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There is continued interest within the Department of Defense to develop new photonic materials to address a wide range of Warfighter needs such as target designation, Soldier identification, communication, visual displays, active and passive optical filtering, and chemical and biological sensing. Optical switching is an area of particular interest. In general, new optical materials are required that can switch their transmission state on and off quickly, that have high optical quality, that can operate over a broad and controllable range of wavelengths, and that are inexpensive and highly manufacturable. As a result of recent progress by researchers at NSRDEC, BEAM Engineering for Advanced Measurements Co. (BEAM). and Massachusetts Institute of Technology Lincoln Laboratory (MITLL), materials now exist that bring us closer to realizing these goals.

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ADVANCES IN ANISOTROPIC MATERIALS FOR OPTICAL SWITCHING

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ABSTRACT

There is continued interest within the Department of Defense to develop new photonic materials to address a wide range of Warfighter needs such as target designation, Soldier identification, communication, visual displays, active and passive optical filtering, and chemical and biological sensing. Optical switching is an area of particular interest. In general, new optical materials are required that can switch their transmission state on and off quickly, that have high optical quality, that can operate over a broad and controllable range of wavelengths, and that are inexpensive and highly manufacturable. As a result of recent progress by researchers at NSRDEC, BEAM Engineering for Advanced Measurements Co. (BEAM), and Massachusetts Institute of Technology Lincoln Laboratory (MITLL), materials now exist that bring us closer to realizing these goals.

1. INTRODUCTION

Electro-optical systems have a number of fundamental limitations when it comes to controlling light beams: they require power supplies that are typically bulkier and heavier than the optical system that needs to be controlled; they require electrodes in the path of the beam, and these are sources of absorption and losses; their speed is limited by the speed of electronic processes; and above all, they need to have highly elaborate sensor subsystems incorporated into the overall system to identify the radiation, determine its specifics, and provide feedback to the control electronics, and these electronic subsystems contribute further to the bulkiness and the electric power consumed by the system. Materials that directly respond to light beams by changing their optical properties would perform many of the tasks attempted by electro-optical systems while overcoming their limitations in dramatically simpler, lighter, and thinner packages, even in the form of thin coatings on conventional optics.

Anisotropic materials are the best candidates for this purpose since a change in the magnitude of their optical anisotropy and/or in the orientation of their optical axis can yield a sufficiently large change in the effective refractive index of the material, comparable to that obtained at transformation of a liquid into vapor. Liquid crystalline materials (LCs), both low-molecular weight as well as polymeric, make feasible such large changes of effective refractive index without a change in their physical state and shape, and therefore, with small energy expenditures. By that, LCs allow optical axis modulation at high spatial frequencies and thus are uniquely suitable for designing optical structures that maximize the effect of changing birefringence/orientation on propagation of light beams. Other advantages of LCs for all-optical system developments include inexpensive synthesis, straightforward customization of their molecular architecture to produce desired properties, compatibility with nanotechnologies and the possibility of using nanomaterials for further enhancing their functions and performance. This work reviews the main concepts, and presents the state of current achievements and remaining challenges.

1.1 Azobenzene: highly efficient photoswitchable molecule

Anisotropic molecules based on azobenzene are among the most promising materials for optical switching applications. Azobenzene is a photosensitive molecule that undergoes geometrical isomerization when absorbing light, Figure 1.[1,2] The photoisomerization is fully reversible, and there is no limit to the number of isomerization cycles that the molecule can undergo. Change in the shape of the molecule as a result of photoisomerization can strongly influence the macroscopic material properties: optical, mechanical, rheological, transport, binding, etc.[3-9]

