

# Chiral nematic order in liquid crystals imposed by an engineered inorganic nanostructure

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Control over the orientational order of liquid crystals (LCs) is critical to optical switching and display applications. Porous polymer networks have been used to influence the orientation of embedded chiral liquid crystals<sup>1</sup>, yielding for example reflective displays. Here we show that inorganic films with a porous structure engineered on the submicrometre scale by glancing-angle deposition<sup>2,3</sup> can be used to control the orientation of LCs impregnated into the voids. The inorganic material contains helical columns that orient rod-like nematic LCs into a phase similar to a chiral nematic<sup>1,4</sup> but with direct control of the local molecular arrangement (for example, the helical pitch) imposed by the inorganic microstructure. We also show that reactive LC molecules in this composite material can be crosslinked by photopolymerization while retaining the imposed structure.

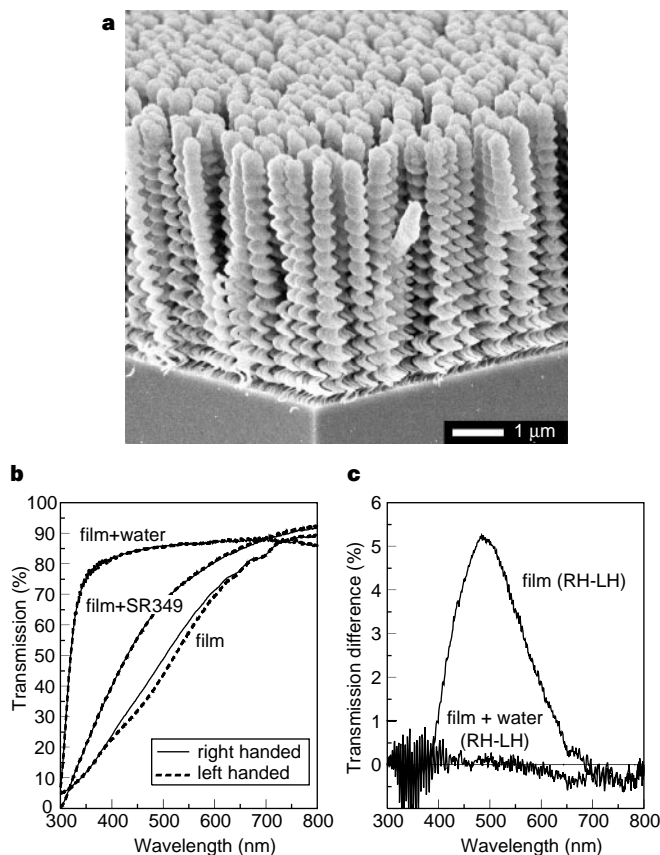
Thin films deposited at an oblique angle onto rotating substrates were first investigated in 1959<sup>5</sup>, and were found to display optical activity at one optical wavelength. In 1992, Azzam<sup>6</sup> described a number of optical properties and devices that might be expected to result from thin films with a helical variation in optical anisotropy, based on oblique deposition (see, for example, refs 7, 8) onto rotating substrates. Robbie and Brett<sup>9</sup> found in 1994 that porous films could be fabricated with submicrometre control of the constituent columnar structure. With motivation from theoretical investigations by Lakhtakia and Weiglhofer<sup>10</sup>, we then fabricated thin films with porous helical structures and demonstrated optical activity over a range of optical wavelengths<sup>11–13</sup>. The films exhibit optical rotation and circular dichroism as would be predicted from comparisons with other chiral systems, including isotropic chiral mediums such as solutions of chiral molecules<sup>14</sup>, and chiral LCs<sup>15</sup>. This technique, which we named glancing-angle deposition (GLAD), was then used to produce a wide range of porous thin-film structures with various materials<sup>2,16</sup>, was expanded to allow greater structural control<sup>3</sup>, and was investigated for use with sputtered films<sup>17</sup>.

