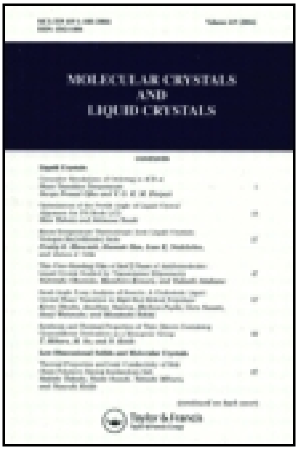

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Nano-Architecture of Self-Assembled Monolayer and Multilayer Stacks of Lyotropic Chromonic Liquid Crystalline Dyes

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Nano-Architecture of Self-Assembled Monolayer and Multilayer Stacks of Lyotropic Chromonic Liquid Crystalline Dyes

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The mesomorphic state of the lyotropic chromonic liquid crystal (LCLC) materials allows one to prepare mono- and multimolecular thin films with a distinct feature of a long-range orientational order in the plane of the film that makes the dried LCLC films drastically different from the classic Langmuir-Blodgett surfactant films. The thin (1–10 nanometers) LCLC films are deposited by the electrostatic layer-by-layer technique, with alternating monolayers of LCLC and oppositely charged polyions. In this work, we report on a new scheme of electrostatic layer-by-layer deposition, in which the passive polyion layers are eliminated: The film is deposited by alternating positively and negatively charged homologs of a LCLC material with the same molecular core structure. The assembled dried films demonstrate long-range orientational order as evidenced by the measurements of absorption and dichroic ratio as a function of the angle between the deposition direction and polarization of probing light.

Keywords: dye; lyotropic chromonic liquid crystal; nano-architecture; self-assemble

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INTRODUCTION

The LCLCs represent a broad class of lyotropic liquid crystals that are fundamentally different from the better studied amphiphilic (surfactant)-based lyotropic systems [1,2]. Qualitatively, the difference is that LCLC molecules are plank-like rather than rod-like, rigid rather than flexible, aromatic rather than aliphatic [3–4]. The polar hydrophilic ionic groups at the periphery of the molecules make the material water-soluble: the side groups dissociate in aqueous solutions, leaving the molecular periphery (partially) charged. As the central core is relatively hydrophobic, the LCLC molecules tend to stack face-to-face into supramolecular aggregates of a columnar type. Correlations between elongated columns give rise to the nematic N phase (orientational order of columns) and to a variety of translationally ordered phases. The columnar type of aggregation is preserved even when the LCLC film is cast by shearing the material onto the substrate and then left to dry [5]. The LCLC films, usually of the thickness 0.5–1 micron, can be used in a number of applications, for example, as the polarizing films in the flexible plastic displays [6,7].

A different technique to prepare aligned LCLC films of a nanometer thickness in the form of monomolecular layer and multi-layered stacks is the electrostatic layer-by-layer deposition from the mesomorphic state of the LCLC [8]. The principal difference of these nanofilms from the Langmuir-Blodgett films is a long-range in-plane orientational order [9]. The electrostatic layer-by-layer deposition is a reliable and simple strategy of non-covalent self-assembly [10,11] that allow one to assemble many other materials, such as polyelectrolytes [12], non-mesomorphic dye monolayers [13], proteins [14], SiO_2 nanoparticles [15], etc. In the original technique described in Ref. [8], the thin films were deposited by alternating the LCLC monolayers with a layer of an oppositely charged polyion, to lock the structure along the normal to the substrates. In this work, we report on the technique that allows one to eliminate the polyion layer, by using positively and negatively charged versions of a LCLC material with the same molecular core structure. The assembled dried films demonstrate a long-range orientational order as evidenced by the measurements of absorption and dichroic ratio as a function of the angle between the deposition direction and polarization of probing light.

EXPERIMENT

The positively, Perylene-3, 4:9, 10-bis(dicarboximide)-N,N’-bis(1-methyl-3-pyridinium) bis-n-toluenesulfonate (Red 2416), and negatively, Perylene-3,4:9,10-bis(dicarboximide)-N,N′-bis(3-benzene sulfonic acid) bis-sodium salt (Red 2304), charged dyes used in experiments (Fig. 1) were synthesized at the Institute of Organic Chemistry, Kiev. They have a structure common for many other molecules of the chromonic class: a rigid planar poly-aromatic core with zwitterionic groups at the periphery [1–4]. The two dyes have the same core structure and oppositely charged peripheries; as a result, their solubility in water is somewhat different.

The dyes were dissolved in distilled water by heating to about 40°C. The solutions were kept for stabilization for about 24 hours in the dark. Oxygen was removed by bubbling nitrogen trough the solutions. Both dyes demonstrate the nematic N phase when dissolved in water with concentrations of about 10 Wt.%.

