# Fluorinated metallomesogens – lamellar versus columnar phase formation<sup>†</sup>

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Two series of tetradental *cis*-enaminoketone Ni(II) and Cu(II) complexes with their mesogenic core substituted by different combination of hydrocarbon or fluorocarbon chains have been synthesized. Depending on the type and position of the substituted groups, compounds reveal either calamitic or columnar mesophases. Replacing the alkyl chains by perfluorinated chains stabilizes the columnar phase. A unique phase sequence of isotropic–columnar hexagonal–re-entrant isotropic–smectic (I–Col<sub>h</sub>–I<sub>re</sub>–SmA) has been observed on cooling for some of the obtained compounds.

# Introduction

It is generally accepted that the type of liquid-crystalline phase depends primarily on a molecular shape, which is determined by the anisotropy of the molecular rigid part - the mesogenic core.<sup>1</sup> Molecules with rod-like or disc-like cores form lamellar or columnar phases, respectively.<sup>2,3</sup> However, some compounds have been synthesized, for which this rule is not fully applied. It has been established that for some compounds even a minor changes within the mesogenic core can lead to major differences in molecular organization and therefore in liquid-crystalline behaviour.<sup>4</sup> There have been reported homologous series of compounds in which both types of phases, lamellar and columnar, occur upon changing the number and the position of substituents<sup>5-8</sup> or upon changing the length of peripheral alkyl chains.9 Also, temperature can influence the type of molecular packing.<sup>10-14</sup> Lamellar-to-columnar phase transition induced by temperature has been observed for molecules with overall rodlike,15 disk-like16 and polycatenar17,18 shapes. The transition between mesophases might be direct,<sup>10</sup> or in some cases the phases are separated by intermediate structures: bicontinuous cubic phase (Cub)<sup>11,19</sup> or fluid, optically isotropic phase (I<sub>re</sub>).<sup>13,14</sup>

Here, we present the synthesis of another type of mesogenic system exhibiting the lamellar-to-columnar cross-over behaviour, which was achieved by incorporation into molecular structure perfluorinated chains, which affects the flexibility of the molecule.<sup>20-22</sup> Previously, it had been reported that the replacement of hydrocarbon by fluorocarbon chains enhances the thermal stability of mesophases.<sup>23</sup> Careful studies on fluoroalkylated liquid crystals have revealed that fluorocarbon substituents stabilize the smectic, columnar and cubic phases compared to their hydrocarbon analogues by increasing their clearing points.<sup>24</sup> This effect is due to the incompatibility of fluoroalkyl chains with alkyl groups caused by the fluorophilic effect with a strong affinity of neighbouring fluorinated chains.<sup>25,26</sup> Moreover, it is also well known that fluorophobic interactions between fluorocarbon and hydrocarbon chains cause the microsegregation of molecular fragments within the mesogenic structure, and in some cases a new type of liquid-crystalline phases are expected to occur.<sup>26-30</sup>

In this paper, we describe mesogenic properties of Ni(II) and Cu(II) complexes with a disc-shaped core substituted by fluorocarbon and/or hydrocarbon chains. The triangular core is made of two *cis*-enaminoketone moieties (Scheme 1). Compounds of series I have at least one fluorocarbon chain in their molecular structure, while the compounds of series II have only hydrocarbon chains. In series I, the perfluorinated chain R<sub>1</sub> is attached to the tetrasubstituted phenyl ring and the substituents R<sub>2</sub> and R<sub>3</sub> at both disubstituted phenyl rings are either octyloxy or perfluorooctyl groups. For the series II, R<sub>1</sub> substituent is a nonyl chain, whereas R<sub>2</sub> and R<sub>3</sub> substituents are octyloxy or nonyl groups.

# Experimental

## Synthetic procedure

The synthetic procedure for Ni(II) and Cu(II) complexes of two designed series of compounds is sketched in Schemes 2–4. The aminophenyl derivatives containing various substituents ( $\mathbf{f}$  and  $\mathbf{I}$ ) were obtained in six-step reaction procedures starting from commercially available substances: *N*-(4-hydroxyphenyl)-acetamide and *N*-(3-hydroxyphenyl)acetamide (Scheme 2 and 3).



