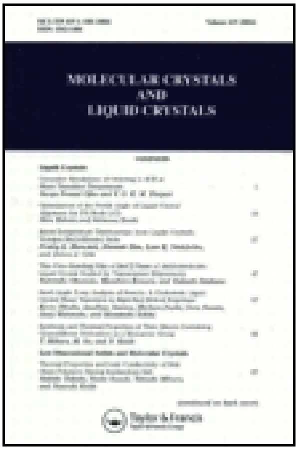

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Nano-Dispersed Organic Liquid and Liquid Crystals for All-Time-Scales Optical Switching and Tunable Negative-and Zero- Index Materials

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Nano-Dispersed Organic Liquid and Liquid Crystals for All-Time-Scales Optical Switching and Tunable Negative-and Zero- Index Materials

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We present an overview of recent results obtained in nano-dispersed nonlinear neat organic liquids and liquid crystals. Experimental observations confirm the enhancement of nonlinear absorption in gold nano-spheres doped neat nonlinear liquids and extension of the bandwidth of efficient all-optical switching operation for visible-near infrared lasers in time scales ranging from sub-picoseconds through nanoseconds and microseconds and longer. Similar nano-particulate doped liquid crystal films also exhibit efficient all-optical switching capabilities for microseconds – cw lasers. Meta-materials fabricated with core-shell nano-spheres dispersed nematic liquid crystals show effective refractive indices that are tunable from negative through zero to positive values.

Keywords: all-time-scales; liquid crystal; neat organic liquid; negative and zero refractive index; passive optical switching; sensor protection

I. INTRODUCTION

Recent rapid development and widespread use of high power lasers have intensified the development efforts for sensor protection devices capable of clamping the laser power to below the Maximum Permissible Exposure (MPE) level [1]. Against such agile frequency lasers, fixed filters are ineffective. A preferable alternative is passive

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all-optical switching that utilizes the nonlinear optical responses of the materials to trigger intensity/power control [2–10]. The incident light self-induces spatial and/or temporal changes in its phase and/or amplitude and emerges from the materials with a transmission level clamped below the MPE levels. In these contexts, nonlinear organic liquids and liquid crystals have been actively investigated [2–4,9–13]. In particular, liquids which possess strong two-photon and excited state absorption have proven to be quite effective for picoseconds and nanoseconds laser pulses [4,9,10]. Nevertheless, such dependence on the intensity of the laser renders all nonlinear absorbers ineffective for longer laser pulses. On the other hand, liquid crystals, particularly nematics, possess extraordinary large optical nonlinearities that enable all-optical switching with very low threshold but at much slower response speed, typically in the milliseconds region [2,3,11–13], except in some special cases where the response speed can be shorter [12,14–18].

Many approaches have been employed to improve the response speed in both classes of materials, in order to bridge the temporal gap in which they do not operate satisfactorily. In this paper, we describe recent results obtained in nano-dispersed nonlinear neat organic liquids and liquid crystals that exhibit extraordinary properties. These nano-particulates, such as gold (Au) and silver (Ag) nano-spheres enhanced the nonlinearities of the host materials, and/or introduce new nonlinear optical mechanisms for passive optical switching in time scales not possible with the hosts. As a result, one could envision integrated compact liquid/liquid-crystal structures for all-time-scale switching applications.

II. NANO-DISPERSED ORGANIC LIQUIDS FOR MULTIPLE TIME SCALE ALL-OPTICAL SWITCHING

Perhaps the most noteworthy nonlinear neat organic liquids developed for passive optical switching application is L34 [9]. Its molecular structure and (linear) transmission spectrum is depicted in Figure 1. Embedded in this rather broadband [$\sim$400 nm–1600 nm] linear transparent spectral window is a much-sought-after nonlinear multi-photon absorption pathway. The molecular photonic transitions start with two-photon absorptions (TPA) from the ground state; from there the molecule can make single photon transitions to high lying singlet excited state, and/or undergo intersystem crossing to a triplet manifold followed by a (single-photon) transition to higher excited state. Since the initial transition is a two-photon process, the molecule

