Induced Liquid Crystallinity in Switchable Side-Chain Discotic Molecules

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Here, we present a strategy whereby a water-soluble tricycloquinazoline (**TCQ**) core is generated by hydrolysis of the corresponding nonionic hexaacetate, presenting itself as a potential (discotic) mesogen. The in situ generated core fragment was then used as a hexaanionic building block (or tecton) for assembly into ordered liquid-crystalline aggregates using the Ionic Self-Assembly (ISA) technique. The success of this “liquid-crystal-on-demand” strategy is demonstrated by a simple example.

Introduction

Discotic liquid-crystalline materials are attractive for applications in electronic devices (solar cells,[1−4] OFETs,[4] OLEDs[5]) owing to their unique charge transport properties. This includes high anisotropy of charge carrier mobilities, high mobilities in the direction of the columns,[3] and low intercolumn mobilities—due to the unique solid-state structure.[2] A large number of discotic ensembles with p-type character (supporting hole transport) are known (e.g., hexabenzocoronenes from Müllen et al.[1]). Studies of electron-deficient core molecules with an n-type character are becoming more frequent, as seen with, for instance, perylenebisimides,[1] phthalocyanines,[6] triphenylene,[7,8] triazine,[9] and triimide[10] derivatives. With some promising developments[11] over the past few years, the need for such materials for applications in electronic devices[1,4,12] has increased.

The materials discussed so far were all synthesized via classical covalent chemistry routes. However, over the past few years, several noncovalent and nonclassical strategies have emerged for the production of liquid-crystalline materials. Metallomesogens as a class of such LC materials is probably one of the best examples for the production of a variety of materials, not only containing many different metal species, but also exhibiting a variety of phases. This topic has been thoroughly covered in, for instance, ref 13 and in a more recent review,[14] where the potential for application of these materials was critically examined.

The supramolecular assembly of discotic materials is a further example where noncovalent strategies (and combinations of) have been applied. The assembly of disks by H-bonding,[15] or through charge-transfer interactions and volume consideration, as exemplified in the work by Percec et al.,[16] are but a few examples in a very active field. Ziessel et al.[17] recently presented another strategy where metal coordination and volume considerations (i.e., wedge-shaped precursors) were utilized to form columnar LC materials. Noncovalent interactions are also exploited where interdisk H-bonding is used to strengthen, increase, or enforce columnar order (for a recent example, see ref 18).

One noncovalent strategy that has recently emerged for the production of organized materials is the so-called

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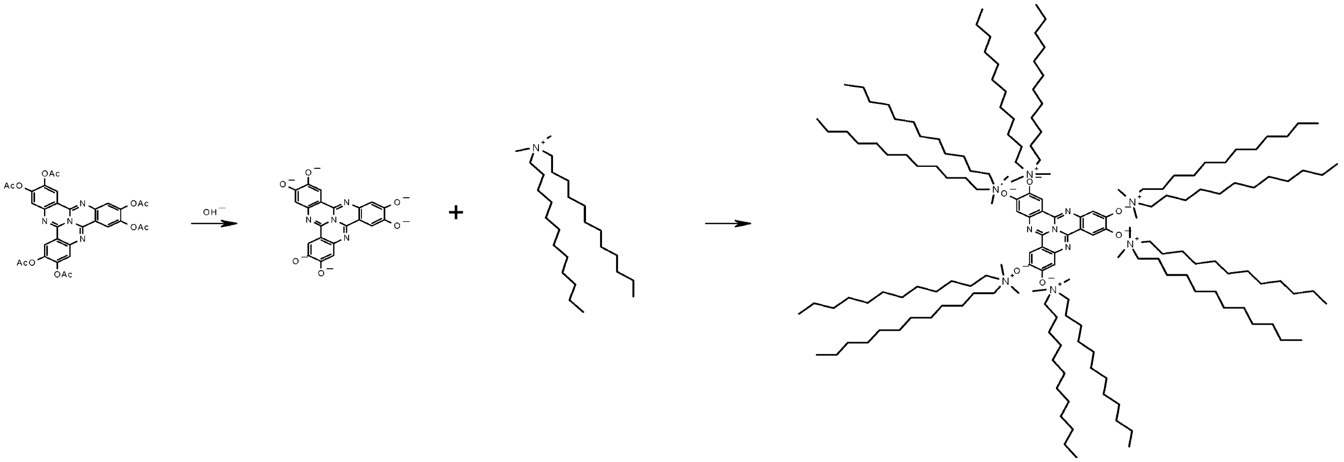
Scheme 1. In Situ Mesogen Formation Process and Consequent Liquid Crystal Formation via the ISA Route