Scheme 1 General structure of complexes studied

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Scheme 2 Synthetic route to 4-octyloxy-5-perfluorooctyl-1,2-phenylenediamine



Scheme 3 Synthetic route to 4-octyloxy-5-nonyl-1,2-phenylenediamine

The condensation at room temperature between appropriate formyl ketone sodium salts (**m**, **n** or **o**) obtained by the Claisen formylation reaction and 1,2-phenylenediamine component (**f** or **l**) proceeds selectively at only one amino group, resulting in crystalline monosubstituted (**p**, **q**, **r** or **s**) products (Scheme 4). The remaining unsubstituted amino group reacts further at higher temperature with proper formyl ketone derivative to give free ligands, which were used without purification in the next reaction step. To obtain designed structures of final Ni( $\pi$ ) and Cu( $\pi$ ) complexes metal acetates were used.<sup>16</sup> Detailed descriptions of the syntheses as well as analytical data of all compounds studied are presented in the ESI<sup>†</sup>.



Scheme 4 Synthetic route to *cis*-enaminoketone complexes

#### **Results and discussion**

#### Mesophase behaviour

The mesophase sequences, phase transition temperatures and enthalpy changes for studied complexes are summarized in Table 1. All compounds of series II without fluorinated chains show direct transition from crystalline-to-isotropic liquid phase, for some of them monotropic lamellar phase (SmC) was observed, when the samples were supercooled. Introducing at least two fluorinated alkyl chains into molecular structure (series I) increases significantly the clearing temperatures of materials by more than 100 degrees. The above observation agrees with the common idea in the chemistry of fluoroalkylated liquid crystals that the stability of their mesophases is significantly enhanced compared to their hydrocarbonated counterparts.<sup>23</sup> However, for studied materials the increase of mesophase stability is also clearly accompanied by the change of the phase type, from lamellar to columnar. In the case of mono-fluoroalkylated I-1 · Ni and I-1 Cu complexes, no increase in clearing temperatures compared to their analogues of series II was observed, neither was the change in type of the formed mesophases - they exhibit lamellar phase.

All of the LC phases were fully characterized by microscopic observation of optical textures and X-ray diffraction studies. In the small-angle region of X-ray patterns of smectic phases only commensurate signals related to layer thickness were observed, while the hexagonal columnar phase was distinguished by the set

**Table 1** Liquid-crystalline phases, phase transition temperatures (in °C) and enthalpy changes (in  $J \times g^{-1}$ ) for complexes studied

Compound	R <sub>1</sub>	R <sub>2</sub> OC <sub>8</sub> H <sub>17</sub> OC <sub>8</sub> H <sub>17</sub>	$\frac{R_3}{\begin{array}{c} OC_8H_{17} \\ C_8F_{17} \end{array}}$	Nickel(II) complexes	Copper(II) complexes	
I-1 I-2	$\begin{array}{c} C_8 F_{17} \\ C_8 F_{17} \end{array}$			Cr 126.8 (34.9) [SmA 125.3 (3.7)] I Cr 138.1 (11.7) [I <sub>re</sub> 86.6 (1.1)] Col <sub>h</sub> 277 <sup>a</sup> I	Cr 141.6 (38.4) [SmA 114.6 (3.2)] I Cr 121.4 (20.0) [SmA 64.0 (1.7) I <sub>re</sub> 101.9 (0.8)] Col. 290 <sup>a</sup> I	
I-3	$C_8F_{17}$	$C_8F_{17}$	$OC_8H_{17}$	Cr 140.7 (27.0) Col <sub>h</sub> 215 <sup>a</sup> I	$\operatorname{Cr} 105^{a} \operatorname{Col}_{h} 267^{a} \operatorname{I}$	
I-4	$C_8F_{17}$	$C_8F_{17}$	$C_8F_{17}$	$Cr 139^a Col_h 270^a I$	$\operatorname{Cr} 120^a \operatorname{Col}_h 270^a \mathrm{I}$	
II-1	$C_{9}H_{19}$	$OC_8H_{17}$	$OC_8H_{17}$	Cr 127 <sup><i>a</i></sup> I	Cr 105 <sup><i>a</i></sup> I	
II-2	$C_9H_{19}$	$OC_8H_{17}$	$C_9H_{19}$	Cr 95.0 (26.5) [SmC 90.0 (8.0)] I	Cr 87.7 (26.5) [SmC 69.1 (6.2)] I	
II-3	$C_{9}H_{19}$	$C_9H_{19}$	$OC_8H_{17}$	Cr 116.0 (34.5) [SmC 96.4 (8.5)] I	Cr 103.4 (32.7) [SmC 73.4 (7.5)] I	
II-4	$C_9H_{19}$	$C_9H_{19}$	$C_9H_{19}$	Cr 93.9 (23.6) [SmC 74.8 (8.4)] I	$\operatorname{Cr} 92^a \mathrm{I}$	

