

Cascade of Molecular Order by Sequential Self-Organization, Induced Orientation, and Order Transfer Processes

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Considerable research effort has recently been focused on the interplay between molecular architecture, molecular order, and macroscopic properties.¹ Many of these studies involve self-assembly or self-organization processes in which molecules associate spontaneously into ordered aggregates as a result of noncovalent interactions and/or entropic factors. In contrast to self-assembly that involves atom-specific interactions producing assemblies with definable structures,² self-organization involves less specific interactions generating aggregates with less definable structures such as cell membranes.³ Many self-organized materials are liquid-crystalline; molecules in this intermediate phase are mobile as in liquids and yet show short-range orientational order as in crystals.⁴ Tremendous success has been achieved in the control of self-assembly or self-organization in solutions,⁵ monolayers,⁶ and thin multilayer films,⁷ tailoring their macroscopic properties. The manipulation of structural order and macroscopic properties of thick films and bulk solids, however, remains a major challenge.⁸ While liquid-crystalline mesophases are of *short-range* structural regularity only, induced alignment of the self-organized ensembles under an external force can increase the degree of orientational order over a *substantially longer range* in the desired direction. This phenomenon has long been observed and employed in many important applications.⁹ By preserving this long-range anisotropic (direction-dependent) order during the transition from liquid to solid phase, a solid matrix with desirable structural regularity and anisotropic properties persisting to the macroscopic scale could be obtained. Surprisingly, this straightforward and promising approach to manipulating properties of solid-phase materials has not been widely used.¹⁰

In this communication, we report the unprecedented control of molecular orientation in solid films of an amphiphilic polyaromatic compound, **1**, using this approach. As a result of the

hydrophobicity of its aromatic core, cation **1** undergoes entropically driven self-organization into lyotropic liquid-crystalline phase in aqueous solution.¹¹ The mechanical force used in spreading this liquid-crystalline solution to form a liquid film on a solid support simultaneously induces the alignment of the aggregates along the direction of spreading. Moreover, this order is then transferred to the solid state upon removal of solvent. Thus, a cascade of molecular order (Figure 1) is generated starting with an isotropic (random) solution and ending with an *anisotropically* ordered solid film that linearly polarizes light.¹²

We chose the 3,4,9,10-perylene diimide hydrophobic core because it is widely used in pigments and organic semiconductors with applications in optical films, photoconducting materials, sensors, and electroluminescent displays.¹³ As a result of the shape anisotropy of perylene diimides, these molecules are dichroic and exhibit anisotropic absorption (light with a polarization axis parallel to the long axis of the molecule is absorbed.) However, in most known applications the molecules are isotropically oriented and their intrinsic dichroic properties have not been fully exploited. This is partly due to the low solubility of perylene diimides in common solvents,¹⁴ hampering processing of the material and precluding convenient techniques for orienting the molecules on a macroscopic scale in the solid phase. We anticipated that the functionalization of the hydrophobic perylene core with cationic groups would impart amphiphilicity, rendering it soluble in water. These water-soluble dyes are then good candidates for exhibiting lyotropic liquid-crystalline behavior because their “plank” shape allows them to stack.¹¹ We thus converted the known diimides **2 a–b**¹⁵ into their corresponding salts **1a–b** and explored the formation of lyotropic mesophases from these cationic perylene compounds (Scheme 1).

Aqueous solutions of **1a** exhibit the liquid-crystalline nematic marbled texture (Figure 2a) when observed under a polarizing microscope.¹⁶ We then simultaneously deposited and aligned these mesophases on glass slides.¹⁷ The molecules in the liquid film were *uniformly aligned over a large area and polarized light*. Significantly, the transition from lyotropic to solid phase upon drying does not disrupt the alignment or the optical properties of the film. As shown in Figure 2b, visible light is transmitted when its polarization axis is parallel to the spreading or shearing of the film. In contrast, only red light is transmitted when the polarization axis of incident light is orthogonal to the shearing direction (Figure 2c). These results indicate that the majority of the amphiphiles

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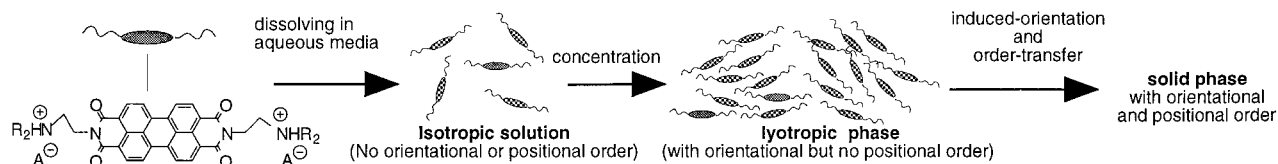
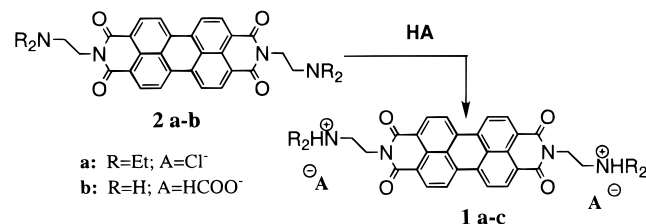