Ionic Self-Assembly (ISA) route.[19] Ionic interactions between charged surfactants and charged oligoelectrolytes are used to direct the formation of highly organized nanostructures. It has been shown that ISA can also be used for the production of a variety of thermotropic liquid-crystalline materials (both metallomesogen-like[20] and perylene-based systems[21]). A combination of the ISA and H-bonding motifs also proved to be successful to not only form thermotropic columnar mesophases, but also enhance the intertecton interactions to such an extent that organogels could be formed.[22]

In this study we have concentrated on the interesting class of tricycloquinazoline cores (**TCQ**, containing four N heteroatoms) as potential mesogens. The presence of the heteroatoms should contribute to increasing the first reduction potential, thereby facilitating electron injection and high electron mobility.[7,23] These materials have previously been investigated in their covalently derivatized hexaalkoxy[24,25]and hexathioalkoxy[26] forms, and all form columnar phases (see below).

Here, we now present results from a new multi-motif strategy, where a **TCQ** tecton is used in the ISA process to form a liquid-crystalline material. However, the difference of this study compared to other previous ISA investigations is the fact that the charged core to be used here is generated in situ by hydrolysis of the corresponding nonionic hexaacetate and then assembled into a nanostructured material. This is outlined in Scheme 1.

We discuss this in situ mesogen formation at the hand of a simple example, the complexation of the **TCQ** hexaanion with the double-tail surfactant didodecyldimethylammonium bromide (**DiC$_{12}$**). The very interesting and unexpected phase behavior of the obtained material is discussed. As further comparison, the complexes of the single tail analogue, dodecyltrimethylammonium bromide (**C$_{12}$**), as well as two longer double-tail analogues (dihexadecyl (**DiC$_{16}$**) and dioctadecyl (**DiC$_{18}$**)), are prepared and characterized.

Experimental Section

Materials. All surfactants (dodecyltrimethylammonium bromide, (**C$_{12}$**), didodecyldimethylammonium bromide (**DiC$_{12}$**), dihexadecyldimethylammonium bromide (**DiC$_{16}$**), and dihexadecyldimethylammonium bromide (**DiC$_{18}$**)) were obtained from Aldrich Chemical Co. and used as received.

Synthesis. The synthesis of the hexamethoxy-**TCQ** was performed according to published procedures[24,25] in a three-step synthesis. Hexaacetoxy-**TCQ** was prepared from hexamethoxy-**TCQ** by (i) ether cleavage with molten pyridinium hydrochloride followed by (ii) an in situ esterfication with acetanhydride/pyridine. The procedures are provided in detail as Supporting Information.

Preparation of the ISA LC Material. 2,3,7,8,12,13-Hexaacetoxytricycloquinazoline was dissolved in a NaOH solution (pH > 10) to form a 2% solution and stirred until clear. The surfactant of interest was dissolved in a NaOH solution (slightly heated when needed) to form a 2 wt % solution and stirred until clear. The surfactant was added to the formed hexaanionic **TCQ** in a 1:1 charge ratio. A precipitate forms immediately and is left to stir for another 24 h. The precipitate is then removed by centrifugation, washed with deionized water, and dissolved in a suitable organic solvent (chloroform) and films were cast from solution. In the case of the **TCQ-C$_{12}$** system, precipitation only occurred to a low degree and obtained samples were dissolved in DMSO or DMF with limited success.

Resulting Materials Were Analyzed by the Following Methods. Thermogravimetric analysis (TGA) was performed on a Netzsch TG 209. The samples were examined at a scanning rate of 20 K·min^{-1}.

