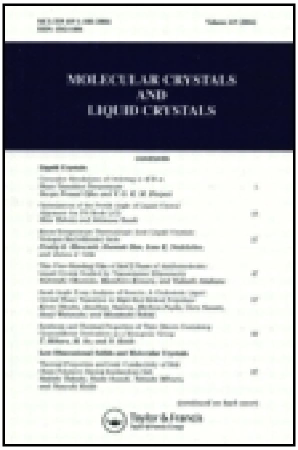

Molecular Crystals and Liquid Crystals

Liquid-Crystalline Materials by the Ionic Self-Assembly Route

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Liquid-Crystalline Materials by the Ionic Self-Assembly Route*

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The novel synthesis method of Ionic Self-Assembly (ISA) for the production of thermotropic and lyotropic LC materials is presented and discussed at the hand of several examples. The use of this alternative synthesis route to well-defined and functional LC materials is discussed.

Keywords: ionic self-assembly; noncovalent interactions; novel LC materials; self-organisation; supramolecular chemistry

INTRODUCTION

In the field of low-molecular weight liquid crystals, the classical covalently assembled mesogens have been developed, characterized and extensively utilized for a variety of high-end devices and applications. However, the construction of well-ordered three-dimensional arrays in a facile way from easily accessible tectons (or building blocks) is essential for the next generation of low-cost (and even disposable) devices.

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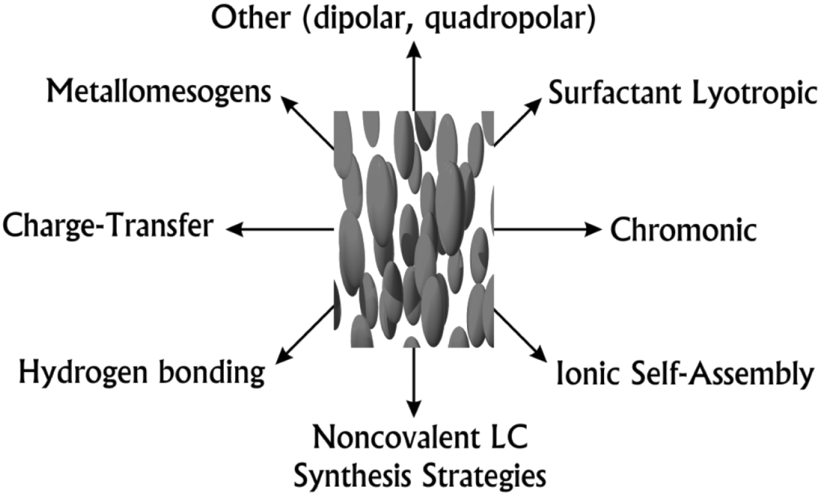
The costs and synthetic effort involved in the development and production of covalent mesogenic materials has, on the one hand, caused scientist active in this field to look for alternatives to these classical approaches. On the other hand, the recent advances made in the fields of self-organisation (or self-assembly) and supramolecular chemistry [1] has focussed attention on the non-classical pathways that are also available to the modern materials chemist.

Seen as part of the general drive in investigating noncovalent interactions as basis for the formation of new materials, several pathways have been developed for the production of mesogens (see Scheme 1). In addition to precise control over the structures, self-assembly can also lead to properties that can be controlled by external conditions or triggers. These interaction strategies include, amongst others, the following (with the name of selected researchers active in these fields in parentheses): hydrogen bonding (Kato [2,3] and Meijer [4,5]), metalomesogens (Serrano [6,7]), charge-transfer (Percec [8,9]) and so-called complimentary polytopic interactions (Bushby [10,11]). Since this discussion focuses on the use of various interaction strategies, novel mesogenic systems due to varying or anisotropic shape factors are not discussed here. See, for example, Reference [12] for more information on this topic. Two strategies or rather classes of materials that do not fit into the above classification, but is certainly worth mentioning, is firstly the well-known surfactant lyotropic phases (Tiddy [13])

