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Combination of ionic self-assembly and hydrogen bonding as a tool for the synthesis of liquid-crystalline materials and organogelators from a simple building block†

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In this communication we report on the facile combination of hydrogen bonding and the ionic self-assembly (ISA) process to produce organized materials and fiber-containing organogel superstructures from functionalised oligoelectrolytic building blocks.

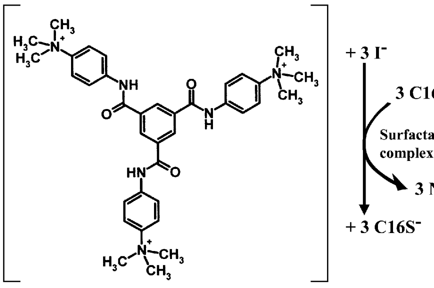
Organised materials, specifically mesogenic materials/molecules, are accessible *via* covalent as well as a range of noncovalent strategies, including coordination chemistry and H-bonding between nonmesogenic molecules.[1]

Recently a facile route for the production of mesogenic building blocks (or tectons) by complexation of oligoelectrolytes with charged surfactants was introduced.[2] This process, so-called ionic self-assembly (ISA), uses electrostatic interactions between the charged species as primary interaction to construct the mesogenic molecule. It was shown[2b,d] that liquid-crystalline properties could be easily tuned by variation of the alkyl volume fraction of the surfactants while leaving the central charged building block unchanged.

So far the ionic self-assembly route has only made use of hydrophobic and π–π interactions as secondary motifs to promote self-organization of charged oligoelectrolytic species. The aim of this study is to show that hydrogen bonding can also be combined with ionic self-assembly as a secondary motif to promote self-organization and to produce ordered and liquid-crystalline materials

Our attention focused on C_3-symmetrical disks. This group of molecules was selected for the following reasons: they bear multiple sites for intermolecular hydrogen bonding formation (amide groups), exhibit liquid-crystalline phase behavior and have been shown to act as organogelators when covalently functionalized with long alkyl chains.[3,4] For the purpose of applying this interesting versatile tecton within the ISA process, a new charged trisamide molecule **1** was synthesized (Scheme 1).

The precursor trisamide molecule bearing three terminal amine functions was synthesized by derivation of the procedure described by E.W. Meijer and co-workers.[4] 1,3,5-benzenetricarbonyl trichloride (Aldrich, 98%) was reacted with *N*,*N*-dimethyl-1,4-phenylenediamine monohydrochloride or *N*,*N*-dimethyl-1,4-phenylenediamine dihydrochloride (Aldrich, 99%) in dry dichloromethane in the presence of triethylamine.[5] The precursor trisamide was obtained as a pure yellow precipitate (51–56%). Methylation of the terminal amine functions was performed in a mixture of methyl iodide and acetonitrile in a 1 : 1 volume ratio to give molecule **1** in high yield with only traces of terminal amine groups. It should be noted that the NH group on the central amide is not affected by the use of a large excess of CH_3I. The synthesis of molecule **1** was confirmed by NMR, IR and elemental analysis.†



Scheme 1

Charged molecule **1** (with iodide counterions) was complexed with three equivalents of commercially available single-tailed sodium *n*-hexadecyl sulfate (C16SNa, Lancaster, 99%) and the double-tailed dihexadecyl phosphate (C16DP) (Aldrich, 99%, neutralized with sodium hydroxide). All solutions were prepared at 0.2 wt% concentration. Complexes were isolated after precipitation. Complexation in a 3 : 1 ratio was confirmed by means of elemental analyses. It was found that the **1**–C16S complex is soluble in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) but not in chloroform. On the contrary, the **1**–C16DP complex was found to be soluble in chloroform but not in DMF or DMSO. The complexes were dissolved in the respective solvents and cast into films.

