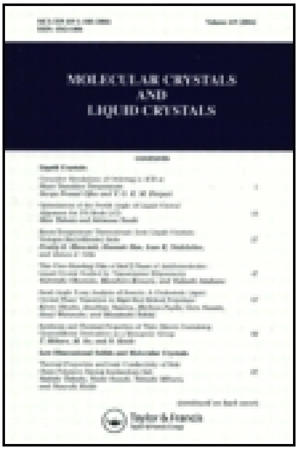

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Enhanced Photorefractive Effect in Hybrid Conducting Polymer - Liquid Crystal Structures

Stanislaw Bartkiewicz [a], Andrzej Miniewicz [a], Francois Kajzar [b] & Malgorzata Zagórska [c]

[a] Institute of Physical and Theoretical Chemistry, WUT Wybrzeze Wyspiańskiego 27, 50-370, Wroclaw, Poland

[b] LETI (CEA - Technologies Avancées), DEIN-SPECE Saclay, F-91191, Gif Sur Yvette Cedex, France

[c] Faculty of Chemistry WUT, Noakowskiego 3, 00-664, Warsaw, Poland

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ENHANCED PHOTOREFRACTIVE EFFECT IN HYBRID CONDUCTING POLYMER - LIQUID CRYSTAL STRUCTURES

STANISLAW BARTKIEWICZ and ANDRZEJ MINIEWICZ
Institute of Physical and Theoretical Chemistry, WUT
Wybrzeze Wyspiańskiego 27, 50-370 Wroclaw, Poland
FRANÇOIS KAJZAR
LETI (CEA - Technologies Avancées) DEIN - SPE, CE Saclay
F-91191 Gif Sur Yvette Cedex, France
MALGORZATA ZAGÓRSKA
Faculty of Chemistry WUT, Noakowskiego 3, 00-664 Warsaw, Poland

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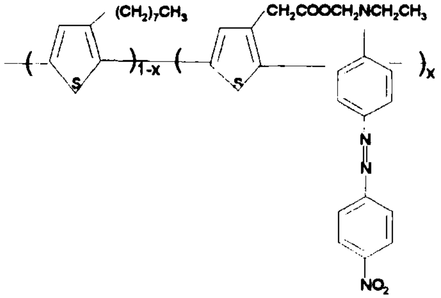
Abstract. We report about a nematic liquid crystal device suitable for efficient coherent beam amplification. A proposed novel hybrid structure is composed of nematic liquid crystal layer sandwiched between suitable ultra thin photoconducting (Disperse Red 1 functionalized polythiophene) polymeric surface layers serving as orienting as well as space charge generating layers upon light incidence. The gain coefficient measured at incidence angle 45° in 10 μm thick liquid crystal layer in a conventional two-wave mixing experiment is one of the highest reported so far for the similar systems and amounts to $g = 7$. The net exponential gain coefficient is very high $\Gamma \approx 2600$ cm^{-1} and is obtained at voltages below 1 V/μm.

INTRODUCTION

A diverse range of applications has arisen that benefit of liquid crystal ability to change their birefringence upon electric field. These applications include liquid crystal (LC) displays, LCTV's, LC spatial light modulators, LC beam deflectors, LC active matrix scattering devices, etc.[1-3]. In recent years this range has been widened by discovery of a new phenomenon: a light induced photoconductivity mediated index grating recording in dye-doped liquid crystals, the effect that mimics a well known photorefractive one[4-10]. Real-time holographic devices like reconfigurable optically addressed spatial light modulators, phase conjugate mirrors, optical pattern recognition systems are the examples of new possible applications for those materials. A rapid progress in material properties and liquid crystal panel design, in just a few years, brought the performance of liquid crystal materials[11,12] to the level reached by the photorefractive polymers, another exciting group of novel materials for photonic applications[13,14]



Scheme 1. Chemical structure of a DR1 substituted poly(3-alkylthiophene).

In a series of recent papers we have described the photorefractive performances of dye-doped nematic liquid crystal panels[15,16]. In these liquid crystal cells index gratings were recorded due to long molecular axis (director) reorientation in an electric field acting on a liquid crystal layer and additionally periodically modulated by light intensity pattern which induced the bulk photoconductivity of the system. The elaborated by us simple model[10] pointed out that the dominant index modulation is local with respect to the light modulation. Local gratings allow for holographic data processing but not for image amplification, in the latter case a nonlocal or shifted index grating with respect to the light intensity pattern is desirable. The same model predicted the existence of the nonlocal effect too, which, however, in standard experimental configuration was of minor importance. In order to take advantage of the existence of the nonlocal grating other liquid crystal panel has been proposed in which nematic liquid crystal was a nonphotoconducting substance and the photoconducting properties were entirely confined in a surface layers of a liquid crystal cell. This allowed us for observation of energy transfer between the beams in a two beam coupling experiment[12]. The exponential gain coefficient Γ observed by us in a liquid crystal panel with E-7 nematic mixture sandwiched between photoconducting surface layers made of poly(3-octylothiophene) polymeric layer approached Γ = 1000 cm^{-1} [12].