A special experimental setup was built to measure the optical polarization anisotropy of the transmitted light (Fig. 2). The light from a $He - Ne$ laser passes through a polarizer and an acousto–optical modulator (AOM). AOM is driven by the square pulse generator with the frequency f_m and its phase retardation amplitude is $\pm\lambda/4$. In this regime it converts linearly polarized incident light into the circularly

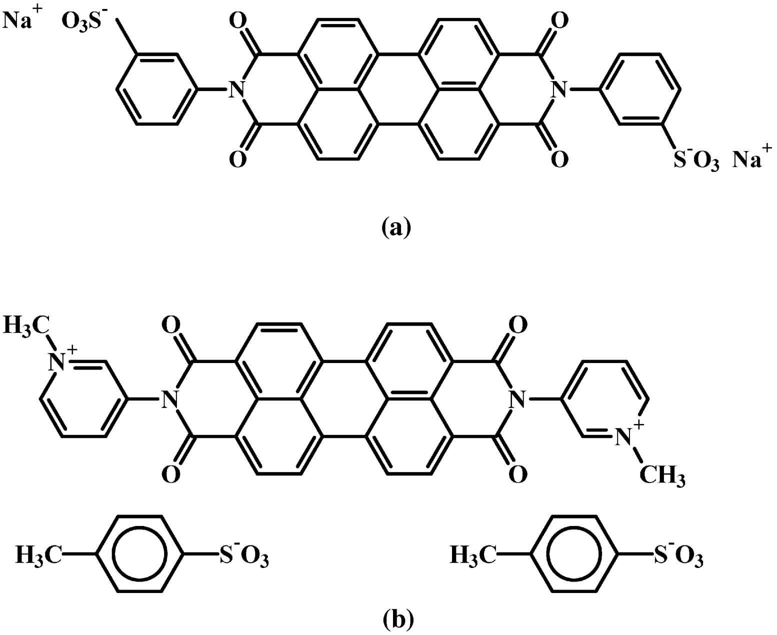

FIGURE 1 Molecular structure of dyes: **a)** Perylene-3, 4:9, 10-bis(dicarboximide)-N,N′-bis(3-benzene sulfonic acid) bis-sodium salt (Red 2304), **b)** Perylene-3, 4:9,10-bis(dicarboximide)-N,N′-bis(1-methyl-3-pyridinium) bis-n-toluenesulfonate (Red 2416).

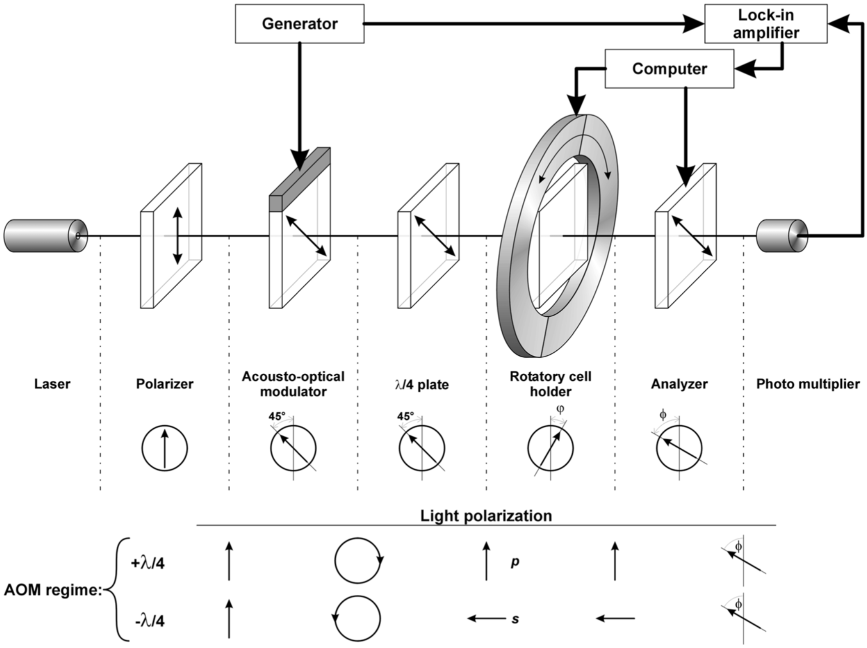

FIGURE 2 Experimental setup to measure transmittance anisotropy. Principle axes for each device and light polarization state is shown for all parts of the light path.