The phase behavior of the complex was investigated by a differential scanning calorimeter (DSC). All DSC measurements were performed on a Netzsch DSC 204. The samples were examined at a scanning rate of 10 K·min^{-1} by applying several heating and cooling cycles.

Small-angle X-ray scattering measurements were carried out with a Nonius rotating anode ($U = 40$ kV, $I = 100$ mA, $\lambda = 0.154$ nm) using image plates. With the image plates placed at a distance of 40 cm from the sample, a scattering vector range of $s = 0.07-1.5$ nm^{-1} was available. 2D diffraction patterns were transformed into 1D radial averages.

Wide-angle X-ray scattering (WAXS) measurements were performed using a Nonius PDS120 powder diffractometer in transmission geometry. A FR590 generator was used as the

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Table 1. Comparison of the Different TCQ Materials

TCQ with branched/linear alkoxy side chains	phase transition	clearing point	phase
pentanoxy[24,25]	184.7	299.2	hexagonal (Col_h) a =2.12 nm (197 °C)
nonyloxy[24]	79.6	237.1	
undecyloxy[24]	71.9	214.7	hexagonal (Col_h) a =2.87 nm (197 °C)
hexadecyloxy[24]	67.1	166.4	
2-ethylhexyloxy[27]		152.8 (mp)	no LC phase observed
3,7-dimethyloctyloxy[27,28]	117.9	190.8	hexagonal (Col_h)[29] a =2.77 nm (118 °C)
3,7,11-trimethyldodecyloxy[27]	n.o.	143.1	hexagonal (Col_h) a =2.90 nm (127 °C)
TCQ-DiC$_{12}$			lamellar (2.98 nm) $d_1 = 1.23$ nm $d_2 = 1.75$ nm (25 °C)
TCQ-DiC$_{16}$, **TCQ-DiC$_{18}$**			crystalline
TCQ-C$_{12}$			nonstoichiometric complexation

source of Cu Kα radiation. Monochromatization of the primary beam was achieved by means of a curved Ge crystal. Scattered radiation was measured using a Nonius CPS120 position-sensitive detector. The resolution of this detector in 2θ is 0.018°.

Elemental analyses (C, H, N, S) were performed on a Vario EL Elementar (Elementar Analyzen-systeme, Hanau, Germany).

^{1}H NMR spectra were recorded in $CDCl_3$, on a Bruker ARX 400 with use of the solvent proton signal as the internal standard at room temperature.

IR spectra were recorded on a Nicolet Impact 400 spectrometer in KBr disks.

Results and Discussion

Previous investigations (synthesis and temperature-dependent X-ray investigations) by Kumar et al. have shown that the phase structures of the liquid-crystalline hexaalkoxy-**TCQ** derivatives are consistent with that of a Col_h phase. The intercolumnar distance is dependent on the alkoxy length (see Table 1 for a comparison), whereas the interdisk distance between the discotic **TCQ** moieties within the columns was estimated to be approximately 0.34 nm. It can be mentioned that, in general, the phase transition and isotropization temperatures decrease gradually with increasing length of the alkoxy groups. In the case of derivatives with long, branched alkoxy substituents (e.g., 3,7-dimethyloctyloxy and 3,7,11-trimethyldodecyloxy) the clearing points are below 200 °C. The $-OC_{15}$ derivative (3,7,11-trimethyldodecyloxy) does not crystallize and forms a stable, discotic LC mesophase also at room temperature. The hexagonal lattice spacing for the linear $-OC_{11}$ (undecyloxy) and the branched $-OC_{10}$ (3,7-dimethyloctyloxy) **TCQ** derivatives are very similar (2.87 and 2.77 nm, respectively); also the longer $-OC_{15}$ derivative (3,7,11-trimethyldodecyloxy) shows an only slightly increased value (2.90 nm).