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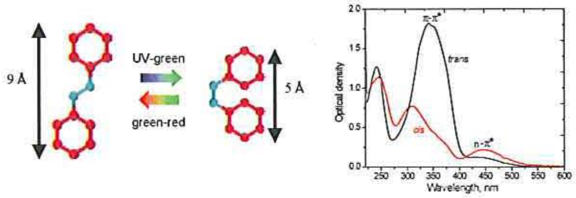
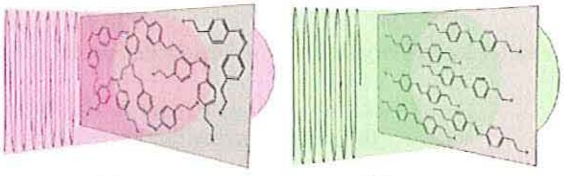


Fig 1. Photoisomerization of azobenzene molecule and absorption spectra of *trans* and *cis* isomers of 0.34 μm-thick layer of room temperature azo LC 1005[10]; π-π^* and n-π^* absorption bands shown in black are designated for the *trans* isomer.

Individual photoisomerization events take place at picosecond time scales and with high quantum efficiency ~ 0.5[11,12]. The π–π^* absorption band of *trans* isomers, most efficient for photoisomerization, is typically in the UV-blue region of wavelengths. *Cis* isomers are more absorptive in the green/red part of the spectrum; however, even at room temperature, they may undergo spontaneous relaxation into the *trans* state due to the relatively small energy barrier between *trans* and *cis* configurations. The peak absorption for a room temperature single component LC D307 (BEAM) containing azobenzene moiety in its molecular structure (azo LC), is at 332 nm, and 443 nm for *trans* and *cis* isomers, with respective absorption constants $1.25 \cdot 10^5$ cm^{-1} and $9.6 \cdot 10^3$ cm^{-1}. In the *trans* state, azobenzene molecules are highly dichroic. The absorption constants of azo LC 1005 at 532 nm are 840 cm^{-1} and 220 cm^{-1} for polarization parallel and perpendicular to the LC optical axis, respectively. The difference in absorption of *trans* and *cis* isomers is considerable over the entire visible spectrum. At 532 nm, a wavelength of great importance for laser technologies, the absorption constants for azo LC mixture 1005 are 450 cm^{-1} and 1480 cm^{-1} for the *trans* and *cis* isomers, respectively.

1.2 Enhancing impact of photoisomerization with azo LCs

The impact of photosomerization on optical properties of materials is particularly significant in azo LCs due to its effect on both the liquid crystalline order and orientation of molecules[13-17]. Photoisomerization may result in substantial changes of the absorption spectrum of azobenzene materials both due to accumulation of *cis* isomers as well as due to molecular reorientation. The effect of radiation on materials containing azobenzene moieties is essentially determined by the wavelength. Radiation of UV-wavelengths, absorbed predominantly by *trans* isomers, leads to accumulation of large concentrations of *cis* isomers, Figure 2(a). Due to comparable photoisomerization rates for both isomers, radiation of blue-green wavelengths may induce repetitive *trans-cis-trans* isomerization cycles resulting in statistical alignment of highly dichroic *trans* isomers of azobenzene molecules perpendicular to the polarization of light, Figure 2(b)[13,14,18,19].



(a) (b)

Fig. 2. The two main effects of photoisomerization of azo LC molecules: (a) UV radiation induces accumulation of *cis*-isomers and isothermal phase transition into isotropic state; (b) azo LC molecules become oriented perpendicular to the linearly polarized light beams of blue/green wavelengths.

Trans isomers are capable of forming LC phases whereas *cis* isomers introduce disorder. Thus, *trans-cis* isomerization makes possible a photoinduced phase transition between LC and isotropic states. Depending on material and temperature, 5-20 wt.% concentration of *cis* isomers is typically sufficient for fully suppressing the LC order[20,21].The azobenzene molecule and LC molecules containing an azo group in their core can be used for imparting photoresponsive features upon both low-molecular as well as polymeric materials and on optical structures based on those materials.