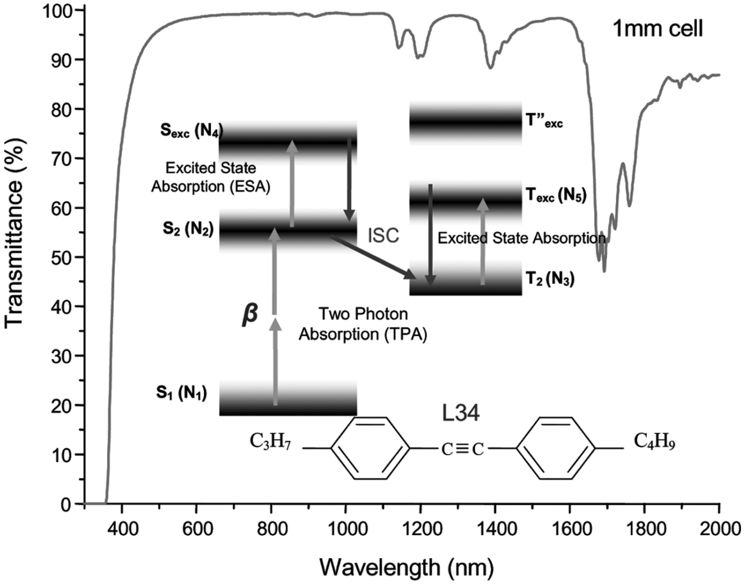


FIGURE 1 Linear transmission spectrum of a neat nonlinear organic liquid L34 showing large transmission window in the spectral region from 450 nm–1600 nm. Insert shows the molecular structure and various photonic transitions.

is essentially transparent at low light level. It becomes increasingly absorptive as the incident laser intensity becomes more intense and facilitates these multi-photon absorption processes; the laser light thus self-attenuates as it propagates through the liquid.

The actual coupled differential equations for the molecular energy level populations and laser pulse propagation are rather complex [9]. To illustrate the physics, a qualitative approach is to describe the evolution of the laser intensity I by an intensity-dependent effective absorption coefficient β_{eff}, i.e. $\mathrm{d}I/\mathrm{dz} \sim -\beta_{\mathrm{eff}}\mathrm{I}$. For purely two-photon absorption, β_{eff} the intrinsic absorption coefficient β becomes dependent on the intensity of the laser as well as the laser pulse duration τ_{p} relative to the inter-system crossing times τ_{is}. Usually τ_{is} is on the orders of nanoseconds. In the femtoseconds–picoseconds time scale, the principal process involved is two-photon transition characterized by the intrinsic coefficient β. For L34, β is on the order of $\sim 4\,\mathrm{cm/GW}$ [9,10]. This is sufficient for clamping the transmission of picoseconds laser pulses to below the maximum permissible exposure MPE level of the eye or optical sensors.

On the other hand, if the impinging laser pulses are in the nanosecond time scale, the two-photon excited state will have time to relax to states that could make efficient single-photon transition to higher lying excited states in the singlet or triplet manifolds. In this case, for L34, β_{eff} can be as large as 230 cm/GW [9,10]. Thus, although nanosecond laser pulses are (for a given laser energy fluence) much less intense than picoseconds and pulses, the larger values of the effective nonlinear absorption coefficient are able to 'compensate' for the lower intensities and maintain the limiting action [9,10].

For longer time scales [100's nanoseconds–microseconds] where the laser intensity is so weak that the initial two-photon transition that generates subsequent nonlinear absorption processes is practically vanishing, all known nonlinear absorbers begin to fail as optical limiters. To circumvent such temporal/intensity limitations, one approach is to synthesize more efficient (larger β or β_{eff}) new compounds but such process invariably alters other desirable properties (e.g. neat liquid form, linear transparency ... etc). To preserve these properties while adding new functionalities and also to enhance the nonlinear responses, we have pursued the guest/host approach whereby nano-particulates are dispersed in the nonlinear liquids. To these ends, we have synthesized gold (Au) and silver (Ag) nanospheres of diameters ranging from 2.5 nm–40 nm and they are functionalized with Thiol to prevent conglomeration and to facilitate their dispersion in L34 and similar organic liquids. Figure 2 shows the absorption spectra of Au-doped L34 (Au/L34) and pure L34; they clearly show a pronounced peak at ~380 nm and enhanced linear absorption that extends from there to the near IR regime. As a result, they give rise to strong nonlinear scattering and thermal/density effects (change of refractive index and defocusing) otherwise absent in the transparent host liquid. Some preliminary picoseconds nonlinear transmission studies at 460 nm also shows that the nonlinear absorption coefficient is enhanced by a factor of ~3 while nanosecond studies revealed even more dramatic reduction in the switching threshold [19].

