A "jellyfish" shaped green emitting gallium(III)-containing metallomesogen†‡

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The synthesis of the first gallium(III)-based liquid crystal has been achieved grafting around the metal centre two chelating 2-methylquinolin-8-olate anions and one monodentate 3,4,5-tris(hexadecyloxy)benzoyloxy ligand, allowing the resulting complex to be a soft luminescent material with the typical high quantum yield of pentacordinated gallium species.

The interest in novel materials with special physical properties and for which combination of order and mobility helps to reach an ordered molecular organization able to change in reply to any external stimuli, has pushed to the design of so-called unconventional liquid crystals (LC), "soft materials" generally higher performing than the classical LC.[1] Thus, a great deal of progress has been made by modulating several factors such as nanosegregation, molecular motifs through specific intermolecular interactions, and molecular shapes.[2–5] Among these approaches, the synthesis of LC based on metal complexes (metallomesogens) has received great attention as an alternative way to obtain a new generation of dynamically functional materials. Therefore, many LC systems based on group 9–11 metals have been synthesized in the last 15 years, for which the presence of the metal centre can promote mesomorphism in non-mesogenic ligands, introduce in the overall system interesting electrical, optical and magnetic properties, and allow the formation of molecular motifs and intermolecular interactions which are unapproachable for organic LC.[6–9]

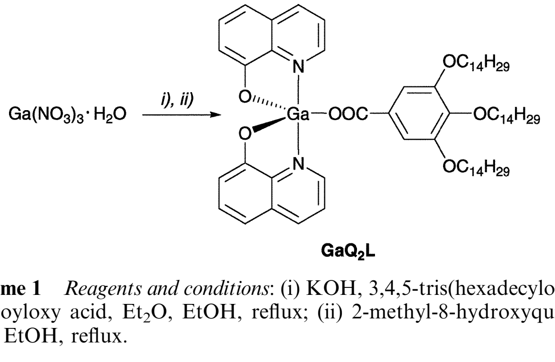
We have been recently interested in the design of metallomesogens with unusual types of molecular or supramolecular organisation able to induce a substantial lowering of the clearing points. This was possible by (i) reaching high coordination numbers around the reactive metal centre,[10] (ii) by changing the molecular topology through the complementary shape approach between hemi-disk molecules[11] and (iii) by the formation of supramolecular arrangements based on several construction motifs ranging from metal coordination, π–π interactions, ionic self-assembly, stereogenic centres or, in ionic species, by modulating the coordinating ability of counter-ions.[12]

Since the nature of the metal centre represents an important tool for tailoring specific molecular shapes and topologies, we have selected gallium(III), never used before in the design of metallomesogens in order to explore the possibility to induce mesomorphism in luminescent metal complexes different than the already well-known lanthanidomesogens.[13] In particular, the pentacoordinate bischelated gallium(III) coordination compounds of general formula **GaQ$_2$L′** where **Q** is the 2-methylquinolin-8-olate anion and L′ is a carboxylate unit, are known to be blue emitting species.[14] Thus, we have explored the possibility of promoting mesomorphism in such systems by introducing several flexible side chains through a polycatenar aromatic function.

Here we report on the synthesis of the first liquid crystal based on gallium(III), consisting of a pentacoordinate complex, **GaQ$_2$L**, where **L** is the 3,4,5-tris(hexadecyloxy)benzoyloxy monodentate ligand. The new **GaQ$_2$L** complex has been synthesized by slow addition of an ethanol solution of the potassium salt of **L** and 2 equivalents of HQ, to a ethanol solution of Ga(NO$_3$)$_3$·xH$_2$O (Scheme 1). The resulting mixture was refluxed overnight to give rise to the desired complex in good yield.§

The molecular structure of **GaQ$_2$L** has been obtained by single crystal X-ray analysis (Fig. 1).¶

The gallium(III) ion is in a pentacoordinated environment with a trigonal bipyramidal geometry, with the two Q ligands in an *N,N-trans* conformation. A strong distortion around the gallium(III) centre is observed in the trigonal plane, where the O(3) oxygen atom is moved away from its regular position [O(2)–Ga–O(3) 130.5(1)°] so that the carboxylic oxygen atom O(4) lies in the same plane and points towards the metal centre, with an O(4)–Ga non-bonding distance of about 3 Å.



