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Mendeleev Commun., 2009, **19**, 185–186
Mendeleev Communications

Homeotropic alignment in films of a mesogenic phthalocyanine depends on the nature of interactions with the surface

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DOI: 10.1016/j.mencom.2009.07.003

Liquid crystalline phthalocyanine bearing eight oligo(ethyleneoxy) peripheral substituents forms homeotropically aligned films on the hydrophilic surface, whereas planar alignment with a random distribution of the column directors occurs on the hydrophobic surface.

Discotic (disc-like) molecules possessing a large, rigid aromatic core decorated with flexible peripheral chains are capable of self-assembly in columnar superstructures and have been attracting considerable interest both for the study of fundamental aspects of charge transport and for potential application in organic electronics.[1–3] A crucial issue in the processing of liquid crystalline (LC) discotic materials is the control of the macroscopic orientation of columnar superstructures on a surface. In particular, homeotropic alignment with the columnar axes perpendicular to the substrate creates a pathway for charge and exciton transport in the direction perpendicular to the electrodes of a device.

Homeotropic alignment can be obtained by a slow cooling from the isotropic phase. The first molecular layers are oriented *face-on* on the surface and act as nucleation sites at which further discs self-assemble in columns that are perpendicular to the surface. Homeotropic alignment between two solid substrates has been reported for various discotic molecules, but 'molecular ingredients' leading to the spontaneous *face-on* orientation of discotic molecules on the surface are not yet identified.[4–9] Published results suggest that homeotropic alignment is independent of the nature of the surface. It was shown, for example, for triphenylenes decorated with partially fluorinated alkyl chains[8,9] and for a phthalocyanine bearing four alkoxy substituents.[10]

Here, we demonstrate that the alignment of phthalocyanine **1** bearing eight hydrophilic oligoether chains strongly depends on the nature of the surface. Phthalocyanine **1** has been synthesized by an earlier described general method.[11,12] The acid-catalyzed esterification of octaacid **2** (prepared from 1,2,4,5-tetracyanobenzene)[11] with $Me(OCH_2CH_2)_3OH$ afforded octaester **1**, which was purified by extensive column chromatography and precipitation from solution.†

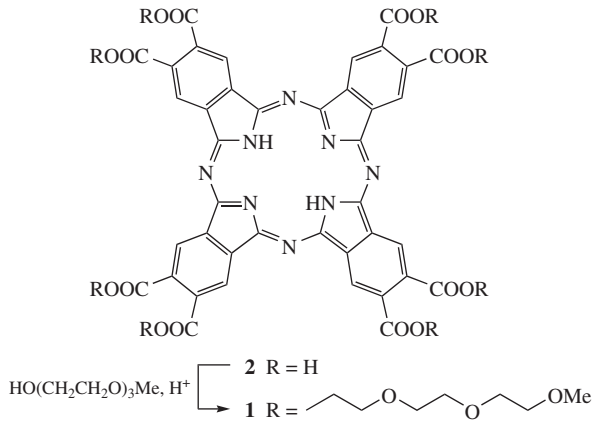

Figure 1 Synthesis and structure of mesomorphic phthalocyanine **1**.

Typically, homeotropic alignment occurs during annealing at the temperature slightly below transition from the isotropic liquid to the LC mesophase, when the viscosity of the LC mesophase is the lowest. Therefore, a reasonably low clearing point (temperature of transition between LC phase and the isotropic liquid) is an important prerequisite. According to differential scanning calorimetry (DSC) and powder X-ray diffraction data, octaester **1** forms a rectangular columnar (Col_r) LC phase above 5 °C (enthalpy of crystalline/Col_r transition 16.1 kJ mol^{-1}) and shows upon heating transitions at 123 °C (1.2 kJ mol^{-1}) to hexagonal columnar phase (Col_h) and then at 245 °C (3.7 kJ mol^{-1}) to the isotropic liquid.

Note that analogues of **1** bearing eight *n*-octyl or *n*-dodecyl ester groups do not show isotropization below 300 °C, when decomposition begins.[11] Hence, substituting the alkyl chains by the $(CH_2CH_2O)_3Me$ groups is crucial to obtaining a material, which can be transformed into the isotropic liquid and, hence, is suitable for the experiments with homeotropic alignment. This effect is due to higher flexibility and, therefore, larger disorder of oligo(ethyleneoxy) chains compared to alkyl ones.