Investigation of the films by polarized optical microscopy shows strong birefringence, indicative of anisotropic and ordered materials. Schlieren-type textures were detected. From thermogravimetric analyses (TGA) the degradation temperature of the complexes was found to be around 200 °C, whereas the thermal stability of **1** (with iodide counter-ions) was determined to be around 150 °C. Differential scanning calorimetric analyses (DSC) show that the films obtained exhibit reversible thermal transitions. In the case of the **1**–C16S complex cast from DMSO, a broad transition was found at −23.3 °C on the second heating curve and is attributed to structural rearrangements of the side chains. **1**–C16DP films cast from chloroform displayed two reversible thermal transitions on the second heating curve at 29.6 and 59.6 °C.

To elucidate the morphology of these materials, a range of temperature-dependent wide-angle (WAXS) and small-angle X-ray scattering (SAXS) measurements was performed.[6] WAXS experiments show that **1**–C16S (at room temperature) and **1**–C16DP films (above 59.6 °C) are non-crystalline materials with a broad reflection at approximately 20° in 2θ (*d*-spacing ~0.45 nm, indicative of a liquid-like arrangement of alkyl tails).

The SAXS pattern of the **1**–C16S complex obtained at room temperature clearly shows that the film is organized, with a set of peaks which can be indexed to a hexagonal array with a lattice parameter a = 4.08 nm (Fig. 1a).

The **1**–C16DP complex also forms highly ordered liquid-crystalline materials, but at temperatures above 59.6 °C. Below this temperature one sharp reflection is observed at 0.40 nm (WAXS) and is attributed to a partial crystallization of the alkyl chains. Temperature-dependent SAXS measurements confirm the formation of a highly ordered columnar phase which can be indexed to a monoclinic 2D lattice (a = 4.24 nm, b = 3.61 nm, γ = 94°) (Fig. 1b). A reflection at 2.94 nm (s = 0.34 nm^{-1}), as well as the second order reflection at 1.53 nm^{-1} is also observed on all the SAXS patterns. This could not be included in the

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† Electronic supplementary information (ESI) available: IR, NMR, DSC and TGA data of the organic core and complexes. See http://www.rsc.org/suppdata/cc/b3/b303552b/

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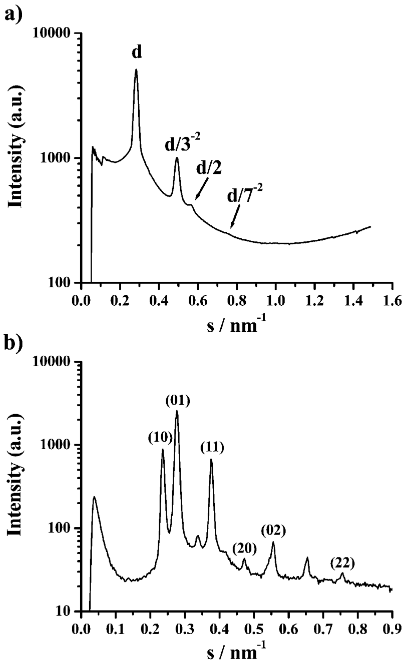

Fig. 1 SAXS pattern of: a) **1**–C16S cast from DMSO at RT and b) **1**–C16DP cast from chloroform at 100 °C.

indexation of the proposed 2D columnar phase structure. The observed columnar phases are to be expected, since the presence of amide groups on such C_3-symmetrical disks generally leads to the formation of columnar phases *via* hydrogen bonding.[3]

Since the related materials are known organogelators, we investigated the gelling properties of these complexes. As stated, the **1**–C16DP complex is not soluble in DMF and DMSO at room temperature. Heating leads to the dissolution of the complex. Clear solutions are obtained at 100 °C and, after cooling to room temperature, formation of gels is observed. It should be noted that pure C16DP does not form a gel in DMF. **1**–C16S did not form a gel in the explored solvents (1-butanol, toluene, hexane, DMF, DMSO, octanol, hexadecane, cyclohexane, water, 1,2-dimethoxyethane).

