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Bending and shaping: cubics, calamitics and columnars†

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The mesomorphism of a series of complexes of Pd(II), Pt(II) and Ag(I) is discussed and systematic structural variations are highlighted which lead to an appreciation of important factors determining the liquid-crystalline polymorphism of these complexes. Models are proposed for cubic phase formation and the occurrence of an unusual lamellar phase in-between a SmC and a columnar phase is discussed.

Introduction

In about the last twenty years, the chemistry of liquid crystals has changed in considerable measure. Following the discovery of the cyanobiphenyls and their subsequent commercialisation in the early 1970s, there was great interest in straightforward, calamitic systems with device potential. Interest continued into the 1980s with the search for suitable materials for application in ferroelectric device configurations. Indeed, this is still an important and fertile area as new device geometries emerge along with advances such as microdisplays and various non-display applications. While the challenges in realising some of these materials were not inconsiderable, individuals began gradually to question the design rules that suggested that simple, anisotropic molecules were those most likely to lead to mesomorphic materials. For example, while columnar phases had been known for many years,[1] the publication in the late 1970s by Chandrasekhar of *disc-like* molecules (Fig. 1A) capable of forming columnar phases[2] opened up a new area in the subject out of which applications have been realised. Also in the late 1970s, Mueller-Westerhoff and Giroud[3] published a paper on mesomorphic nickel dithiolene complexes (Fig. 1B) which is seen as the beginning of the systematic study of metallomesogens, an area which took off in the mid-1980s.[4]

For some time in all of these fields, the emphasis was on rather simple rod- and disc-like shapes, although there was clear evidence from the earlier work of Skoulios with metal soaps that there were other molecular arrangements capable of giving rise to liquid-crystallinity.[5] Of course this emphasis on, for example, rod-like materials has continued to produce new and exciting phenomena, and here one might consider the wide range of new phase types recognised such as the TGB phases[6] and the various antiferro- and ferri-electric smectic phases.[7] Thus it was that through the 1980s and into the 1990s, we saw the development of new molecular motifs giving rise to liquid crystals such as bowlics,[8] polycatenars,[9] dendrimers[10] and bent-core[11] (or banana) mesogens.

However, consider for a moment the theoretical binary phase diagram for an amphiphile in water shown in Fig. 2. In an organised assembly of these surfactant molecules, we can imagine that a surface between the two incompatible parts, that is the hydrophilic and hydrophobic parts, is generated and that

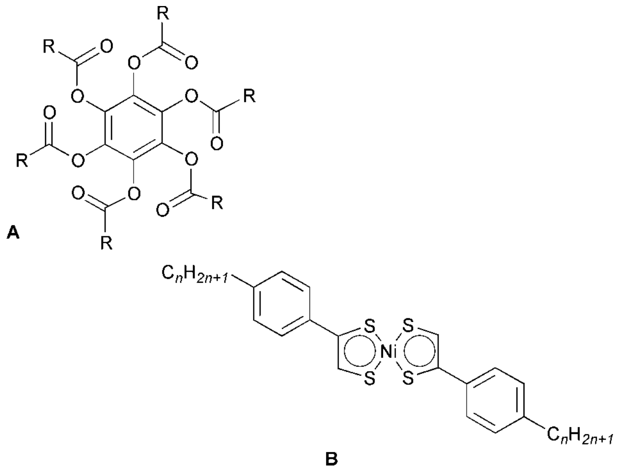

Fig. 1 Discotic benzene derivative (**A**) and mesomorphic Ni dithiolene complex (**B**).

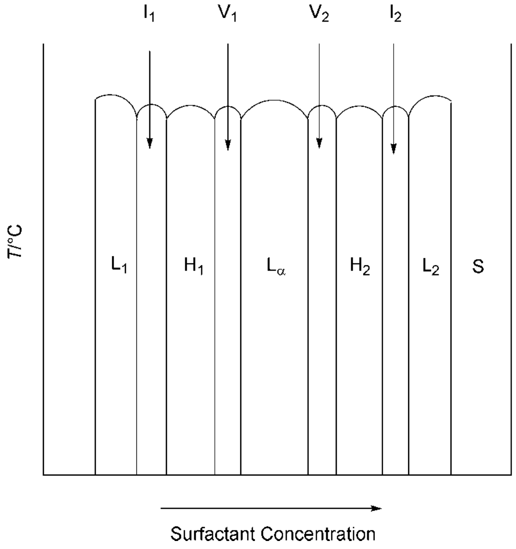

Fig. 2 Theoretical lyotropic phase diagram for an amphiphilic material in water. H represents a hexagonal phase, I a micellar and V a bicontinuous cubic phase, L_α the lamellar phase, L_1 and L_2 micellar solutions and S solid. Subscripts 1 and 2 imply 'normal' and 'reversed' phases, respectively

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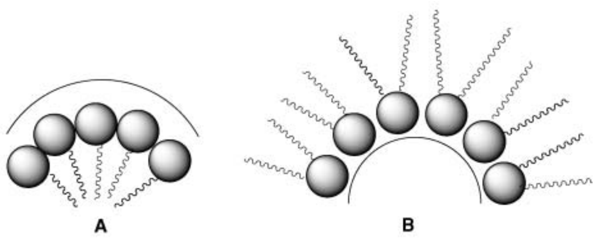

Fig. 3 Diagram to show curvature arising from a large head group (**A**) and a small head group (**B**).

this interface possesses a variable curvature which depends on the size of the headgroup and the volume of the chain. Thus, we start at one end with a simple micellar cubic (I_1) phase with substantial curvature, then gradually, we reduce this curvature through the hexagonal (H_1) and bicontinuous cubic (V_1) phases and then through to zero curvature at the lamellar (L_α) phase, before reversing the nature of the curvature (to form water-in-oil phases) and then increasing it through V_2 and H_2 to I_2. A simple way in which to look at this behaviour is to relate the size of the headgroup to the volume of the alkyl chains and to consider the way in which these can pack through geometric arguments[12] (although clearly these are not the only factors at work). Thus, at one extreme, a very large headgroup will tend to give rise to a large curvature (Fig. 3A), whereas a very small headgroup with a substantial chain volume would also give rise to substantial curvature, but in a reversed sense (Fig. 3B). Of course, the diagram shown in Fig. 2 does not represent all of the lyotropic phase types possible with amphiphilic systems, but it does give a basic picture of the richness of architectures possible in mesophase systems. Yet, if we draw an analogy with thermotropic systems, then at least in terms of calamitic mesogens, we are working only in that small part of the phase diagram where the interfacial curvature is zero (L_α) and while there is great diversity of lamellar phases, we are only scratching the surface.

This geometric approach to the phase diagram has been examined notably by Tschierske[13] and by Goodby[14]—both have shown that a great deal of the 'lyotropic' phase diagram can be reproduced in binary mixtures of carbohydrate compounds. In a complementary approach, they have also taken the geometric view of Fig. 2 and have synthesised a range of materials in which the 'headgroup' and 'chain' sizes have been controlled, allowing the curvature associated with amphiphilic systems to be demonstrated in thermotropic systems (Fig. 4).[14,15]

In these pieces of work, the phase diagram has been reproduced by making compounds whose structure conforms to the geometric requirements necessary to produce the given phases; *i.e.* compounds with the possibility to generate the necessary curvature. However, there are other, slightly more subtle ways in which this curvature can be achieved and here we look to a discussion of the mesomorphism of *polycatenar* mesogens.

The design of polycatenar (literally many-tailed) mesogens is based on that of calamitic mesogens in that the core of the molecule is an extended, rod-like structure which is 'decorated' with several alkoxy chains. *Tetra*catenar mesogens have four, *hexa*catenars six (Fig. 5A) and so on. One of the aspects which quickly becomes apparent is that there are isomeric possibilities. For example, a tetracatenar mesogen may have its terminal chains symmetrically arranged on the 3,4-positions of the terminal ring (Fig. 5B) or in the 3,5-positions, *or* it may have them unsymmetrically disposed-3,4- at one end and 3,5- at the other (Fig. 5C). For reasons that will become apparent, it is the symmetric 3,4-systems which are usually of greatest interest and we will consider these most closely.