In this paper we report on the observation of still higher two-beam coupling gain, $g = \exp(\Gamma L) = 7$ and net exponential gain coefficient $\Gamma = 2600$ cm^{-1} which was achieved in LC panel containing commercially available E-7 nematic liquid crystal with surfaces covered by thin layers of Disperse Red 1 functionalized polythiophene. Polymeric photoactive coatings served both as space charge field formation layers and liquid crystal ordering layers.

EXPERIMENTAL

We used soluble polythiophene derivative containing NLO chromophore commercially known as Disperse Red 1 (DR1). This polymer was prepared via copolymerization of 3-alkylthiophene and 2-[N-ethyl-N-[4-(4-nitrophenylazo)phenyl]amino]ethyl 3-thienylacetate, its structure is shown in Scheme 1 and the details of synthesis will be reported elsewhere[17]. Poly(3-alkylthiophenes) are known as good photoconductors[18,19] and DR1 substituted-thiophenes also exhibit these properties as was proved by the experiments presented in this paper. These polymeric layers simultaneously perform a dual function - that of partially transparent but photoconducting layer and of alignment inducing layer (substituting conventional polyimide layers). Polymer was dissolved in $CHCl_3$ and the layer was prepared by spin-coating (at 2000 rpm for 30 s and 4000 rpm for 40 s) on ITO covered glass plates. After that polymeric layers (on average 100 nm thick) were uniaxially brushed and the resulting plates were sandwiched, with the use of a 10 μm polyester spacer, in parallel to each other so the planar ordering of nematic liquid crystal could be imposed. The layers showed optical uniformity over the whole display area (1 cm x 1 cm) and absorption band with the maximum around 480 nm. The absorption peak characteristic of the chromophore underwent a batochromic shift from 485 nm (pure DR1) to 516 nm[17]. The position of the absorption maximum suggests that the main absorption is due to the π-π^* transition in the polyconjugated backbone. Illumination at 514 nm leads to photogeneration of charge carriers in the system under study. The cells were filled by a capillary action with a multicomponent nematic liquid crystal mixture E7 (Merck KGaA, Darmstadt) and showed homogenous alignment. Such an LC composition at room temperature is characterised by a positive static dielectric anisotropy $\Delta\varepsilon = +13.8$, birefringence $\Delta n = 0.2253$ at 589 nm ($n_e = 1.7464$, $n_o = 1.5211$), viscosity $v = 39\ \mathrm{mm^2 s^{-1}}$ and a clearing point at 331 K[20]. A schematic structure of the described above hybrid conducting polymer - liquid crystal device is shown in Fig. 1. The layered structure is composed of : glass plate, ITO covered glass surface, photoconductive polymer, nematic liquid crystal, photoconductive polymer and ITO covered glass plate. The DC voltage supplier (0 ± 50 V) was connected with the help of thin wires to the ITO surface layers. To study photorefractive properties of such a system we employed a well known method of two-beam coupling[21,22] which allows for recording of refractive index gratings and evaluation of material's fundamental holographic properties. The typical two-wave mixing experiment is shown in Fig. 1 where two coherent (p-polarised) beams from a continuous-wave Ar$^+$ laser (wavelength l = 514 nm) intersect within an optical medium and form a simple interference (intensity) grating. The spacing $\Lambda = \dfrac{\lambda}{2n\sin(\theta/2)}$ of the intensity grating was set between 4 to 80 μm by changing the incidence angle θ between two writing beams. At oblique light incidence angle ($\beta = 45°$) and small wave mixing angle q with p-polarised beams and light electric field vectors along the brushing direction we