Liquid crystals embedded in porous networks have been studied extensively in recent years because of their important present role, and promising future, in electro-optic switching and display technologies<sup>1</sup>. Confining LCs in small-scale porous structures significantly affects the molecular ordering, and response to external fields, of the LC molecules, allowing electro-optic properties to be tailored. In most of this work, LCs are confined to organic polymeric networks formed either by phase separation or by emulsification. Inorganic porous networks, such as porous aerogels, Anopore membranes (aluminium oxide membranes containing cylindrical honeycomb pores) and porous glasses, have also been investigated. Twisted orientational structures have been observed in LCs confined in submicrometre spherical<sup>18</sup> and cylindrical<sup>19</sup> cavities, but elastic energy prevents multiple rotations of the molecular helix without adding chiral additives.

We deposited porous films with helical columns of MgF<sub>2</sub> onto glass substrates (Corning 7059) using GLAD<sup>2,12</sup>. A detailed description of the deposition process is given in ref. 2. The films (Fig. 1a) are composed of helical columns of MgF<sub>2</sub> with 15 turns and a helical pitch of ~350 nm (the pitch of a helix is the distance along the helical axis for one period of revolution of the helix). The density of similar films has been previously measured with a microbalance mass measurement technique<sup>2</sup>, and found to be ~60% of the bulk density. The accuracy of this measurement is limited, as only similar samples were measured.

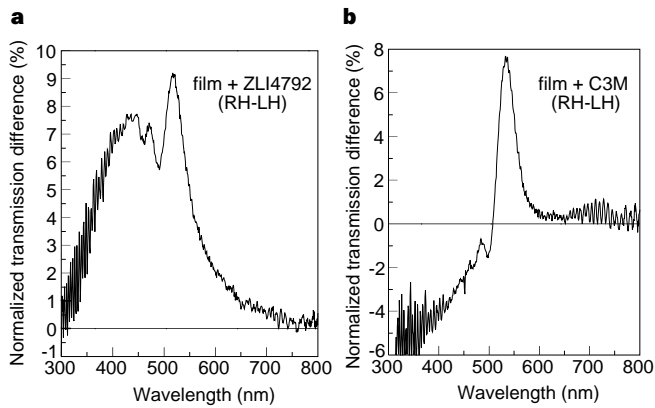
The porous chiral film was impregnated with various materials including: water, an optically isotropic polymer (SR349, Sartomer, West Chester, Pennsylvania), and reactive (C3M) and non-reactive (ZLI4792 and E7) nematic LCs (Merck). To impregnate the film, the sample was covered with a thin glass slide held in place with small pieces of tape at two edges. A small drop of the impregnating material was placed at one of the open edges and rapidly filled the porous film, as observed by a change in light scattering.

To investigate the optical response of chiral films impregnated with LCs, circular polarized spectroscopic optical transmission was measured. The light switching property of chiral (or cholesteric) liquid crystals (CLCs), circular Bragg reflection, occurs between wavelengths  $\lambda_1 = pn_o$  and  $\lambda_2 = pn_e$  where  $n_o$  and  $n_e$  are the ordinary



**Figure 1** Porous inorganic GLAD film impregnated with optically isotropic fluids. **a**, Scanning electron micrograph of as-deposited GLAD thin film of MgF<sub>2</sub> ( $n = 1.38$ ) on glass with 15 helical turns of pitch ~350 nm. **b**, Absolute transmission through the film and substrate for right-handed (RH) and left-handed (LH) circularly polarized light for the as-deposited film, the film impregnated with water ( $n = 1.33$ ), and the film impregnated with an optically isotropic polymer—SR349 ( $n = 1.56$  in bulk), cured with ultraviolet exposure. The difference between the 'film + water' and 'film' transmission spectra is attributed to diffuse scattering from inhomogeneities within the film. Weak transmission below 350 nm is due to absorption in the glass substrate. **c**, Difference spectrum of transmitted right-handed minus transmitted left-handed light for the as-deposited film and with a water impregnate.

