

Self-Alignment of Dye Molecules in Micelles and Lamellae for Three-Dimensional Imaging of Lyotropic Liquid Crystals

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1. INTRODUCTION

Liquid crystals (LCs) are a classic example of soft materials, typically possessing long-range orientational order combined with varying degrees of partial positional order and chirality.^{1,2} The simplest type of LCs, the so-called nematic liquid crystals, are comprised of self-aligned anisotropic molecules or multi-molecular building blocks whose local average orientation is described by the director with nonpolar symmetry $\hat{n} \equiv -\hat{n}$. This orientational ordering is supplemented by unidirectional twist in the ground-state structures of the cholesteric phase, by quasi-long-range one-dimensional positional order in the lamellar phase and by two-dimensional positional order in the columnar phase. LCs have both fundamental and technological importance and are also of profound interest from the biological standpoint because of the liquid crystalline behavior exhibited by lipids, viruses, biopolymers, and membranes.^{3–5} The elasticity- and defect-mediated interactions between incorporated colloidal particles in LCs are markedly different from those in isotropic media, allowing for novel means of nanoscale and microscale colloidal self-assembly that have attracted a great deal of recent interest.^{6–10} Columnar hexagonal, lamellar, and other lyotropic mesophases are frequently used as templates to obtain mesoporous silica structures.¹¹

A remarkable and technologically useful property of the thermotropic LCs is that they can align small dye molecules of

size comparable to that of LC molecules (this is the well-known guest–host effect)² and also nanometer-sized and much bigger micrometer-sized colloidal particles, forcing these foreign inclusions to follow the spatial patterns of orientational order and director structures of LCs. Alignment of anisotropic colloidal particles (such as gold nanorods) in surfactant-based lyotropic LCs has also been achieved.¹² However, long-range ordering of small anisotropic molecules comparable to the size of surfactant molecules and much smaller than the self-organized micelles is presently a challenge. This precludes a number of potential applications that require such alignment (i.e., lyotropic cholesteric LC distributed-feedback lasers) and the use of this alignment for orientation-sensitive fluorescence (1Tj/i3.5(e)14a5(o)Tg(ic)T278.6(Imag

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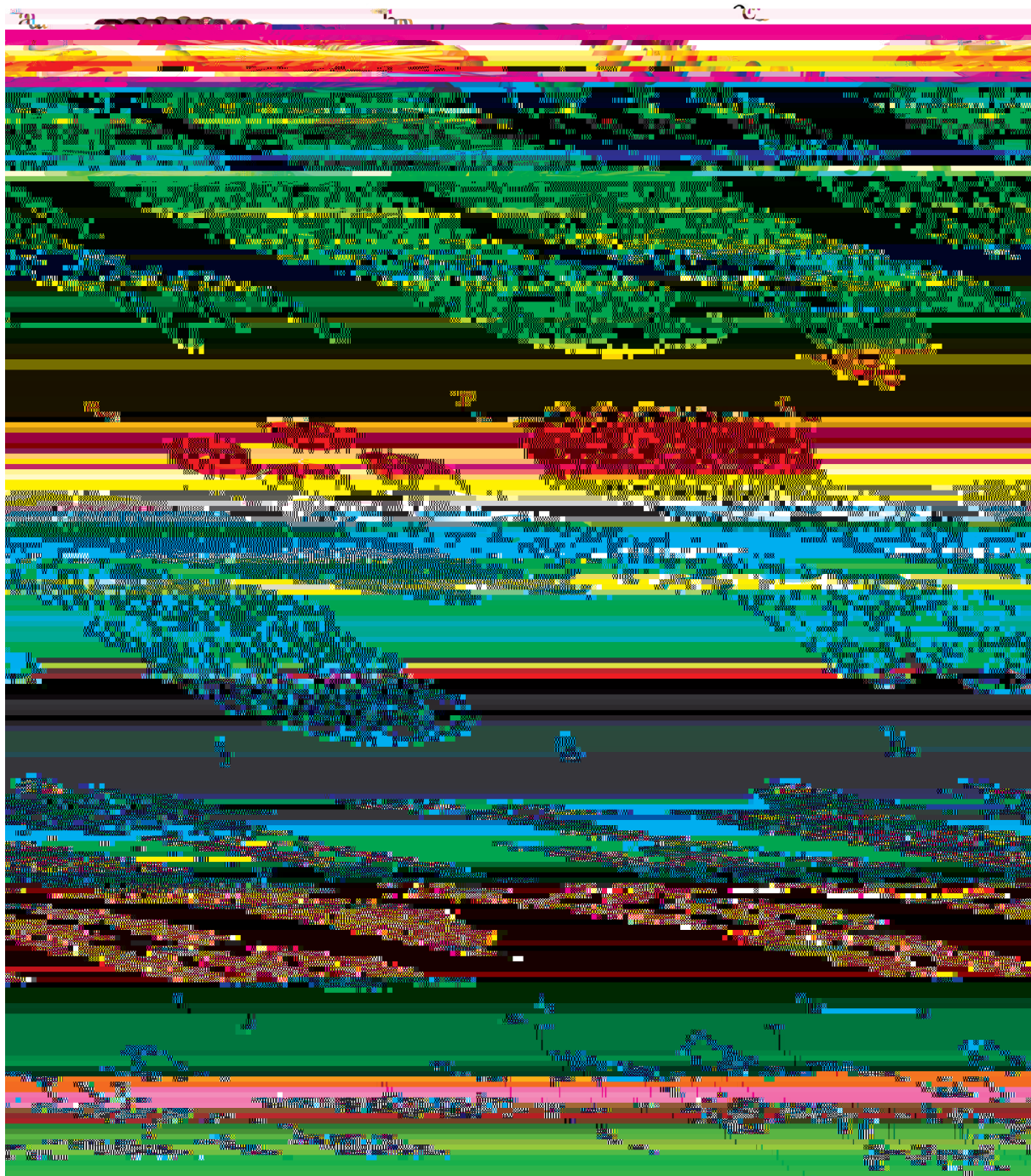


