Chiral Amplification in Columns of Self-Assembled *N,N',N''*-Tris((*S*)-3,7-dimethyloctyl)benzene-1,3,5-tricarboxamide in Dilute Solution

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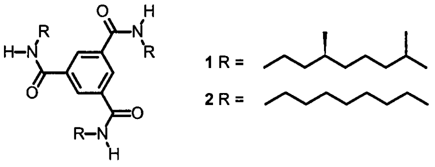
Remarkable control of chirality within a long and stable columnar self-assembly of *N,N',N''*-Tris((*S*)-3,7-dimethyloctyl)benzene-1,3,5-tricarboxamide in dilute solution is achieved by strong, unidirectional hydrogen bonding and cooperative side-chain interactions; IR and CD-spectroscopy have been used to elucidate these features.

From an esthetic and practical point of view, C_3-symmetrical molecules are highly attractive building blocks for the formation of supramolecular architectures. Especially those compounds that feature amide bonds have extensively been utilized for the formation of organic gels by Shirota et al.[1,2] and Hanabusa et al.[3,4] It has nicely been proven that the formation of such organogels is governed by intermolecular hydrogen bonding and intermolecular hydrophobic interactions between the side chains. Recently, the presence of helical columns in the solid state of such a C_3-symmetrical trimesic amide has been shown, mediated again by intermolecular hydrogen bonding.[5] We have demonstrated the formation of chiral columnar structures by C_3-extended-core discotic molecules bearing chiral side-chains.[6] These C_3-symmetrical molecules first self-assemble into columnar architectures in dilute solution. At higher concentrations these columns aggregate, resulting in the formation of an organogel. In order to elucidate the formation of gels formed by trialkyl-1,3,5-benzenetricarboxamides and the nature and importance of the secondary interactions, we synthesized enantiomerically pure **1** and studied its self-assembly in dilute solution with IR, UV and circular dichroism (CD) spectroscopy. Chiral amplification within mixtures of chiral **1** and achiral **2** was investigated to reveal the cooperativity within the stacks. Within columnar self-assemblies of compound **1**, cooperative directional hydrogen bonding as well as cooperative side-chain interactions are operative and these account for the formation and order within the well-defined columnar self-assemblies.



N,N',N''-Tris((*S*)-3,7-dimethyloctyl)benzene-1,3,5-tricarboxamide (**1**) was synthesized by reacting 1,3,5-benzenetricarbonyl trichloride with three equivalents of (*S*)-3,7-dimethyloctylamine in methylene chloride, using triethylamine as a base. The compound was identified using ^{1}H- and ^{13}C-NMR, elemental analysis and MALDI-TOF mass spectrometry.[7] Achiral **2** was synthesized in a similar fashion and has been reported previously.[8] Compound **1** showed liquid crystalline behavior at elevated temperatures in accordance with its achiral analogue **2**.[8] Melting into the mesophase occurred at 119 °C (16 kJ/mol) with evidence of a low enthalpy pre-transition at 105 °C. The mesophase extended until 236 °C (21 kJ/mol). Textures grown under the optical microscope show malthese crosses, pointing to the formation of a columnar mesophase.[8] The large energy of the transition at the clearing temperature is most probably due to melting of the three intermolecular hydrogen bonds.

The formation of self-assemblies in dilute solution and the involvement of hydrogen-bonding was studied using IR-spectroscopy. The N-H stretching vibration in the solid state occurred at 3223 cm^{-1} due to intermolecular hydrogen bonding.[2,4] In a hexane solution (10^{-4} M) this band had remained (3242 cm^{-1}) showing that hydrogen-bonding still persisted in solution. In a tetrachloromethane solution of 10^{-2} M this band could be discerned as well, although upon further dilution to 10^{-4} M an upcoming band at 3458 cm^{-1} could be discerned, attributable to molecularly dissolved molecules. In chloroform, **1** dissolved molecularly as could be deduced from the presence of a band at 3450 cm^{-1} only.