2. AZOBENZENE LIQUID CRYSTALS IMPROVED FOR FAST VISIBLE RESPONSE

Since *trans* is an anisotropic state for azobenzene LCs that can rotate the state of polarization of incident light and *cis* is an isotropic state for which no rotation is possible, the *trans* to *cis* conversion can act like an optical switch that is triggered by the incident light itself. There are several areas where materials performance improvements are required: 1) still large improvements are needed in the sensitivity of azobenzene molecules for visible wavelengths; and 2) azobenzenes alone are too highly absorbing for most practical applications. One of the issues till recently was also the rather slow spontaneous relaxation of *cis* isomers.

The peak absorption wavelengths for azobenzene isomers can be shifted towards visible wavelengths, thus enhancing its photosensitivy, by modifying their molecular structure. Peak wavelengths exceeding 575 nm have been obtained by attaching donor and acceptor groups at the opposite ends of the molecule without sacrificing mesogenic ability in some cases[22]. Spectra of different classes of azo LCs are shown in Figure 3. The graphs correspond to the material compositions 1) BA 1005, 2) CPND8(10%)/5CB, and 3) NB6CBZ(5%)/5CB wherein BA stands for 4-n-butyl-4'-n-alkoxyazobenzenes; CPND8 corresponds to 1-(2-Chloro-4-N-octylpiperazinylphenyl)-2-(4-nitrophenyl) diazene, and (NB6CBZ) is the working name for 2-(4-N-hexylpiperazinylphenylazo)-6-nitrobenzothiazole. Figure 3 also shows the relaxation dynamics measured in a standard pump/probe setup of crossed polarizers comprising the LC cell. Single laser pulses of ~ 8 ns duration were used as pump.

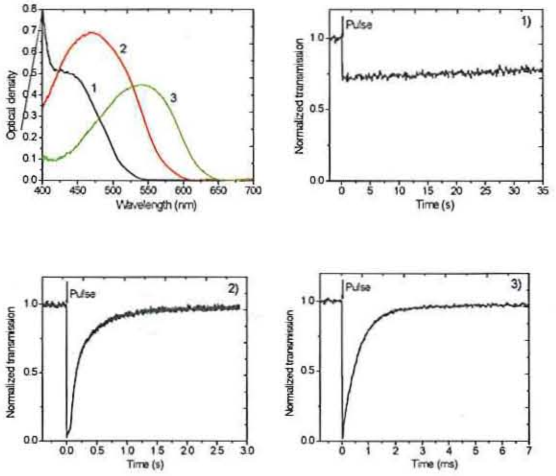


Fig. 3. Absorption spectra of 1.6 μm-thick layers of BA (1), CP (2) and NB (3) series azo dyes characterized by relaxation times of days (1), seconds (2), and milliseconds (3), correspondingly.

Such modifications of molecular properties of azo LCs proved to reduce the lifetime of *cis* isomers by many orders of magnitude, from days up to milliseconds[23]. The change in optical properties of an azo LC determined by the concentration of *cis* isomers obtained within the pulse of light, depends on the ratio of the lifetime of isomers to the pulse duration. The widest spread in lifetime values τ allows obtaining three groups of materials that exhibit: a) high sensitivity to CW radiation and low sensitivity for short (nanosecond) laser pulses (materials with nearly symmetrical $\pi-\pi$ conjugation characterized by $\tau \sim 10^5$ s); b) high sensitivity to both CW and pulsed beams (materials containing two benzene rings with donor-acceptor, or push-pull, $\pi-\pi$□ conjugation, characterized by $\tau \sim 1$ s); and c) high sensitivity to short pulses with low sensitivity to CW (materials ontaining two benzene rings with enhanced push-pull, $\pi-\pi$ □conjugation, characterized by $\tau \sim 0.001$ s) [Error! Bookmark not defined.].

Azo LCs that combine the high photosensitivity of azobenzenes with the high transmission and efficient polarization rotation of liquid crystals are ideal for optical switching applications because they exhibit both an *active* and a *passive* switching response. Azo LCs can be actively switched with an applied voltage or change in temperature, and they can be passively switched in response to an incident light beam. The combination of azobenzenes with liquid crystals greatly reduces absorption losses.