The exact mechanism(s), including plasmonic field enhancement by the Au nano-spheres or its intra- band transitions nonlinearities [20,21] ... etc underlying these enhanced performances remain to be quantitatively ascertained. Nevertheless, nonlinear transmission experiments with microseconds lasers have demonstrated that Au/L34 is capable of efficient passive optical switching as a result of the nonlinear absorption, nonlinear scattering and self-defocusing. Figure 3 shows a plot of the output vs. input of q-switched (300 ns full width) 750 nm laser through a 2 mm thick Au-L34 sample in a

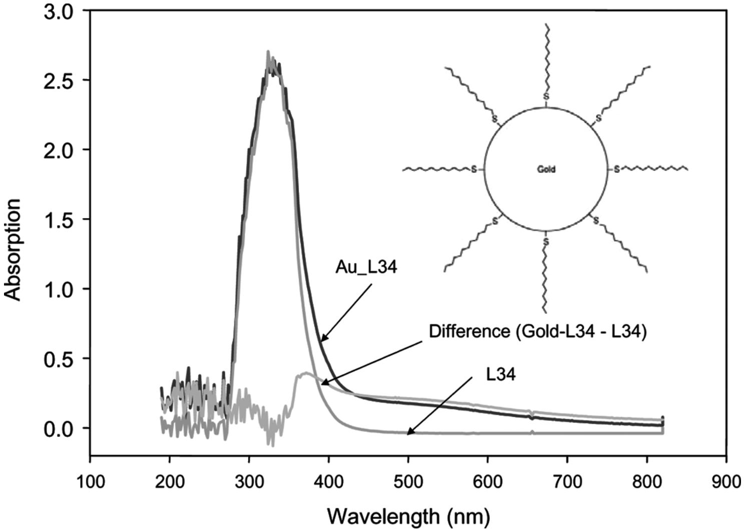


FIGURE 2 Schematic depiction of the dodecanethiol – coated gold nanospheres and the resulting absorption spectra of L34 and the Au-Nano doped L34 and the. Bottom right curve shows the differential absorption spectrum of dodecanethiol – coated gold.

closed aperture set-up. The concentration of Au is such that the linear transmission of the sample is ~50%. The laser is focused by a lens of focal length 5 cm to an estimated spot size of ~100 μm. The size of an aperture placed downstream in a F6 set-up allows the low energy (< 1 μJ) laser pulses to pass through. At high power, it is observed that the laser is strongly scattered and defocused. The 2 mm bulk cell, with the help of the aperture in front of the downstream detector, is able to clamp the transmission to ~2 μJ for input up to 2 mJ.

We have repeated the experiment with the laser operating in the (multiple-spikes) free-running mode (30 μs total pulse duration), and observed similar nonlinear transmission performance (Fig. 4). Au-doped L34, therefore, could be used for clamping pulsed lasers over the vast time scale ranging from picoseconds through nanoseconds to microseconds. In some preliminary studies, we have also observed similar nonlinear transmission behaviour for milliseconds – cw lasers, and so Au/L34 could be an all-time-scale optical switch. However, its performance in the microseconds – cw time scales may not be able to match other materials such as liquid crystals that are more suited to slower time scales operations.