CD spectroscopic measurements were performed in order to investigate the self-assembly of **1** in dilute solution and the expression of chirality and cooperativity. As detected with IR-spectroscopy, **1** dissolves molecularly in chloroform and no detectable Cotton effect could be found, as expected. The UV spectrum of **1** in heptane is depicted in Figure 1 (top) and shows the absorption of the benzene and amide chromophores. Aggregation of **1** in heptane occurs, indicated by the appearance of a negative Cotton-effect (Figure 1). This effect is due to

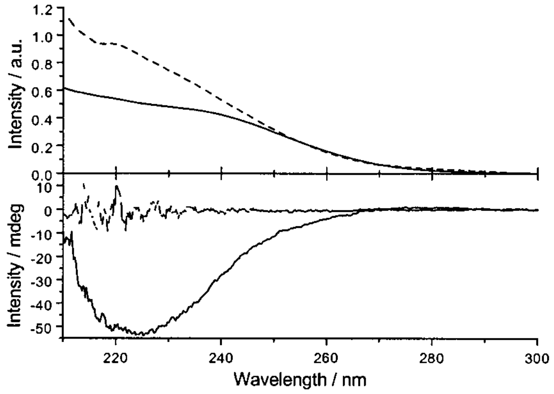


Figure 1. Absorption (top) and CD (bottom) spectra of **1** in heptane at 10 °C (——) and at 90 °C (----). Concentration = $6.5 \cdot 10^{-5}$ M.

the formation of a chiral superstructure. In this superstructure the molecules have to be highly ordered in order to give rise to a Cotton-effect. The peripheral side-chains interact due to the self-assembly, which allows them to transfer their chirality to the core.[9,10] The intermolecular hydrogen bonds apparently lock the molecules on top of each other and give directionality to the stacking of the molecules within the columns.[6] Upon increasing the temperature, a clear change of the UV and CD spectra between 50 and 80 °C could be observed. Over this temperature range, the Cotton-effect disappears and the UV spectrum changes significantly, because the columns break up into single molecules (Figure 1).

The cooperativity within the columns was proven by chiral amplification in accordance with the "Sergeant and Soldiers" principle.[11] Chiral **1** was used as the sergeant to direct the packing of the soldiers: achiral discs **2**. Figure 2 shows the intensity of the Cotton-effect as a function of the amount of sergeant added. As becomes evident from the figure, after addition of only 2.5% sergeant all columns have gained the same chirality as columns exclusively consisting of sergeants. Based on these data we calculated a cooperativity length of at least 80 molecules, illustrating the high positional order within the columns due to the chiral directionality of the amide groups. These amplification results of **1** and **2** are similar to the results of the extended C_3-symmetrical molecule previously reported.[6]

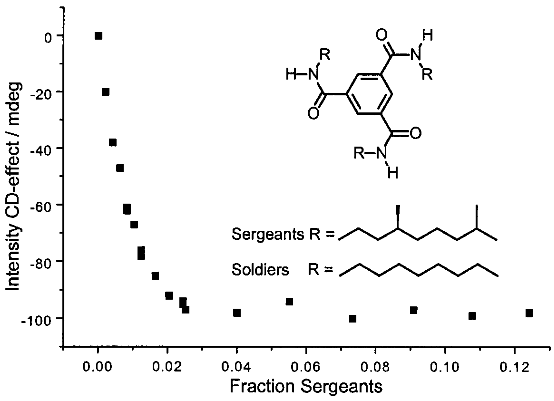


Figure 2. Plot showing the chiral induction, expressed in terms of the Cotton-effect (mdeg), as a function of the fraction of sergeants added. Measurements have been performed in heptane at 20 °C at a concentration of $7.9 \cdot 10^{-5}$ M. Data have been recorded at 224 nm.

We conclude that intermolecular hydrogen bonds within the self-assembled columns of **1** are highly directional and cooperative. The side-chain interactions, occurring upon self-assembly, give rise to large chiral superstructures over a long distance. With this study we disclosed detailed information on several aspects of the hierarchical growth of organic gels.

References and Notes

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7 Spectral data of **1**: ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.30 (s, 3H), 6.73 (t, *J* = 5.2 Hz, 3H), 3.45 (m, 6H), 1.62 (m, 3H), 1.51 (m, 6H), 1.42 (m, 3H), 1.28 (m, 9H), 1.15 (m, 9H), 0.93 (d, *J* = 6.4 Hz, 9H), 0.86 (d, *J* = 6.4 Hz, 18H); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ =165.7, 135.3, 127.9, 39.2, 38.5, 37.1, 36.6, 30.7, 27.9, 24.6, 22.7, 22.6, 19.5. MALDI-TOF [$M+Na^+$] = Calcd. 650.4 Da. Obsd. 651.0 Da. Elemental analysis: Found: C, 74.19; H, 11.30; N, 6.69%. Calcd for $C_{39}H_{69}N_3O_3$: C, 74,59; H, 11.07; N 6,69%.

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