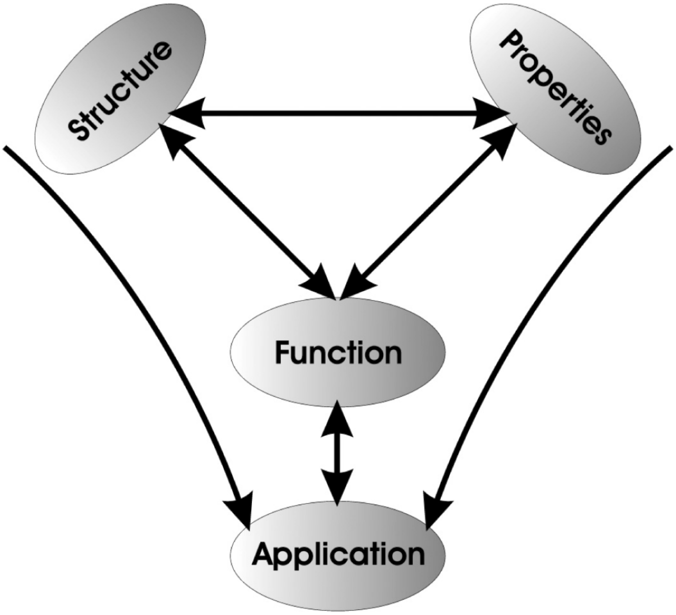


SCHEME 1 Routes to the production LC materials by noncovalent interactions.

and secondly, the chromonic lyotropic liquid crystals (Lyddon [14,15]). Here the formation of lyotropic phases at low concentrations by charged dyes characterise these interesting nonclassical systems. (Noncovalent) Stacking interactions combined with further geometrical factors dictate the formation of mesophases.

One set of interactions that has featured, but only on a very limited scale in the case of the polycatenar LC materials, is ionic interactions. The use of surfactant counterions with silver systems are demonstrated [16,17] and the influence of the counterion on the phase formation was studied for a few species. Variation of the counterion was performed in another study, but the authors concentrated on small (inorganic) counterions in most cases [18]. In the case of the chromonic materials mentioned above, these materials are charged but possess small inorganic counterions when they form mesophases.

In contrast to this, the Ionic Self-Assembly (ISA) strategy was recently introduced for the production of supramolecular materials [19]. Here, the mostly neglected ionic interactions are exclusively



SCHEME 2 The interaction and balance between tectons' structure and properties, and how that leads to specific function and application (Reprinted from Synthetic Metals, 147, CFJ Faul, Structure–function relationship in optically and electronically active ISA materials, 63-65 (2004). Copyright (2004), with permission from Elsevier).

utilised to combine two mutually repulsive molecular tectons to form a charge-neutralised supramolecular complex. More specifically, the addition of charged surfactants to oppositely charged oligoelectrolytic species yield nanostructured bulk materials in a cooperative process [20]. The fact that the starting materials are easily accessible, cheap (in the case of surfactants) and available in a large variety of different structures, makes this strategy attractive for the formation of a wide range of materials. Due to the modular approach of the ISA strategy, it is possible to include organic and inorganic central oligoelectrolytes [21] of varying charge, number and function into these nanostructured materials. Variation of the surfactant structure (length and number of tails [22], presence of branching in the tails and inclusion of specific function [23]) also has a significant effect on the materials properties, and has ultimately led to the formation of liquid-crystalline materials using this strategy [24]. The interaction and balance between the tectons' structure and properties, and how that leads to specific function and finally application of the newly formed materials, has been discussed elsewhere [25], and can be summarised by Scheme 2.

In this contribution, the facile formation of liquid-crystalline materials and their (unexpected) phase behaviour and function is discussed at the hand of several examples from recent work.

DISCUSSION

Before the discussion of the thermotropic phase behaviour and the formation of lamellar phases in discotic premesogenic units, the formation of lyotropic phases in ISA materials will be discussed briefly.