We have improved Azo LC sensitivity through the development of new molecules and by employing nanotechnology-based field enhancement techniques. This has enabled *trans/cis* conversion at very low light levels as well as faster LC reorientation. The improved sensitivity also allows for thinner films, which further reduces absorption losses.

3. ANISOTROPIC NANO/MICRO-STRUCTURES FOR EFFICIENTLY CONTROLLING LIGHT

Aligned anisotropic molecules are commonly used to rotate the state of polarization of incident light to transmit it through crossed polarizers in the "on" state. Incident light can be blocked by the crossed polarizers in the "off", non-rotational state. Polarized light is generally created by the absorption of one orthogonal electric field component of the incident light. This is an inefficient and costly waste of over 50% of incident light. Thus, there is a need for a fundamentally new optical element that can eliminate the crossed polarizer configuration that is commonly used with anisotropic materials such as LCs to efficiently transform changes in their birefringence into changes in the transmission of the optical system.

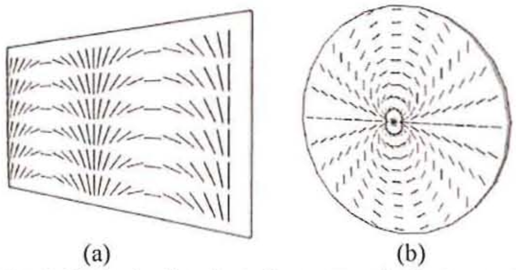

(a) (b)

Fig. 4. Optical axis orientation pattern in the two main classes of diffractive waveplates: (a) cycloidal; (b) axial (of $q_\varphi = 2$ topological charge).

To overcome this challenge we have developed a fundamentally new concept of optically switchable elements based on diffractive waveplates (DWs). DWs are nanostructured, LC-based, polarization rotating elements for which the axis of orientation is continually varying in space. Thus, it works equally well regardless of the state of polarization and can have practically 100% transmission. The diffractive waveplate can take a number of forms: cycloidal wherein the optical axis rotates in space along a single Cartesian coordinate axis x, $\theta = qx$, Figure 4(a), and its polar analog – the axial diffractive waveplate (ADW) – wherein the optical axis rotates in space as a function of the azimuthal angle φ, $\theta = q_\varphi \varphi$, Figure 4(b).

Upon fulfillment of the half-wave retardation condition, these DWs strongly affect the propagation properties of a light beam. CDWs are capable of deflecting a circular polarized beam at large angles, like a prism, along +1st or -1st diffraction angles, depending on the sign of polarization. Hence, both orders are present for an unpolarized beam, Figure 5(a). The diffraction pattern is wrapped around the axis outputing a doughnut beam, for axially symmetric structures of ADWs, Figure 5(b). The role of the spatial frequency q here is played by the "topological charge" of the ADW; higher charge corresponds thus to larger "doughnut" size.

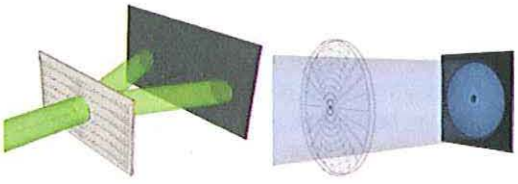

(a) (b)

Fig. 5. Schematic representation of the optical functions of (a) CDW and (b) ADW. CDWs output only one beam for a circular polarized incident light.

Note that LCs, including LC polymers (LCPs) are the only material systems that allow fabrication of DWs with continuous modulation of optical axis orientation practical for most applications[24,25]. They are transparent in visible/Near IR spectral range and, due to their high optical anisotropy ($n_e - n_o \sim 0.2$), the half-wave phase retardation condition is achieved in thin material layers (~ 1 μm). LCs uniquely allow obtaining optical axis deformation patterns at high spatial frequencies.

These components are inherently broadband and, as half-wave plates, can be made practically achromatic for wide wavelength ranges by stacking layers with mutually shifted orientation angles. We have fabricated CDWs that can switch over 300 nm bandwidth of light with nearly 100% efficiency (Figure 6).