polarized one. During the one half driving period the polarization of the emerging light changes from right-hand to left-hand. Then light passes the quarter–wave plate. Its optical axis is set parallel to the AOM optical axis. As a result, the light becomes linearly polarized alternatively along two mutually perpendicular directions, vertical and horizontal, that we label as p- and s-directions, respectively. This cycle of the polarization switching is repeated with the frequency f_m. Then light beam goes through the sample, which axis is set at the angle φ with respect to the p-direction, and second polarizer (analyzer). This analyzer serves as a compensator and is initially set at the angle $\pm 45^\circ$ with respect to p and s directions. The direction of the polarization of the compensator can be changed for an angle ϕ, required to achieve a complete compensation. The angle ϕ is then transformed into an electrical signal fed to a computerized acquisition system.

The intensity of the light is measured by a photomultiplier (PM). If the transmission of the light passed through the sample is different for the two polarizations, p and s, a component with the frequency f_m

appears in the registered signal. This signal of frequency f_m is picked up by a lock-in amplifier whose reference signal comes from the generator. The output signal of the lock-in amplifier is fed to the step motor that turns the analyzer–compensator. The compensating polarizer will then rotate until the component of a PM signal with the frequency f_m becomes zero.

The angle ϕ between the direction p and the polarization direction of the analyzer is given by the ratio

$$\phi = \arctan\sqrt{\frac{T_s}{T_p}}, \tag{1}$$

where T_p and T_s are the transmission coefficients for the light polarized along the p and s directions respectively. Therefore measuring the angle ϕ of the analyzer one can obtain the optical polarization anisotropy value. In case when the optical polarization anisotropy value is very small we align the analyzer along p or s direction. Rotating the sample for 360° the output signal of the lock-in amplifier has the minimal and maximal values, $U_{\min}$ and $U_{\max}$ respectively. The optical polarization anisotropy value can be obtained from the following relationship:

$$\frac{U_{\max} - U_{\min}}{U_{\max} + U_{\min}} = \frac{T_s - T_p}{T_s + T_p}. \tag{2}$$

RESULTS AND DISCUSSIONS

Figure 3 shows the absorption spectra of Red 2304 in water solution. Up to the concentration of about 10^{-5} wt.% the spectra are characterized by an intense absorption band near 500 nm (curve **a**) and an additional molecular peak at 539 nm. With the increasing dye concentration, one observes pronounced peaks at 584 nm, 502 nm, and 485 nm, in additional to the molecular peak, which points to the aggregation process. The absorption spectrum of Red 2416 is shown in Figure 4. The dye demonstrates similar absorption peaks with maxima at 523 nm, 487 nm and 457 nm as in the case of Red 2304.

As follows from Figure 1, the molecular structures of Red 2304 and Red 2416 are complementary in terms of the polarity of electric charges at the two opposite ends of the molecules. We used this feature to alternate the two dyes in the layer-by-layer electrostatic assembly technique. As a control sample, we used a system prepared by alternating the oppositely charged layers of a polyion and Red 2304. The preparation technique is similar to that described in [8].

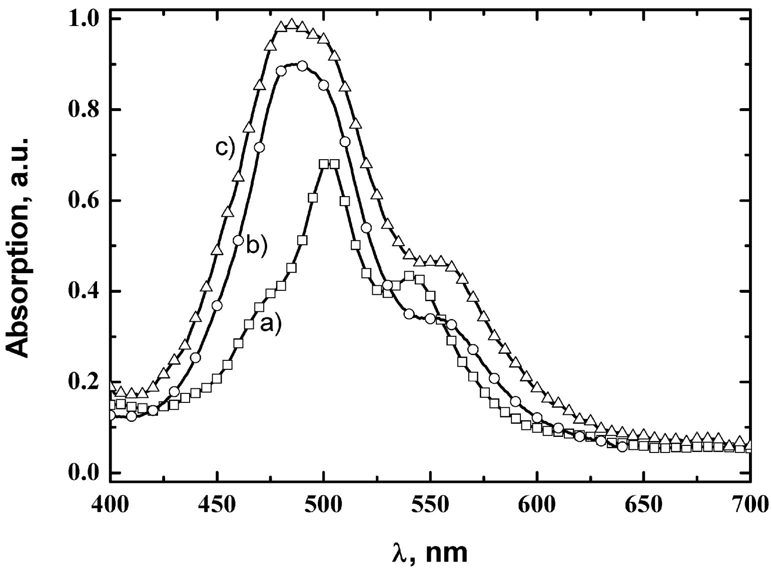

FIGURE 3 Concentration dependence for the absorption of the Red 2304 in water at T = 293 K: **a)** 10^{-3} wt.%, **b)** 1 wt.%, **c)** dried film.

