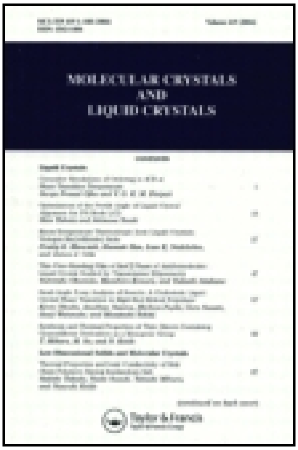

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Photorefractive Properties of Undoped Chiral Smectic C Phases of Cyclopalladated Complexes

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The photorefractive properties of chiral smectic C phases formed by cyclopalladated complexes were studied. The complexes were not doped with photosensitizers. A gain coefficient higher than 100 cm^{-1} at an applied field of 5.4 V/μm was measured. Measurements of phase shift between interference fringes and index grating were also performed. By using a previously developed model, the amplitude of the space-charge field was estimated and shown to be much smalled than what predicted by the commonly used model for photorefractive inorganic crystals.

Keywords: liquid crystals; non-linear optics; photonics; photorefractivity; smectics

INTRODUCTION

In recent years, intense efforts have been devoted to the study of organic materials that could replace inorganics in several applications in which electrical conductivity is a crucial parameter. In fields such

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as photovoltaics or LED's the performance of organic materials has neared, and for some parameters is already better than, the performance of inorganics. In particular, optical media for data transfer and storage and image treatment are the focus of intense research, including substances in which optical encoding is based on the modulation of the refractive index induced through the photorefractive effect [1,2]. In photorefractive materials, charges created as a result of light absorption are redistributed in space by diffusion or under the effect of an applied electric field. Through such mechanism it is possible to set-up a non-uniform space distribution of charges which reflects the light illumination pattern: the resulting electric field is called space-charge field. If the material exhibits a field dependent refractive index, a volume hologram is written which is a replica of the light distribution in the material. The refractive index distribution will be phase shifted with respect to the light intensity, since the space-charge field depends on the gradient of the charge density, and in this sense photorefractive holograms are often described as non-local. Several other physical mechanisms (photoinduced reactions, photoisomerizations etc.) can be associated with light induced refractive index changes but in all these cases the index change is proportional to the local light intensity. The unique property of non-locality of photorefractive holograms is important since it is the origin of energy exchange, for example, between the same two coherent beams which write a periodic refractive index modulation in the medium, a property that can be exploited in a variety of applications.

Several different physical mechanisms can be at the origin of the field induced refractive index variation in photorefractive materials. Second-order nonlinear optical effects are active in traditional inorganic crystals, as well as in amorphous organic polymers or glasses [3,4]. In these last materials a contribution from orientational birefringence is also present [5]: the birefringence is induced by the total electric field, the sum of an applied field, which is used to pole the sample in order to achieve noncentrosymmetry, and of the photoinduced space-charge field. The molecular dipole moments of the nonlinear chromophores are partially oriented by the field and, since its space-charge component is space modulated, a spacially periodic refractive index is obtained. The understanding that such orientational effects are the dominant index modulation contribution in most highly efficient polymers [6,7], led the way to the development of liquid crystalline photorefractive materials, in which birefringence is high and spontaneous. Both bulk [8–10] and dispersed [11,12] nematic liquid crystals have been shown to exhibit excellent photorefractive performances and, more recently, also chiral smectics [13–15], where the field induced refractive index modulation is not a consequence, like in nematics, of dielectric anisotropy, but of different linear interactions. In most of the reported investigations, the liquid crystalline phase is not intrinsically photoconducting, so that the space-charge field set up is achieved either by dissolving a light sensitizer (and often a charge transport agent as well), or by placing the mesophase within (like in dispersed systems), or between layers of, a photoconducting material. In this work we present instead an example of a smectic mesophase that exhibits photorefractive behaviour without any doping [16]. We will also describe a measurement of the photorefractive space-charge field in a chiral smectic C phase [17], which is not obtained through any of the models developed for crystalline or amorphous media, but instead considering the specific properties of the SmC* mesophase [18]. We will also see how the use of the standard models for inorganic materials would have given results which are considerably different.

