

Functional dyes in electro-optic and imaging applications

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Abstract: This paper provides a brief overview of the use of functional dyes in electro-optic and imaging applications with an emphasis on liquid crystalline (LC) materials as host matrices. In such systems switchable colour displays, large area projection devices, analog recording fiches, holographic storage media, holographic optical elements and photocontrolable LC alignment layers have all been enabled through the interplay of functional dyes with functional hosts.

The switching of colour, or between colours, by the incorporation of small loadings of guest dye molecules in liquid crystalline (LC) host matrices is one of the best known examples of the use of functional dyes in electro-optic applications. In its simplest embodiment, the so-called guest-host (GH) effect operates by cooperative alignment of the dichroic (orientation dependent absorption characteristics in one wavelength region) or pleochroic (orientation dependent absorption characteristics in different wavelength regions) dye molecules by LC host molecules as illustrated schematically in Fig. 1. The device shown in Fig. 1 describes the negative image contrast mode which utilises nematic LCs with positive dielectric anisotropy. Linearly polarised white light incident on the cell is efficiently absorbed by aligned dye molecules in the OFF state. Electric field switching rotates the dye to an orthogonal disposition which has minimal absorption thereby creating optical contrast in the addressed pixel.

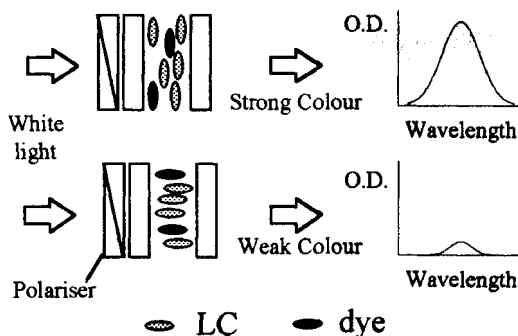


Fig. 1 Schematic representation of the Guest Host effect in negative image LCDs. Upper diagram corresponds to OFF state and lower diagram corresponds to electrically switched ON state - when backlit, switched pixels appear transmissive and virtually colourless against a highly coloured background.

Double GH (DGH) displays operate on the same principle but exploit a second independently switchable layer which is arranged behind the first. The cells are configured so that they inherently act as efficient polarisers at a selected wavelength only. Thus the neutral polarisers required in conventional GH displays, which absorb heavily across the spectrum, can be dispensed with and a brighter display results [1]. Tri layer displays have also been described which incorporate a different colour dye in each layer that can be selectively switched to produce a gamut of colours [2].

With regard to the design of functional dyes for these applications a number of criteria are important including colour (of dye or dye mixtures), solubility, stability (photo-, electro-, thermal) and above all, the order parameter of the transition moment of dye absorption [3,4]. The latter criterion, which is related to the ordering of the dye in the host, has a profound effect on optical contrast. Detailed reviews of functional dyes suited to LC application have been published by Ivashchenko and Romyantsev [3] and recently by Bahadur [4]. Among the more novel dyes developed for this application are two-coloured dichroic dyes [3], anisotropic fluorophors [5] and dichroic or photochromic dyes incorporated into liquid crystalline polymers (LCPs) [6]. The two-coloured dyes enable switching between colours in the same LCD, the fluorescent dyes provide bright, partially emissive displays with good viewing angle characteristics and the polymers provide a means of solubilising higher dye loadings and preventing separation of the dye from the host on cooling.

An alternative display mode which utilises LC-functional dye mixtures involves the use of polymeric binders. The LC-polymer or monomer mixture, starts off as either an aqueous emulsion which is subsequently dried (so-called Nematic Curvilinear Aligned Phase or NCAP approach), or as an isotropic solution which phase separates on polymerisation (so-called Polymer Dispersed Liquid Crystal or PDLC approach [7]). Dry solid films of these materials sandwiched between plastic optically transparent electrodes provide an effective means of constructing large area chromogenic devices [8]. Isotropic or pleochroic dyes have been used in these embodiments to enhance contrast. Thus the absorption of isotropic dyes may be modulated through dyed PDLC films due to increase in optical path length in the scattering OFF state relative to that in the transparent ON state [9(a)]. In this particular case, it makes no difference whether the dye is incorporated in the polymer binder or the LC droplet [9(b)]. Because of their very high brightness and wide viewing angle, PDLCs are well suited to TFT driven reflective mode LCDs and large active matrix, full colour projection TV screens based on this technology have been demonstrated [10].

