

Clustomesogens: Liquid Crystal Materials Containing Transition-Metal Clusters**

Yann Molard,* Frederick Dorson, Viorel Cîrcu, Thierry Roisnel, Franck Artzner, and Stéphane Cordier*

Dedicated to Dr. Christiane Perrin

Octahedral metal atom clusters in which metallic atoms are held together by metal–metal bonds are commonly found in solid-state compounds prepared by high-temperature synthesis.^[1] The metallic octahedron is surrounded by eight face-capping and six terminal ligands to form a $[M_6Q_8Q_a^a]^{2-}$ nanosized unit (Q = chalcogen/halogen, i = inner, a = apical). Many routes^[2] afford soluble discrete $[M_6Q_8X_6]^{2-}$ units (X = halogen) that exhibit, either in the liquid or solid state, specific electronic, magnetic, and photophysical properties related to the number of metallic electrons available for metal–metal bonds.^[3] In particular, they are highly emissive in the red–NIR region, have photoluminescence quantum yields of up to 0.23,^[3d] display long excited-state lifetimes,^[3d,4] and undergo facile ground- and excited-state electron transfer by electrogenerated luminescence.^[5] Owing to the stronger covalent nature of the $M-Q^i$ bond relative to the $M-X^a$ one, halogen apical atoms can be replaced by inorganic or organic ligands without any alteration of the $(M_6Q_8)^{m+}$ core, leading to functional building blocks usable for the design of supramolecular architectures, polymeric frameworks, or nanomaterials with unique properties.^[6] Although many examples of hexasubstituted $[M_6Q_8L^a_6]^{x-}$ units (L = organic ligand) have been reported,^[6d,7] their integration in macroscopic devices by a bottom-up approach remains a challenge. This task requires systems with self-organization abilities on

the one hand and fluidity on the other hand, to correct automatically the positioning errors that can occur during the assembly process. Metal-containing liquid crystals (metal-lomesogens) are the typical examples in which the unique properties of anisotropic fluids are combined with the specific properties of metals (e.g. geometry of coordination, optic, electronic, magnetic).^[8] However, mesomorphic materials containing covalent metal–metal-bonded entities are rare, and all examples described up to now, since the pioneer work of Marchon and co-workers,^[9] are based on dinuclear metal–metal-bonded species.^[10] The association of mesomorphism with the peculiar properties of metallic clusters should lead to clustomesogens that offer great potential in the design of new electricity-to-light energy conversion systems, optically based sensors, and displays.

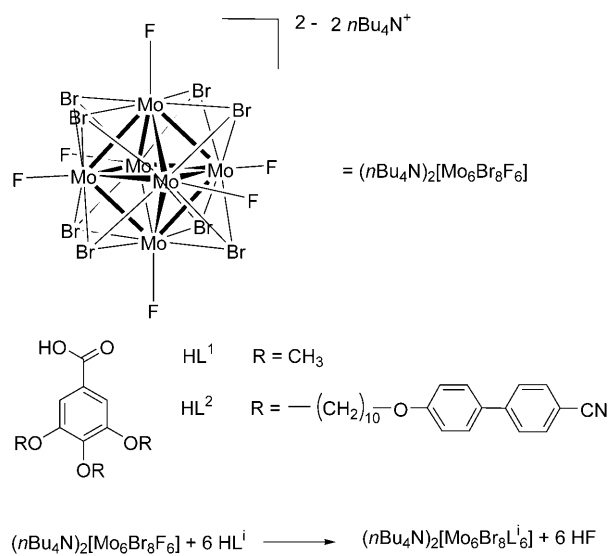
In the scope of our work dedicated to transition-metal-cluster based multifunctional materials,^[11] we report herein the elaboration and characterization of liquid-crystalline materials based on a Mo_6 cluster. The synthesis is straightforward and consists of the one-step reaction of $[Mo_6Br_8F_6]^{2-}$ units with carboxylic acid derivatives (Scheme 1), which results in the *in situ* exchange of apical F^- by carboxylate anion along with the formation of HF.