FIGURE 1. Alignment of amphiphilic dye molecules in the calamitic and discotic micelles. (a) A schematic of the self-oriented DiOC₁₈(3) dye molecules (red) having anisotropic aromatic cores along the axis of a cylindrical SDS/1-decanol micelle. (b) A schematic of alignment of the dye molecules along \hat{n} in the calamitic nematic phase. (c) A schematic of alignment of the dye molecules along \hat{n} in the cholesteric phase formed by the cylindrical micelles. (d) A schematic of the oriented self-assembly of DiOC₁₈(3) dye molecules (red) in a discoid SDS/1-decanol micelle (note that the hydrocarbon chains of the dye molecule are about 2 times longer than those of SDS). (e) A schematic of alignment of the dye molecules in the discotic nematic phase. (f) A schematic of alignment of the dye molecules in the cholesteric phase formed by the discoid micelles. (g) The orthorhombic micelles of nematic liquid crystals originate the different nematic phases by different orientational fluctuations, giving rise to (h) discotic nematic phase and (i) calamitic nematic phase. Molecular structures of (j) the amphiphilic molecule of sodium decyl sulfate (SDS), (k) chiral agent molecule of brucine sulfate heptahydrate, and (l) the dye molecule of DiOC₁₈(3). We note that the schematics a–i represent highly idealized models of micelles and their self-

microscopy (FCPM).^{13–19} In this approach, the absorption and fluorescence transition dipoles of the dye molecules spontaneously

follow \hat{n} while the dye molecules homogeneously distribute within the LC sample. Two-photon excitation fluorescence

polarizing microscopy (2PEFPM) works in a similar way but excites the dye molecules through the two-photon absorption process using a pulsed laser beam and provides images with higher spatial resolution with a stronger sensitivity to the molecular orientations patterns.^{16–18} By use of linearly polarized excitation and fluorescence detection, the FCPM and 2PEFPM techniques yield 3D patterns of fluorescence intensity that visualize the 3D structures of ().^{14–18} Furthermore, 2PEFPM is capable of dynamic imaging of various fast processes related to field-induced transformation of 3D director fields in thermotropic liquid crystals.²⁰ The rodlike fluorescent probe dyes are commonly employed to visualize () of thermotropic LCs by detecting the polarized fluorescence of probe dyes aligned along the director and parallel to the calamitic LC molecules. Dye intercalation between

micelles of the surfactant-based nematic LCs, orientational
uctuations of micelles that predetermine the symmetry axis of

polarizing microscopy. This approach can be further extended to imaging of lyotropic LCs composed of biaxial micelles, undulating bilayers, as well as to studying the features of orientational ordering in uniaxial and biaxial nematic phases, ripple phases, etc.^{29,34,35} 3D imaging of lyotropic surfactant-based LCs with similar molecular labeling can be also further extended to the use of various other nonlinear optical microscopy techniques, including coherent anti-Stokes Raman scattering polarizing microscopy,^{18,36} multiphoton excitation fluorescence and multiple harmonic generation microscopies,^{16,17,37} and multimodal nonlinear optical polarizing microscopy.^{18,38} The nonlinear optical microscopy based on stimulated Raman scattering³⁹ and several new techniques enabling subdiffraction-limited high-resolution optical imaging (see, for example, refs 40 and 41) can be extended to the use for purposes of orientation-sensitive imaging as well. The demonstrated capability of 3D imaging of orientational ordering in these lyotropic mesophases will further expand their utility in optical, photonic, biodetection,³ templating, and other applications¹¹ and enhance our fundamental understanding of these intriguing soft matter systems.

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