



## Review

## Liquid–crystalline metallodendrimers



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## ABSTRACT

The state of the art of liquid–crystalline metallodendrimers, i.e. metal-containing dendritic molecules displaying mesomorphic properties, is reviewed. This class of metallomesogens is an emerging and potentially important sub-area of liquid–crystalline dendrimers since they combine within one single molecule the outstanding conformational properties and structural versatility of dendrimers, the self-organizing abilities of liquid–crystalline materials and the intrinsic physical properties of the metallic ions (optical, magnetic, electronic, ...). Designs and synthetic strategies used for the preparation of LC metallodendrimers, their various molecular structures and topologies, along their mesomorphic and other physical properties will be discussed. New trends in this area will also be evoked.

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**Bertrand Donnio** was born in Bretagne (France) in 1967. He graduated in Mathematics, Physics and Chemistry from the University of Rennes (France) in 1991, and was granted his PhD in 1996 from the University of Sheffield (UK), under the supervision of Professor D. W. Bruce, on metal-containing liquid crystals. He then undertook two consecutive research postdoctoral fellowships with Professors R. Deschenaux (Institut de Chimie, Neuchâtel, CH, 1996–1997) and H. Finkelmann (Institut für Makromolekulare Chemie, Freiburg, D, 1997–1999), where he synthesized organometallic mesomorphic complexes and designed a novel method for the synthesis of main-chain liquid crystalline elastomers, respectively. In 1999, he joined the Institut de Physique et Chimie des Matériaux de Strasbourg (UMR 7504) as an appointed CNRS researcher. He received his Research Habilitation from the University of Strasbourg in 2009, and was promoted to Director of Research in 2010. In 2013, he joined the Complex Assemblies of Soft Matter Laboratory (UMI 3254, CNRS-Rhodia/Solvay-University of Pennsylvania) in the USA (Bristol & Philadelphia), for a two-year scientific venture. His current research interests focus on the design and synthesis of multifunctional liquid-crystalline, supramolecular materials (e.g. oligomers, dendrimers, polymers and elastomers, metal complexes, hierarchical hybridized clusters and nanoparticles) and on the structural elucidation of the various low-dimensional organizations they formed by small- and wide-angle X-ray diffraction methods and their magnetic/optical properties. He has co-authored some 200 publications and several book chapters. He is currently member of the editorial board of *Liq. Cryst.*

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## 1. Introduction

### 1.1. Liquid crystals

In the liquid crystal true state of matter, which occurs between the crystalline solid and the amorphous liquid, the *mesogens* i.e. molecules endowed with liquid-crystalline (LC) properties, possess orientational correlations of their main molecular axis and various degrees of positional molecular orderings, reminiscent of the crystalline state, and they flow like normal liquids. Liquid-crystalline materials are therefore unique soft self-assemblies in that they combine the anisotropy of the physical properties (due to molecular ordering) and the fluidity within components self-organizing into various low-dimensional, periodic supramolecular structures [1]. In addition to their dynamic and adaptive nature [2], their ability to evolve towards more complex forms of matter, to integrate and amplify various functions through specific molecular interactions, to tolerate defects and to respond to external stimuli render them extremely attractive for widespread high-tech and biological applications. Although essentially unavoidable components within the LC displays industry (e.g. ultra-large area displays, e-paper, ...), worth circa 50 billions per annum, liquid crystals, due to their pervasive nature, are also more and more found in highly selective sensing-based applications for biological (DNA, bacteria, virus, prions, genes, toxins, ...), chemical (explosives, gases, ions, toxics, pollutants, ...), pressure, heat and electromagnetic radiations detections (and/or selections) [1,3], biomimicry [4], as well as in the so-called “plastic” molecular electronics (e.g. organic field-effect transistors (OFETs), photovoltaic cells (OPVs) and light-emitting diodes (OLEDs)) [5,6] and nanophotonics [7].