Owing to the bulkiness of the cluster unit and to its octahedral coordination,^[12] we used a strategy based on the

[*] Dr. Y. Molard, F. Dorson, Dr. T. Roisnel, Dr. S. Cordier
Université de Rennes 1
UMR "Sciences Chimiques de Rennes", UR1-CNRS 6226
Campus de Beaulieu, CS 74205, 35042 Rennes Cedex (France)
Fax: (+33) 2-2323-6799
E-mail: yann.molard@univ-rennes1.fr
stephane.cordier@univ-rennes1.fr
Homepage: <http://scienceschimiques.univ-rennes1.fr>
Dr. V. Cîrcu
Department of Inorganic Chemistry, University of Bucharest
Dumbrava Rosie 23, Bucharest 020464, sector 2 (Romania)
Dr. F. Artzner
Université de Rennes 1
UMR "Institut de Physiques de Rennes", UR1-CNRS 6251
Campus de Beaulieu, CS 74205, 35042 Rennes Cedex (France)

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Scheme 1. Schematic representation of $(nBu_4N)_2[Mo_6Br_8F_6]$ and the gallic acid derivatives HL^1 and HL^2 .

grafting of mesomorphic promoters through a flexible aliphatic spacer that was successfully applied to obtain thermotropic mesophases in the case of polyoxometalates,^[13] octahedral coordination complexes,^[14] fullerenes,^[15] rotaxanes,^[16] catenanes,^[17] or bulky lanthanidomesogens.^[18] The ligand HL² is based on a gallic acid scaffold and was synthesized according to reported procedure.^[19]

The hybrids were easily and quantitatively obtained by heating a mixture containing one equivalent of $(n\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Br}_8\text{F}_6]$ ^[20] and six equivalents of the corresponding gallic acid derivative. Dissolution of HL¹ in THF was necessary prior heating to obtain a homogeneous medium, while for HL² the reaction took place without solvent in the melted ligand (see the Supporting Information). The grafting of ligands was revealed by ¹H NMR spectroscopy with a small downfield shift of the singlet corresponding to the aromatic protons of the ligand gallic moiety and by ¹⁹F NMR spectroscopy with the disappearance of the signal at $\delta = -203$ ppm corresponding to the starting material $(n\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Br}_8\text{F}_6]$ and the appearance of two signals at $\delta = -138$ and -151 ppm corresponding to the formation of HF and $n\text{Bu}_4\text{NF}$, respectively. IR measurements confirmed the grafting by the shift of the $\nu_{\text{C=O}}$ stretching band from 1714 cm^{-1} (dimer of the acid) or 1685 cm^{-1} (monomer) to 1630 cm^{-1} , and the disappearance of the OH carboxylic acid band at 3300 cm^{-1} together with the appearance of the intense and broad band of the $\nu_{\text{H-F}}$ vibration at around 3440 cm^{-1} .^[21] Indeed, as already discussed by Clark,^[22] F[−] reacts like a Brønsted base with carboxylic acid, leading to the formation of HF and carboxylate. Single crystals of $(n\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Br}_8\text{L}^1_6] \cdot x\text{HF} \cdot 1\text{ THF}$ were obtained by gas diffusion of diethyl ether into a THF solution. The crystal structure of $(n\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Br}_8\text{L}^1_6] \cdot 5\text{HF} \cdot 1\text{ THF}$ determined by single-crystal X-ray diffraction confirmed the grafting mode of the gallic acid moieties on the cluster through one oxygen atom of the carboxylate.

The thermal and liquid-crystal (LC) properties of $(n\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Br}_8\text{L}^2_6] \cdot 6\text{HF}$ were investigated by differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction. The phase transition and thermodynamic data are reported in Table 1. The modified cluster showed broad transition ranges, presumably because of its high viscosity (see the Supporting Information). The formation of one LC phase could be detected by DSC ranging from 22.7°C to 103.2°C on the second heating cycle. Focal conic fans textures of smectic-type phase could be obtained by POM on cooling from the isotropic melt after several hours of annealing (inset Figure 1). The appearance of transition bars in the back of some fans, together with their smoothness and their truncated aspect in some other places, could be indicative of the formation of a highly ordered hexatic