High order parameter pleochroic dyes have been used in NCAP systems which offer the advantage of larger electro-optic contrast over PDLCs since the dye is substantially confined to the nematic droplets rather than partitioned between LC and polymer phases [11]. Polymer bound dye cannot respond to the switching field and reduces display contrast. More recently a variant of PDLC, the so-called glass dispersed LCs (GDL), has been reported in which LCs and/or dyes are dispersed in silica gel-glasses [12]. The partitioning of dye between the organic LC and inorganic glass phases would be further enhanced in these systems. The mode of operation of NCAP, PDLC and GDLs is summarised in Fig. 2.

It is interesting to note that organic doped sol-gel glasses have also been examined as hosts for laser dyes and photochromic spiropyran. The former offer certain advantages for laser rods over dyed PMMA systems, for example, and the latter enable a plethora of organic photochromes to be incorporated into inorganic glasses. The inner pore surfaces in the silica cages can be modified so as not to adversely effect the kinetics of reversible photochromic reactions [12] (and references within).

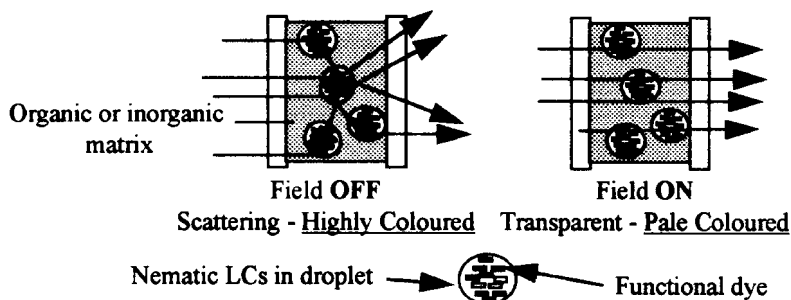


Fig. 2 Schematic representation of dyed LC droplets dispersed in polymeric matrices for large area, lightweight, flexible display applications. In PDLC systems, the dye will carry over into the matrix.

Functional dyes enable optical recording in LC host materials. Laser induced storage systems have been realised by several different modes of perturbation of liquid crystalline order by photochemical, photophysical, thermal or combined effects. Purely photonic recording is discussed in detail later. In thermo optic recording the pleochroic dye absorbs strongly at the laser wavelength and hence facilitates the transfer of thermal energy from the beam to the matrix which is typically a smectic LC or LCP [13, 14]. In Fig. 3 the initial recording state is depicted as a homeotropically aligned monodomain in (a) and is hence transparent. The write event from the laser causes a temperature jump, the magnitude of which is selected to exceed the clearing temperature of the LC matrix as shown in (b). Writing thus causes disordering of the previously aligned host at the local level. When the addressed spot is quenched below the clearing temperature of the LC host it appears as a scattering pixel as shown in (c). In the case of LCP storage devices, durable storage of high resolution images is possible by exploiting the glassy phase of the polymer [14]. These devices are particularly interesting as analog optical recording microfilms or fiches. They offer the possibility of both bulk and selective erasure by a combination of thermal and electric field addressing at the device or pixel level respectively. Many variants of the technique have been reported [15] all of which are contingent on functional dyes, particularly those which absorb at near infra red wavelengths. In addition to the prerequisites of high absorption coefficient, high dichroic ratio and adequate solubility in LCs, dyes used in this application must be durable since the destruction of LC alignment layers has been noted by decomposition products of cyanine dyes. In this regard, squarylium dyes such as **1** offer optimal properties [16].

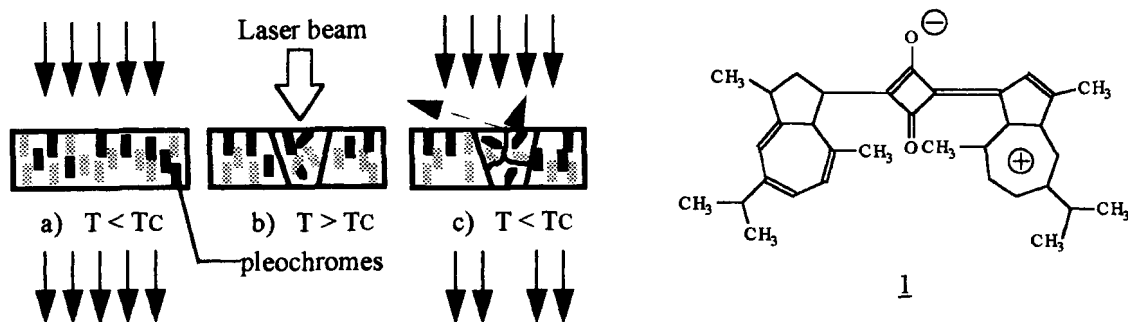


Fig. 3 Laser addressed thermo-optic recording in a dyed Smectic LC or LCP (see text for detail).