In general, the core of a polycatenar mesogen consists of at least four rings, usually aromatic, which are joined by groups commonly found in calamitic mesogens, such as esters and

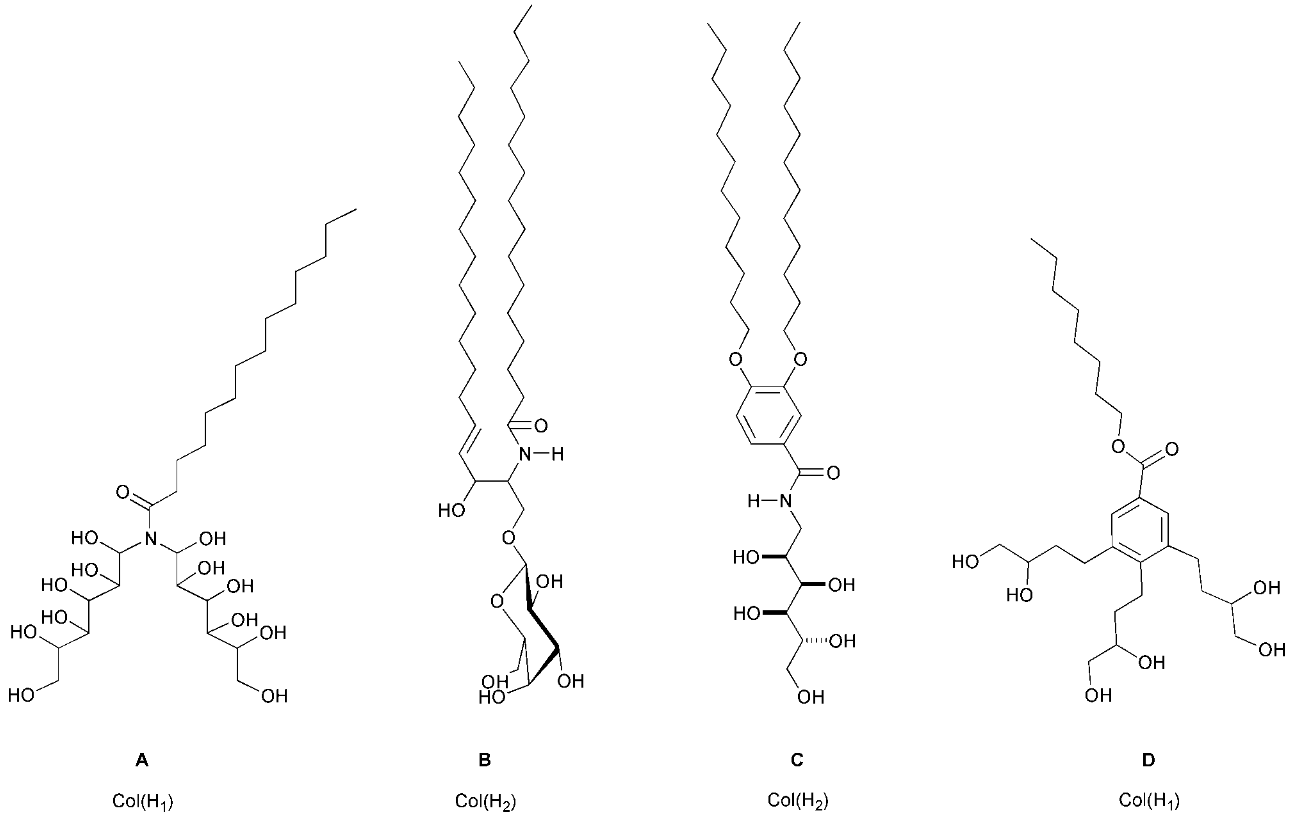

Fig. 4 Carbohydrate liquid crystals designed to show particular mesophases. A large head group example (**A**) showing a 'normal' phase and a small head group case (**B**) showing a 'reversed' phase from Goodby and a similar pair from Tschierske (**C** and **D**).

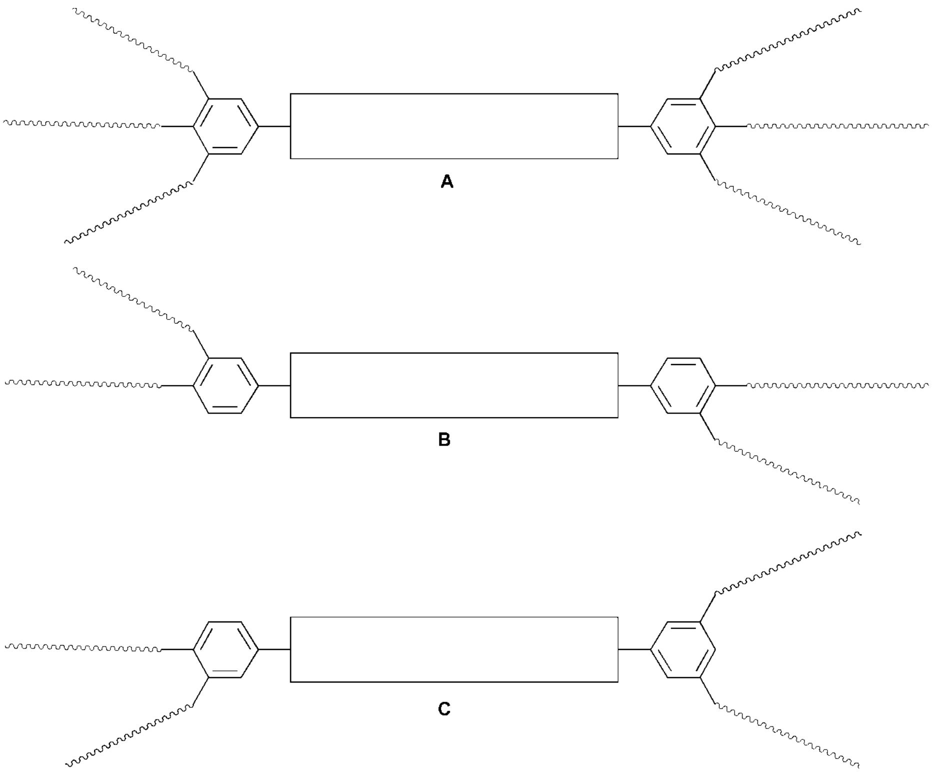

Fig. 5 Schematic of polycatenar mesogens showing a hexacatenar system (**A**), a symmetric tetracatenar system (**B**) and an unsymmetric tetracatenar system (**C**).

imines. Indeed, there is a 'rule of thumb' which suggests that the core of a polycatenar mesogen must have as many rings as terminal chains. Focussing now on symmetrically substituted tetracatenar mesogens, we find that when the terminal chain lengths are short, nematic and smectic C phases are found. The important factors at play here are two-fold and relate to the formation of the SmC phase. First, there is the idea of microphase separation at the molecular level, where the aromatic cores prefer to be together while the alkyl chains also prefer to be together—regarded as a standard driving force for the formation of lamellar phases. Second, there is the idea of the discrepancy between the cross-sectional area of the core and the chains at their interface. In a conventional, calamitic mesogen, there is no great incompatibility between these two quantities and so both the core and the chain are free to dispose themselves as they will, allowing the full range of smectic phases, both orthogonal and tilted, to form. However, in the polycatenar systems, the existence of the extra chain means that the cross-sectional area of the chains at the interface is greater than that of the core, causing the core to tilt (Fig. 6) forming a SmC phase (indeed, the SmC phase is the only smectic phase seen in such systems).

When the chain lengths are extended in these systems, the nematic and SmC phases are replaced by the columnar phase, revealing the interest in these materials, namely that they can form the mesophases characteristic of rods and those characteristic of discs. How then can the formation of the columnar phase be explained? X-Ray diffraction shows that the column diameter in the columnar phases of these molecules is the same as the molecular length which places the molecules in a plane perpendicular to the column direction. Further, a combination of X-ray diffraction and dilatometry suggests that there are three or four of these polycatenar molecules present in each repeat unit (Fig. 7), which implies that the lamellae have broken up into smaller aggregates (groups) of molecules.[16] The driving force for this is held to be the greater volume occupied by the chains as they increase in length which makes the maintenance of a simple lamellar phase impossible, causing the layers to break up.[16]

Reconsideration of the hypothetical phase diagram for amphiphilic systems shows that between each pair of phases, the possibility exists for a cubic phase to form, and these cubic phases are of two different types, namely micellar (I_1 and I_2) and bicontinuous (V_1 and V_2). In surfactant systems, the formation of these cubic phases is rather well understood and can readily be explained in terms of a curvature model of the sort outlined above. Cubic phases are common in surfactant systems.