Scheme 1 *Reagents and conditions*: (i) KOH, 3,4,5-tris(hexadecyloxy)-benzoyloxy acid, Et$_2$O, EtOH, reflux; (ii) 2-methyl-8-hydroxyquinoline, EtOH, reflux.

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‡ Electronic supplementary information (ESI) available: DSC traces and H NMR. CCDC 672320. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b800030a

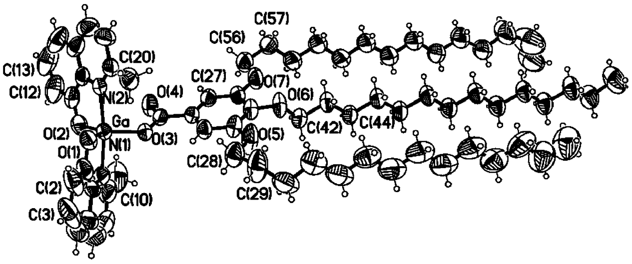

Fig. 1 Perspective view of the complex **GaQ$_2$L** with atomic numbering scheme (ellipsoids at the 50% level).

The other bond distances and angles around the metal centre are similar to those recently reported for other gallium(III) pentacoordinated hydroxyquinolinate derivatives.[15] The alkoxy chains on the carboxylate ligand are all oriented in the same direction, exerting to each other a strong hydrophobic interaction and dividing the molecule into polar and apolar parts. The solid-state packing of **GaQ$_2$L** shows the presence of π–π stacking interactions between the aromatic rings of the **Q** ligands of neighbouring molecules (Fig. 2(a)), which are the most remarkable structural features already observed in gallium(III) pentacoordinated hydroxyquinolinate solids.[15] The repetition of the so formed dimers along the *c* direction gives rise to a crystalline bilayer type architecture, with the aliphatic chains highly interdigitated (Fig. 2(b)). The corresponding interlayer distance is about 23 Å.

Optical microscopy and differential scanning calorimetry has been used in order to verify the thermal behaviour of the light-green solid **GaQ$_2$L**. Despite of its unusual molecular shape, **GaQ$_2$L** shows thermotropic mesomorphism, as evidenced by a blue birefringent texture between 66 and 145 °C. On cooling from the isotropic phase the same texture is retained from 144 °C to room temperature where it is frozen (see ESI‡). XRD has been able to identify the mesophase. The observed pattern (Fig. 3) shows an organization where the molecules align to form a lamellar phase with short range columnar order within the layers, *i.e.* a lamello-columnar phase (L$_{col}$), similar to what has been recently found for both inorganic and organic liquid crystal materials.[16,17] Three sharp reflections with reciprocal spacings in the ratio 1 : 2 : 3 are observed in the small-angle region at 32.3, 16.1 and 10.8 Å and assigned as (001), (002) and (003) reflections. The presence of these equidistant reflections shows that the molecules are arranged in regularly spaced layers with lamellar period *d* of 32.4 Å. This value is larger than the molecular dimension of **GaQ$_2$L** calculated from its observed crystal structure ($L \approx 25$ Å), but smaller than $2L$, indicating a severe degree of interdigitation of the alkoxy chains. Within the methylquinoline-gallium layers, a two-dimensional order is observed. A number of reflections in the middle-angle region of the XRD spectrum are related to the internal structure of the metal-rich sublayers and can be indexed as reported in Table 1. The cell parameters of 18.8 and 3.6 Å originate from the π–π stackings between the aromatic rings of the two different **Q** ligands of neighbouring molecules in the two directions. Starting from the crystal packing observed in the crystalline solid state, we can extrapolate the packing necessary to describe the molecular organization of the lamellar phase (Fig. 3).