In the case of the ISA material **TCQ-DiC$_{12}$**, complex formation was, except for the fact that precipitation occurred with addition of surfactant, confirmed by solution ^{1}H NMR studies. The absence of a singlet at 2.34 ppm, corresponding to the methyl group of the $-$OAc group, indicated that all the acetoxy groups were removed. The ^{1}H NMR spectrum furthermore shows a singlet signal at 7.5 ppm for the aromatic protons H1, H6, and H11 (that are somewhat downfield compared to the aromatic protons H4, H9, and H14 which shows a singlet signal at 7.1 ppm). A triplet signal at 3.17 ppm is also observed, accounting for the 24 α CH_2 protons of the alkyl chains (four per surfactant, six surfactants per **TCQ** molecule). Multiplet signals are furthermore observed at 1.6−0.96 ppm, accounting for the rest of the alkyl protons. IR measurements also confirmed the absence of the acetoxy groups (no band at 1776 cm^{-1} from the C=O group). Repeated elemental analyses, even after prolonged periods of extraction in water, indicated the presence of some impurities (possibly water and hydroxide from NaOH). These consistently lower than calculated values however did not affect the found phase morphology.

Polarized light microscopy investigations revealed a strongly absorbing birefringent material, exhibiting very small domains and no typical texture. TGA showed an onset of decomposition at relatively low temperatures (125−150 °C), with almost full decomposition at 250 °C. DSC investigations (below the onset of decomposition) showed a reversible thermal transition below room temperature, at 10.1 °C (on the heating curve). WAXS and consequent SAXS analyses at room temperature showed that this material was already in a liquid-crystalline state at room temperature (Figure 1a and b). Further temperature-dependent WAXS analyses showed that phase transition observed in the DSC curve was only due to a partial crystallization of the alkyl tails since only a narrowing of the alkyl halo could be seen at −25 °C rather than any sharp reflections typical for crystalline surfactant alkyl tails.

The most interesting and striking feature of the **TCQ-DiC$_{12}$** material was however observed in the WAXS diffractograms recorded at room temperature, namely that the well-known (and expected) packing of the discotic mesogens ($d = 0.34$ nm) was not observed at all. In addition to this observation, the SAXS diffractograms recorded showed a very clear peak ratio of 1:2:3, very typical for a lamellar phase (see Figure 1b), with a lamellar d-spacing of 2.98 nm. This is indeed a very interesting phenomenon since it is not expected that a discotic mesogen will arrange itself into a lamellar architecture, but rather form a columnar structure of some kind. After the sample was annealed at 100 °C (to allow for possible thermal rearrangements within the material) and cooled back to room temperature