MATERIALS, SAMPLES PREPARATION AND EXPERIMENTAL METHODS

The chemical structure of the materials which were used in the present investigation is shown in Figure 1. They are two heteroligand cyclopalladated complexes, [(Az)Pd(Lm)] containing one or two stereogenic centres, obtained by reaction of the chiral 4-tetradecyloxy-4′-S-(-)-β-citronelloloxyazobenzene (HAz) with a Schiff base, namely the N-[4′-(dodecyloxy) resorcylidene]-4-(S-(-)-β-citronellolloxy)aniline (HL1) and the N-[4′-(dodecyloxy)resorcylidene]-4-octylaniline (HL2), as previously reported [19]. In both cases, after each synthetic step the resulting product was purified by recrystallization. The purity of the intermediate and final products was controlled by elemental

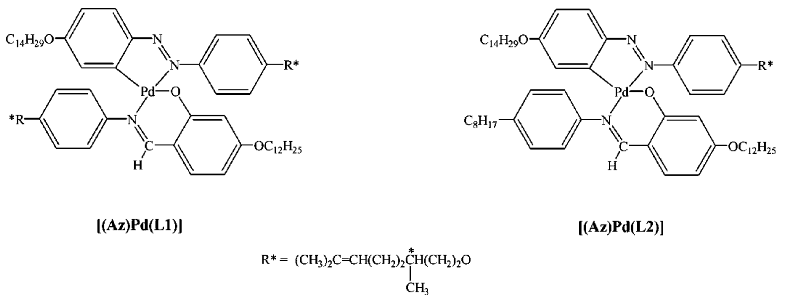

FIGURE 1 Chemical structure of the mesogenic cyclopalladated complexes.

analysis and spectroscopic techniques (IR, NMR, UV/VIS). No evidence of the presence of contaminants was found. Both complexes show an enantiotropic smectic C* phase (with the typical broken focal-conical texture, at 67 and 85°C, respectively) which trasforms at 77°C, into a N* phase for [(Az)Pd(L1)] (with an oily streaked texture) or, in the [(Az)Pd(L2)] case, into a SmA phase with a fan-shaped texture, at 90°C. Both complexes melt below 100°C and, on cooling from the isotropic liquid, the mesophase remains stable until −30°C.

Samples of the two materials were placed between ITO covered glass slides. On one of the two glass slides a layer of Nylon 6 or polyimide was spin-coated on ITO from solution. The polymer was then rubbed unidirectionally and cells were prepared by joining one glass treated as described with another glass where a layer of (3-glycidoxypropyl)-trimethoxysilane was spin-coated from a water/isopropanol 1:9 solution. The second slide was not rubbed. The thickness of the liquid crystal was controlled by using spacers ranging between 1.7 and 9 μm. Interferometric measurements of the thickness of empty cells were performed. Cells were then filled by capillarity with the liquid crystal and slowly cooled in order to obtain a good orientation of the director within the SmC* phase.

The spontaneous polarization was measured by using the well known triangular waveform voltage method [20]. Photorefractive properties were investigated by using the two-beam coupling technique, i.e. by monitoring the intensities of two p-polarized coherent He-Ne laser beams superimposed on the sample. The intensity of both beams was 3 mW and their diameter 0.9 mm. The sample normal was tilted by 56° with respect to the beams bisector and the direction of rubbing on the polymer layer was in the s plane. As usual with organic materials, a DC field was applied on the sample to increase photogeneration efficiency and provide a drift mechanism.

For the measurement of the phase shift, the intensity of both laser beams was recorded while the sample was translated at constant speed along the grating wavevector. The total translation time was chosen to be much smaller than the grating formation time. Phase measurements are usually affected by a large error. We were able to considerably reduce the error by repeating the measurements several times and by averaging the measured phase shift values.