**Table 2** Calculated unit cell parameter *a* [in Å] for Col<sub>h</sub> phase and  $\rho$  - density [in g/cm<sup>3</sup>] calculated from X-ray data, assuming one molecule per crystallographic unit cell and 3.4 Å of the columnar slide dimension along the column

	Nickel(II) complexes			Copper(II) complexes		
Compound	<i>T</i> /°C	а	ρ	<i>T</i> /°C	а	ρ
I-2	155	25.8	1.286	150	25.8	1.290
I-3	180	25.9	1.276	150	25.8	1.290
I-4	165	28.7	1.238	180	29.4	1.183

of reflections with relative positions  $q_1 : q_2$  as  $1 : 1/\sqrt{3}$  and 1 : 1/2. The lattice parameters for columnar hexagonal phase of compounds of series I calculated from the X-ray data are collected in Table 2. The obtained intercolumnar distance (*a*) was smaller than the calculated molecular dimension for the most extended molecular conformation. It suggests that molecules from neighbouring columns interdigitate their terminal chains at a distance of about four carbon atoms. Assuming one molecule per crystallographic unit cell, the density of the Col<sub>h</sub> close to 1 g cm<sup>-3</sup> can be obtained, confirming that the columnar cross-sections are made of a single molecule. In the SmA phase of compound I-1, the layer distance is 29.3 Å and close to molecular length (Fig. 1).

For materials of series I, in the wide-angle region of the X-ray pattern, apart from diffused signal corresponding to the average distance between discs in the column (at ~3.5 Å), the broad signal related to the average distance of  $-CF_2$ - groups of molten terminal chains was detected at ~5.6 Å (Fig. 2).



**Fig. 1** Proposed structure of smectic (a) and hexagonal columnar (b) phase made of complexes with fluorinated alkyl chains (dark green).



**Fig. 2** 2-D X-ray patterns for complex **I-2** in Col<sub>h</sub> phase at 150 °C. The Bragg reflection at 22.3 Å is due to the hexagonal arrangement of the columns. The diffused signals at 3.4 Å and 5.6 Å are related to the average distance between discs within the column and between CF<sub>2</sub> groups in the molten fluorinated chains, respectively.

Remarkably, it was found that complexes  $I-2 \cdot Ni$  and  $I-2 \cdot Cu$ form the re-entrant isotropic liquid phase below the columnar hexagonal phase. The isotropic phase was identified from nonbirefringent texture re-appearing on cooling the Colh phase. Moreover, it was observed that the X-ray signal related to columnar organization that was sharp and Bragg-type in the columnar phase weakens and becomes diffused as the isotropic phase re-enters. (Fig. 3). This reflects that the order of molecules becomes short range. In both isotropic phases the average distance between molecules (24.6 A for I-2 · Cu complex) and correlation length (2-3 molecular distances) is nearly the same. It is worthwhile to mention that no changes in the wide-angle region of the X-ray pattern were observed. Moreover, for compound I-2 Cu below re-isotropic phase the lamellar (SmA) phase was detected. The layer spacing for the SmA phase was slightly larger (28.9 A) than the intercolumnar distance (25.9 A). Both phase transitions Colh-Ire and Ire-SmA were also detected by calorimetric method and found to be exothermic on cooling.



**Fig. 3** 2-D small-angle X-ray patterns for partially aligned sample (surface free drop) of complex **I-2**  $\cdot$  **Cu** in I, Col<sub>h</sub> and I<sub>re</sub> and SmA phases. The Bragg reflection with six-fold symmetry observed in the Col<sub>h</sub> phase becomes diffused and without azimuthal modulation in both, I and I<sub>re</sub>, phases. In the SmA phase, Bragg reflections from layers are visible.

# Conclusions

Summarizing the experimental results, it is apparent that the type of molecular organization, lamellar or columnar, for the studied group of materials can be engineered by the type of the terminal chains attached to the mesogenic core. The tendency to form the columnar phase increases with the number of introduced fluorocarbon chains. For mono-fluoroalkylated molecules the SmA phase occurs, for di-fluoroalkylated compounds SmA and Col<sub>h</sub> phases are observed, while for tri-fluorosubstituted molecules only the Col<sub>h</sub> phase is detected. The effect is related to much stiffer structure of perfluorinated chains compared to hydrocarbon chains, making the molecular core broaden. the re-entrant isotropic phase to be below the columnar phase. Such re-appearance of isotropic phase is due to the competing tendency to form the columnar and lamellar structures over a specific temperature range.

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