By contrast, cubic phases are much less common in thermotropic systems, although now that they are more widely recognised, they are becoming more common. The origins of cubic phase formation in simple, calamitic materials was the report by Gray in 1957[17] of a phase, later termed 'smectic D' and found to be optically isotropic, in two homologues of some 4-alkoxy-3-nitrobiphenylcarboxylic acids. The term smectic D is no longer used as it is recognised[18] that the phase is not layered at all, and the abbreviation 'Cub' now tends to be used. The phase remains rather uncommon in calamitic systems and we shall return to this aspect later. The cubic phase is also found in polycatenar mesogens and here, it is possible to offer a sensible explanation for its occurrence. Thus, as the formation of lamellar and columnar phases in tetracatenar mesogens can be explained in terms of interfacial effects and the volumes of the terminal chains (determined by both chain length and temperature), then at short chain lengths, lamellar phases are seen while at longer chain lengths the columnar phase prevails. However, in certain systems and at intermediate chain lengths, the cubic phase is found between the SmC and columnar phases, representing an intermediate state of affairs. We have previously investigated the mesomorphism of some tetracatenar 2,2′-bipyridine derivatives[19] and the phase diagram of this homologous series shows the progression from lamellar to cubic to columnar phase rather well (Fig. 8) and shows that these transitions can be effected by temperature and chain length alike. Curiously however, there are examples of so-called 'swallow-tail' mesogens (which may be considered to be somewhat similar in structure to tetracatenar mesogens) in which the cubic phase is found between the SmC and N phases.[20]

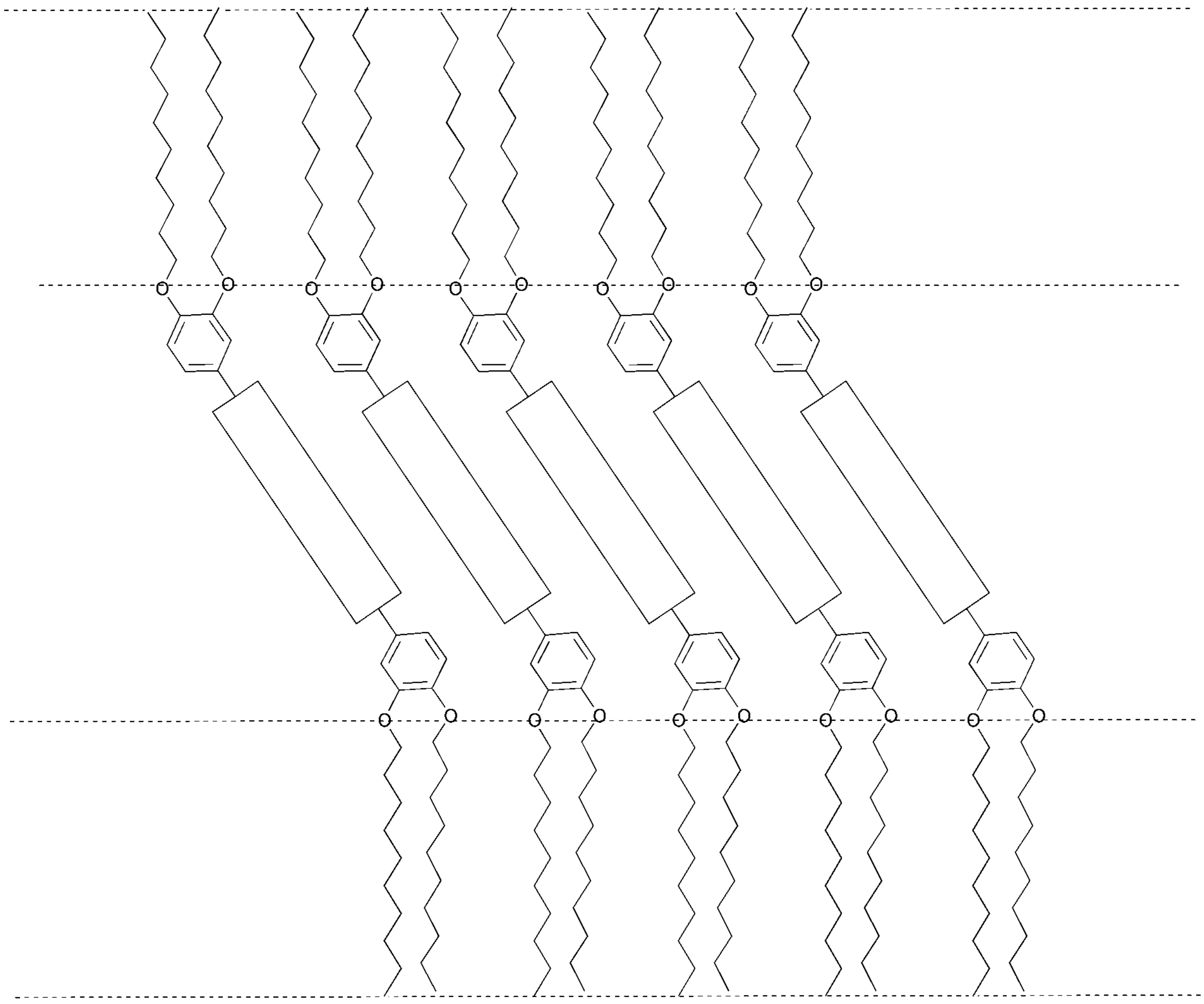

Fig. 6 Schematic figure to show the origin of the tilt in the SmC phase of polycatenar mesogens.

The thermotropic/lyotropic analogy

At this point, it is perhaps worth considering some analogy between the phase behaviour and structure of lyotropic and thermotropic mesophases, because in certain aspects of the discussion, the language used is rather similar.[21] A useful starting point is the lyotropic L_α phase which is directly analogous to the thermotropic smectic phases, all of which are characterised by flat interfaces, either between layers or between different parts of the layers. Moving to the 'oil-rich' side of the lyotropic phase diagram (Fig. 2) gets us to the reversed hexagonal (H_2) phase which is characterised by a polar core surrounded by apolar chains. This is, of necessity, the analogue of the thermotropic columnar hexagonal phase in which the polar(isable) parts of the molecule are found at the centre of the column surrounded by apolar chains.

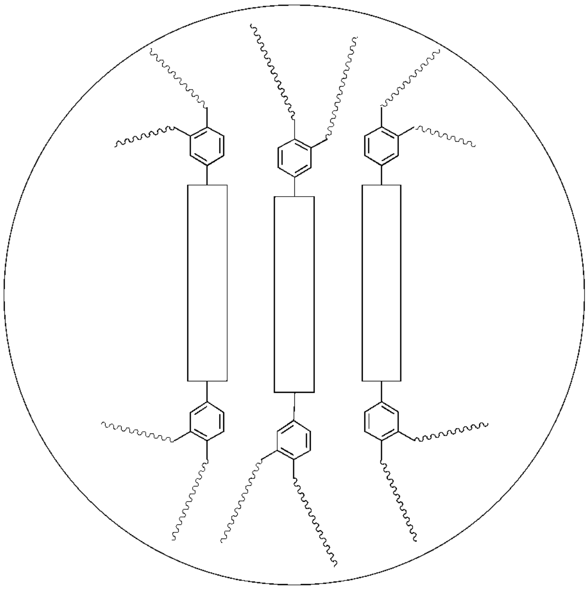

Fig. 7 Schematic representing a possible arrangement of polycatenar mesogens in the hexagonal columnar phase.

Here, it is perhaps instructive to consider three different ways in which the 'thermotropic H_2' phase might be formed. The first uses simple discotic molecules such as phthalocyanines or triphenylenes where the 'polar core' is in fact the centre of an individual molecule which is then surrounded by aliphatic chains.[22] The second might be viewed as a direct thermotropic equivalent of the lyotropic system and here, the phase is comprised of, for example, carbohydrate mesogens with 'headgroups' and 'chains' radiating out (Fig. 9).[14] Here, geometric examination of the materials shows a substantial volume for the 'chains' which is large compared to the 'headgroup', leading to organisation directly analogous to the lyotropic H_2 phase. Another expression of this mechanism is found in the columnar phases of certain dendrimer systems[10c] (schematised in Fig. 10) where the periphery of the columnar unit is formed of the terminal chains of the mesogenic unit, the very centre is composed of the fluid, hyperbranched units and the polarisable, mesogenic units sit in-between the two in a microphase-separated arrangement. Finally, we consider a third option which is the hexagonal phase of polycatenar