The CDW is particularly useful when paired in series with a complimentary CDW, which exactly compensates for the diffraction caused by the first; similar to assembling a pair of prisms into a plane optical window, Figure 7.[26] The light emerging from the pair is unaffected by diffraction. The pair appears as a perfectly transparent optical element. With CDWs, optical switching can be accomplished by making one of the elements switchable. The switching can be either *active* or *passive* or both!

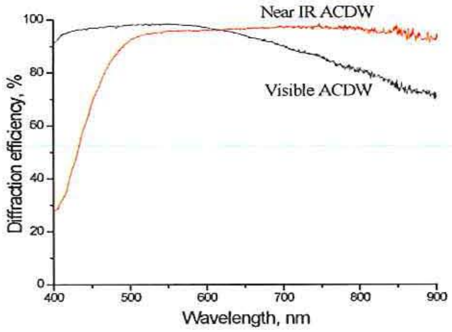


Fig. 6. Diffraction efficiency as a function of wavelength for visible and near IR achromatic CDWs fabricated at BEAM Co.

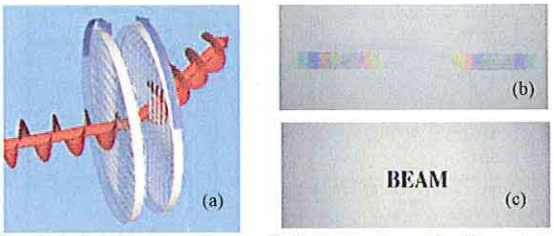


Fig. 7. (a) Adjusting the angle between two similar CDWs, one can deflect a light beam and even images at double the angle obtained with a single CDW (b), or cancel the deflection at all (c).

The development of this fundamentally new type of optical element is a significant step in the transition of azo LC switching technology for many Soldier-based applications. It can be combined with nonlinear dyes, plasmonic field enhancement techniques, and advances in electronic switching. This new set of components has brought researchers closer to their goal of developing new optical materials and systems that can switch quickly, have high optical quality, can operate over a broad and controllable range of wavelengths, and that are inexpensive and highly manufacturable.

4. ANISOTROPIC DIELECTRIC COATINGS WITH PATTERNED OPTICAL AXIS ORIENTATION

As mentioned above, LCs and LCPs provide a unique opportunity of continuous modulation of optical axis orientation with high spatial resolution. Different modulation patterns can be obtained by directly acting on the orientation of the LC with the aid of electric and optical fields. This approach is essentially limited to LCs in case of electrical control. Optically, one can control

LCPs as well if they contain azobenzene moieties in their molecular stucture.

4.1 Materials

The most versatile technique for producing optical axis orientation patterns in all kinds of LC material systems is based on so-called photoalignment materials[27,28]. These materials, coated in few nanometer thin layers on substrates for LC cells or LCPs, are capable of undergoing anisotropic stuctural changes according to the polarization direction of light, and they are thus capable of orienting LCs that are brought in contact with them. The technique consists of producing desired boundary conditions for orientation of LCs with the aid of a polarization modulation pattern of linearly polarized UV light, Figure 8.

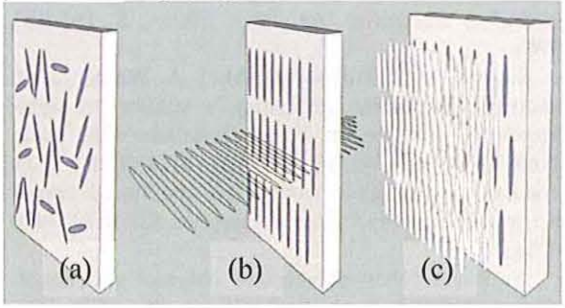


Fig. 8. The Photoalignment process. The substrate for making an oriented LC cell or an LCP layer is coated with the photoalignment material. The anisotropic molecules of the material are initially randomly oriented (a), however they are capable of being realigned perpendicular to the polarization direction by a UV light beam (b). The LC (LCP) brought afterwards in contact with the photoaligned layer becomes oriented accordingly.