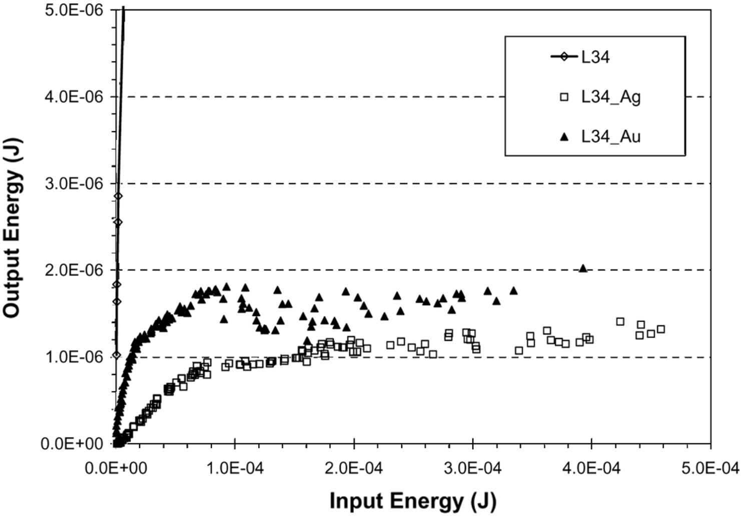


FIGURE 3 Plot of the output versus input of a 750 nm Q-switched lasers (~100 ns duration) through 2 mm Au (2.5 nm) and Ag (4–5 nm) nano-sphere doped L34 bulk liquids. Almost linear curve is from pure L34.

III. NANO-DISPERSED LIQUID CRYSTALS FOR ALL-OPTICAL SWITCHING AND NEGATIVE-ZERO REFRACTIVE INDEX MATERIALS

Nematic liquid crystals (NLC) are perhaps the most widely studied liquid crystals for nonlinear optics. The principal mechanism employed in these studies is the optically controlled birefringence ($\Delta n = n_e - n_o$) of NLC. The birefringence change can be effected by polarized laser light induced crystalline (director) axis reorientation. The reorientation changes the refractive index as 'seen' by the laser, giving rise to an optical intensity dependent refractive index. This process is however quite slow, with response times ranging from milliseconds to seconds, although there were studies [12,14–18] that showed that intense nanosecond laser pulses could create director axis reorientation in that time scale.

A faster mechanism to effect birefringence changes is laser induced order parameter (S) and/or temperature (T) modification. A reduction in the order parameter and/or rise in temperature will reduce the birefringence of the liquid crystal as it approaches the isotropic disordered phase. These processes originate from photo-absorption and can be enhanced if the liquid crystal is absorptive or doped with appropriate photosensitive azo-molecules or nano-particles [12,22–24].

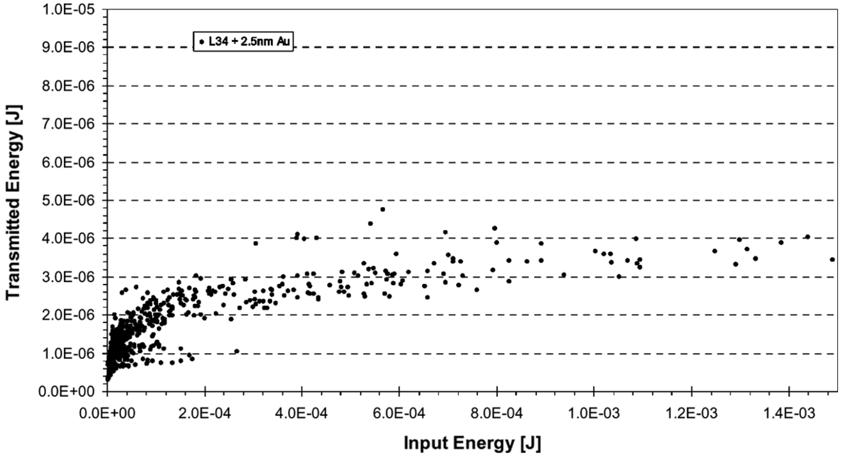


FIGURE 4 Plot of the output versus input of a 750 nm free running (30 μs) pulsed lasers through 2 mm Au (2.5 nm) nano-sphere doped L34 bulk liquid.

Photo-absorption gives rise to conformational changes of the dopants [e.g. trans-cis isomerism in azo-molecules] and/or increase in the temperature; the order parameter S and therefore the birefringence of the nematic will be reduced, i.e. $\Delta n \rightarrow 0$ as the laser intensity is increased. Such laser induced index or birefringence changes, so-called optically controlled birefringence (OCB) are characterized by response times ranging from 10's nanoseconds–microseconds.