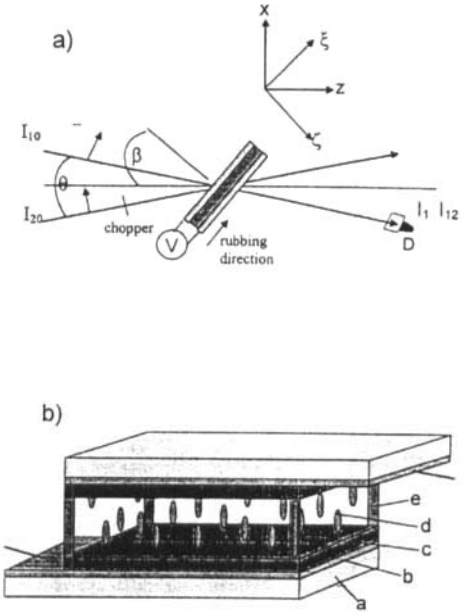


FIGURE 1. (a) Schematic configuration for beam coupling in a tilted thin nematic liquid crystal cell equipped with polymeric photoconducting layers. The pump I_{20} and probe I_{10} beams are polarised in a plane of the paper. The co-ordinate system and wave mixing q and incidence b angles are also indicated. (b) Simplified schematic structure of the device. Here a - is the glass plate, b - is the ITO conducting and transparent layer, c- is the photoconducting polymer, d - nematic liquid crystal mixture, e - denotes the polyethylene spacers. DC voltage is applied to the ITO electrodes.

observed an efficient self-diffraction with a multiple orders of diffraction visible in far field, providing that a suitable external electric field E_a ($0 < E_a < 10$ kV/cm) was externally applied. In such a case one deals with the Raman-Nath type[23] of diffraction in which the angular spread of the grating wave vector is larger than the Bragg angle. No self diffraction occurred for normal light incidence ($\beta = 0°$) neither at zero external electric field. The latter eliminates the possibility of grating formation due to pure thermal effects.

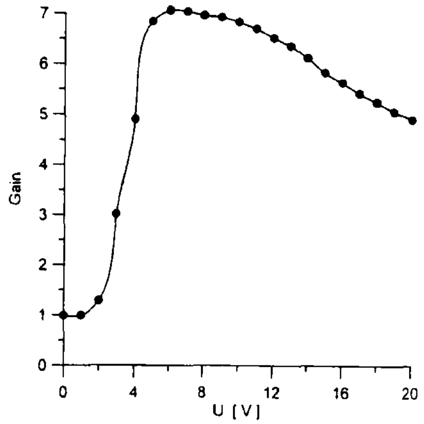


FIGURE 2. Probe beam gain g as a function of voltage U applied to the above described liquid crystal panel measured in two-beam coupling configuration. The thickness of E-7 nematic liquid crystal layer is $d = 10$ μm. Probe to pump beam intensity ratio $m = 10$, $I_{20} = 100$ mW/cm^2, $\lambda = 514$ nm, $\beta = 45°$, $\theta = 0.6°$, both beams are p-polarised. The line serves as a guide for eyes only.

RESULTS AND DISCUSSION

The index grating inside the nematic liquid crystal arise due to electric field driven reorientation of nematic director as a result of a spatially modulated space charge field created by a light intensity pattern in two surface layers of polymeric photoconductor. Light intensity pattern formed by two intersecting beams (plane waves) of intensities I_1 and I_2 has the form[23]:

$$I(x) = (I_1 + I_2)[1 + \frac{2\sqrt{I_1 I_2}}{I_1 + I_2}\cos(Kx)] \qquad (1)$$

where $K = 2\pi/\Lambda$, and Λ is the grating spacing. The respective sinusoidal space charge [2] grating is created under steady state illumination conditions in a photoconductive layers due to photogeneration and diffusion of charge carriers. The period of this grating, due to a tilting by angle β, will be higher $\Lambda_\beta = \Lambda/\cos\beta$ than the period Λ. The space charge electric field along the surface layers can

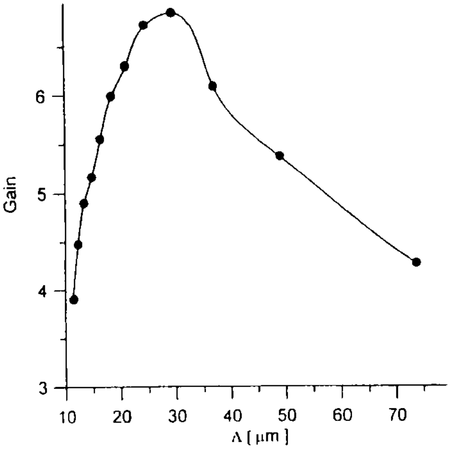


FIGURE 3. Plot of the net probe gain *g* as a function of grating spacing *Λ*. Other experimental conditions as in Fig. 2. The line serves as an guide for eyes only