Item code	λ_{max}, nm	E, J/cm^2		
		$\lambda = 458$ nm	$\lambda = 325$ nm	$\lambda = 365$ nm
PAAD-22	367	0.6	0.3	0.5
PAAD-23	403	4.5	7.2	9
PAAD-26	429	3	12.6	14.4
PAAD-27	393	0.3	2.7	1.1
PAAD-29	404	3	12.6	n/a

Table 1. Azobenzene-based photoalignment materials optimized for different wavelengths.

A number of different types of photoalignment materials have been developed so far. The photoalignment phenomenon of azobenzene is widely used for developing anisotropic thin films[28-32]. We have developed azobenzene photoalignment materials that provide strong anchoring and high quality adequate for fabrication of DWs. Their high sensitivity, hence smaller exposure times, would help fabricating CDWs with large diffraction angles, and reducing the area of the defect when recording ADWs. Using different molecular structures allows us to make materials optimized for different radiation wavelengths, Table 1. The alignment axis is perpendicular to polarization and is reversible when used with liquid crystals.

4.2. Printing technology of Diffractive Waveplates

CDWs are typically obtained using a holographic recording process wherein two coherent laser beams of orthogonal circular polarization overlap on the substrate carrying the photoalignment layer. The conventional technique for fabrication of ADWs is based on mechanical rotation of the substrate that carries the photoalignment material in a narrow strip of a linear polarized UV light beam. This polarization direction has to be rotated as well for producing ADWs of higher than 1 topological charge. Due to sensitivity of such setups to ambient and mechanical noise, they are not well fit for fabrication of large area high quality DWs, particularly, in large quantities.

The DW printing technology developed by us employs linear-to-cycloidal or linear-to-axial polarization converters, Figure 9.[33,34] DWs themselves play the role of such components for the light beam wavelength that meets the half-wave phase retardation condition. This technology is much simpler, does not require mechanical motions, is robust and insensitive to noises. Using a DW as a polarization converter allows for also obtaining CDWs with doubled spatial frequency, and can double the topological charge of ADWs. Thus, the noise or inaccuracies introduced by mechanical motions are eliminated, and are replaced by precisely controlled optical processes. Using a projection setup, we can smoothly vary the spatial frequency of DWs.

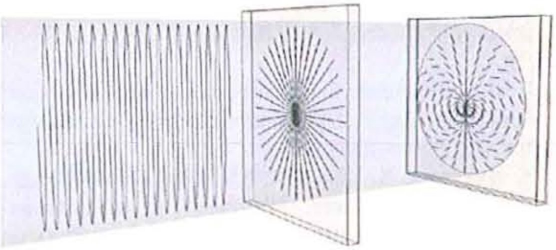


Fig. 9. Schematic of the setup for printing DWs and doubling the spatial frequency of CDWs and topological charge of ADWs. An ADW acting as a radial-to-axial polarization converter is shown as an example. The topological charge of the pattern printed at the photoalignment layer is double of that of the converter

5. CONCLUSIONS

Thus, there was remarkable progress made in the recent years towards the development of materials and technologies that make possible a number of applications where the propagation of light beams is self-controlled. Those applications, including, optical switching, steering, shaping and combining of laser beams, important for different DoD and commercial purposes, may eliminate or reduce the need for laser beam sensing, identification electronics, feedback and control systems, and related electric power sources. The all-optical technologies would allow one also to overcome speed limitations of electronic systems, and to eliminate electrodes from the path of the beam. The technology we have developed extends the capabilities of multilayer dielectric coating technology by adding new control parameters for each layer – the optical axis orientation patterns. These new technologies still require extensive functional material development, both for fabrication process as well as for further enhancing their optical functionality.