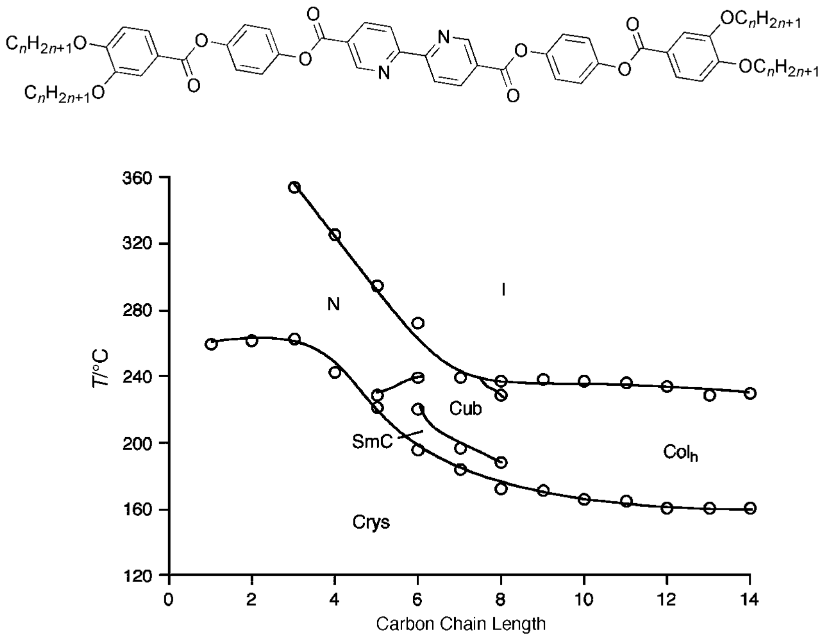

Fig. 8 Phase diagram for some tetracatenar bipyridines.

mesogens (Fig. 7). This can be regarded as somewhat intermediate between the other two cases in that like the simple discotic system, there is a polarisable core and attached apolar chains, and like the carbohydrate systems, there are geometric factors concerned with chain volume which determine the phase formation.

It is also worth pointing out some distinguishing features between these three possibilities, as this will add to the appreciation of some of the discussion below. First, we note that purely discotic molecules will form, for the main part, either nematic (rather rarely) or columnar phases and so the mesomorphism is limited. The mesomorphism of the second class is also somewhat limited as the work by Goodby has shown that in order to move around the phase diagram, it is effectively necessary to make a different molecular variation each time. However, the third type, particularly when we consider the tetracatenar mesogens, are somewhat different in that we can move around between lamellar, cubic and columnar phases as a function of chain length and, in many cases, simply as a function of temperature for a given chain length.

In the majority of cases, the cubic phase of polycatenar mesogens lies between a lamellar and a columnar phase and so we would regard these cubic phases as analogues of the lyotropic V_2 phase, that is to say they have a bicontinuous structure. Systems are known which give rise to thermotropic micellar cubic phases (I_1 and I_2), but these do tend to be rather specific systems. As far as the cubic phases of simple, calamitic materials are concerned, we might intuitively assign these as analogues of the lyotropic V_2 phase. However, the lyotropic analogy is not so clear here as in the majority of cases, the phase is found either:

(1) between pairs of lamellar phases (SmC and SmA);

(2) *or* between a SmC and isotropic phase;

(3) *or* between a SmC and a nematic phase;

(4) occasionally below a SmC phase;

(5) *and* often associated with a tetragonal phase (the 'S_4' phase)

(6) *but never* below a columnar phase.

This difference between the cubic phases of calamitic and polycatenar mesogens will arise again below.

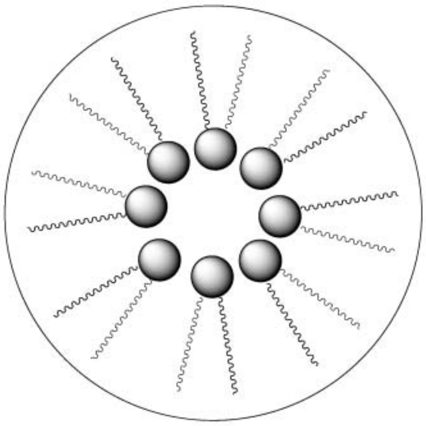

Fig. 9 Possible packing of carbohydrate mesogens in a 'thermotropic H_2' phase (Col(H_2)).

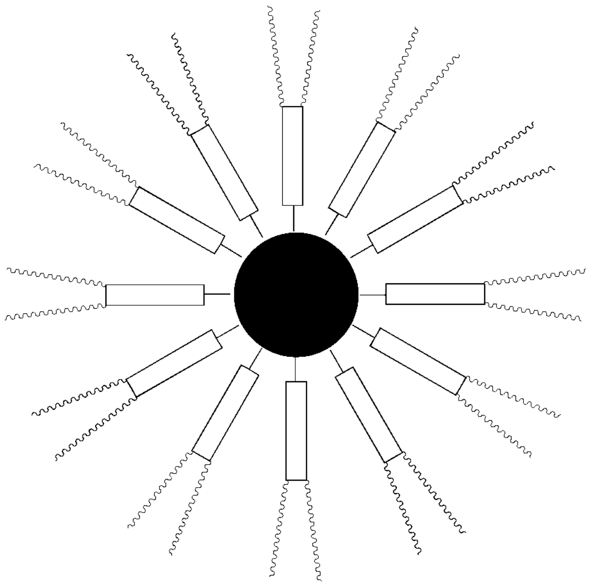

Fig. 10 Schematic diagram to show the arrangement of dendrimer mesogens in a 'thermotropic H_2' phase. The dark central part represents the hyperbranched dendrimer chains.

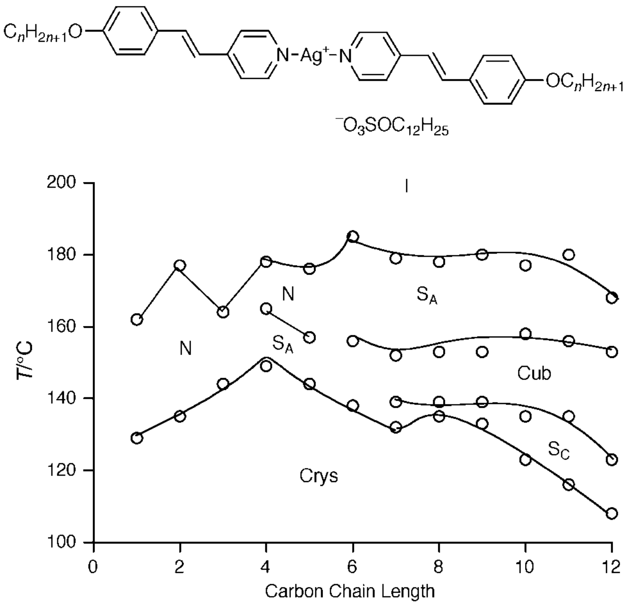

Fig. 11 Phase diagram of silver(I) dodecyl sulfate complexes of 4-alkoxystilbazoles.

Setting the scene

The thrust of this paper is a reflection on the formation of lamellar, columnar and cubic phases in families of calamitic and polycatenar mesogens and the discussion of some new findings to try to understand and rationalise how the formation of these phases might be influenced and even controlled. The story begins with some of our early work on stilbazole complexes of silver(I) which has been reviewed recently,[23] and so only a brief overview is given here.

The starting point is the phase diagram for the silver(I) dodecyl sulfate complexes of 4-alkoxystilbazoles which is reproduced in Fig. 11.[24] The salient features are now given.

(1) At short ligand chain lengths, there is a nematic phase in complexes which are formally ionic.

(2) Conductivity measurements imply that the anion and cation are closely associated (there is no conductivity in the mesophase), which is backed up by single crystal X-ray studies[23] and so we can regard the materials as calamitic mesogens bearing a lateral chain. As such, the formation of nematic phases would be *expected.*

(3) At longer chain lengths, we see two smectic phases and a cubic phase; as stated above, cubic phases remain rare in purely calamitic systems.

(4) The presence of the smectic phases *is* rather surprising, for as we are now considering these mesogens as calamitic with a lateral chain, then we would not expect the formation of any phase other than a nematic.

(5) When we look at complexes of silver octyl sulfate, we find that the phase diagram is very similar *except* that the cubic phase is *absent*, and so clearly the anion chain has a rôle to play in stabilising this phase.

We then turned our attention to polycatenar analogues using various di- and tri-alkoxystilbazoles and two phase diagrams are reproduced below, namely for tetracatenar and hexacatenar complexes of silver dodecyl sulfate (Figs. 12 and 13, respectively). Again, we summarise the main findings.

(1) As is fairly typical for tetracatenar systems, the phase diagram is dominated by the cubic and columnar phases, although there is no evidence of a smectic phase. Based on detailed studies of this system, we proposed a model for the cubic-to-columnar transition.[25]

(2) The mesomorphism of the hexacatenar mesogens is typical, showing a columnar phase across the phase diagram.

