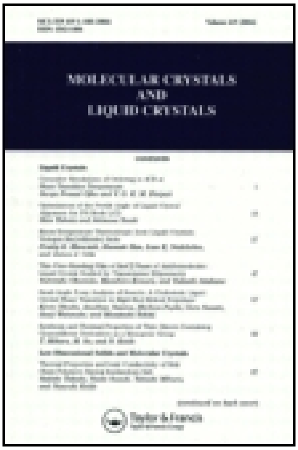

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Wide Temperature Range Azobenzene Nematic and Smectic LC Materials

U. Hrozhyk [a], S. Serak [a], N. Tabiryan [a] & T. J. Bunning [b]

[a] Beam Engineering for Advance Measurements Co., Winter Park, Florida, USA

[b] Air Force Research Laboratory, Wright Patterson Air Force Base, Ohio, USA

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Wide Temperature Range Azobenzene Nematic and Smectic LC Materials

U. Hrozhyk
S. Serak
N. Tabiryan
Beam Engineering for Advance Measurements Co.,
Winter Park, Florida, USA

T. J. Bunning
Air Force Research Laboratory, Wright Patterson Air Force Base,
Ohio, USA

We have developed a series of azobenzene liquid crystals (azo LC) compounds, both multicomponent as well as single component, that possess room temperature nematic and smectic phases. Some of these materials have a wide mesophase temperature range which makes them useful for a variety of practical applications. Two main strategies were used for controlling the temperature range of these mesogenic azo LC materials: 1) chemical modification of azobenzene molecules with different terminal pendants; and 2) development of multicomponent compositions. These materials were highly photosensitive exhibiting nonlinear refraction and transmission at nanowatt/microwatt power levels. Physical, electro- and nonlinear-optical parameters of many of these materials have been characterized in detail.

Keywords: azobenzene; liquid crystals; multicomponent compositions; thermal phase transitions

INTRODUCTION

Azobenzene based molecules are among the most significant chemical structures for developing optically controlled devices and photonic systems. The interest on azobenzene based materials has been sustained

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Address correspondence to N. Tabiryan, Beam Engineering for Advance Measurements Co., 809 S. Orlando Ave, Suite I, Winter Park, FL 32789, USA. E-mail:nelson@beamco.com

at a remarkably high level during the last three decades [1]. The enormous variety of such materials relies on a simple structural unit, the nitrogen–nitrogen double bond −N=N−.

Many azobenzene based materials are mesogenic, most of them, however, in a temperature range considerably exceeding room temperature. Development of a wide assortment of azo LCs possessing different mesophases including room temperature liquid crystallinity is a viable task for modern chemistry using new advanced techniques in the organic synthesis field. We have undertaken that task focused on low-molecular liquid crystalline azocompounds and their compositions.

Two main strategies can be used for controlling the mesophase temperature range of azo LC materials: 1) chemical modification of the azobenzene molecules with different lateral and terminal pendants; and 2) development of multicomponent compositions. The first substantial work on the synthesis of an "interesting new class of nematic liquid crystals" was published in 1971 by R. Steinstrasser and L. Pohl [2]. They synthesized 43 azocompounds with alkyl terminal substituents C_nH_{2n+1} belonging to 6 homologous series (n = 1 to 6)

$$H_{2n+1}C_n{-}C_6H_4{-}N{=}N{-}C_6H_4{-}R$$

where alkyloxy ($C_mH_{2m+1}{-}O{-}$) or acyloxy ($C_mH_{2m+1}{-}COO{-}$) pendants were used as opposite terminal R.

Many of those compounds possessed an enantiotropic nematic phase and the melting points of some were close to room temperature. The most known of these azo LCs, 4-butyl-4′-methoxyazobenzene (BMAB, or BAAB-1)

$$H_9C_4{-}C_6H_4{-}N{=}N{-}C_6H_4{-}OCH_3$$

has a nematic phase in the temperature range 32 to 47°C and can exist in a supercooled nematic phase at room temperature.

The phase behavior of those newly obtained azo LCs and their mixtures were not studied in details. However, it was demonstrated that low melting point azo LCs can be created on the basis of simple combinations of alkyl- and alkoxy-terminal pendants. Analogous nematic azocompounds were synthesized also by H. Kelker [3] and K. Murase [4].

J. van der Veen *et al.* in 1972 [5] and M. Moriyama *et al.* in 2001 [6] synthesized a homologous series of symmetrical dialkylazobenzenes

$$H_{2n+1}C_n{-}C_6H_4{-}N{=}N{-}C_6H_4{-}C_nH_{2n+1}$$

with n up to 16. Most of those compounds had no mesophase or possess only a monotropic nematic or smectic phase only.

Even though publications on the synthesis of azo LCs are scant, including isolated works on the synthesis of low molecular azo LC structures for special applications [7,8], these can be used to conclude that the presence of two polar terminal pendants like the alkoxy group leads to azocompounds with high melting temperatures whereas azocompounds with symmetrical non-polar terminal pendants have a poor ability to form nematic phases. Hence, azobenzene molecules with one non-polar alkyl or two alkyl, but nonsymmetrical, terminal pendants are the most promising candidates to exhibit mesophases at room temperature.