6. REFERENCES

1. H. Knoll, "Photoisomerism of azobenzenes", in *Organic Photochemistry and Photobiology*, ed. by W. Horspool, F. Lenci, 2-nd ed., CRC Press, Boca Raton, 2004, pp. 89/1 – 89/16.
2. J. Griffiths, "Photochemistry of azobenzene and its derivatives," Chem. Soc. Rev. **1**, 481-493 (1972).
3. R. H. El Halabieh, O. Mermut, C. J. Barrett, "Using light to control physical properties of polymers and surfaces with azobenzene chromophores," *Pure Appl. Chem.* **76**, 1445–1465 (2004).
4. T. Hugel, N. B. Holland, A. Cattani, L. Moroder, M. Seitz, H. E. Gaub, "Single-molecule optomechanical cycle," *Science*, **296**, 1103–1106 (2002).
5. E. Jeoung, V. M. Rotello, "Photochemical control of molecular recognition on self-assembled monolayer-protected gold clusters," *J. of Supramol. Chem.*, **2**, 53-55 (2002).
6. J. M. J. Paulusse, R. P. Sijbesma, "Molecule-based rheology switching," *Angewandte Chemie International Edition*, **45**, 2334 – 2337 (2006).
7. H. Asanuma, X. Liang, H. Nishioka, D. Matsunaga, M. Liu, M. Komiyama, "Synthesis of azobenzene-tethered DNA for reversible photo-regulation of DNA functions: hybridization and transcription," *Nature Protocols*, **2**, 203 – 212 (2007).
8. G. Miller, "Optogenetics: shining new light on neural circuits," *Science*, **314**, 1674 – 1676 (2006).
9. K. G. Yager, C. J. Barrett, "Novel photo-switching using azobenzene functional materials," *J. of Photochem. and Photobiol. A: Chemistry*, **182**, 250–261 (2006).
10. U. Hrozhyk, S. Serak, N. Tabiryan, T. J. Bunning, "Wide temperature range azobenzene nematic and smectic LC materials," *Mol. Cryst. Liq. Cryst.*, **454**, 235-246 (2006).
11. L. K. Lendev, T.-Q. Ye, P. Matousek, M. Towrie, P. Foggi, F.V.R. Neuwahl, S. Umapathy, R.E. Hester, J.N. Moore, "Femtosecond time-resolved UV-visible absorption spectroscopy of *trans*-azobenzene: dependence on excitation wavelength," *Chem. Phys. Lett.*, **290**, 68-74 (1998).
12. J. Wachtveitl, S. Spoerlein, H. Satzger, B. Fonrobert, C. Renner, R. Behrendt, D. Oesterhelt, "Ultrafast conformational dynamics in cyclic azobenzene peptides of increased flexibility," *Biophysical Journal*, **86**, 2350-2362 (2004).
13. L. M. Blinov, "Photoinduced molecular reorientation in polymers, Langmuir–Blodgett films and liquid crystals," *J. Nonlinear Opt. Phys. Mater.*, **5**, 165–187 (1996).
14. K. Anderle, R. Birenheide, M. J. A. Werner, J. H. Wendorff, "Molecular addressing - studies on light-induced reorientation in liquid-crystalline side chain polymers," *Liquid Crystals*, **33**, 1421–1427 (2006); J. H. Wendorff, "Holographic storage via the liquid crystal state: a success story," *Liquid Crystals*, **33**, 1419–1420 (2006).
15. Y. Zhao, "New photoactive polymer and liquid-crystal materials," *Pure Appl. Chem.*, **76**, 1499–1508 (2004).
16. C. H. Legge, G. R. Mitchell, "Photoinduced phase transitions in azobenzene-doped liquid crystals," *J. Phys. D.: Appl. Phys.*, **25**, 492–499 (1992).
17. T. Ikeda, O. Tsutsumi, "Optical switching and image storage by means of azobenzene liquid crystal films," *Science*, **268,** 1873–1875 (1995).
18. A. Makushenko, O. Stolbova, B. Neporent, "Reversible orientational photodichroism and photoisomerization of aromatic azo-compounds," *Opt. Spectr.* **31**, 295- 302 (1971).
19. C. Kempe, M. Rutloh, and J. Stumpe, "Photo-orientation of azobenzene side chain polymers parallel or perpendicular to the polarization of red He-Ne light," *J. Phys.: Condens. Matter.*, **15**, S813-S823 (2003).
20. N. V. Tabiryan, S. V. Serak, V. A. Grozhik, "Photoinduced critical opalescence and reversible all-optical switching in photosensitive liquid crystals," *J. Opt. Soc. Am. B*, **20**, 1-7 (2003).
21. T. V. Truong, C.-Y. Chen, N. V. Tabiryan, Y. R. Shen, "Phase transition induced by two-photon absorption in azobenzene liquid crystals," *J. Opt. Soc. Am. B*, **24**, 2623-2626 (2007).
22. U. A. Hrozhyk, S. V. Serak, N. V. Tabiryan, L. Hoke, D. M. Steeves, B. Kimball, and G. Kedziora, "Systematic Study of Absorption Spectra of Donor–Acceptor Azobenzene Mesogenic Structures," *Mol. Cryst. Liq. Cryst.*, **489**, 257[583]–272 [598] (2008).