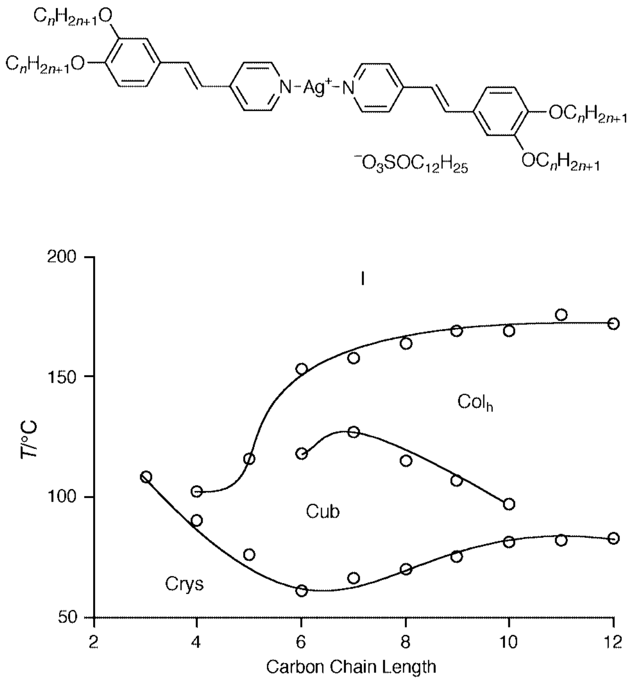

Fig. 12 Phase diagram of silver(I) dodecyl sulfate complexes of 3,4-dialkoxystilbazoles.

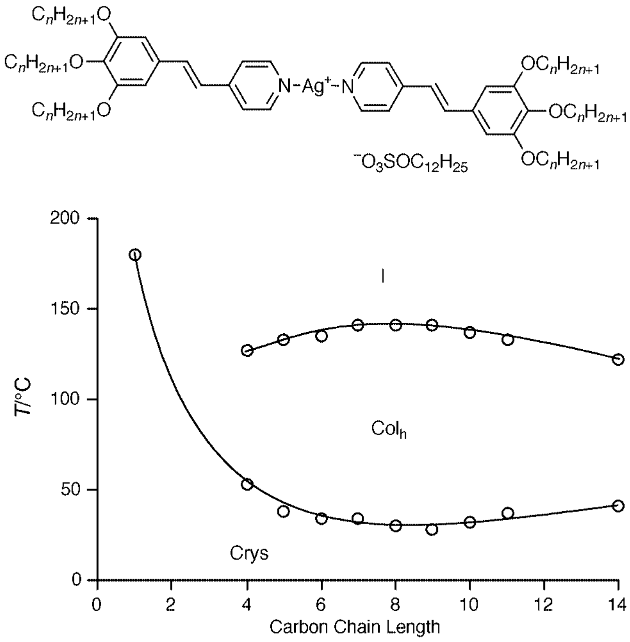

Fig. 13 Phase diagram of silver(I) dodecyl sulfate complexes of 3,4,5-trialkoxystilbazoles.

(3) In an examination of tetracatenar complexes using 3,5-dialkoxystilbazole, we observed columnar phases for several homologues—many more than is typically the case in tetracatenar systems with such a substitution pattern which implies that there is something different about these systems with their attendant anion.

The final part of the 'scene-setting' is to relate the behaviour of dichloro-palladium(II) and -platinum(II) analogues (Fig. 14)[26] of these various silver complexes.

(1) Complexes of 4-(mono)alkoxystilbazole complexes of Pd(II) show mesophases at elevated temperatures (>220 °C), where they tend to decompose.

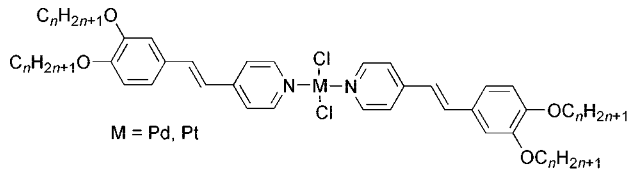

Fig. 14 Structure of the Pd and Pt analogues of the silver(I) stilbazole complexes. Example is a tetracatenar mesogen.

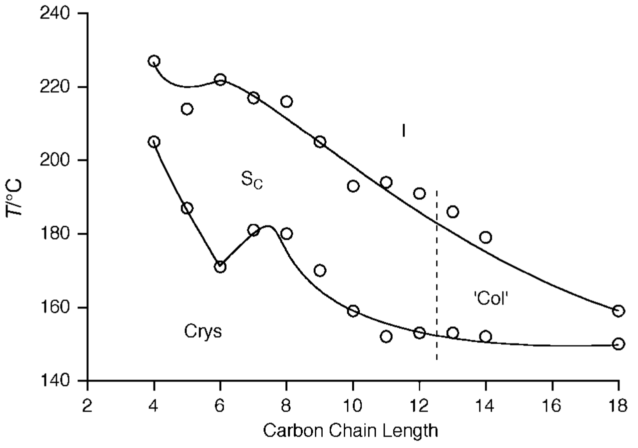

Fig. 15 Phase diagram for the dichloropalladium(II) complexes of 3,4-dialkoxystilbazoles.

(2) Replacement of the chloride ligands by alkylcarboxylates leads to nematic phases at lower temperatures.[27]

(3) Hexacatenar complexes of Pd(II) (based on 3,4,5-trialkoxystilbazoles) showed the expected columnar mesophase in addition to a rectangular phase. Similar behaviour was found for hexacatenar complexes based on 2,3,4-trialkoxystilbazoles, although the symmetry of the two-dimensional rectangular cell is different.[28]

(4) Tetracatenar complexes based on 3,4-dialkoxystilbazoles showed what appeared by microscopy to be a SmC phase at shorter chain lengths, giving way to a columnar phase at longer chain lengths. No cubic phase was seen and no homologue showed more than one mesophase (Fig. 15).

Controlling the 'bends'

Given the difference in behaviour between the silver and palladium systems and the particular fact of the observation of a cubic phase in the tetracatenar silver complexes which was absent in the palladium systems, we were keen to try to identify factors which might turn out to be determining. As such, we undertook some further synthetic work as well as some careful X-ray and mixture studies which are now described. The first, and most obvious, difference between the two series of complexes is the presence of the lateral, anionic chain in the silver systems. Bearing in mind the arguments given earlier about the importance of the relative areas of the core and the chains at the core–chain interface, as well as the issues of the chain volume which relate to core volume in determining the mesomorphism, we decided to see what effect could be observed on the introduction of lateral chains in the polycatenar Pd complexes.

We therefore undertook the synthesis of a range of stilbazole complexes of palladium alkanoates. Palladium alkanoates were synthesised in an exchange reaction starting from palladium acetate, so that reaction of palladium acetate with the appropriate carboxylic acid in benzene under reflux in a flask equipped with a Dean and Stark trap led to the evolution of acetic acid in an azeotrope with benzene, and the formation of the palladium carboxylate, usually isolated as an oil. The resulting palladium precursor was then reacted with the required stilbazole to lead smoothly to the target complex—a polycatenar palladium complex with two lateral alkanoate groups (Fig. 16).[29]

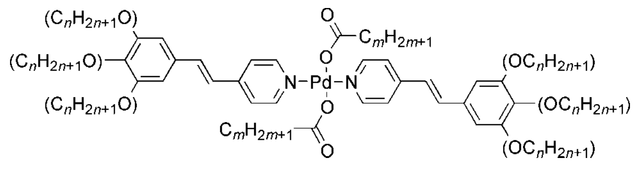

Fig. 16 Polycatenar stilbazole complexes of palladium(II) alkanoates.

While complexes of this type with *mono*alkoxystilbazoles had shown nematic phases, we felt that with the greater surface coverage by the terminal chains found in the polyalkoxystilbazole complexes, we would either see a modification of the SmC/columnar behaviour of the parents or the formation of essentially disc-like mesogens which would show columnar phases. However, we were very surprised to find that, whatever the number, disposition and length of the chains used on the ligand, all of these carboxylate complexes gave only a nematic phase. Thus, from the early examples described with carboxylate ligands and monoalkoxystilbazoles, to these examples with up to eight chains, all form a nematic phase! This behaviour is in itself interesting as it begs questions concerning the nematic phase—for example is there a change at some number/length of chains from it being a nematic phase composed of rods to one composed of discs? The rather high viscosity of some of the materials with many chains precludes simple miscibility studies and this is still an open question, as is the absence of a columnar phase in the eight-chained materials.