Figure 1. Cascade of molecular order: Cartoon representation of the self-organization of amphiphilic dichroic diimide **1** in aqueous media forming lyotropic liquid-crystalline phase and order-transfer to solid phase.



Figure 2. Photomicrographs (a)–(d) from left to right. (a) The lyotropic phase of **1a** in aqueous solution (9 wt %, 0.14 M, 50X); (b) an air-dried film prepared from 15 wt % solution of **1a** with the shearing axis (in verticle direction) parallel to the polarization axis of incident light; (c) the same sample as in (b) except the polarization axis of incident light is rotated 90°; and (d) an air-dried film prepared from a 13 wt % solution of **1b**. (b – d are 750X.)

Scheme 1



are oriented with the long axis of the aromatic core orthogonal to the spreading direction, resulting in anisotropic absorption of light. Analysis at higher magnification by scanning electron microscopy indicated that the optical texture shown in Figure 2b is due to surface topography and not domain boundaries.

As expected, thin films prepared¹⁷ from isotropic solutions (for example, 0.1 wt %) do not exhibit polarization properties since the molecules are isotropically oriented. This confirms that self-organization into the liquid-crystalline phase is prerequisite for generating anisotropic solid films using our strategy.

Similar behavior is observed for **1b**, although the concentration of its solution is different in producing liquid-crystalline mesophase that can be uniformly oriented. For example, at a concentration of 9 wt %, uniform polarizing films are produced. At higher concentrations (e.g., 13 wt %), the lyotropic domain sizes increase, as a result of extensive aggregation. The domains are not uniformly ordered after deposition and alignment (Figure 2d), resulting in minimal bulk-polarizing properties.

We quantified these observations by polarized UV–vis spectroscopy, examining the same air-dried films used in Figures 2b and 2c. The thin films display a broad absorption band that extends from about 400–600 nm (Figure 3). The broadening is significant when compared with absorption bands for dilute aqueous solutions suggesting orbital interactions between the perylene aromatic cores. When unpolarized incident light is used, the maximum degree of polarization of light (V)¹⁸ transmitted by these polarizing films is 99% (Figure 3). The dichroic ratio (R_d),¹⁸ which is equal to the ratio of the two principal absorption coefficients associated with the orthogonal directions in the plane of the film, was determined to exceed the value of 20 at λ_{\max} . To a first approximation, the dichroic ratio is a measure of the degree

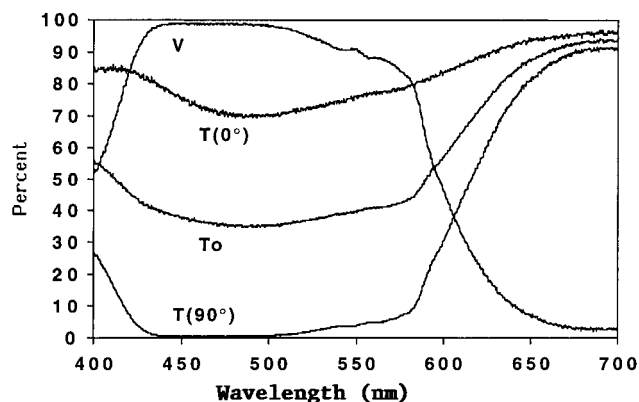


Figure 3. Optical properties of a thin film of **1a** deposited on glass from a 15 wt % aqueous solution. $T(0^\circ)$ is the transmittance when the aligned film's shearing axis is parallel to the polarization of the incident light. $T(90^\circ)$ is the transmittance when it is orthogonal. Mean transmittance (T_0) is a measure of the transmittance of unpolarized incident light.

of anisotropic orientation of the molecules in the film. These optical parameters of the films of **1a** rival commercial polarizers and indicate highly anisotropic orientation of the amphiphiles in the films.¹⁹ Similar optical properties are observed for films prepared from a 9 wt % solution of **1b**.

In summary, the unprecedented control-of-orientation of cationic perylene diimides in solid films is achieved by a combination of self-organization, mechanically induced orientation, and order-transfer processes.

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Supporting Information Available: Experimental procedures and spectral data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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