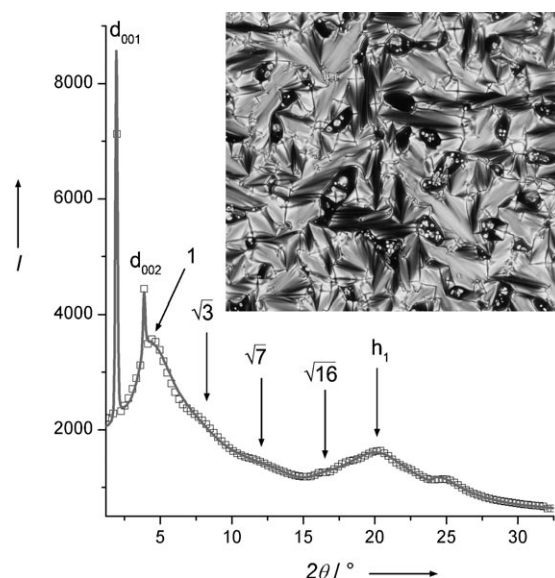


Figure 1. X-ray diffraction pattern of $(n\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Br}_8\text{L}^2_6] \cdot 6\text{HF}$ at 90°C obtained on cooling (solid line), and simulated hexagonal pattern (squares). Inset: Polarized optical micrograph of $(n\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Br}_8\text{L}^2_6]$ at 102.6°C (see the Supporting Information for colored figure).

smectic B phase (SmB).^[23] However, the smectic B focal conic fan texture is paramorphic and is only exhibited upon cooling, when it is inherited from a previous focal conic fan texture of a smectic A or smectic C phase. In our case, no previous smectic phase could be detected either by DSC or POM. We can therefore only conclude at this stage that a smectic-type phase is observed.

Temperature-dependent X-ray diffraction experiments were carried out to identify the exact nature of the obtained mesophase. The X-ray diffraction patterns recorded at different temperatures within the mesomorphic range are all qualitatively equivalent and contain two sharp small-angle reflections characteristic of a layered morphology with a reciprocal spacing in the 1:2 ratio. Thus, by applying the Bragg's law, for example at 90°C (Figure 1), a spacing of 45.5 Å attributed to the interlayer distance was calculated. A diffuse scattering halo in the wide-angle region centered around 4.4 Å (h_1) and corresponding to the lateral short-range order of the molten chains and the cyanobiphenyl moieties confirmed the liquid-crystalline nature of the mesophase. X-ray diffraction patterns exhibit additional intense and very broad reflections that can be indexed in a hexagonal network as $(hk0) = (100), (110), (210), (400)$, corresponding to the reciprocal spacing ratios $1, \sqrt{3}, \sqrt{7}, \sqrt{16}$. These reflections traduce the average lateral organization of the electron-rich cluster cores and are indicative of a local hexagonal ordering within the layers.

Pattern refinement of experimental data obtained at 90°C (Figure 1) using the FullProf program^[24] is in agreement with the nature of an hexagonal arrangement of the clusters within the layers and an average inter-cluster distance of 23 Å . Decreasing the temperature to 20°C induces an increase of the interlayer distance to 46.7 Å together with a shortening of the intercluster distance to 21.6 Å .

Table 1: Phase behavior of $(n\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Br}_8\text{L}^2_6]$ on the second heating cycle.

Compound	Transition	$T\text{ [}^\circ\text{C]}$	ΔC_p [$\text{kJ mol}^{-1}\text{ K}^{-1}$]	ΔH [kJ mol^{-1}]
$(n\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Br}_8\text{L}^2_6]$	$\text{g} \rightarrow \text{Sm X}$	22.7	4.29	–
	$\text{Sm X} \rightarrow \text{I}$	103.2	–	32.94

To understand how the modified clusters are self-assembled, the electronic density profile^[25] was calculated from the intensity of the lamellar Bragg signals at 90 °C and revealed a succession of electron-rich (thickness = 14 Å) and electron-poor (thickness = 31.5 Å) layers corresponding respectively to the cluster layer and the organic layer (Figure 2). As the thickness of the organic layer is roughly equal to the total length of HL², we may consider that it contains fully interdigitated ligands. Moreover, the observed local hexagonal arrangements of the clusters and the thickness of the electron rich layers are indicative of cluster's orientation with their threefold axes perpendicular to the plane of the layers (Figure 2).^[26]

Therefore, we emphasize that the clusters adopt a dendritic-like configuration with an equal repartition of nine cyanobiphenyl groups on both of their sides (Figure 2). In this case, the molecular area per cluster unit was evaluated at 90 °C to 460 Å² from the molecular volume (ca. 21 000 Å³) and the thickness of the layer (45.5 Å). This calculation gives a molecular area per mesogenic moiety of 51 Å², which is more than twice larger than the transverse cross-section of one cyanobiphenyl groups (22–25 Å²). This result is in favor of an interdigitation of the cyanobiphenyl moieties from two adjacent layers giving then an area per mesogenic group of 26 Å².