PHOTOREFRACTIVE BEHAVIOUR

The cyclopalladated complexes that we used in the experiments are not easily aligned by standard aligning methods and materials. Several aligning surfaces were tried and the best results were obtained by

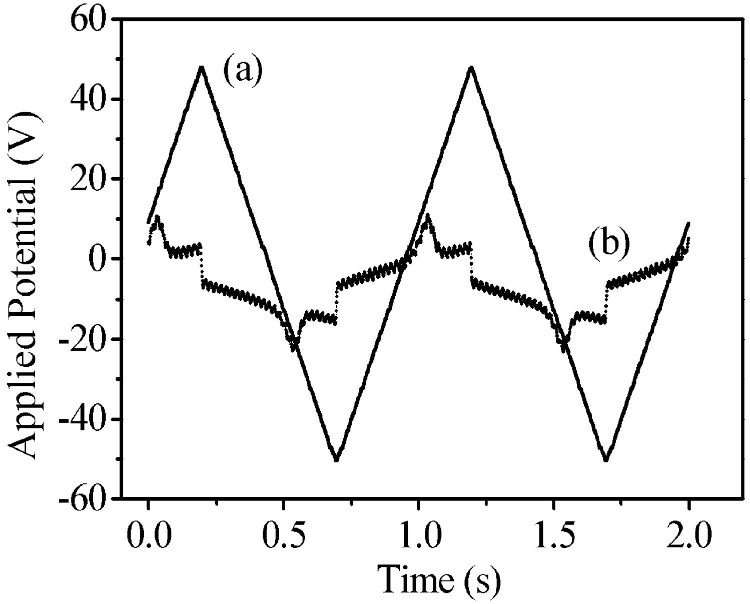

FIGURE 2 Applied voltage (a) and current response (b) of an [(Az)Pd(L1)] sample for spontaneous polarization measurement. The current was measured by monitoring the voltage across a resistor in series with the sample. The vertical scale refers to the applied voltage (a); the scale for curve (b) in this figure is arbitrary.

using the materials described in the experimental section with a very slow cooling rate in the presence of an applied electric field. Nonetheless, without an applied field the alignment was never good over the entire sample and experiments were performed in the better aligned regions.

The first characterization performed was the measurement of spontaneous polarization. This was done by applying a triangular waveform electric field while simultaneously measuring the current through the cell [20]. Typical results are illustrated in Figure 2. The spontaneous polarization, measured five degrees below the transition in the SmC* phase, at the same temperature of the photorefractive characterization, was rather low $P_s = 1.1 \pm 0.1\,\mathrm{nC/cm^2}$. In addition, the reorientation time was also relatively long, in the 100 ms range.

The photorefractive nature of our materials was investigated by using the two-beam coupling technique, as described in the experimental section. The intensity of the one writing beam was followed in time, with an applied field turned on, before and after the turning

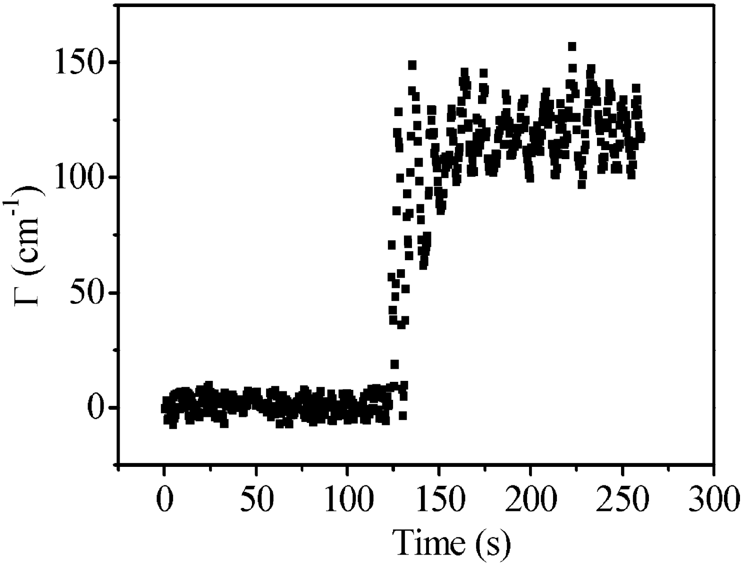

FIGURE 3 Gain coefficient Γ measured in a two-beam coupling experiment as described in the text for a sample of [(Az)Pd(L1)] at an applied field of 5.4 V/μm and a 15 μm grating spacing.

on of the second light beam. In a twin experiment, the role of the two writing beams was reversed. In photorefractive media, the index grating resulting from the simultaneous presence of the two writing beams produces an asymmetric exchange of energy between them. The gain coefficient Γ was calculated using $\Gamma d = [\cos\alpha_1 \ln\gamma_1 - \cos\alpha_2 \ln\gamma_2]$, where $\gamma_i = I_i\,(I_j \neq 0)/I_i\,(I_j = 0)$ (1 and 2 indicate the two light beams), d is the sample thickness and α_i is the internal angle between the sample normal and the i beam. Figure 3 shows the results in the case of a sample of [(Az)Pd(L1)] where a gain larger than 100 cm^{-1} was measured. This is, for what is in our knowledge, the largest gain ever measured in photorefractive SmC* phases. In addition, it should be underlined that such results are obtained from pure samples, without the addition of any dopant to increase photogeneration or conduction.