$$E_\xi = E_{o,\xi}\sin(K_\beta \xi) \qquad (2)$$

where the axis x is turned by angle β with respect to the x axis (cf. Fig. 1). This means that due to pure diffusion process of charge carrier transport the electric space charge field grating is shifted by an angle π/2 with respect to the light intensity grating. The sum of electric space charge field E_x and externally applied electric field along the z-axis E_z form a complex modulated pattern inside a dielectrically anisotropic liquid crystal which leads to the periodic director reorientations along the lines of this resulting electric field. The reorientations of nematic director are possible if the local total field strength exceeds the electric Freedericksz threshold field. Then the director modulation is transformed into the periodic spatial modulation of the refractive index, i.e. into refractive index grating which has no simple sinusoidal form. Moreover, the index grating is not uniform throughout the thickness of the liquid crystal layer, being more pronounced nearby the both photoconducting polymer surfaces and weaker at the centre of the layer. Nevertheless between sinusoidal light intensity grating and refractive index grating exists a phase shift *f* responsible for the energy flow from one to another input beam[23]. The direction of the energy flow is determined be the sign of the angle ϕ. Experimentally it has been show that for a given experimental geometry the magnitude of angle ϕ and even its sign can be changed by the value and sign of the externally applied electric field strength, respectively.

The transfer of energy between the beams was measured by monitoring the (I_1) intensity of beam 1 after the sample without beam 2 applied, and (I_{12}) the intensity of beam 1 after the sample with beam 2 applied. The input beams intensities were different and their ratio $m = I_{20}/I_{10}$ was equal to 10, where the subscript 0 denotes the respective beam intensity before entering the sample. The highest weak beam amplification that we observed in the system studied amounted to $g = 7$ (g is called gain). For I_1 and I_{12} being the signal beam output in the absence (I_1) and presence (I_{12}) of the pump beam I_2 the gain g can be expressed as[24]:

$$g = \frac{I_{12}}{I_1} = \frac{1+m}{1+me^{-\Gamma L}} e^{\ \alpha L} \tag{3}$$

where α is the average absorption coefficient of a liquid crystal at the excitation wavelength, L is the interaction length and Γ is the exponential gain coefficient. This coefficient is expressed for a co-directional two-wave mixing by[24]:

$$\Gamma = \frac{2\pi n_{GA}}{\lambda \cos(\theta/2)} \sin\phi \tag{4}$$

where n_{GA} is the effective (averaged over thickness) amplitude of index of refraction grating. Putting $\alpha \cong 10\ \mathrm{cm}^{-1}$ and $\Lambda = d/\cos\beta'$ (where the inner incidence angle $\beta' = 26{,}22°$ for $\beta = 45°$ with n = 1.6) one finds $L = 11.15\ \mu\mathrm{m}$. The maximum exponential gain coefficient observed in the described system at optimal conditions amounted to $\Gamma \cong 2600\ \mathrm{cm}^{-1}$. This means that even for the thickness $L \approx 10\ \mu\mathrm{m}$ in this device an interesting regime of $\Gamma L > 1$ has been reached (here $\Gamma L = 2.893$) at the electric field strength of only 0.7 V/mm. The value of Γ reported by Wiederrecht et al.[6] for 37 mm thick nematic liquid crystal layer amounted to 640 cm^{-1}. In photorefractive polymers with $\Gamma = 200$

cm^{-1} this field is at least two orders of magnitude higher (120 V/μm) [25].

In the case of studied liquid crystal cell from the relation (4) one can evaluate the maximum refractive index grating amplitude assuming for the measured $G \cong 2600\ cm^{-1}$. Putting $\phi = \pi/2$ the value of averaged over thickness refractive index grating amplitude amounts $n_{GA} \approx 0.02$, which makes near 10% of the nematic liquid crystal birefringence. If in reality the phase shift is smaller f < p/2 then a higher values of refractive index grating amplitudes must be realised in the liquid crystal. In Fig. 2 we show how the beam coupling ratio $g = I_{12}/I_1$ changes in function of voltage applied to the 10 mm thick liquid crystal layer. The intensity of stronger beam was set to I_{20} = 100 mW/cm^2. There is no gain (g = 1) for voltages in the region below the characteristic Freedericksz effect threshold voltage ($U_{th} \sim 2V$). A further increase of voltage causes a steep rise of gain to the maximum value of $g = 7$ which is reached at $U = 6V$. For still higher voltage there is a smooth decrease of gain to the value $g = 5$ at 20 V. The decrease of gain with an increase of voltage in the region 8 - 20 V is connected with the change of refractive index profile across the sample thickness which changes from being sinusoidal for smaller voltages to nonsinusoidal for higher ones[26]. The sharpness of *g(V)* curve corresponds to the sharpness of the derivative of an effective extraordinary index of refraction n_e^{eff} versus voltage[10] in the vicinity of electric Fréedericksz transition in nematics. The levelling off *g(V)* curve seen at higher voltages applied to the sample reflects a state of complete, nearly homeotropic, ordering in LC layer which does not favour further director reorientation.