Lyotropic Phase Behaviour

Initial efforts in the investigations of phase behaviour of ISA materials focussed on their thermotropic behaviour [22,24,26]. The formation of lyotropic phases from ISA materials was not examined in any detail at all, until the formation of large oriented (monodomain) structures became a goal of our investigations. It was then found, in the case of the perylenediimide-AOT complex [27], that lyotropic phase behaviour could be induced by dissolution in either dimethylformamide (DMF) or 1-methyl-2-pyrrolidone (NMP). Indications from X-ray analyses were that a hexagonal columnar phase was formed in DMF (at 28 wt%). Formation of oriented domains was then induced at the phase transition front (PTF) between the isotropic and lyotropic phase at elevated temperatures. Detailed investigations using polarized UV-Vis

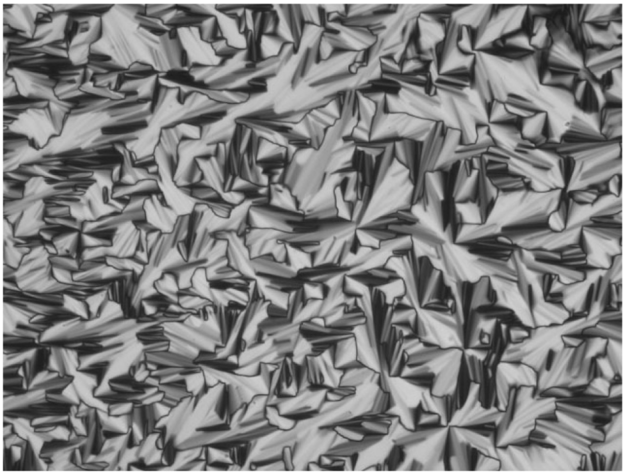


FIGURE 1 Typical texture of a lyotropic phase of a highly luminescent polyoxometalate-surfactant complex (in chloroform (Reproduced from Zhang, T. R., Spitz, C., Antionietti, M., Faul, C. F. J. (2005) *Chem. Eur. J. 11*, 1001, with permission from Wiley).

spectroscopy and null-ellipsometry yielded the following data: dichroic ratio of over 18 was achieved, corresponding to an order parameter of 0.85, while the principle refractive indices for the oriented films were determined to be $n_x = 1.450$, $n_y = 1.615$ and $n_z = 1.575$ at $\lambda = 632.8\,\text{nm}$.

Except for organic tectons, we have also been investigating inorganic tectons for the formation of hybrid nanostructured materials. Recently [28] we also found the formation, for the first time, of a lyotropic phase of a highly luminescent polyoxometalate-surfactant complex in chloroform (see Fig. 1). Unfortunately this phase, tentatively labelled a columnar phase, could not be investigated any further due to the high viscosity at the high solid content. This example however shows that the possibility exists for the formation of lyotropic phases with such functional materials.

Thermotropic Phase Behaviour

Lamellar Phases from Discotic Precursors

In our search to expand our understanding of the factors that influence the phase behaviour of LC ISA materials, the delicate balances that exist between the alkyl volume to central tecton ratio and the structure of both the surfactant tecton and oligoelectrolytic tecton have been investigated. However, the influence of the charge-neutralised groups on the phase formation has not been given any great attention, except for the case of the formation of crystalline materials [29]. In the following cases of two potentially discotic mesogens we have seen the very large influence and role that this factor can play.

Discotic liquid-crystalline materials were discovered by Chandrasekhar in 1977 [30]. These hexasubstituted (hexaester) benzenes introduced a new and exiting class of materials and properties to the field of liquid-crystal research. Since then the use of discotic building blocks/tectons have become wide spread, and their use for the formation of a variety of columnar and even nematic discotic mesophases is well-known and described [31,32].

We therefore proceeded to try and mimic the work of Chandrasekhar by making a hexasubstituted ionic complex, starting from mellitic acid (benzene hexacarboxylic acid) and double-tailed ammonium surfactants [33]. The samples exhibited, after initially exhibiting a fan-shaped texture, very facile alignment into very large monodomains with a negative homeotropically oriented optical axis after heating. We found that instead of the expected columnar phase architecture, a very well-defined lamellar (or more precise, a bilayer Smectic A) phase was formed, with a repeat unit of 3.22 nm (transmission-mode small-angle X-ray scattering (SAXS) on a non-aligned sample). SAXS in both symmetric and asymmetric reflection mode on an aligned sample yielded a repeat unit $d = 3.15\,\mathrm{nm}$. This value fitted very well with the data generated from a model [34] of two alternating types of layers of different electron densities. This model yielded values for the two layers of $d_1 = 1.41\,\mathrm{nm}$ and $d_2 = 1.74\,\mathrm{nm}$, respectively, which also fitted extremely well with a geometrical model of the mellitic acid and surfactant headgroups as the first layer (d_1), and the fully interdigitated alkyl chains as the second layer (d_2) (see Fig. 2).