When a film (5–20 μm thickness) of phthalocyanine **1** was heated between two glass plates to 250 °C and then slowly cooled down, homeotropic alignment was observed: in polarized optical microscopy (POM) experiments, the image appeared black between crossed polarizers. Between parallel polarizers, digitated star-like structures were observed, which are typical

† *Synthesis of phthalocyanine* **1**: a 250 cm^3 round-bottom flask was equipped with a Soxhlet extractor charged with ~20 g of 4 Å molecular sieves and a reflux condenser. The flask was charged with acid **2** (500 mg, 0.577 mmol), $Me(OCH_2CH_2)_3OH$ (1.64 g, 10 mmol), *para*-toluenesulfonic acid (200 mg) and toluene (100 cm^3) and heated at vigorous reflux for 72 h. The reaction mixture was concentrated in a vacuum and poured into Et_2O (300 cm^3). The precipitated solid was filtered off and washed by cold Et_2O. Purification of this solid by column chromatography on SiO_2 (CH_2Cl_2/MeOH, 9:1) afforded **1** as a dark-green waxy solid (118 mg, 10%). R_f 0.6 (CH_2Cl_2/MeOH, 20:1). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si, 25 °C) δ: 9.89 (s, 8H), 4.79 (t, 16H, CH_2O, *J* 4.5 Hz), 4.05 (t, 16H, CH_2O, *J* 4.5 Hz), 3.81–3.87 (m, 16H, CH_2O), 3.75–3.80 (m, 16H, CH_2O), 3.68–3.73 (m, 16H, CH_2O), 3.53–3.58 (m, 16H, CH_2O), 3.33 (s, 24H, MeO), –1.15 (s, 2H, NH). ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si, 25 °C) δ: 167.3, 137.5, 134.2, 124.6, 71.9, 70.70, 70.66, 70.5, 69.0, 65.4, 59.0. MS (MALDI), *m/z*: 2034.81 (M^+); calc. for $C_{96}H_{130}N_8O_{40}$: 2034.84.

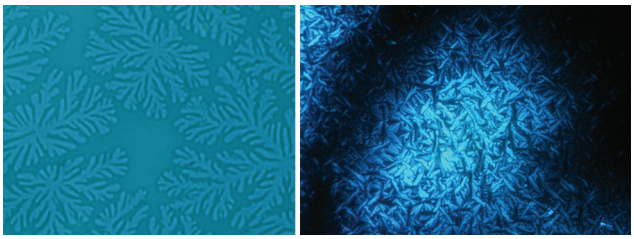

Figure 2 POM images obtained upon cooling of **1** from isotropic melt to room temperature between two solid surfaces. Left: glass, parallel polarizers; right: cross-linked DVS-bis-BCB, crossed polarizers.

of Col_h phases.[13,14] Similar observations were reported earlier for other phthalocyanines bearing oligoether peripheral substituents.[4] On the contrary, when this experiment was performed between two slides coated by the benzocyclobutene-based cross-linked polymer (obtained by the thermal annealing of divinylsiloxane-bis-benzocyclobutene, DVS-bis-BCB),‡ the linear alignment with the random distribution of columnar axes was obtained as confirmed by birefringent textures between crossed polarizers (Figure 2). This difference in alignment behavior apparently originates from different interactions between the substrate and the peripheral chains of phthalocyanine molecule. In case of hydrophilic glass surface, H-bonding between oligo(ethyleneoxy) chains and residual hydroxy groups induces the *face-on* arrangement of the first layer of molecules. In the absence of such interactions on the hydrophobic surface of the cross-linked polymer, the *edge-on* orientation of molecules is preferred.

A possibility to enforce the homeotropic alignment of discotic mesogens by means of substrate–molecule interactions has been demonstrated earlier. Nolte and co-workers[15] used specific interactions between a 'command layer' of anchored amine ligands and molecules of Zn phthalocyanine to induce a *face-on* arrangement of the latter. Kato and co-workers[16] induced homeotropic alignment of an imidazolium-derived mesogen by modifying the glass surface with amino groups. In this study, we demonstrated an example when the alignment of one and the same material can be switched by a simple change of a solid substrate from a hydrophilic to hydrophobic one.

‡ Glass slides were covered with cross-linked polymer by spin-coating with neat DVS-bis-BCB (Cyclotene 4026-46, Dow) at 1500 rpm followed by thermal annealing at 70 °C for 90 s.

This work was supported by the European Union (FP6-NAIMO integrated project NMP4-CT-2004-500355). We are grateful to P. Heremans and S. de Jonge (IMEC, Leuven, Belgium) for the gift of DVS-bis-BCB.

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Received: 21st January 2009; Com. 09/3271