A further feature of interest that emerges from the work of Urabe et al. [17] in this area, is that modulation of dye absorption can be discerned within the write pulse which may offer the possibility of 'direct read during write' (DRDW) data verification in digital optical recording.

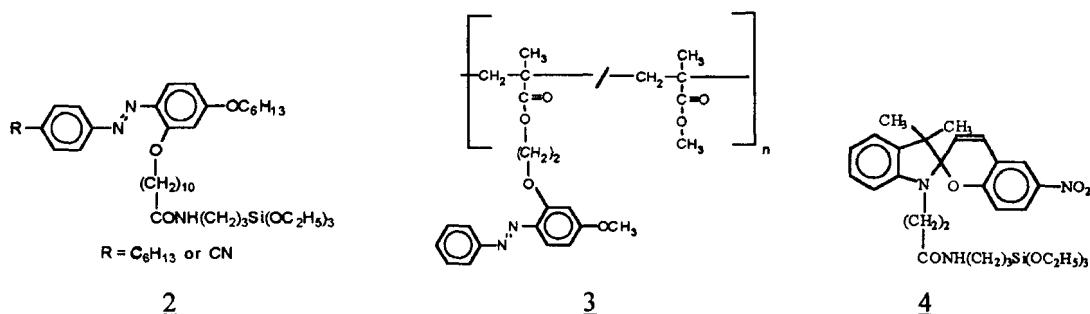
Polarisation sensitive media allow the recording of polarised light and its reconstruction by holographic techniques. Thus two separate holograms can be recorded at the same spatial frequency in the same volume by using two plane waves with orthogonal polarisations. Depending on the polarisation of the read out light, the two images can be reconstructed either individually or simultaneously and their common part subtracted from their sum so that optical logic operations can be performed (AND, EXCLUSIVE OR). The basis of this means of recording is in the induction of birefringence and anisotropy in the optical absorption of the medium. Todorov et al. [18] studied this phenomenon using xanthene dyes in an orthoboric acid matrix and azo dyes in organic polymer matrices. The former example exploits the transient absorption induced by triplet photochromism whereas the latter exploits *trans-cis* photoisomerisation. These authors have postulated that irradiation with linearly polarised light causes the dye molecules to order so that their long axes lie perpendicular to the polarisation direction of the recording light. Thus dichroism (and birefringence) is induced and locally varied in accordance with the spatial modulation of the recording light. The kinetics of induced dichroism were faster in second and subsequent irradiation duty cycles relative to the first due to preordering effects. The greater than expected birefringence exhibited by these recording materials was attributed to local perturbation of the polymer matrix itself by the included photochromic species.

Eich et al. [19] were first to extend the work of Todorov and co-workers into liquid crystalline polymer matrices. The materials again exploited *trans-cis* isomerisation of now mesogenic azo dyes appended to polyester or acrylic backbones. Purely photonic recording was induced in these materials by locally reordering an initially homeotropically aligned monodomain film. Due to the liquid crystalline nature of these materials, high values of optically induced birefringence were recorded (0.01) together with high diffraction efficiencies (~50%). These functional dye - polymer matrices were found to be useful not only for holographic recording but also for the construction of holographic optical elements (HOEs). Thus a radial-symmetric variation in refractive index may be recorded for the production of Fresnel zone plates. These materials offer the ability to construct two dimensional lenses which can be 'erased' thermally then reconstructed at will to generate elements with different optical performance characteristics simply by annealing the photochromic film and rerecording different spatial patterns. Electrical erasure of the patterns is also possible in these systems which may be assisted thermally and facilitated by judicious molecular design [20].

More recently, Ivanov et al. [21] have shown that even in the glassy state of photochromic LC copolymers, photoinduced reorientation of a minority of azo chromophores triggers the physical reorientation of other mesogenic groups in a direction perpendicular to the plane of polarisation of incident light. These workers have shown that while the *trans-cis* isomerisation of the azo dye establishes equilibrium within minutes of irradiation, photoinduced birefringence proceeds on a much longer timescale (~3 hours). Thus, non dye mesogenic groups are affected by photoselection of azo moieties and the latter are reoriented in a multistep process. Photoinduced dichroism and birefringence are frozen in even after relaxation of the *cis* isomer back to its *trans* form. It has been suggested that the effect results from successive reversible isomerisation steps. These cause rotational diffusion of azobenzene side chains such that the angle between the axis of the azo chromophore and the plane of polarisation of incident light is continuously enlarged to a maximum, which is a perpendicular to the incident light. The dynamics of the process are strongly affected by the molecular environment of the chromophores.