In Fig. 3 we plot the dependence of gain g on grating spacing Λ. It is clearly seen that there is an optimum grating spacing ($\Lambda \cong$ 30 μm) for which the gain is at its maximum. A fast gain decrease is seen when grating spacing decreases and slower when grating spacing increases. However, a high gain $g >$ 4 can be observed within a L range 5 - 80 mm. One can tentatively explain the

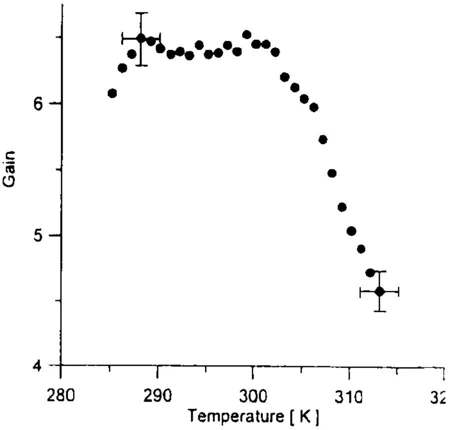


FIGURE 4. Plot of the probe beam gain as a function of temperature of liquid crystal panel.

gain reduction at lower grating spacings by elasticity of liquid crystal which resists to modulate its structure when period of modulation becomes small. This was proved both experimentally and by Monte Carlo simulation techniques applied to liquid crystal placed in the sinusoidally modulated electric field [26]. Explanation of gain drop at higher grating spacings can not be connected with the liquid crystal properties, then we linked it with the properties of the photoconducting polymer itself. The amplitude of space charge field generated by sinusoidal light intensity pattern in polymer depends on the effective charge transport length L_{eff}. For no applied field L_{eff} can be found from the carrier diffusion length L_D and the grating wavevector K_β[22]:

$$L_{eff} = \frac{K_\beta L_D}{1+(K_\beta L_D)^2} L_D \qquad (5)$$

where $L_D = (\frac{\mu \mathbf{k}_B T}{e} \tau_{rec})^{1/2}$ is the carrier diffusion length, μ is the carrier mobility, t_{rec} is the recombination time and k_B is the Boltzmann constant. L_{eff} is then a function of grating spacing ($K_\beta = 2\pi/\Lambda_\beta$) and has the maximum L_{eff} = 0.5, L_D at $L_{eff}K_b = 1$. Assuming that the observed by us maximum of gain in function of L_b can be attributed to the process of space charge field formation photoconducting polymer one can estimate the value of the product $\mu t_{rec} \approx 4\text{x}10^{-}$

^{9} m^2V^{-1}. Knowing, from separate measurements, either μ or τ_{rec} values the other can be estimated from grating measurements as presented in this work. The above estimation, however, should be treated with limited confidence as the position of the maximum of gain function may be apparent, being also dependent on the way of measurements e.g. for higher grating spacing less number of fringes is contained within a beam diameter what leads to the weaker diffraction of light, too.

Temperature dependence of gain within 285 - 315 K range has been presented for the studied sample in Fig. 4. Starting from 300 K a noticeable decrease of gain occurs. We believe that this decrease of gain is connected with the increase of disorder when temperature of the E-7 mixture approaches the clearing point temperature (331 K) and possible induced by temperature gradients flows of liquid crystal which partially destroy the refraction index gratings.

CONCLUSIONS

We have demonstrated how the use of a novel hybrid structure composed of nematic liquid crystal layer sandwiched between suitable ultra thin photoconducting polymeric surface layers can produce a photorefractive device with the ability of coherent beam amplification. The gain coefficient $g = 7$ obtained for only 10 μm thick liquid crystal layer in a conventional two-wave mixing experiment is one of the highest reported so far for the similar systems. The net exponential gain coefficient $\Gamma \approx 2600$ cm^{-1} is obtained at voltages smaller than 1 V/ μm. Devices of this type after maturation can easily be exploited in optical systems performing image amplification, image correlation or incoherent-to-coherent image conversion.

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