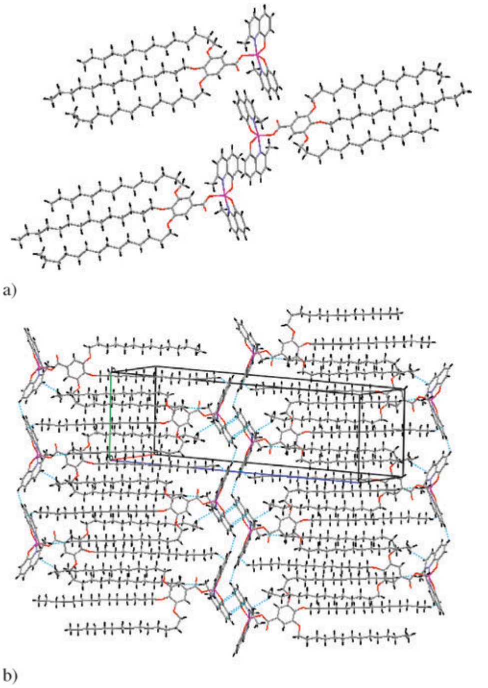

Fig. 2 Crystal packing views showing (a) the formation of the chains of molecules of **GaQ$_2$L** through π–π stacking interactions and (b) the crystalline bilayer architecture obtained along the *c* direction.

The pseudo-columns, formed by the metal-rich sublayer, are still present in the mesophase, as confirmed by the lattice constants calculated from the XRD pattern, and are separated

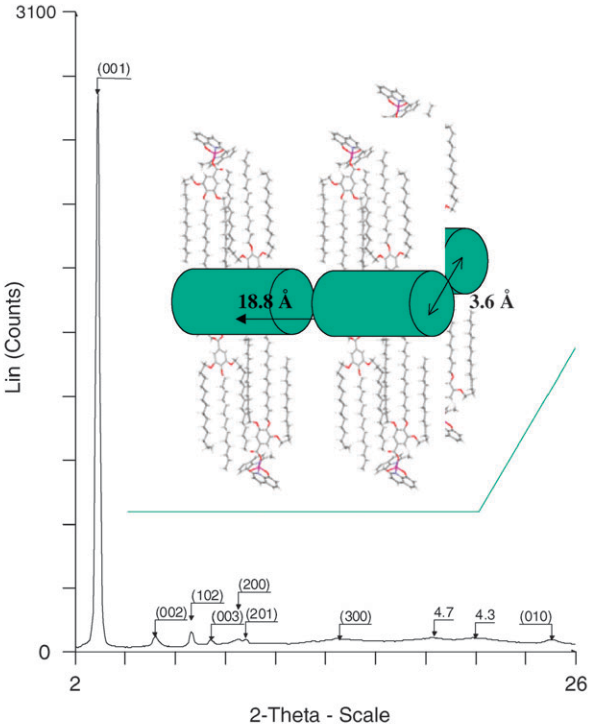

Fig. 3 X-Ray diffraction pattern of **GaQ$_2$L** obtained at 120 °C on heating. In the inset a proposed packing diagram for the L$_{col}$ phase using the molecular packing observed in the single-crystal X-ray structure.

Table 1 Experimental and calculated Bragg peaks and the corresponding Miller indices for the L_{col} phase of **GaQ_2L**, recorded at 120 °C

Reflection	d_{obs}/Å	hkl	d_{calc}/Å	Lattice constants/Å
1	32.3	001	32.4	
2	16.1	002	16.2	a = 18.8
3	12.2	102	12.3	b = 3.6
4	10.8	003	10.8	c = 32.4
5	9.3	200	9.4	
6	9.01	201	9.02	
7	6.3	300	6.3	
8	4.7	alkyl chains		
9	4.3	h1		
10	3.6	010		

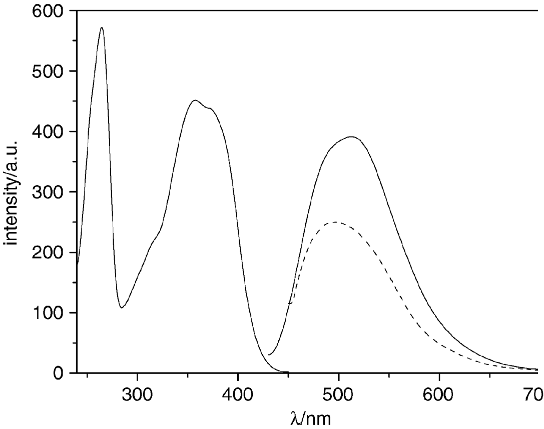

Fig. 4 Solid line: emission (λ_{ex} = 370 nm; on the right) and excitation (λ_{em} = 515 nm; on the left) spectra of **GaQ_2L** in dichloromethane solution. Dotted line: emission (λ_{ex} = 370 nm) spectrum of emission **GaQ_2L** film spin coated onto quartz.