Stumpe et al. [22] have studied similar systems to Ivanov and co-workers. In their work with homogeneously aligned monodomains of photochromic LCPs, they showed that reorientation of the optic axis depends on light power and exposure time and that a stationary state occurs when the optic axis of the azo and non dye mesogens is perpendicular to the exciting light polarisation. This is a significant result because it means that the optic axis in the sample can be adjusted by polarisation, power and exposure time so that optical storage elements can be realised with pixels of different orientation as well as with high lateral resolution. These systems may be bulk erased by heat, but are selectively erasable with light. Selective erasure requires re-irradiation with light having a polarisation perpendicular to that of the initial activating light.

It is not necessary for the polymeric media to be liquid crystalline to exhibit this angular dependent photoselection. Thus Lasker et al. [23] have observed the phenomenon in glassy acrylic comb polymers which had azo chromophores in their side chains. Jones et al. and Kozak and Williams [24, 25] have reported the anisotropic photobleaching of photochromic fulgide dissolved into in glassy acrylic polymers and recognised the grey scale capabilities of these recording materials due to the angular dependence of optical properties.



The above mentioned work exemplifies light induced macroscopic orientation of a polymer structure leading to applications in photonic recording. These systems could also function as so-called

'command surfaces' to control the bulk orientation of overlying films of low molar mass LCs. The concept of command surfaces was introduced by Ichimura et al. [26] as a novel approach to the photo control of LC alignment. These workers described an elegant photocontrolable memory effect in a nematic LCD using photosensitive surfactants and photochromic side chain polymer alignment layers to treat device substrates. The photosensitive alignment layers are coined 'command surfaces' because the isomerisation of one azo unit in the surface layer can result in the reorientation of several thousand overlying LC molecules. One effect, illustrating photoinduced switching between homeotropic and homogeneous orientations, is illustrated schematically in Fig. 4 and requires non polarised light. When chromophoric groups were attached in a lateral configuration relative to surfactant segments or to spacer groups in polymeric systems, as indicated in structures 2 and 3, reversible photocontrol of in-plane LC alignment could be achieved with linearly polarised light as illustrated schematically in Fig. 5.

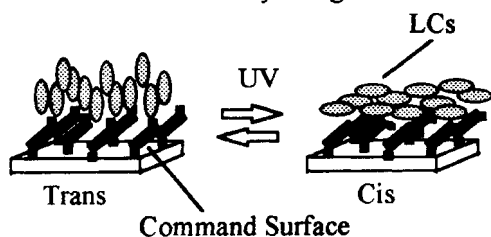


Fig. 4 Photoinduced homeotropic to homogeneous alignment by Functional Dye surface.

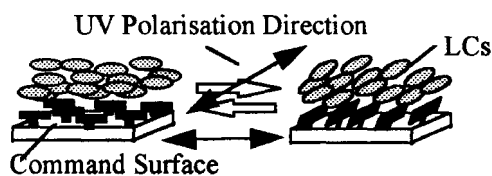


Fig. 5 In-plane photoinduced alignment of LCs by Functional Dye molecular rotors (see text).

The spacer segments act as axes and the functional dyes as molecular rotors, both axle length and rotor length affect the efficiency of the process [26(e)]. In this embodiment much less energy is required to realise photoinduced bulk alignment of nematic LCs. Photochromic spiropyran surfactants such as 4 also function as command surfaces when irradiated with linearly polarised UV light [26(d)]. The in-plane alignment displayed excellent storage stability, in the dark at room temperature, when acrylic copolymers with laterally attached functional azo dyes were used. Alignment could be completely and rapidly destroyed by heat treatment [26(c)]. Photocontrol of in-plane LC alignment has also been demonstrated using surface-selective modification of PVA films by the same group [26(e)].

The objective of this paper has been to provide a flavour of some of the synergistic effects that can be exploited by combining functional dyes and functional hosts. Many further interesting examples, such as organic photorefractive and non linear optic materials have been excluded due to restrictions in space (for recent reviews see [27]).

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