Figure 5 shows an exemplary illustration of how OCB in a 90°-twist aligned nematic liquid crystal cell can be used for passive optical switching [13,23]. A polarized laser incident with the polarization vector parallel to the director axis at the entrance plane will follow the rotation of the director to emerge with the polarization vector rotated by 90° at the exit plane, and is thus maximally transmitted by the exit polarizer. If the intensity of the laser is increased, Δn will decrease through temperature rise and/or order parameter reduction, the twist alignment will be degraded, and the polarization rotation action on the laser diminished. The transmitted laser intensity is therefore also reduced.

Such dye-doped liquid crystals have been found to yield very efficient and high extinction optical switching results with response times that can be in the sub-milliseconds regime [see also Ref. 14]. From the previous section on Au/L34 liquid for passive switching in the microsecond time scales, we expect Au nano-spheres to perform similarly in liquid crystals. This is indeed borne out in our recent

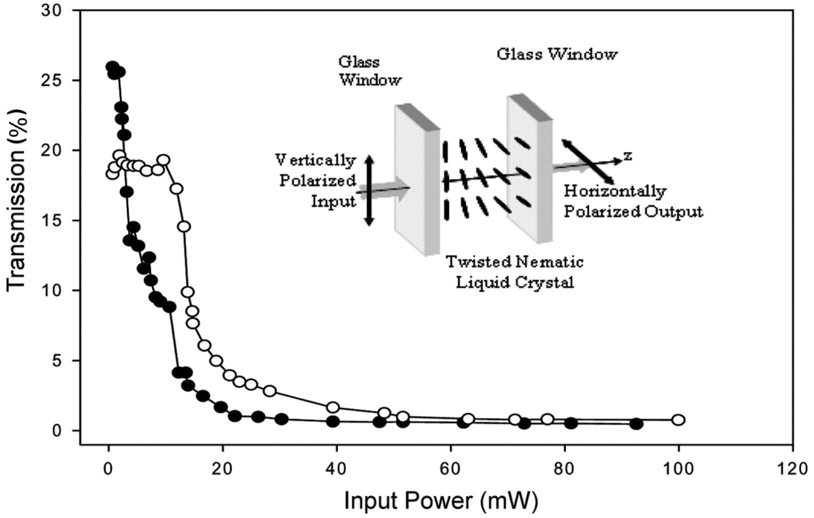


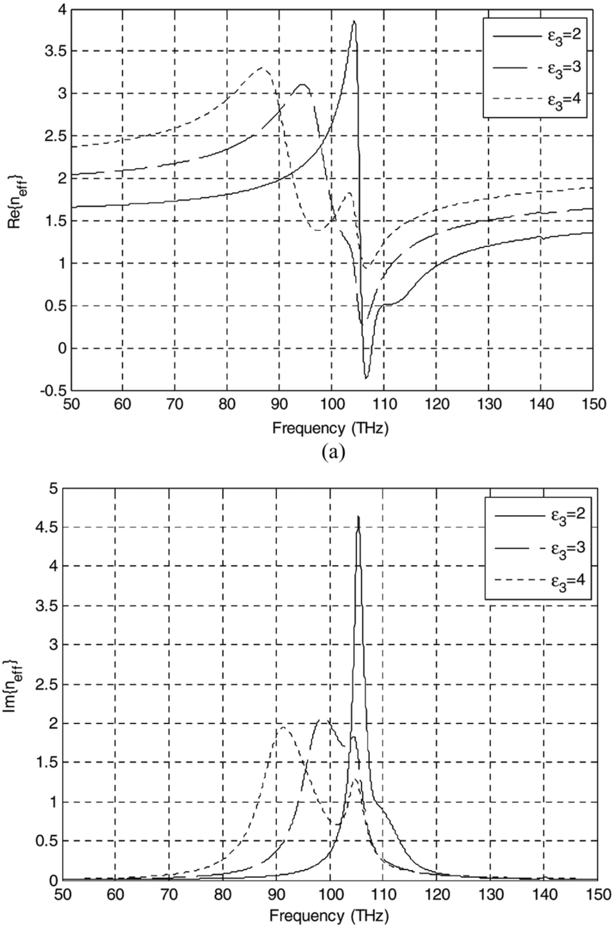
FIGURE 5 Power dependence of the transmission of a linearly plolarized 488 nm cw laser through a Au-doped 90° twist alignment nematic liquid crystal cell of two different thickness.