To ascertain the order of the complexes within aligned films, angular dependent polarised UV and IR measurements where measured at a range of temperatures. A summary of the results obtained from these investigations are provided: From the UV measurements we could calculate the order parameter for the benzene rings $S = 0.92 \pm 0.01$ (rings oriented parallel to the plane of the substrate). The surfactant tails (from IR measurements) are aligned perpendicular to the plane of the benzene rings with an order parameter $S = 0.75 \pm 0.02$. Temperature-dependent investigations showed, in short, that the alkyl tails of the surfactant retain a high degree of order, even at high temperatures. However, the material does not fully crystallize either, and the order parameter for the alkyl tails at low (-40°C) temperature stays below 1 (0.89 ± 0.03). A full and in-detail discussion is provided in the original publication [33].

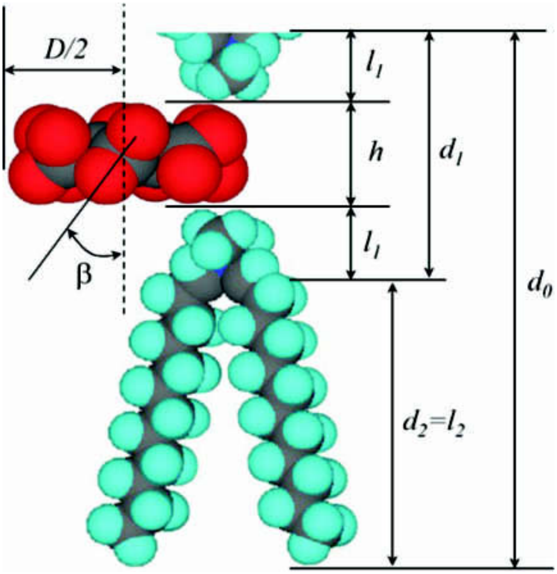


FIGURE 2 A geometrical model of the mellitic acid-surfactant complex: the mellitic acid and surfactant headgroups form the first layer (d_1), and the fully interdigitated alkyl chains the second layer (d_2) (Reprinted with permission from Y. Zakrevskyy, B. Smarsly, J. Stumpe, and C. F. J. Faul, (2005). *Physical Review E*, *71*, 021701. Copyright (2005) by the American Physical Society).

The fact that the central tecton in the above-mentioned case was very small when compared with the size and number of the charge-neutralised groups on the outer edge, does influence the formation of the phase found from purely geometrical considerations. We have, however, also investigated a much larger, electron-deficient discotic core, and found very similar behaviour in particular cases [35]. In the case of the covalently modified tricycloquinazoline (TCQ) core, columnar phases spanning a wide range of temperatures are mostly found [36,37]. In the case of the hexaacetoxy derivative it was found that this potentially discotic mesogen would undergo hydrolysis at high pH to yield a hexacharged species. Complexation with double-tailed ammonium surfactants did however not produce the expected columnar phases. Although not all of the complexation reactions yielded 1:1 charge ratio complexes (and therefore made the characterisation of the obtained products obsolete), in the case of the didodecyldimethylammonium surfactant this was not the case. It was furthermore rather interesting to note, once again, that this material did not produce columnar phases, but rather a lamellar phase with a d spacing of 2.98 nm.

The SAXS data obtained was of high quality, and could therefore also be used to model the system using a similar two-layer model as discussed above. This yielded values of $d_1 = 1.75$ and $d_2 = 1.23$ nm, respectively. If the length of a stretched C_{12} alkyl chain is calculated, a value of 1.67 is found. This would indicate that the alkyl fraction is accommodated in d_1, and in a fully interdigitated arrangement. The core and charge-neutralised groups would therefore be accommodated within d_2, as depicted in Figure 3 below.

Switchable Function in Thermotropic LC ISA Materials

Finally, the importance of the development of switchable materials is also highlighted. Switchable behaviour (in terms of phase and function switchability) is well-known in classical low molecular weight LC materials. In the case of supramolecular-based materials switchability is still a sought-after feature [38] and the research focus of many groups.