Thick samples, as the ones used for the experiments described in Figure 3, are not bistable and in order to achieve bistability, samples with a thickness within the 1.5–2 μm range were prepared. In this case bistability was observed, as described in Figure 4. In such experiments a DC pulse was applied and the light transmission through the sample placed between crossed polarizers was followed. Although bistability is

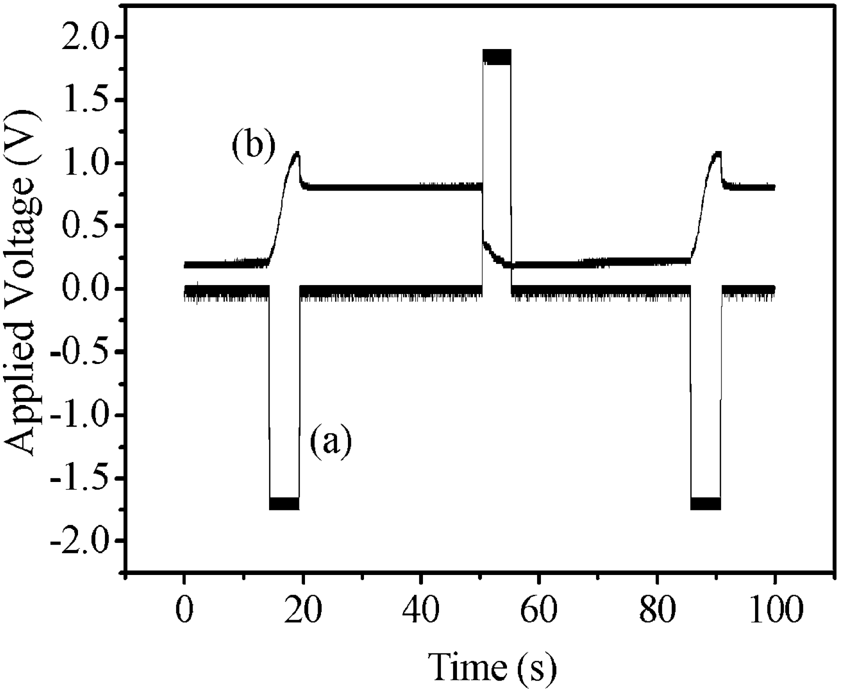

FIGURE 4 Applied voltage (a) and optical response (b) for an [(Az)Pd(L2)] sample 1.7 μm thick. The sample was placed between crossed polarizers.

clearly demonstrated, the response to the applied pulses is much slower than the response of spontaneous polarization illustrated if Figure 2. We did not investigate this in detail but we believe that the behaviour might be associated with some kind of surface dynamics that, with our materials, seems to be necessary to obtain bistability. Unfortunately, in thin samples two beam coupling, if present, was below the detection limit of our set-up. In fact, given the exponential nature of intensity gain in photorefractive media, with a gain coefficient $\Gamma = 100\,\mathrm{cm}^{-1}$, the intensity variation of the interacting beams is more than 10% in samples around 10 μm thick but for thicknesses below 2 μm it decreses to below 2%, too low to be separated from noise in our experimental conditions. For such reason, even if photorefractive thin bistable films are potentially very interesting, such experiments did not have a follow-up.