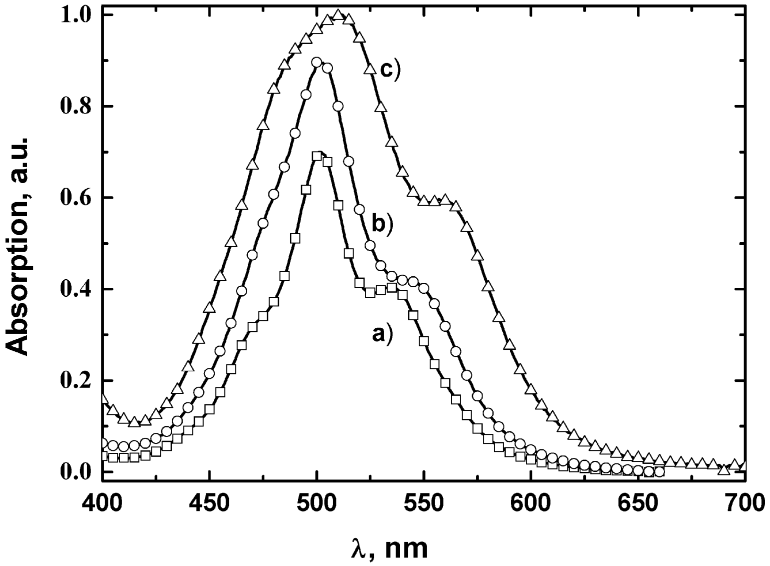

FIGURE 4 Concentration dependence for the absorption of the Red 2416 in water at T = 293 K: **a)** 10^{-3} wt.%, **b)** 10^{-1} wt.%, **c)** dried film.

Polyion – Red 2304 System

A glass substrate was prepared by covering it with a polyion. We used poly(diallyldimethylammonium chloride) (PDDA) purchased from Aldrich. PDDA becomes positively charged in the aqueous solution. The glass substrate was ultrasonically cleaned in an alkaline bath consisting of 5 g of KOH pellets, dissolved in 30 g of water, and 500 mL of 2-propanol for about an hour. This modifies the glass substrate by etching the surface layer away and exposing a clean negatively charged surface. The substrate is rinsed for 30 s and then placed into a 2 mg/mL aqueous solution of (positively charged) PDDA for 20 min. Once a layer of PDDA is adsorbed, the substrate is rinsed for 30 s to remove the excess of polymer. The next step is deposition of Red 2304 prepared as a 10% (weight) solution in water; at this concentration, the solution exhibits the N phase. In aqueous solutions, the end groups of dye molecules are negatively charged, Figure 1. The solution is sheared onto the glass substrate with the PDDA layer. After 5 min, the excess of LCLC is rinsed off for 30 s. The macroscopically thick LCLC layer is reduced to a monomolecular film as described in [8,9].

The resulting nanofilm consists of two monolayers of PDDA and Red 2304, with the plausible structure shown schematically in Figure 5a.

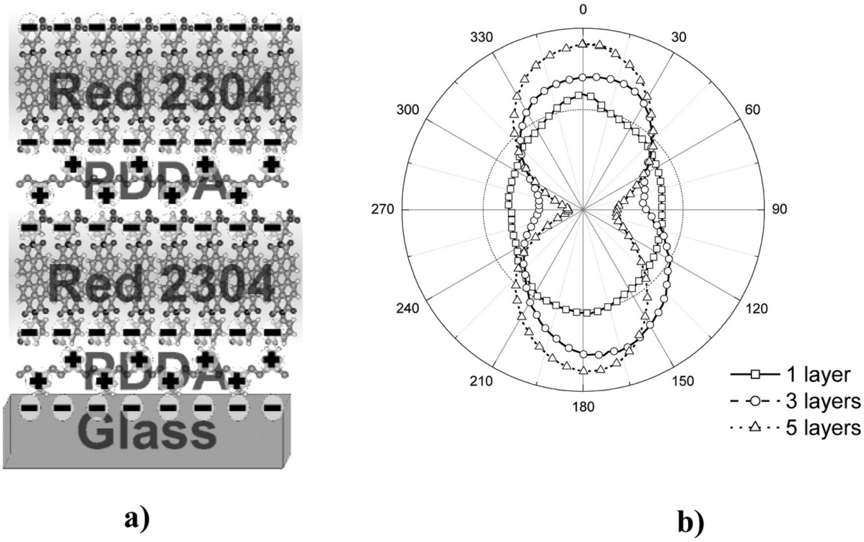

FIGURE 5 **a)** Geometry of the assembled PDDA/Red 2304 layers. **b)** Transmittance anisotropy of multi-layered structures of PDDA/Red 2304 for 1, 3 and 5 dye layers.