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**Figure 2** Transmission of circularly polarized light through a porous inorganic GLAD film with LC impregnates ZLI4792 and C3M. Difference spectra are shown for right-handed minus left-handed transmitted light through the film shown in Fig. 1a impregnated with **a**, a non-reactive LC blend, ZLI4792 ( $n_o = 1.479$  and  $n_e = 1.573$ ), and **b**, a LC diacrylate, C3M ( $n_o = 1.5488$  and  $n_e = 1.6880$ ) polymerized at 80 °C. The difference has been normalized to the transmittance of the right-handed circularly polarized light to minimize diffuse-scattering contributions. Absolute transmission was comparable to that observed for the film impregnated with SR349 (Fig. 1b), with the ZLI4792 impregnate exhibiting slightly higher transmission and the C3M exhibiting slightly lower transmission.

and extraordinary refractive indices of the locally uniaxial structure, and  $p$  is the pitch of the helical structure. Within this reflection band, right-handed circularly polarized light is reflected from a right-handed helix, and light with left-handed circular polarization is transmitted. Alternatively, left-handed circularly polarized light is reflected from a left-handed helix, and light with right-handed circular polarization is transmitted. Wavelengths outside the reflection band are transmitted in all polarizations. The width of the reflection band is less than  $\sim 100$  nm for typical materials with  $n_o \approx 1.5$  and  $n_e \approx 1.7$ . An approximate expression for the reflectivity  $R$  can be derived<sup>4</sup>:

$$R(\lambda) = \frac{k^4 \delta^2 \sin^2(\beta L)}{4q_0^2 \beta^2 + k^4 \delta^2 \sin^2(\beta L)} \quad (1)$$

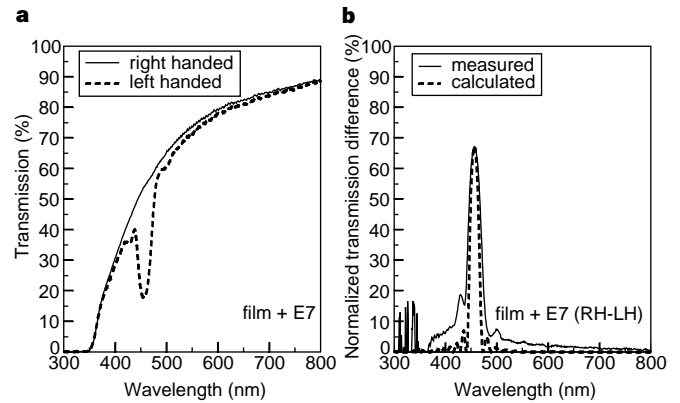
where

$$\beta^2 = k^2 + q_0^2 - k\sqrt{4q_0^2 + k^2 \delta^2}, \quad (2)$$

$$k = \frac{\pi(n_o + n_e)}{\lambda}, \quad \delta = \frac{n_e^2 - n_o^2}{n_e^2 + n_o^2}, \quad q_0 = \frac{2\pi}{p}$$

The peak theoretical reflectivity can be very high for thicker layers of CLCs; up to  $R \approx 99.988\%$  (a contrast ratio of  $\sim 40$  dB) for a 5- $\mu\text{m}$ -thick layer of a typical LC material with  $n_o \approx 1.5$  and  $n_e \approx 1.7$ . For thinner, or less than ideally aligned, layers, the observed reflectivity can be considerably less. High contrasts have been difficult to realize in bulk CLCs because of loss of alignment with thicker layers. In most display applications, however, very high contrast is not necessary, and the need for low switching voltages makes thinner LC layers more desirable. In other optical switching applications, such as for optical communications, higher contrast than that obtainable with bulk or polymer stabilized LCs is required. A more accurate numerical method for describing Bragg reflection in CLC layers is given by Berreman<sup>20</sup> and was used recently<sup>21,22</sup>.