One important consequence of the non-local nature of the photorefractive index modulation is its displacement with respect to the light pattern from which it originates. With light patterns that derive from

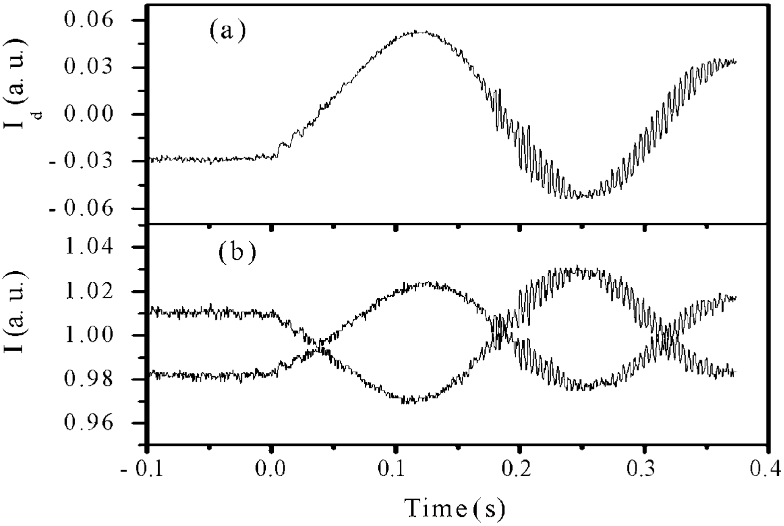

FIGURE 5 Time evolution of the writing beams intensities (b) in a two-beam coupling experiment under a sample translation starting at a time t = 0, for an [(Az)Pd(L1)] sample. The difference between the two beams intensities, from which the phase shift can be extracted, is shown in (a).

the interference of two coherent beams, as in our case, this means that there is a phase shift Θ between interference fringes and refractive index grating. This parameter was measured by monitoring the intensities of the beams in two-beam coupling experiments during a fast (compared to the grating erasure time $\tau \sim 2\,\mathrm{s}$) displacement of the sample along the grating wavevector after grating formation [21]. A typical resulting time evolution of the beams intensity is illustrated in Figure 5. From these data the value of Θ for the phase grating can easily be extracted: at $E_0 = 5.4\,\mathrm{V}/\mu\mathrm{m}$ we obtain $\Theta = 31^\circ \pm 4^\circ$. This value of applied field was chosen because it was high enough to induce a clearly observable index modulation without dielectric breakdown.

MEASUREMENT OF THE PHOTOREFRACTIVE SPACE-CHARGE FIELD

Since the gain coefficient Γ can be expressed as [1]:

$$\Gamma = \frac{2\pi}{\lambda}\Delta n \sin\Theta \tag{1}$$

where λ is the light wavelength and Δn is the refractive index modulation amplitude, the measurements of gain coefficient and phase shift described in the previous section can be used to obtain values of Δn by using Eq. (1). These results can then be compared with calculations of Δn obtained from a model [18] that was recently developed to describe, in simple terms, the director distribution and the associated refractive index modulation in SmC* phases, in the simultaneous presence of a homogeneous and a space modulated (in our case the photogenerated one) electric fields. In this model a number of parameters are considered, and in particular sample orientation relative to light direction, light polarization, spontaneous tilt angle, ordinary and extraordinary refractive indices of the liquid crystal and the ratio k between the amplitudes of the modulated and the uniform electric fields. As all these parameters but the last one can be controlled during experiments or measured, the model provides a dependence of Δn as a function of the ratio k between the space-charge and the uniform applied field. In order to increase the accuracy of the comparison, both measurements and calculations were carried out as a function of light polarization. The resulting polarization dependence of Δn, obtained from Eq. (1) by inserting the measured values of Γ and

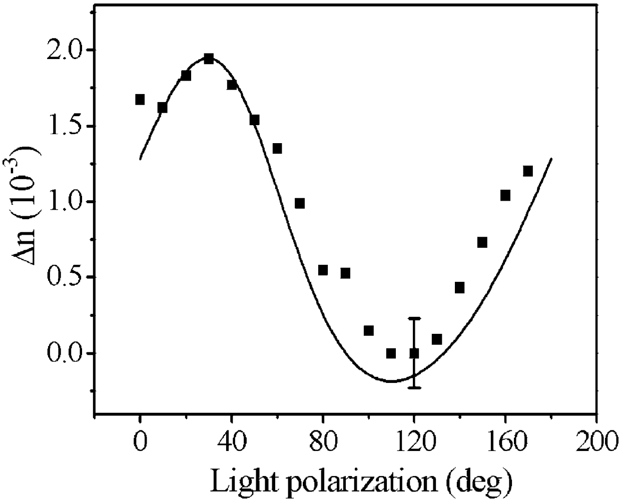

FIGURE 6 Refractive index modulation Δn measured as a function of the polarization of the writing beams at E = 5.4 V/μm (dots) for an [(Az)Pd(L1)] sample. The 0 of polarization is set for light polarized in the p-plane. Data have been obtained for a 15 μm grating spacing. The refractive index modulation Δn (full line) was calculated by using the model described in Ref. [18].

