecular rearrangement of the TTF units. We therefore observe the hierarchical level at which the helicity is inverted, from the single columns to the nanoscopic fibres, as seen in some other systems.<sup>13</sup>

Another notable feature of the CD spectra are the bands of opposite sign above 500 nm, where the spectra cross. There is no significant absorption band at this position (unlike compounds with near IR absorption<sup>14</sup>), and therefore it must be assigned to chiral scattering of the light caused by its interaction with the nanostructures whose size coincides with its wavelength. The more intense band for the larger aggregates supports this hypothesis. Curiously, no CD spectrum could be recorded for the higher order aggregates reported by us previously.<sup>8</sup>

When a hot  $10^{-3}$  M solution of **1** is allowed to cool on the bench, long macroscopic visibly chiral fibres are formed. In an effort to explore further the association pathway up from the chiral nanoscopic fibres to the macroscopic helices, we changed the cooling rate: a hot  $10^{-3}$  M solution of **1** was cooled slowly (at a rate of approximately 1 °C per minute) in the oil bath or thermo-shaker in which it had been heated. The resulting precipitate shows an unprecedented morphology, short scrolls which appear to be microscopic croissants (Fig. 4). Unlike the macroscopic fibres, the helical sense is always evident, and for the *S* enantiomer is *P*. An end view of one of the croissants shows the rolled up structure seemingly to be made of sheets, yet no individual sheets are observed, only occasional short and thin (approximately 250 nm wide) fibres. It therefore appears that the fibres role and associate in a side-on fashion to generate this object, which is well ordered: optical micrographs of the microcroissants show that they polarise light, and powder X-ray diffraction in a General Area Detector Diffraction system shows a reflection corresponding to approximately 3.5 Å corresponding to the  $\pi$ - $\pi$  stacking interaction inferred by modelling<sup>8</sup> (this reflection is also present for the macroscopic helical fibres prepared by fast cooling). While a change in morphology has been observed in the cooling of an organogelator,<sup>15</sup> the dramatic change in morphology seen for **1**





**Fig. 4** Scanning electron microscope images of the “micro-croissants” formed by molecule **1** upon slow cooling of a dioxane solution of the compound. Note the small fibres in some areas of the sample.

on changing the cooling rate of the precipitation (both enantiomers display the phenomenon) is new.

To conclude, the chiral morphology of **1** is not evident until microscopic (1 micron in width at least) fibres or croissants are formed, despite the clear presence of chirality in the aggregates as witnessed by CD spectroscopy. This technique shows that the optical activity inverts its sign when single helical strands of the molecule come together to form the larger fibres after hierarchical self-assembly. AFM measurements seem to indicate that the fibres may be made up of sheet-like aggregates as other helical fibres, but which nonetheless is surprising given the  $C_3$  symmetric and non-amphiphilic nature of the molecular component. Achiral analogues have shown fibrous morphology,<sup>16</sup> but not the behaviour shown in these chiral materials. The truly remarkable range of morphologies provided by processing the molecule under different concentrations and temperature cycles provides an opportunity to study tremendously complex nucleation, growth, and organisation of molecular matter where a hierarchy of chiral expression is witnessed.

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