The circularly polarized transmission through the film shown in Fig. 1a without any impregnate is shown in Fig. 1b and c. Figure 1b shows the transmission through the film/substrate system ('film'), as measured. Figure 1c is the difference spectrum where the left-handed transmission is subtracted from the right-handed transmission to show the differential effect of the film on the two circular polarizations. The transmission difference has a peak at  $\sim 480$  nm



**Figure 3** Transmission of circularly polarized light through a porous inorganic GLAD film with LC impregnate E7, and comparison with theory. Absolute (**a**) and difference (**b**) transmission spectra are shown for a GLAD film similar to that shown in Fig. 1a impregnated with E7 LC ( $n_o = 1.5211$  and  $n_e = 1.7476$ ). In **b**, a calculated spectrum is shown assuming chiral nematic alignment of the LC within the voids of the GLAD film.

which corresponds (within experimental uncertainty) with the estimated peak wavelength of  $\lambda = pn_{\text{avg}} = 350 \times 1.2 = 420$  nm, where  $n_{\text{avg}}$  is an effective refractive index of the film which is estimated as the density (60%) weighted sum of the refractive index of the  $\text{MgF}_2$  columns ( $n = 1.38$ ) and the index of the air in the voids ( $n = 1.00$ ). The slightly low prediction of peak wavelength could be a result of some water absorption within the voids which would tend to increase the effective index and shift the peak wavelength to higher values.

When the film was impregnated with water ( $n = 1.33$ , chosen to closely match the index of  $\text{MgF}_2$ ,  $n = 1.38$ ), all transmission difference was lost, as is shown in Fig. 1b and c ('film + water'). The difference spectrum (Fig. 1c) shows some structure with differences less than 1%, but this may be due to imperfections in the spectrometer configuration. The second optically isotropic impregnating material tested was an ethoxylated bisphenol diacrylate (SR349), an optically isotropic polymer that has an index of 1.56 after curing with ultraviolet exposure. The transmission spectra are shown in Fig. 1b ('film + SR349'). As with water, no significant difference between right- and left-handed transmission is seen ( $< 1\%$ ). Also, transmission reduction from diffuse scatter is less than found for the film alone, but not as low as for water. This is attributed to the larger index mismatch between the polymer and the film  $\text{MgF}_2$ . From the transmission spectra through the film with and without the optically isotropic impregnates, we conclude that the chiral optical response seen in the as-deposited film arises from scattering at the film/air interfaces of the helix-shaped columns of  $\text{MgF}_2$ . When the voids are filled with an optically isotropic index-matching material, the effects disappear.

When optically anisotropic impregnates such as LCs are used, there is a significant effect. An area of the film shown in Fig. 1a was filled with the reactive LC diacrylate C3M and polymerized at 80 °C, and another area was filled with the non-reactive LC blend ZLI4792. Another  $\text{MgF}_2$  film, with a slightly larger pitch, was impregnated with a non-reactive nematic LC, E7. All three of these LC materials usually exhibit nematic phases at room temperature, and as such have no differential effect on circularly polarized light. The difference spectra for the films impregnated with ZLI4792 and C3M are shown in Fig. 2. If the LC impregnates are induced into a chiral nematic order by the helical structure of the GLAD films, the circular Bragg reflection will have a maximum at  $\lambda = pn_{\text{avg}}$ . Taking a simple mixing rule of the density-weighted sum of the index of  $\text{MgF}_2$  and the average index of the LCs  $\lambda_{\text{C3M}} = pn_{\text{avg}} = 350(0.6 \times 1.38 + 0.4(1.5488 + 1.6880)/2) = 520$  nm, the maxima should occur at  $\sim 520$  nm for C3M and 500 nm for

ZLI4792. Measured transmission difference maxima agree within experimental error, confirming that chiral GLAD films induce a type of chiral order in simple nematic LCs, similar to the chiral nematic phase seen in CLCs, and with the pitch matching the physical pitch of the GLAD helical columns.

Absolute transmission and normalized transmission difference through the film impregnated with the nematic E7 are shown in Fig. 3. Here the observed transmission difference is much stronger than that observed with the C3M and ZLI4792 impregnates. Again, the maxima occurs (within experimental error) at the wavelength predicted assuming chiral nematic order of the LC within the GLAD film. Figure 3b shows a calculated curve from equation (1) where the transmission difference peak magnitude and wavelength have been chosen to match the measured spectrum. In matching the measured curve, an average index of  $n_{\text{avg}} = 1.43$  and an anisotropy  $\delta = 0.024$  were used. The simple mixing rule described above predicts an average index of  $n_{\text{avg}} = 1.47$ , again within experimental error. The optical anisotropy is much less than that of E7 alone ( $\delta \approx 0.14$ ), but as the hybrid is composed of 60% isotropic  $\text{MgF}_2$ , and 40% LC, this is not unexpected. It is quite difficult to estimate the anisotropy for the composite material and this was not attempted.