Note that Figure 5a is not supposed to reflect the actual degree of order in the orientational distribution of the molecules and the possible existence of columnar aggregates at the absorbed monolayers of the dye similar to those described in Ref. [9]. Figure 5b show the transmittance anisotropy for a multi-layered structures of PDDA/Red 2304 containing one, three and five layers of Red 2304. Transmittance anisotropy is about 2% for one layer and increases with increasing a number of Red 2304 layers. The results are similar to those described in Ref. [8] and imply that a single monolayer of dye molecules is aligned very weakly; one of the reasons might be the non-flat surface profile of the glass substrate; the anisotropy increases as the number of layers increases.

Red 2416 – Red 2304 System

To eliminate the polyion layers, we performed layer-by-layer deposition by alternating the oppositely charged dye layers, Figure 6a.

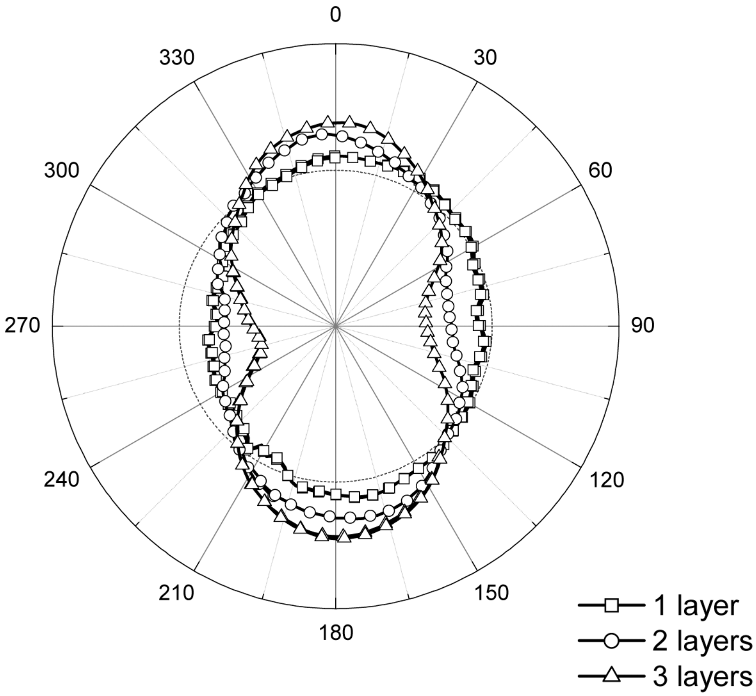

FIGURE 6 Transmittance anisotropy of multi-layered structures of PDDA/Red 2304 (1 layer), PDDA/Red 2304/Red 2416 (2 layers) and PDDA/Red 2304/Red 2416/Red 2304 (3 layers).

The deposition procedure is almost the same as described above, with that difference that PDDA is replaced by Red 32416 for all the layers except the very first one, adjacent to the glass. Once the sequence glass/PDDA/Red 2304 is created, the dye Red 2416 is deposited on the top of Red 2304 layer and sheared in the same direction as the Red 2304 layer. Since the cores of Red 2416 molecules become positively charged in water, the monolayer of this dye acts similarly to the positively charged polyion PDDA. An important difference is that Red 2416 is deposited from the liquid crystalline phase; by shearing it in the pre-set directions, one can control the structural and optical anisotropy of the structure. In the case when the shear directions of the two dyes were the same, we expected an enhancement of the anisotropy, however the structure did not show any increase of the anisotropy, compare Figure 5b and Figure 6; the latter shows the transmittance anisotropy for the films that consist of 1, 2 and 3 dye layers. The possible reason of a decreased anisotropy is that the electrostatic interaction between differently charged dye layers is much stronger than that for alternative deposition of the dye and polyion; the two dye subsystems can penetrate each other, at least partially. Another possible reason might be a lower orientational order of the dried Red 2416. For large number (3 and more) of positive charged dye layers the films became unstable and may be easily removed from the glass substrate even by gentle washing.

CONCLUSION

Our experiments show that the transmittance anisotropy of the films with the architecture "polyion-dye" and "positive-negative dye" demonstrates no reliable difference, however in the later case the thickness of the film is less that may be sufficient for many applications. Furthermore, the fabricated multilayer LCLC films that consist of oppositely charged LCLC dyes eliminates the polyion layers and thus expand the possibility of electrostatic deposition techniques to create certain film architecture with desirable properties.

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