So, it would seem that we can learn little from these complexes in trying to effect a comparison between the silver and palladium complexes. However, as these new Pd complexes bear two lateral chains and the silver complexes only one, then perhaps the comparison is not well made. Thus, we undertook a search for some complexes of palladium where we might introduce only one lateral chain. One of the drawbacks in making lower symmetry complexes of certain metals is a tendency to disproportionation (eqn. 1), and so it is often advisable to seek inert metals for this kind of chemistry.

$$2[MXYL_2] = [MX_2L_2] + [MY_2L_2] \qquad (1)$$

Palladium does have a tendency to lability and so we quickly realised that we would have to change metals to pursue our aim. In fact, the required change was not great for we knew already that the platinum analogues of our palladium stilbazole complexes have an extremely similar mesomorphism. Coupled with the fact that Pt(II) complexes tend to be much more inert than their Pd(II) congeners, we alighted on platinum as our way forward. We then identified mixed chloride–thiolate complexes as our targets and decided to try first with what should have been the easier palladium chemistry. In our search (Fig. 17) for even symmetric thiolate complexes of palladium or platinum, we attempted to replace the chloride ligands by thiolates using silver thiolate,[30] or remove them using triflic acid and then reacting with a thiolate anion and we also pre-formed palladium thiolates and attempted to react them with stilbazoles, but none of these approaches was successful and we were not able to establish the synthesis of thiolate complexes of palladium or platinum stilbazoles.

We therefore sought another ligand type and decided on acetylides, following the reports by Raithby of acetylide complexes of Pt(II) bound to pyridines.[31] The coupling of acetylides to Pt is well established and uses the acetylene, the platinum chloride and usually Cu(I) and a Pd(0) catalyst. Using such an approach, we were easily able to obtain a series of symmetric, bis(acetylide) complexes based on aliphatic acetylenes, although it is interesting to note that formation of these

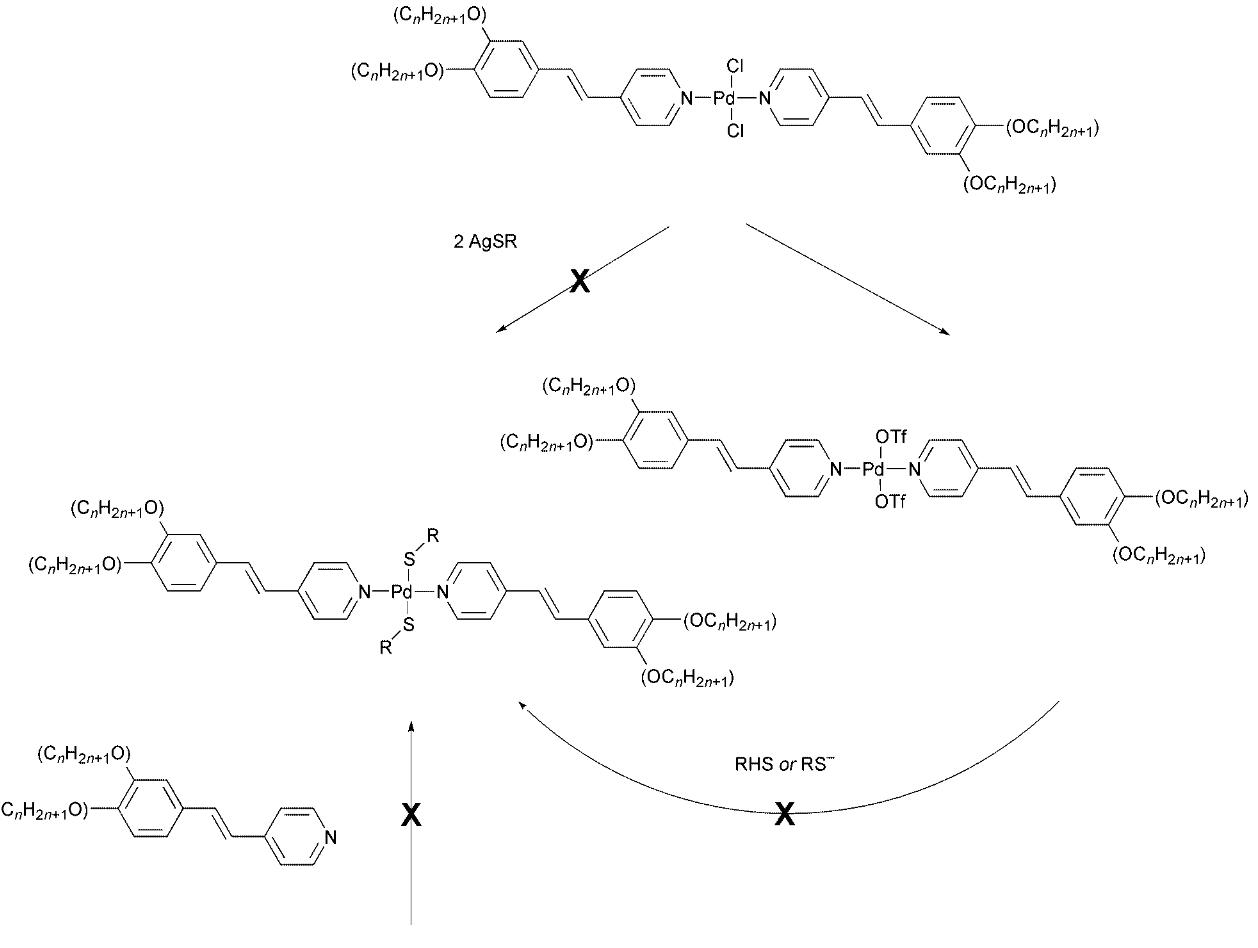

Fig. 17 Attempted syntheses of Pd thiolate complexes.

complexes required the use of several equivalents of acetylene. However, the monoacetylide equivalents were more difficult to obtain. Eventually, we established conditions for their formation (Fig. 18) which required the use of three equivalents of acetylene and rather short reaction times (sometimes only ten minutes).[32]

The mesomorphism of these new complexes was established by optical microscopy and, perhaps unsurprisingly, we found that the bis(acetylide) complexes showed a nematic phase as we had found with the alkanoate complexes, although curiously, we were also able to observe a SmC phase, too. However, we were most keen to find out about the behaviour of the monoacetylide complexes, for now we had direct analogues of the silver complexes except that these platinum complexes have a single chain but no ionic component to the metal–ligand interaction. Most interestingly, these complexes also showed the nematic phase and once more, there was evidence for the formation of a SmC phase.

Discussion

In our initial discussion of the mesomorphism of the silver complexes based on monoalkoxystilbazoles, we commented briefly on the observation of smectic phases in mesogens which possessed a lateral chain—something not observed elsewhere.[33] In a discussion of this behaviour, Levelut[34] argued that this observation was so unprecedented that it required explanation and she advanced the idea that it is intermolecular, electrostatic interactions arising from the silver cation–alkyl sulfate anion combination which can stabilise the observed SmC and SmA phases. It is clear that these interactions are not too strong, for we observe nematic phases at short ligand chain lengths, and so we argue that it is a combination of the electrostatic interactions and the ligand chain length (microphase separation) which allows the lamellar phases to form. Can we then learn anything about the formation of the cubic phase in these systems using these arguments? The answer is in two parts. First, we believe that we can eliminate the possibility that intermolecular, electrostatic interactions alone are responsible for the occurrence of the cubic phase, for while we do observe several homologues with a cubic phase when we have a dodecyl sulfate anion, this is not the case when the anion is octyl sulfate.[35] We were able to obtain a single crystal X-ray structure of one octyl sulfate complex and it showed[35] that the anion chain did not extend beyond the rigid core of the molecule. Modelling shows that a dodecyl sulfate chain is necessary for this to be the case. Thus, we must consider the possibility that the extension of the anion beyond the core contributes to a mismatch between the core and chain area at the interface and that this effect is significant, as advanced by Levelut.[34] However, what is absolutely clear is that we are not in a situation analogous to that found in the polycatenar mesogens we discussed above, for there it was interfacial mismatch and chain volume which drove the phase transitions which lead (with either increasing chain length or temperature) to a lamellar-to-cubic-to-columnar phase sequence. Rather here, we have a lamellar-to-cubic-to-lamellar sequence, which suggests that a slightly different mechanism is in operation. So where do the platinum acetylide complexes fit in to all this? Crucial evidence comes from the use of the pentadecynyl ligand (Fig. 18 $m = 13$) as this contains the same number of atoms (fifteen) as the dodecyl sulfate anion and, whereas silver stilbazole complexes with this anion are shown to form a cubic phase, those with the acetylide do not. In both cases, the