23. U.A. Hrozhyk, S.V. Serak, N.V. Tabiryan, L. Hoke, D.M. Steeves, and B.R. Kimball, "Azobenzene liquid crystalline materials for efficient optical switching with pulsed and/or continuous wave laser beams," *Opt. Express* **18**, 8697-8704 (2010).

24. S. Nersisyan, N. Tabiryan, D.M. Steeves, B.R. Kimball, "Fabrication of liquid crystal polymer axial waveplates for UV-IR wavelengths," Opt. Express, **17**, 11926-11934 (2009).

25. S.C. McEldowney, D.M. Shemo, R.A. Chipman, P.K. Smith, "Creating vortex retarders using photoaligned liquid crystal polymers," *Opt. Lett.* **33**,134-136 (2008).

26. S.R. Nersisyan, N.V. Tabiryan, L. Hoke, D.M. Steeves, B. Kimball, "Polarization insensitive imaging through polarization gratings," Opt. Express, **17** (3), 1817-1830 (2009).

27. V.G. Chigrinov, V.M. Kozenkov, and H.S. Kwok, "Photoaligning: Physics and Applications in Liquid Crystal Devices" (Wiley VCH, 2008).

28. K. Ichimura, Photoalignment of Liquid-Crystal Systems, *Chem. Rev.* **100**, 1847-1873 (2000).

29. S. Ishihara, "How far has the molecular alignment of liquid crystals been elucidated?" *IEEE/OSA J. of Display Technology*, **1**, 30-40 (2005).

30. V. Chigrinov, H.S. Kwok, H. Takada, H. Takatsu, "Photo-aligning by azo-dyes: Physics and applications," *Liquid Crystals Today*, **14**, 1–15 (2005).

31. M. Schadt, K. Schmitt, V. Kozinkov, and V Chigrinov, "Surface-induced parallel alignment of liquid crystals by linearly polymerized photopolymers," *Jpn. J. Appl. Phys.* **31**, 2155-2164 (1992).

32. W. M. Gibbons, P. J. Shannon, S.-T. Wu, B. J. Swtlin, "Surface-mediated alignment of nematic liquid crystals with polarized laser light," *Nature* **351**, 49 - 50 (1991).

33. S.R. Nersisyan, N.V. Tabiryan, D.M. Steeves, B. Kimball, "Optical Axis Gratings in Liquid Crystals and their use for Polarization insensitive optical switching," Journal of Nonlinear Optical Physics & Materials, **18**, 1–47, 2009.

34. S.R. Nersisyan, N.V. Tabiryan, D.M. Steeves, and B.R. Kimball, "Characterization of optically imprinted polarization gratings," *Appl. Optics* **48**, 4062-4067 (2009).