experiment with Au nano-spheres doped nematic (Pentyl-Cyano-Biphenyl 5CB) 90° twist-alignment cell [13,23]. The laser light used is the 488 nm line of an Argon laser focused to a spot diameter of ~150 μm. As shown in Figure 5, the transmission of the [40 ms long square pulse] laser begins to drop dramatically above a certain threshold power [~10 mW and 1 mW for the 10-μm and 40-μm thick samples, respectively]. The clamped transmission can be reduced to a few 10's of μW for input power of 100 mW. With tighter focusing, the threshold can be reduced to sub-mW level and the switching-off time to the microseconds.

IV. TUNABLE NEGATIVE- AND ZERO- INDEX MATERIAL WITH NANO-DISPERSED NEMATIC LIQUID CRYSTALS

Photo absorption is associated with the imaginary part of the complex refractive index. The gold nano-dopant actually introduces modification to the real part of the refractive index. The modification can be substantial if the filling fraction (concentration) of the gold nano-spheres is sizeable; the effective refractive index of the resulting meta-material can be less than unity or negative, as illustrated in recent studies of nano-spheres doped nematic liquid crystals [25].

Furthermore, since the host liquid crystal's refractive index can be optically modified (or 'tuned'), such meta-materials thus possess nonlinear (or tunable) zero- and negative refractive indices. As the process involves random distribution of nano-particles, it is considerably simpler than other techniques that involve precise 3-D periodic arrangement [26–28] of nano-sized particles to yield bulk meta-materials.



(a)

(b)

FIGURE 6 Real [upper curve] and Imaginary [lower curve] parts of the complex effective refractive index of the core-shell nano-spheres dispersed nematic liquid crystals showing tunable refractive index from negative-positive values.

The nano-spheres can be in the form of simple single constituent metallic (gold, silver, and semiconductor) spheres or in core-shell structures. As an illustration, consider the case of a nematic host (dielectric constant ε_3) containing core-shell nanospheres made of a (Polaritonic) core and a (Drude, e.g. gold) shell [21,25,29,30]. The relevant parameters for various oscillation frequencies and damping constants: $\varepsilon(\infty) = 17$, $\omega_L/2\pi = 570\,\mathrm{THz}$, $\omega_T/2\,\pi = 240\,\mathrm{THz}$, $\gamma_1/2\,\pi = 2.5\,\mathrm{THz}$, $\mu_1 = \mu_2 = \mu_3 = 1$, $\gamma_2 = \omega_p/60$, $\omega_p/2\,\pi = 134.0\,\mathrm{THz}$. Using an effective medium theory [31], we have calculated the effective medium responses and specifically the effective refractive indices. Figure 6 shows the exemplary results for a filling fraction $f = 0.1$, $r_1 = 0.13\,\mu\mathrm{m}$, $r_2 = 0.143\,\mu\mathrm{m}$ As a result of the doping, the effective birefringence of the meta-materials is generally higher. In the low-loss (small imaginary part of n_{eff}) regimes around 50–70 THz, Δn is ~0.75 to 0.9 respectively. At 80 THz, where the loss is still acceptably low, the effective Δn is even larger [~1.1]. Note that there are regions [at ~105 THz] where the effective refractive index can assume negative-, zero- or sub-unity values as the liquid crystal host dielectric constant is varied.

V. CONCLUSION

In conclusion, we have demonstrated how nano-particulates could improve liquids and liquid crystals to yield new functionalities while preserving the desired properties of the pure materials. We show that gold-nano spheres can extend the bandwidth of operation from visible to the near infrared regime over all time scales. These liquids and liquid crystals could be placed in tandem for optical switching of lasers ranging from picoseconds through nanoseconds, microseconds to the cw regimes. They can also possess effective refractive indices below unity, zero or negative values.

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