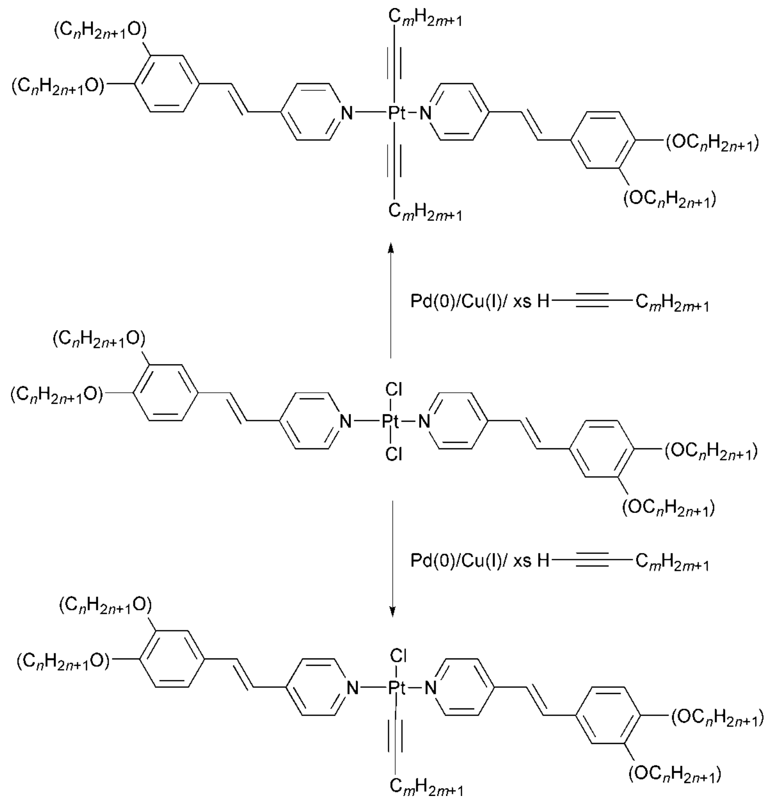

Fig. 18 Synthesis of the platinum(II) acetylide complexes.

extension of the ligand chain would reach the core/chain interface and so the prime difference is the presence of electrostatic interactions for silver and their absence for platinum. Thus, while we cannot attribute cubic phase formation solely to intermolecular electrostatic interactions, we can identify these interactions as crucial.[32]

Now, is this explanation specific to these complexes, or does it find resonance in the structures of other calamitic mesogens which form cubic phases? The answer, we believe, is that the explanation is not strictly specific, rather that it hints at another factor. Recall that it is the lamellae of the SmC phase which break up giving way to the cubic phase and recall also that in the model of the lamellar-to-columnar transition in polycatenar mesogens, we consider the break-up of the lamellae to give columns which are composed of three or four molecules. Thus, perhaps a crucial feature is the formation of these 'aggregates' of molecules, but why might we argue for aggregates when in the case of our mesogens and in those of most other calamitic mesogens forming cubic phases, we can point to rather specific intermolecular interactions?[36]

The reason comes with another set of calamitic mesogens which we have made and which show a cubic phase (Fig. 19). These are four-ring mesogens terminated at each end by a single perfluoroalkyl chain and we have shown that they form a SmC and a cubic phase which then clears to the isotropic liquid.[37] The microphase separation found in perfluoroalkyl-substituted mesogens is much greater than that found in hydrocarbon systems to the extent that calamitic perfluorinated systems form exclusively lamellar phases. We would argue that in these systems, it is the driving force to maintain this separation which acts to keep the mesogens in the lamellae and that this acts as a kind of pseudo-attractive interaction which, at the transition out of the SmC phase, allows molecular aggregates to be created and, hence, the cubic phase to form. Similar explanations would also account for the observation of cubic phases in the unfortunately named 'rod–coil' mesogens shown in Fig. 20 which possess a polar chain at one end.[38]

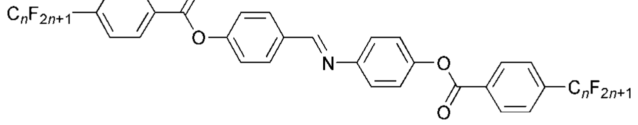

Fig. 19 Cubic-phase-forming imine mesogens.

This might then suggest a common factor in cubic phase formation, namely the formation of these aggregates, which could be applied to the consideration of both polycatenar and calamitic systems. This has its attractions because it then allows simply for the formation of a SmA phase above the cubic in calamitic systems (where the terminal chain volume is not so large) and the columnar phase above the cubic phase in polycatenar systems (where the terminal chain volume is much larger). The model would still allow for a curvature argument to be applied to the SmC-to-cubic transition in polycatenar systems, but it does still leave some question concerning the driving force of this transition in calamitic mesogens.

This model also explains the formation of cubic phases in the elegant work of Yoshizawa and collaborators[39] with molecules possessing two chiral centres (Fig. 21). Cubic phases are

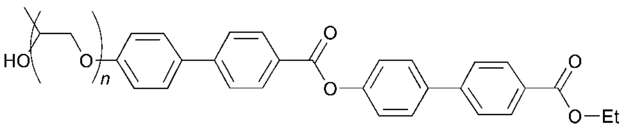

Fig. 20 So-called 'rod–coil' mesogens.

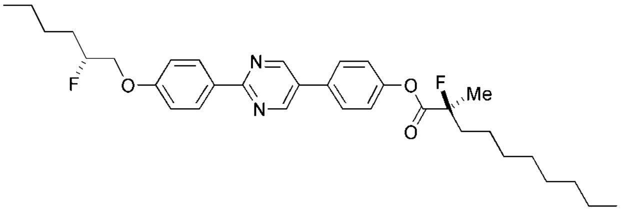

Fig. 21 Chiral mesogens which form cubic phases.

observed when the molecules are (*R*,*S*) or (*S*,*R*), but not (*R*,*R*) or (*S*,*S*), although a cubic phase is injected in mixtures between the (*R*,*R*) and (*S*,*S*) isomers. The behaviour has been interpreted in terms of intermolecular recognition and is, therefore, consistent with ideas of aggregate formation.‡

One final thought for this part. Throughout the literature of calamitic mesogens, it is observed that the introduction of a lateral chains results in the formation of the nematic phase *only*; indeed, we have used these arguments above. What we now find, however, is that in our acetylide complexes, we see, in addition, a SmC phase. For now, we have not considered the how and the why of it. Just as one door appears to close…

The lamellar-to-columnar transition in polycatenar mesogens

When we constructed[27] the phase diagram for the tetracatenar palladium mesogens shown in Fig. 15, one thing that we found a little strange was the abruptness of the transition from the SmC to the columnar phase, by which we mean that when dodecyloxy chains were used we observed a SmC phase, while with tridecyloxy chains we saw a columnar phase. Each homologue showed only one phase. In order to investigate this system further, the materials were subjected to a detailed investigation by X-ray diffraction, some results of which are now reported. Thus, for the complexes (Fig. 14; M = Pd) with $12 \geqslant n$, the X-ray experiments confirmed the presence of a lamellar phase, consistent with the assignment as SmC; similarly, for $n = 18$, X-ray diffraction confirmed the presence of a $\mathrm{Col_h}$ phase. However, for $n = 13$ and 14 (at that time we had not synthesised homologues with $n = 15$ to 17), X-ray diffraction showed a lamellar pattern, and periodicities corresponding to d_{001} and d_{002} reflections were observed, yet this was at odds with the optical microscopy which implied the presence of a columnar phase, probably with a two-dimensional hexagonal lattice. Subsequent studies have shown that the homologues with $n = 15$ and 16 also show this lamellar phase, while $n = 17$ is columnar hexagonal.

There are, we believe, two explanations. First, is that the X-ray pattern *is* that of a hexagonal phase, except for some reason, the structure factor for the d_{11} reflection is extremely small. At present, we believe that this is less likely. The second explanation is that the phase is, in fact, lamellar and that there were subtleties in the optical microscopy which we failed to pick up. Indeed, careful re-examination of the optical textures revealed that there were, in fact, such subtle differences between the texture of the $\mathrm{Col_h}$ phase and the texture of the phase we observed, namely that whereas in the hexagonal phase, Maltese crosses are apparent due to the meeting of lines of optical interference in the sample; in this lamellar phase, these lines did not meet (Fig. 22). Clearly then, there were textural differences which might support the existence of a separate phase. We also know that the phase is tilted, as the observed layer spacing is always substantially less than the calculated molecular length. Further, X-ray measurements show that this tilt increases with *n* (Fig. 23) and that for $n < 11$, the tilt is temperature-invariant, while for $n > 10$ the tilt increases as the clearing point is approached. The increase of the apparent tilt with *n* is, of course, consistent with the general mechnism for the transition between the SmC and $\mathrm{Col_h}$ phases of polycatenar materials. X-Ray diffraction did not, however, show any evidence of in-plane order in this phase.

Keen to pursue this further, we first undertook some mixture studies between the homologues with $n = 12$ and $n = 13$, and between the homologues with $n = 16$ and $n = 17$. Aspects of these investigations are still ongoing, but essentially what we found was:

Fig. 22 Optical texture of the lamellar phase of the tetracatenar palladium(II) complexes.