TEM was used to provide further evidence of the organogel nature of these materials. Micrographs obtained from a solution of **1**–C16DP (0.5 mg mL^{-1}) dried onto a carbon-film covered grid reveals the presence of a 3D network of twisted fibers with diameter of 10–40 nm extending over several micrometres (see Fig. 2). The twisted nature of the fibers can be attributed to the drying process, as has been observed for other organogels.[7] CD measurements confirmed that no preferred twist orientation existed.

In order to ascertain whether H-bonding does play any role in the formation of the observed superstructures, both IR and ^1H NMR investigations were performed on these materials. Infrared spectra of films of the complexes were recorded. This showed that H-bonding does indeed take place during the formation of the organised superstructures, but does not involve all of the C=O groups. This is indicated by the splitting of the single C=O band (1664 cm^{-1} in CCl_4 for **1**–C16DP) into two bands: 1606 and 1672 cm^{-1} for **1**–C16S complex; 1608 and 1672 cm^{-1} for **1**–C16DP complex.[4] The band with lower frequency arises from C=O···H–N hydrogen bonds, whereas that with the higher frequency is due to the non-hydrogen bonded C=O group.[8]

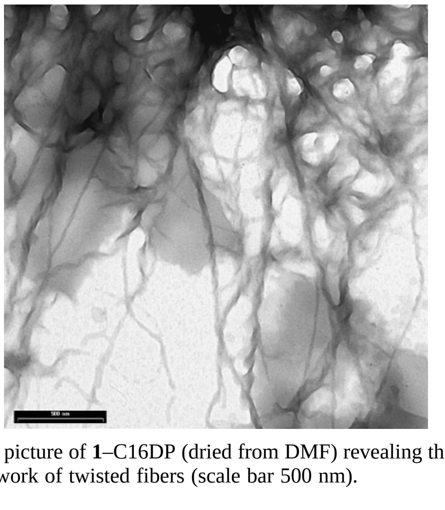

Fig. 2 TEM picture of **1**–C16DP (dried from DMF) revealing the presence of a 3D network of twisted fibers (scale bar 500 nm).

Temperature-dependent ^1H NMR spectroscopy[9] in d_7-DMF was used in this study to investigate the extent of H-bonding and its involvement in the gelation behaviour. At 100 °C, the NMR spectra displayed the characteristic signals of the hydrogen atoms of the NH groups of the amide at 12.46 ppm. The observation of the resolved resonances of both the amide protons as well as the aromatic protons (8.85 (3H), 8.36 (6H), 8.05 (6H) ppm) indicate that the core part of the complex can freely rotate.

However, upon cooling to room temperature, these resonances are completely dampened by motional broadening. The effect is so severe that the signals are hardly detectable and only signals from the surfactants were observed. These results show that the core of the complex, *i.e.* the triamide molecule, is involved in the gelation process upon cooling and that the NH group (hydrogen bond donor) is taking part in the aggregation.

A very important fact to mention here is that no π–π stacking could be detected by WAXS experiments (performed on both concentrated organogels and films). This, in conjunction with the NMR data presented, clearly shows that the aggregation of the complex into elongated fibers in solution is induced by a directional extended network of hydrogen bonds.

Here we presented results from the combination of hydrogen bonding and ISA to produce columnar thermotropic liquid-crystalline materials and fiber-containing organogel superstructures. The flexibility, tunability and ease of implementation of this approach (using one core, varying the surfactant to tune the properties, minimal covalent synthesis) highlights the potential for use in industrial organogelator applications such hydrometallurgy, cosmetics, food processing and lubrication.

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6 X-Ray measurements were performed after heating to 130 °C and 180 °C respectively, to ensure the removal of residual solvent in the films (as determined by TGA analyses). This was done to ensure that solvent-swollen (lyotropic) phases were not investigated, but true (solvent-free) thermotropic LC phases.

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