In this example it can be shown that very basic temperature-dependent switchability of the function of a thermotropic LC ISA material is possible [39]. A group of functional supramolecular materials were synthesized based on the complexation of phenyl-capped tetraaniline, phenyl-capped octaaniline and polyaniline with various phosphate surfactants (also acting as dopants). Complexation leads to the formation of a variety of highly organised LC materials showing thermotropic phase behaviour.

In the case of the phenyl-capped tetraaniline (TANI) systems the following very interesting behaviour was detected. Since polyaniline

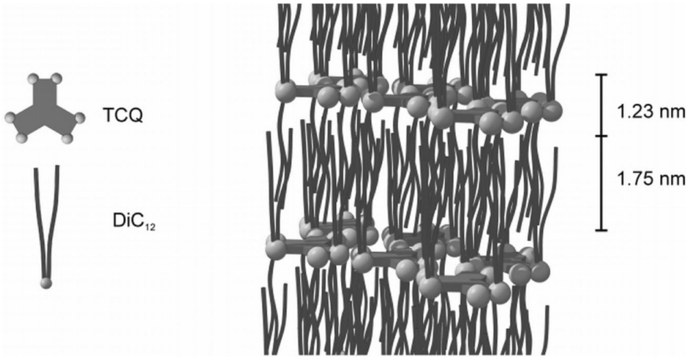


FIGURE 3 A model of the lamellar phase produced from the discotic tricycloquinazoline (TCQ) core (Reproduced with permission from *Chem. Mater*. 2004, *16*, 3867. Copyright 2004 American Chemical Society).

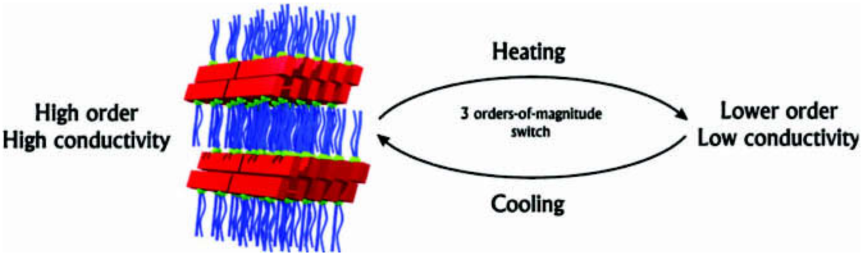


FIGURE 4 The influence of changes in temperature on the conductivity and phase behaviour of TANI-surfactant LC materials.

is a very well-known conducting polymer [40], the conductivities of the results oligomer-based systems were also investigated. It was found that these materials were indeed conducting (as indicated by their UV absorption spectra). SAXS analyses of the TANI-surfactant complexes indicated extremely well-organised columnar phases ($A = 2.35\,nm$, $B = 2.7\,nm$ and $\gamma = 80^\circ$). Volume calculations indicated that 2 TANI-surfactant complexes would fit into such a unit cell arrangement, with stacking of the TANI molecules found to be extremely strong (stacks of larger than 15 nm).

Investigations of the temperature-dependent conductivity of the TANI-surfactant complexes at different doping ratios showed remarkable reversible functionality – the conductivity of these materials could, in some cases, be switched over more than three orders of magnitude in a reversible and repeatable way. This was attributed to an order-disorder phase changes in these thermotropic LC materials, with consequent decrease (but not loss) of conductivity. These results were confirmed by temperature-dependent X-ray and UV analyses, and are summarised in Figure 4.

CONCLUSION

It was the goal of this short overview of the latest results obtained from investigations using LC ISA materials to show the potential of this approach for future LC materials production. Not only does this route have the advantage of facile synthesis, but also presents, owing to the modular approach in that two separate components are utilised, the possibility for investigating a broad range of structural influences on the phase behaviour of such formed LC materials.

It was furthermore shown that, due to the presence of the charge-neutralised groups within the complexes, new factors have to be kept in mind when the aim is to design LC materials of specific phase structure.

The fact that functionality can be included in the ISA materials with great ease has been combined with phase changes induced in the formed thermotropic materials to show rudimentary switchability of function.

LC materials from the ISA approach therefore seem to hold promise for the future for the production of a wide variety of different kinds and classes of (LC) materials.

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