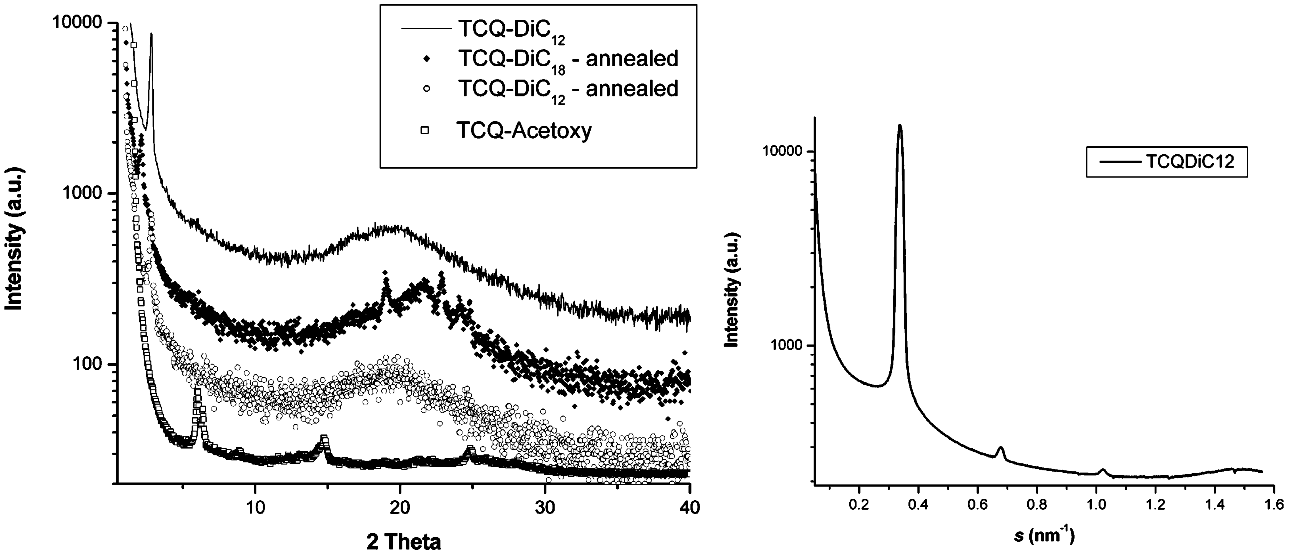

Figure 1. (a) WAXS diffractogram of the pure hexaacetoxy-**TCQ** material and **TCQ-DiC$_{12}$** LC material (before and after heating to 100 °C, recorded at RT) as well as that of the **TCQ-DiC18** (after heating). (b) SAXS diffractogram of the **TCQ-DiC$_{12}$** material, clearly showing a lamellar phase structure (peak ratios 1:2:3).

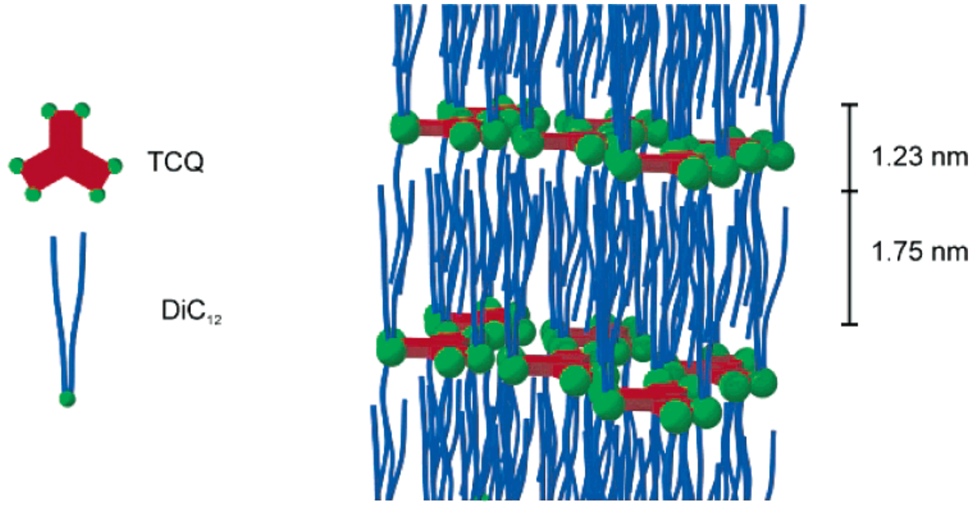

Figure 2. Respective thicknesses of the lamellar structure as obtained from the stacking model.

(Figure 1a), the same organization (i.e., lamellar phase and no typical packing) was still present.

To evaluate the X-ray data obtained from the lamellar **TCQ-DiC12** material, a so-called stacking model, recently developed by Smarsly and Ruland,[29] was applied. This is used to determine the respective thickness of layers within lamellar-structured materials from X-ray data. This model was applied to the obtained data and the thicknesses d_1 and d_2 of the individual sublayers could be calculated. As mentioned before, the *d*-spacing was found to be 2.98 nm (directly from the diffractogram), and d_1 and d_2 were calculated to be 1.75 and 1.23 nm, respectively. When the formula developed by Tanford[30] is used to determine the critical length (l_c) of an extended saturated hydrocarbon chain with *n* carbon atoms, a value of 1.67 nm is found for a C_{12} chain. If we assume that d_1 can be assigned to the hydrocarbon phase, this would indicate that an extremely high degree of interdigitation of the surfactant tails exists. We have estimated in previous investigations that the contribution of the ammonium headgroup is approximately 0.4 nm, and this value, in combination with the contribution from the ionic groups and the rest of the **TCQ** moiety, would account for the 1.23 nm of the second layer (see Figure 2).

From previous studies[20,31] it is known that both tail length and tail number of the surfactant tectons used in the ISA process have a significant influence on the materials properties. To investigate the observed unexpected phase behavior as seen for the **TCQ-DiC$_{12}$** material, the following materials were therefore also prepared: the double-tail species (**TCQ-DiC$_{16}$** and **TCQ-DiC$_{18}$**) as well as the single-tail derivative **TCQ-C$_{12}$**.