[Mo₆Q₈X₆]²⁻ cluster units (Q = Cl, Br, I; X = F, Cl, Br, I) are known for their remarkable luminescence properties, such as high quantum yields and significant microsecond emission lifetimes.^[3d,4] Note that those compounds present also electroluminescence properties.^[5] Thus, emission measurements were carried out for all compounds in solution and in the solid state (on powder for (nBu₄N)₂[Mo₆Br₈F₆] and on a sample deposited by spin coating on a silica glass slide for (nBu₄N)₂[Mo₆Br₈L²₆]) giving the same emission profile in

both cases. As depicted in Figure 3, all clusters show a broad luminescence in the red–NIR area ranging from 570 to more than 900 nm with a maximum located at 745 nm for (nBu₄N)₂[Mo₆Br₈F₆] and 735 nm for (nBu₄N)₂[Mo₆Br₈L²₆].

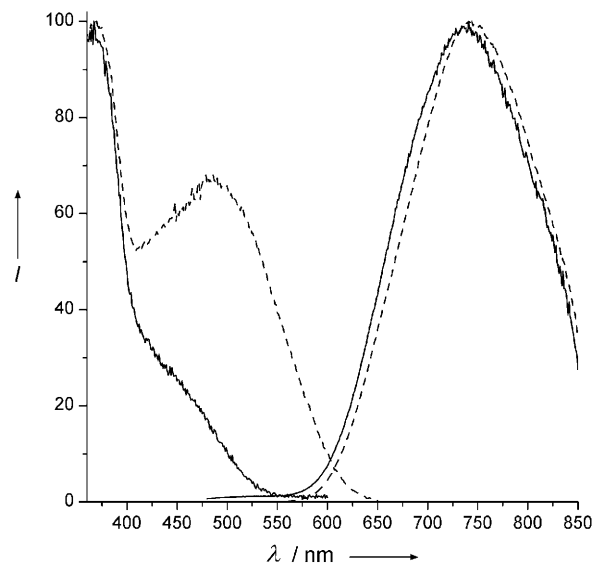


Figure 3. Corrected excitation and emission spectra of (nBu₄N)₂[Mo₆Br₈F₆] (dashed line) and (nBu₄N)₂[Mo₆Br₈L²₆].6HF (solid line) in the solid state. λ_{exc} = 450 nm.

This luminescence is obtained for a wide range of excitation wavelength starting from 300 nm to 550 nm. The presence of the ligand around the cluster induces slight changes to its luminescence spectrum, revealing that the electronic transition responsible of the emission is mainly of