Θ, is shown in Figure 6. In the same figure the values of Δn calculated by using the previously mentioned model for the index modulation in photorefractive SmC* phases are shown. The geometrical parameters used in the simulation were the same as in the experimental setting. In addition, experimentally determined values for the spontaneous tilt angle ($\Psi = 36.5^\circ$, from polarized optical microscopy and powder X-Ray diffraction), and for the mesophase optical anisotropy ($\delta n = n_e - n_o = 0.45 \pm 0.05$, from phase retardation measurements) were used. The best fit of the experimental data is obtained for $k = 9 \pm 1 \times 10^{-3}$, which gives for the amplitude of the space-charge field $E_{SC} = 2.5 \times 10^{-2}\,\mathrm{V}/\mu\mathrm{m}$.

This result should be compared with the standard model developed for the calculation of the space-charge field in inorganic crystalline materials [1,2,22], where light absorption is due to impurity levels within the electronic band gap and conduction is treated by considering electron bands. This model is often used to calculate space-charge field values in organic amorphous materials as well, since similar models developed for organic materials [23,24] contains a large number of parameters, often unknown, a fact that prevents a realistic comparison with experimental data. In our model instead, the space-charge field is derived from its effect on the director orientation and refractive index modulation. Within the frame of the model valid for inorganic photorefractive crystals the space charge field is given by:

$$E_{SC}^2 = E_q^2 \frac{E_d^2 + (E_0 \sin\theta)^2}{(E_q + E_d)^2 + (E_0 \sin\theta)^2} \tag{2}$$

and its phase difference with the interference fringes by:

$$\tan\Theta = \frac{E_d^2 + E_d E_q + (E_0 \sin\theta)^2}{E_q (E_0 \sin\theta)} \tag{3}$$

where $E_d = 2\pi k_\mathrm{B} T / e\Lambda$ is the so-called diffusion field and E_q is the trap-limited field. Here $\mathrm{k_B}$ is the Boltzman constant, T the temperature, e the electron charge and Λ the period of the space-charge field. Using Eqs. (2) and (3) and the measured value for Θ, we obtain $k \sim 0.85$, i.e. a space-charge field two orders of magnitude higher than what derived with our model. This result suggests that the model developed for inorganic crystalline materials to describe the set-up of a photorefractive space-charge field cannot always be extended to amorphous phases or mesophases, as it is instead very often found in the literature [3,25].

CONCLUSIONS

We have shown the properties of the first smectic liquid crystal in which photorefractivity is an intrinsic property, not induced by the addition of photosensitive dopants. The material used are mononuclear chiral cyclopalladated complexes [(Az)Pd(L1)] and [(Az)Pd(L2)]. Since the conduction is in our case due to electron hopping, rather than ionic transport as in doped systems, this work is a significant step towards the development of high performance photorefractive materials, although this implies the use of slightly higher applied fields. The use of relatively elevated temperatures (60–70°C) is not instead a necessary requirement in principle, since synthetic work may produce in the future a photoconducting medium with a SmC* phase at room temperature. A gain coefficient Γ higher than $100\,\mathrm{cm}^{-1}$ was measured at an applied field $E_0 = 5.4\,\mathrm{V}/\mu\mathrm{m}$ in two-beam coupling experiments.

We have also shown that it is possible to derive the amplitude of the space-charge field in photorefractive SmC* phases. The field was measured independently from existing models for crystalline or amorphous media. At an applied field $E_0 = 5.4\,\mathrm{V}/\mu\mathrm{m}$, results show that the photoinduced space-charge field is about two orders of magnitude smaller than the applied field. Nonetheless, given the high spontaneous birefringence typical of liquid crystals, the resulting refractive index modulation is of the order of 10^{-3}. The use of the existing standard model for photorefractive inorganic materials would have given a modulated field two orders of magnitude higher. These results indicate that caution should be used when experimental results on photorefractive organic materials are interpreted in terms of models developed for inorganic systems, at least in the case of liquid crystals.

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