In the case of the double-tailed species, complex formation was also confirmed (as above) by NMR, IR,

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and elemental analysis. Decomposition temperatures (from TGA) were significantly higher than those for the **TCQ-DiC$_{12}$** species. DSC curves showed, after strong transitions in the first heating curve (probably due to thermal rearrangement within the material), no further significant thermal transitions. WAXS investigations showed that both the double-tail materials were crystalline at room temperature (exhibiting a number of sharp reflections in the range $2\theta = 18-24°$, which is typical for the crystalline arrangement of surfactant alkyl side chains, see Figure 1a). These reflections were still present, even after heating the samples to 100 °C and cooling back to room temperature. The SAXS diffractograms of these materials were, due to the crystalline character of the alkyl chain, complicated and showed mixed phase structures. The **TCQ-C$_{12}$** material was found to be a hard, nonbirefringent material, exhibiting low solubility and high-temperature stability. The elemental analysis of this material also showed very low carbon content (<20%), indicating that complexation was not successful in this case. This was already hinted at by the fact that precipitation did not occur to the same extent as for the other materials.

From the comparison of the different **TCQ** materials and their properties, the importance of the size of the alkyl volume fraction is once again evident. A fine balance is evidently needed to ensure that LC materials are actually produced (and not crystalline or amorphous (nonstoichiometric) materials as found). In the case of the very long alkyl tails, the possibilities exist for crystallization at the ends of the oligomethylene chains. This phenomenon has already been reported for polyelectrolyte-surfactant systems.[32] This was also found here in the case of the complexation of the **TCQ** hexaanion with the longer (C_{16} and C_{18}) double-tail surfactants.

In the case of the short **TCQ-C$_{12}$** materials, the alkyl volume provided by the single C_{12} surfactant tails was not enough to ensure the organization of the hexaanionic species, and therefore the formation of well-ordered materials does not take place.

The influence of the presence of a large number of ionic “docking sites” on the perimeter of the **TCQ** hexaanion furthermore plays a very large role in the formation of the found LC phase. This was evidenced by the absence/total lack of stacking of the discotic tectons in the case of the **TCQ-DiC$_{12}$** liquid-crystalline system. This stands in stark contrast to the ordered columnar phases of the covalent analogues, with interdisk spacings of 0.34 nm. This absence of stacking in ISA materials has previously been observed in the case of double-charged perylenediimide derivatives,[21] even though perylenes dyes form stacked aggregates at low concentrations. In the case of the **TCQ** hexa-anion, the high charge density makes stacking even less favorable and, in conjunction with the influence from the alkyl volume fraction, leads to the formation of lamellar phases. This phenomenon has very recently also been observed for other hexaanionic ISA systems.[33]

Conclusions

Here, we have presented a strategy where, through the in situ generation of a charged tecton, liquid-crystalline materials are constructed in a facile way by the Ionic Self-Assembly route. It was found that the balance between alkyl volume, tecton shape, and number of charges (that is, the charge density of the central **TCQ** tecton) plays an important role in the formation of the phase architectures and tuning of phase properties.

We therefore found that, instead of the expected columnar phases, a liquid-crystalline material with a lamellar phase structure was formed. Application of a stacking model enabled us to extract the thicknesses of the two layers of the lamellar phase. This fits well with a highly interdigitated arrangement of the alkyl tails.

Because phases and properties can be adjusted very easily through the choice of surfactant, future work would include the use of branched single- and double-tail surfactants to study the influence of branching on the phase formation. The influence of the charges on the packing of the tectons could be further investigated by moving the charges away from the core through the use of spacer chains. Once better understanding of the various parameters influencing phase behavior is obtained, this concept can be used for the design, facile tuning, and production of functional liquid-crystalline materials. Charge-carrier mobilities should then be measured to have any indication if these materials would be suitable for the fabrication of devices. The removal of solvent (H_2O) and other impurities from the materials presents a further challenge for such future investigations.

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Supporting Information Available: Full description of the synthetic methods as well as all relevant TGA, NMR, EA, IR, and X-ray data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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