(1) Mixture of compounds with $n = 12$ and 13: The SmC phase of the derivative with $n = 12$ persisted to around 70% composition and then there was an apparent 10% biphasic region (L + SmC), after which the lamellar phase was seen.

(2) Mixture of compounds with $n = 16$ and 17: Here, the phase diagram was dominated by the lamellar phase which persisted through to 80% of the complex with $n = 17$, after which there was pure columnar phase. However, there was also a large biphasic region (L + I) from 30–80% of the complex with $n = 17$. In both this and the previous case, the lines representing the clearing temperatures and the melting points were essentially linear across the phase diagrams.

From these results, it appears that the SmC phase is tolerant of a good amount of lamellar-forming complex before the mesomorphism changes, while the columnar phase does not tolerate much perturbation.

We then constructed some binary phase diagrams between pairs of adjacent complexes which both show the lamellar phase and to our surprise, we found that for a good deal of the phase diagram, polarised optical microscopy suggested that a columnar phase was injected. We await X-ray results to confirm this observation.

So what is this lamellar phase and how do we account for its formation? To date in polycatenar mesogens, transitions from the SmC to the columnar phase have either been direct or have occurred *via* the intermediacy of a cubic phase, yet here we have a different situation. We also have a problem, for we do not

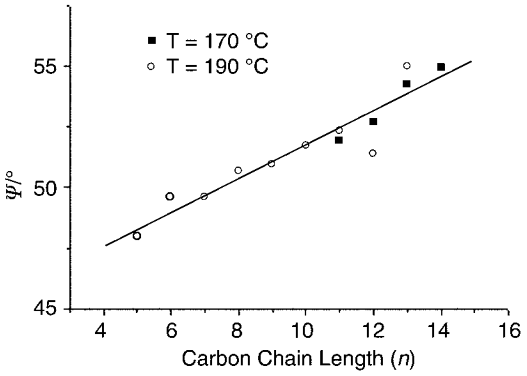

Fig. 23 Plot of tilt angle (ψ) against *n* for the tetracatenar palladium(II) complexes from Fig. 14.

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‡In a poster presented at MD4, Yoneya and Yokoyama from Tsukuba, Japan, showed the formation of the rod model for the *Ia*3*d* cubic phase in a molecular dynamics simulation in which molecules were allowed to form aggregates based on lateral interactions created through hydrogen bonding.[44]

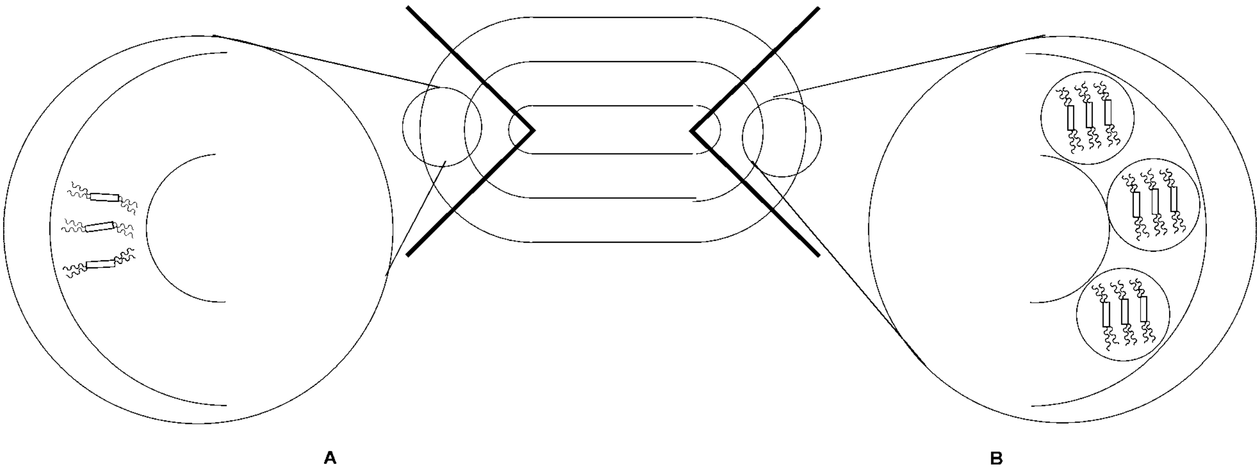

Fig. 24 Schematic to show two possibilities for the molecular organisation in the lamellar phase. **A** represents a straightforward lamellar phase, while **B** represents a columnar lamellar phase. The dark lines are extinction lines parallel to the polariser or analyser.

know what is the nature of the lamellar phase. We believe that there are two possibilities. In the first (Fig. 24A), we recognize cylindrical domains in the texture with typical optical fringes arising from two 'eyes'. These cylindrical domains are focal conics and developable domains at the same time. They indicate that the structure is lamellar, but that the layers are stiff and that they cannot elongate, similarly to sheets of paper. This mechanical property, which does not exist in the SmA phase, could arise from a higher molecular order inside the layers. In the second explanation (Fig. 24B), we analyze the texture of Fig. 22 as due to developable domains. The phase is then essentially columnar ($\mathrm{Col_L}$). In this case, we are led to suppose that the SmC layers observed by X-ray scattering, have been disrupted due to the terminal chain volume, but they remain unable to form a hexagonal arrangement. Stacking periodicities would not be observed by X-ray methods as is common in polycatenar systems.

If this latter explanation is correct, why is it that this phase has formed in preference to either the cubic or the columnar hexagonal phase? One explanation comes from the examination of a single crystal structure of some cyanobiphenyl complexes (not so structurally different from the Pd–stilbazole complexes) which we synthesised some time ago[40] and a particular structure, that of *trans*-$[\mathrm{PtCl_2(6CB)_2}]$,[41] is shown in Fig. 25. What the molecular structure reveals when shown as a space-filling model, is that the ligated chloride ligands extend laterally beyond the organic extremes of the molecule to the point where they could interact, repulsively as it turns out, with the similar group in a neighbouring complex. Thus, it may well be the case that while the chain length on the ligands is sufficient to break up the simple lamellar structure, the lateral chlorides prevent close association of the molecules. This would then prevent the formation of the aggregates which we proposed above were responsible for the formation of cubic phases and which are also required for the formation of the columnar phase. Thus, while the lamellae are broken up with a tridecyloxy chain, it requires the extra volume of a heptadecyloxy chain to ensure the microphase separation is sufficient to overcome these repulsive forces. While this does not *explain* why the lamellar phase forms in particular, it does offer an explanation for the appearance of another phase between SmC and $\mathrm{Col_h}$, and it does account for the non-observance of the cubic phase.

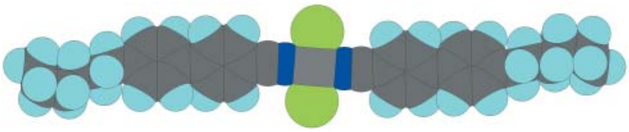

Fig. 25 Space-filling representation of the molecular structure of *trans*-$[\mathrm{PtCl_2(6CB)_2}]$.

Interestingly, Tschierske[42] has recently drawn attention to the 'transition' from columnar to lamellar organisation in discotic systems in which he charts the progression from $\mathrm{Col_h}$ to $\mathrm{Col_r}$ to $\mathrm{Col_L}$ to SmA. Here, he argues that the intermediacy of the $\mathrm{Col_r}$ and $\mathrm{Col_L}$ phase arises from the inability of the discotic systems to access a cubic intermediate. In our case, we are not dealing with a discotic material, but the underlying cause is arguably the same, namely that the cubic phase is inaccessible, suggesting a parallel between the two lines of argument.

Concluding remarks

In this article, we have discussed the behaviour of a range of organic and metal-containing mesogens which exhibit a rich and diverse mesomorphism. We have attempted to rationalise factors influencing cubic phase formation and we have suggested a mechanism which can unite the formation of the cubic phase in both calamitic and polycatenar systems. We have then explored a polycatenar system where the cubic phase does not form and where we find a lamellar phase between the SmC and $\mathrm{Col_h}$ phase. In comparing the behaviour of this system with discotic systems which also undergo the columnar-to-lamellar transition *via* a lamellar phase, we have identified as a common factor the inability to form the cubic phase and we have identified a potential reason why the cubic phase does not form in these systems which is consistent with the model which we proposed earlier to account for cubic phase formation.

We are still a little way from *predicting* why cubic phases form in thermotropic systems, but we are in a better position to rationalise a number of important factors. What we do learn, as with many things in liquid crystals, is that they really do constitute 'Nature's Delicate Phase of Matter'[43] and that the factors at work are strongly inter-related and rather subtle.

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