from each other by a dense layer of aliphatic chains, running perpendicular to the longest columnar axis. Moreover, the two halos observed in the wide angle part of the XRD spectrum, at 4.7 and 4.3 Å (hl), correspond, respectively to the liquid-like order to the molten chains and to the columnar stacking within the methylquinoline-gallium layers.

Photophysical studies performed in CH_2Cl_2 solution and on a pure thin film spin coated from CH_2Cl_2 solution of **GaQ_2L**, showed very interesting results with reference to possible practical applications. Indeed **GaQ_2L** is luminescent (515 nm in solution and 495 nm in film, Fig. 4) with the typical high quantum yield of pentacordinated gallium complexes (40% in solution).[15]

In conclusion, the results of the present investigation demonstrate that it is possible to expand the pool of metals able to induce mesomorphism and, through the appropriate choice of the metal ion, obtain novel, non-conventional structures which represent interesting candidates for laser diodes or LC displays technology.

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Notes and references

§ *Synthesis* of **GaQ_2L**: An EtOH solution (5 ml) of potassium hydroxide (45 mg, 0.78 mmol) was added to an Et_2O solution (5 ml) of 3,4,5-tris(hexadecyloxy)benzoyloxy acid (296 mg, 0.39 mmol). The resulting solution was slowly transferred to a refluxing EtOH solution of $Ga(NO_3)_3 \cdot xH_2O$ (100 mg, 0.39 mmol); the mixture was stirred further for several minutes and a solution of 2-methyl-8-hydroxyquinoline (62 mg, 0.78 mmol) in EtOH (5 mL) was slowly added. The reaction mixture was refluxed overnight. After cooling, a greenish solid was filtered off, washed with H_2O, EtOH and Et_2O. The crude product was recrystallized from $CHCl_3$–Et_2O (1 : 3) solution. Green crystals of **GaQ_2L** were collected in 35% yield. Elemental analysis (%) calc. for $C_{69}H_{105}N_2O_7Ga$: C, 72.42; H, 9.25; N, 2.45. Found: C, 72.39; H, 9.01; N, 2.32%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, 9H, J = 6.7 Hz, CH_2CH_3), 1.22 (m, 60H, $(CH_2)_{10}CH_3$), 1.42 (m, 6H, $OCCH_2CH_2CH_2$), 3.06 (s, 6H, CH_3), 3.86 (t, 4H, J = 6.7 Hz, OCH_2), 3.92 (d, 2H, J = 6.7 Hz, OCH_2), 7.17 (m, 6H, H^5, H^7, H^a, $H^{a'}$), 7.40 (t, J = 8.55 Hz, 2H, H^3), 7.47 (t, J = 7.94 Hz, 2H, H^6), 8.25 (d, J = 8.55 Hz, 2H, H^4). IR (cm^{-1}): 2917 (w), 2851 (w), 1683 (s), 1649 (m), 1579 (w), 1507 (m), 1468 (s), 1427 (s), 1341 (m), 1271 (m), 1218 (s), 1115 (w), 869 (s), 836 (s), 754 (w), 651 (s).

¶ *Crystal data* for **GaQ_2L**: monoclinic, space group $P2_1/c$, a = 11.6814(7), b = 12.7385(8), c = 44.889(2) Å, β = 94.647(2)°, V = 6658(1) Å^3, T = 298 K, Z = 4, $\mu(\lambda = 0.71073$ Å$)$ = 0.464 mm^{-1}, D_c = 1.142 g cm^{-3}, 47 267 reflections measured, 9677 unique, 6232 ($I > 2\sigma(I)$) used in the calculations; $R1$ = 0.0593, $wR2$ = 0.1396.

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