Thermotropic LC mesophases [1] are generated as a function of temperature. On heating, mesogens will pass from the crystal to the isotropic liquid states through various intermediate, thermodynamically stable, supramolecular organizations, by the progressive loss of the positional and orientational molecular orders according to a multiple step melting process, a consequence of their molecular structural anisotropy and amphiphathic nature (vide infra) [8]. Mesophases produced this way are subdivided into various subclasses, depending on the packing symmetries and geometries of the self-assemblies. The least ordered of all is the nematic phase (N), and is characterized by the one-dimensional orientational order of the molecules via correlations of their principal molecular axis, usually the axis of highest symmetry [1]. The structure of the smectic “SmX” [9] and laminated “Lam<sub>x</sub>” phases [10], a subgroup of the smectics, consists of the one-dimensional stacking of equidistant 2D molecular layers (Sm) or sheets (Lam), with orientational (and rotational) correlations of the principal mesogen axis with respect to the layer normal. In the Sm phases, the mesogens orient parallel or make a tilt with respect to the layer normal, whilst in the Lam phases, they lie perpendicular to the layer normal and adopt various in-plane orientations and arrangements. Depending on the various degrees of positional (translational) registry of the molecules within the layers and between the layers, orientations, packing constraints and polar orderings, numerous smectic and laminated phases modifications (SmA, SmB, SmC, ... and Lam<sub>iso</sub>, Lam<sub>N</sub>, Lam<sub>Sm</sub>) have been recognized [1,9,10]. Columnar

phases (Col<sub>x</sub>) result from the self-assembly of the molecules into one-dimensional columns (by molecular stacking or aggregation processes) [11], which are then further self-organized parallel to each other and positioned at the nodes of various 2D lattices (e.g., hexagonal, x = hex; rectangular, x = rec; oblique, x = obl; x = square, squ) [12]. As for the three-dimensional mesophases (Cub, cubic; Tet, tetragonal; Mon, monoclinic; ...) [10,13], not as commonly observed as the previous ones, they have a discontinuous structure (ordered 3D arrays of micellar aggregates or bundles) or possess infinite, interwoven continuous sub-networks, both morphologies that can be theoretically described by any of the 7 crystalline systems [14]. In addition to this already impressive collection, some mesophases may possess intertwined morphologies, such as lamello-columnar structures (Lam<sub>Col</sub> or Col<sub>Sm</sub>) resulting from the simultaneous interlocking of lamellar and columnar sub-lattices within the mesophase, or preserve some reminiscent ordering of the preceding mesophases such as the nemato-lamellar and nemato-columnar phases (e.g. N<sub>Lam</sub>, N<sub>Col</sub>, Col<sub>N</sub>) [15]. Polygonal “honeycomb” LC phases represent an emerging family of original and complex columnar systems: such mesophases indeed possess a multi-compartmentalized structure, composed of extended honeycomb networks made of self-assembled rigid molecular segments, usually rods (Fig. 1), describing single or mixed polygonal tessellation (i.e. periodic arrays of triangles, squares, rhombs, pentagons, hexagons, octagons, ...). The voids within such polygonal arrays are either filled by one single component, referred to as single-color tiling, or selectively by different incompatible molecular fragments, such as aliphatic and fluorocarbon chains, according to specific and symmetrical patterns (i.e. multi-color tiling) [16]. Chirality also affects considerably the structures of the mesophases and usually conducts to helical, symmetry-reduced, and/or frustrated superstructures, due to additional packing constraints brought by this asymmetry [17].

Recall that commonly, a mesogen has an *amphiphathic* character [8] i.e. a molecule which is composed of at least two portions of contrasting structural and/or chemical character, namely a rigid *anisotropic* segment, the core, which usually consists in a succession of connected or fused phenyl rings, from whose extremities or periphery radiate flexible aliphatic, polyethylene oxide, even semi-rigid perfluorinated chains. Apart from the nematic phases, whose formation solely requires some degrees of molecular shape anisotropy (e.g. rod, lath, disc, ring, star or bent cores, Fig. 1), LC mesophases formation is essentially driven by nanophase separation between the incompatible constitutive chemical moieties, which generates long-range periodic alternations of non-miscible sub-networks: these low-dimensional arrays are stabilized by intermolecular interactions i.e. dipolar, electrostatic, van der Waals, hydrogen bonding, and dispersive (anisotropy) and repulsive (amphiphathy) forces. Self-assembly driven by shape or by amphiphathy may be cooperative (as in most cases) or in competition, depending on the chemical nature, the volume fractions of the respective constitutive blocks and the degree of the core anisotropy. Essentially two core-shape anisotropies have been considered for the design of low-molecular weight LC materials, namely the rod-like (*calamitic*) and the disc-like (*discotic*), (Fig. 1, I and II) [1]. Whereas the former is much longer than it is broad and hence possesses one long

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