



## Review

## Liquid crystalline metal phthalocyanines: Structural organization on the substrate surface

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## ABSTRACT

The use of metallo phthalocyanines (MPcs) in technological applications requires certain methodological approaches for thin film fabrication. Among these applications the implementation of MPc films is in electronic devices such as organic field-effect transistors (OFETs) and photovoltaic (PV) devices. For such applications the control of alignment and ordering of MPc molecules within the films remains a considerable challenge. This review provides an overview of films' growth of mesogenic MPcs offering systematic analysis of the influence of different factors on the structural organization of liquid crystalline phthalocyanine films, including phthalocyanines molecular structure, regimes of heating, substrate materials, and type of interfaces. The achievements in the development of methods and approaches for the formation of liquid crystalline phthalocyanine films with controllable alignment and ordering are discussed in sufficient details.

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## 1. Introduction

The unique physicochemical properties of phthalocyanines and their metal complexes (MPcs) have made them subjects of numerous fundamental and applied studies. The ability to tailor their chemical structure allows their semiconducting properties to be modified to suit a broad range of technological applications. This can be controlled through the synthesis process of the MPcs altering parameters such as central metal atoms, peripheral substituents and conjugated structure [1]. In dependence on molecular structure, MPcs can be volatile or unvolatile in vacuum, soluble or insoluble in organic solvents and in water [2]. They can form liquid crystalline phases [3,4], different linear, net and 3D polymeric structures [5]. The choice of thin films deposition method is dependent on MPc molecular properties [6].

Methods like vacuum evaporation, spin coating and Langmuir–Blodgett (LB) technique have been extensively used to produce thin films of MPcs. The morphology and structure of the MPc films have strong bearing on their electrical and optical properties as well as on the films' sensing characteristics. Therefore in order to optimize the properties of the films for one or another technological application it is crucially important to produce films with sufficient level of uniformity as well as controllable architecture and molecular ordering.

Self-alignment of MPc molecules into columnar molecular stacks is the consequence of the strong overlap between the  $\pi$ -orbitals of adjacent molecules. This alignment results in the formation of one-dimensional wires which are surrounded by an insulating sheet that are produced by the aliphatic chains. Such films with ordered columnar structure demonstrate anisotropic properties including a highly anisotropic charge carrier mobility. The latter is an electronic feature which is found of crucial importance in electronic device applications. Metal phthalocyanines have wide application as active layers in various electronic devices such as organic solar cells [7,8], organic light-emitting diodes (OLED) [9–11], organic field effect transistors (OFET) [12,13], chemical sensors [14,15] as well as several other applications. For all these applications, ordered structures and smooth surfaces of the MPc films play significant role in achieving devices with significantly improved performance.

Organization of monolayers and ultrathin films of porphyrin and phthalocyanine derivatives on surfaces has been extensively discussed in several reviews [16–18]. These reviews describe a number of approaches which are implemented in order to achieve nanoscale architectures on different substrates. Among these approaches are sublimation under ultrahigh vacuum conditions, immersion of surfaces into solutions to form adlayers as well as the deposition of solutions directly onto substrates in order to directly investigate the liquid–solid interface properties.

In general deposition of materials from solution followed by thermal annealing is a remarkably more simple and inexpensive method in comparison with vacuum-processing techniques for the manufacturing of organic electronic devices [6]. Film deposition of phthalocyanine compounds by Langmuir–Blodgett method is a very useful approach, however this method imposes many restrictions and requirements to the molecular structure. Some aspects of the effect of different parameters on the orientation of MPc molecules at the air–water interface and in the LB thin layers are discussed in the literature [19].

Since the pioneering work in 1982 by Piechocki and co-authors [20], mesogenic phthalocyanines have attracted significant attention due to their intriguing optical and electronic properties making them attractive in optoelectronic device applications. These materials are able to self-organize into mesophases possessed order and mobility. Being an intermediate state between the crystal and the isotropic liquid, the macroscopic behavior of these mesophases is

determined by the molecular structure and properties. Disc-like phthalocyanines stack as columnar structures, leading to the formation of 1D conductors along the columns axis. This is the result of the efficient overlap of the  $\pi$ -orbitals in adjacent macrocycles, whereas the surrounding long alkyl chains play the role of a laterally isolating shield [21–23]. Within this type of structure the molecules are arranged in stacks on top of one another forming columns of molecules which assume a regular 2D lattice which are predominantly classified in terms of their symmetry. In a similar fashion as the smectic counterparts, these columnar structures exhibit a rich poly-mesomorphism. Columns packed as a regular hexagonal lattice are called  $Col_h$  and on a rectangular lattice,  $Col_r$ ; an oblique lattice packing is called  $Col_{ob}$ , and so on (Fig. 1).

Columnar liquid crystals (LC) exhibit large charge carrier mobilities as well as large exciton diffusion lengths along the columnar stacks axis; these are essential electronic characteristics that make these materials of significant importance in organic electronic applications [21,24–28]. As pointed out earlier such characteristics are the result of  $\pi$ -orbitals overlapping between adjacent discotic molecules within the columns, providing 1D charge transport pathway. When layers of these columnar liquid crystalline molecules are aligned between two metal electrodes they can form active layers in organic optoelectronic devices. The latter is a relatively new field of research where the unique properties of this class of materials play critical role in the development of simple, low cost and mechanically flexible device fabrication route. Discotic liquid crystals however are already in use as active layers of some electronic devices as OFET, light-emitting devices, photovoltaic cells and electronic nose.

A key issue for discotic LCs is the alignment of their disc-like molecules which self-assemble into columnar aggregates and exhibit one-dimensional charge transport along the columnar axes [29]. The columnar axes should be oriented perpendicular to the metal electrodes for efficient charge injection and collection. In photovoltaic applications [13,30] the homeotropic alignment of the molecular columns, that facilitate the current flows between the top and bottom electrodes, is required (Fig. 2a). On the other hand, planar or homogeneous alignment, where the columnar axes are oriented parallel to the substrate surface, should be achieved, for device applications as in field effect transistors (Fig. 2b).

The molecular design of discotic liquid crystals, as well as their structure–property relationship, has been the subject of several reviews [21,31,32]. A review article written by S. Kumar [32] was devoted to chemical aspects of the formation of supramolecular assemblies of discotic molecules with more emphasis placed on basic design principles and synthesis of some frequently used discotic liquid crystals (DLC), while the problems of structural organization of DLC films on substrate surfaces were not discussed. Another critical review published by Geerts et al. in 2007 [21] covers aspects associated with molecular design, supramolecular structure and deposition of ordered films of DLCs. However most published data in this field are devoted to hexabenzocoronene, triphenylene derivatives as well as polycyclic aromatic hydrocarbons. Very limited examples of mesogenic phthalocyanine derivatives are also described, however a range of questions concerning the influence of the phthalocyanine molecular structure and the substituents type on the films alignment were not sufficiently answered. It is also worthwhile mentioning that the number of published work (about 50 references) on the investigation of the alignment of mesogenic MPc films have been published after 2007. In a mini review written by Martínez-Díaz and Botari [33] a brief overview was provided describing the work of Spanish researchers in preparing organized phthalocyanine-based supramolecular systems. In a more recent review [31] Fleischmann et al. have summarized state of the art applications of different classes of DLCs in some electronic devices.

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