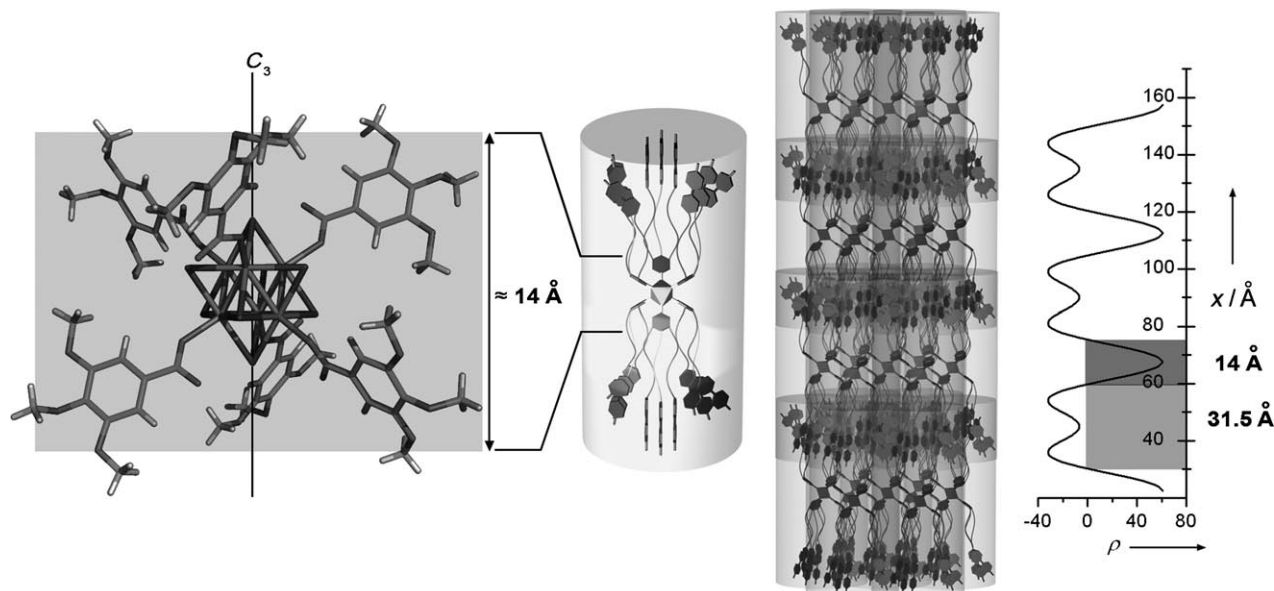


Figure 2. Representation of the [Mo₆Br₈L¹₆]²⁻ building block according to single-crystal X-ray diffraction analysis of (nBu₄N)₂[Mo₆Br₈L¹₆].x HF·1 THF (left side) and illustration of the lamellar packing in the smectic X layer of (nBu₄N)₂[Mo₆Br₈L²₆].6 HF along the C₃ axis of the clusters according to the calculated electronic density profile at 90 °C (right side). The (nBu₄N)⁺ cations and HF molecules are omitted for clarity.

metal–metal charge transfer type and therefore that the bright luminescence properties of the cluster unit are preserved upon complexation.

In summary, we report an original synthesis and characterization of the first clustomesogen, that is, a mesomorphic material containing a transition-metal cluster core. The $[\text{Mo}_6\text{Br}_8\text{L}_6]^{2-}$ building blocks self-organize in layered Sm phase over a wide temperature range from 22 °C to 103 °C after the first heating cycle. The luminescence properties of the native cluster are preserved upon complexation of the ligand leading to a bright red–NIR luminescent liquid-crystal material with high potential in the design of red–NIR signaling or displays. Studies with other kinds of mesogenic ligands are underway to control the mesomorphic behavior of the obtained complexes and will be reported in due course.

Experimental Section

Crystal data for $\text{C}_{60}\text{H}_{66}\text{Br}_8\text{Mo}_6\text{O}_{30} \cdot 2(\text{C}_{16}\text{H}_{36}\text{N}) \cdot \text{C}_4\text{H}_8\text{O} \cdot 5(\text{HF})$: $M_r = 3135.07 \text{ g mol}^{-1}$, $0.28 \times 0.22 \times 0.19 \text{ mm}^3$, triclinic, $P1$, $a = 17.838(3)$, $b = 19.896(4)$, $c = 22.761(4) \text{ \AA}$, $\alpha = 68.599(9)$, $\beta = 89.531(10)$, $\gamma = 67.421(9)^\circ$, $V = 6862(2) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.517 \text{ g cm}^{-3}$, $\mu = 2.929 \text{ mm}^{-1}$, $\lambda = 0.71073 \text{ \AA}$, APEXII, Bruker-AXS diffractometer, 0.97 to 27.56° , $T = 100(2) \text{ K}$, 103 040 reflections, 30 936 independent reflections ($R_{\text{int}} = 0.0704$), 1313 parameters, 0 restraints, full-matrix least-squares refinement on F^2 , multiscan absorption correction, final $R1$ ($I > 2\sigma(I)$) = 0.0734, final $wR2 = 0.2243$, largest difference peak and hole 5.121 and $-2.139 \text{ e}^- \text{ \AA}^{-3}$. The structural resolution is detailed in the Supporting Information. CCDC 758965 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. All other experimental data are found in the accompanying Supporting Information.

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