Differential transmission of circularly polarized light through the hybrid thin-film/LC material shows that some chiral ordering of the LC is induced by the helical backbone of the porous film fabricated with GLAD. However, a true single-domain 'planar' chiral nematic texture, where all LC molecules lie parallel to the substrate with the helical axis perpendicular, is not the only possible molecular orientational texture. The observed differences in effect with varying material (E7 produced much stronger Bragg reflection than the other LCs), as well as the low anisotropy needed to match theory to observations in Fig. 3b, suggest that a more complicated alignment in fact occurs. One peculiarity of the LC E7 is that there is a cyano group at the end of the rod-like molecules. Dipole interactions of this group with polar surfaces (such as glass) make these molecules susceptible to alignment perpendicular to the surface (homeotropic alignment). It is therefore likely that at the surfaces of the  $\text{MgF}_2$  helices, the E7 molecules will align homeotropically. But in the larger voids between the helical  $\text{MgF}_2$  columns, the complex mix of alignments arising from homeotropic alignment onto helical columns must resolve to reduce elastic energies. One possible texture is a tilted orientation that follows the rotation of the nearby helices. The 'bulk' void regions would have a chiral texture that imitates the nearby helices, but with a tilt to reduce elastic energy and eliminate domain boundaries. Another possibility would be a tube-like structure with homeotropic alignment (perpendicular to the substrate) within the 'bulk' void regions. This texture is more like that seen in the absence of a helical backbone, where all molecules are aligned homeotropically (perpendicular to the substrate). The  $\text{MgF}_2$  columns would then introduce small but periodic variations in the local orientation of the LC near the columns. These two possible textures probably describe the limits of a continuum of alignments; the alignment that occurred would depend on the inorganic film material and surface treatments, LC chemistry, temperature and applied fields. Both possibilities would help to explain the low observed anisotropy of the E7 mixture, as the full anisotropy of the tilted LC is not seen for light propagating along the helical axis.

As an example, and as a comparison to conventional LC techniques, one of us (D.J.B.) has shown that the small bandwidth of transmission/reflection (usually  $<100$  nm) of a CLC layer can be increased by producing a structure with a graded pitch. This was accomplished by crosslinking reactive CLCs by photopolymerization of a diffusion-controlled concentration gradient of CLC<sup>23</sup>. This produced a solidified structure, however, and does not allow for switching. The GLAD technique allows LC alignment structures, such as graded pitches, to be engineered for a desired optical response, and will still allow switching of the LC. GLAD films

composed of multiple layers with different pitches, handedness and structure have been fabricated, and will be investigated in future work. □

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## A reversibly antigen-responsive hydrogel

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Stimuli-responsive hydrogels that undergo abrupt changes in volume in response to external stimuli such as pH, temperature and solvent composition have potential applications in biomedicine and the creation of 'intelligent' materials systems, for example as media for drug delivery, separation processes and protein immobilization. Hydrogels have been reported that respond to pH<sup>1–3</sup>, temperature<sup>4–13</sup>, electric fields<sup>14–16</sup> and saccharides<sup>17–22</sup>. For some biomedical applications it would be very useful to have a material whose swelling response was dictated by a specific protein. Here we report such a material, which swells reversibly in a buffer solution in response to a specific antigen. The hydrogel was prepared by grafting the antigen and corresponding antibody to the polymer network, so that binding between the two introduces crosslinks in the network. Competitive binding of the free antigen triggers a change in gel volume owing to breaking of these non-covalent crosslinks. In addition, we show that the hydrogel displays shape-memory behaviour, and that stepwise changes in antigen concentration can induce pulsatile permeation of a