Both directions discussed above have been utilized in this work including: 1) the study of two and multicomponent compositions based on 4-*n*-alkyl-4′-*n*-alkoxy(acyloxy)azobenzenes; and 2) synthesis of new potentially mesogenic azocompounds based on nonsymmetrical 4,4′-di-*n*-alkylazobenzenes

$$H_{2n+1}C_n{-}C_6H_4{-}N{=}N{-}C_6H_4{-}C_mH_{2m+1}$$

and 4-*n*-alkyl(alkoxy)-4′ -cyanoazobenzenes

$$H_{2n+1}C_n(O){-}C_6H_4{-}N{=}N{-}C_6H_4{-}C{\equiv}N$$

Nonsymmetrical 4,4′-di-*n*-alkylazobenzenes are interesting due to the anticipated low melting temperatures whereas 4-*n*-alkyl(alkoxy)-4′-cyanoazobenzenes are expected to possess a large positive dielectric anisotropy. In addition, the presence of the strong electron acceptor $-C{\equiv}N$ group could lead to acceleration of the dark reverse *cis-trans* transition.

PREPARATIVE ROUTES

The syntheses of the 4-*n*-alkyl-4′-*n*-alkoxy(acyloxy)azobenzenes and 4-*n*-alkoxy-4′-cyanoazobenzenes were performed by alkylation of the appropriate azophenols (obtained by azo coupling of diazonium salts of 4-alkylanilines or 4-aminobenzonitrile with phenol) with the alkyl halides by the Williamson reaction

$$\begin{gathered} R_1(CN){-}C_6H_4{-}N{=}N{-}C_6H_4{-}OH + R_2Hal \\ \rightarrow R_1(CN){-}C_6H_4{-}N{=}N{-}C_6H_4{-}OR_2 \end{gathered}$$

where $R_1 = -C_nH_{2n+1}$, $R_2 = -C_mH_{2m+1}$, or by the acylation of the potassium salts of the appropriate azophenols with acyl chlorides:

$$\begin{gathered} R_1{-}C_6H_4{-}N{=}N{-}C_6H_4{-}OK + R_2{-}COCl \\ \rightarrow R_1{-}C_6H_4{-}N{=}N{-}C_6H_4{-}OOC{-}R_2 \end{gathered}$$

with $R_1 = -C_nH_{2n+1}$ and $R_2 = -C_mH_{2m+1}$.

The syntheses of nonsymmetrical 4-*n*-alkyl(R_1)-4′-*n*-alkyl(R_2) azobenzenes and 4-*n*-alkyl-4′-cyanoazobenzenes were performed by coupling 4-alkyl or 4-cyano nitroso benzene with 4-alkylanilines in glacial acetic acid:

$$R_1(CN){-}C_6H_4{-}N{=}N{-}C_6H_4{-}NO + H_2N{-}C_6H_4{-}R_2$$
$$\rightarrow R_1(CN){-}C_6H_4{-}N{=}N{-}C_6H_4{-}R_2$$

with $R_1 = -C_nH_{2n+1}$ and $R_2 = -C_mH_{2m+1}$.

Phase transition temperatures were measured using polarizing microscope equipped with a hot stage although in cases of low melting points, the obtained data were corrected by DSC measurements.

ROOM TEMPERATURE COMPOSITIONS

4-*n*-alkyl-4′-alkoxy(acyloxy)azobenzenes with the lowest mesophase range have, as a rule, even numbers of carbon atoms (n = 2, 4, 6) in the alkyl terminal substituent R_1. However, all of them are in the mesophase above room temperature. We chose compounds of 4-*n*-butyl-4′-alkoxyazobenzene series (BAABs, n = 4) as the main components for developing room temperature compositions.

Increasing the number m of the carbons in the alkoxy terminal chains of these homologoues, generally increases the melting temperatures. In addition, they become more smectogenic with elongation of the alkoxy tails. Smectogenic ability in the BAAB series starts from the sixth carbon in the alkoxy chain leading, first, to appearance of monotropic smectic A and then to an enantiotropic smectic A phase for the eighth homolog.

In order to check this tendency we synthesized homologs with m = 11–16. BAAB-11 and BAAB-12 proved to be pure smectogens with no nematic phase at all and with smectic ranges 62 to 68°C and 54 to 64°C, respectively. Further elongation of the terminal alkoxy- pendant decreases the extent of participation of the highly polarizable aromatic azobenzene core. The mesogenicity is lost after the 12-th carbon atom since the physical properties of BAABs start to be defined by the predominantly isotropic intermolecular interactions of the hydrocarbon tails. The highest obtained homologs appeared as wax-like substances with their melting points very close to each other: 53–55°C for BAAB-13; 56–58°C for BAAB-14; and 55–57°C for BAAB-16.

In summary, the development of wide temperature range azo LC compositions was accomplished using BAAB homologs with 10 or less carbon atoms in the alkoxy pendant. Several materials consisting of two to four components proved practically useful possessing room temperature liquid crystalline phases. Some of the compositions include other 4-*n*-alkyl-4′-alkoxy(acyloxy)azobenzenes with $R_1 = C_2H_5$- and $R_1 = C_6H_{13}$- alkyl pendants as well as nonmesogenic azodopants. Mesophase ranges of 12 compositions possessing nematic and smectic A phases are presented in Figure 1. The melting point of the lowest melting quaternary composition 4915 is as low as −7°C. DSC curves of this composition at heating and cooling of the sample are shown in Figure 2 as an example.

The main physical, electro- and nonlinear optical properties of several compositions are presented in Table 1. Brief definitions of the main parameters characterized in Table 1 are summarized below, see also [9].

The "Constant of nonlinear refraction n_2" determines the change in the refractive index $n - n_0$ of the material under the influence of a light beam of power density I according to the formula $n - n_0 = n_2 I$. It was measured for planar oriented 10 μm thick layer of the material with a laser beam of $\lambda = 532\,\text{nm}$ wavelength and $I = 4.4 \cdot 10^{-7}\,\text{W/cm}^2$ power density, polarized parallel to the orientation of the LC. The "incubation energy E_{inc}" determines the amount of light energy that

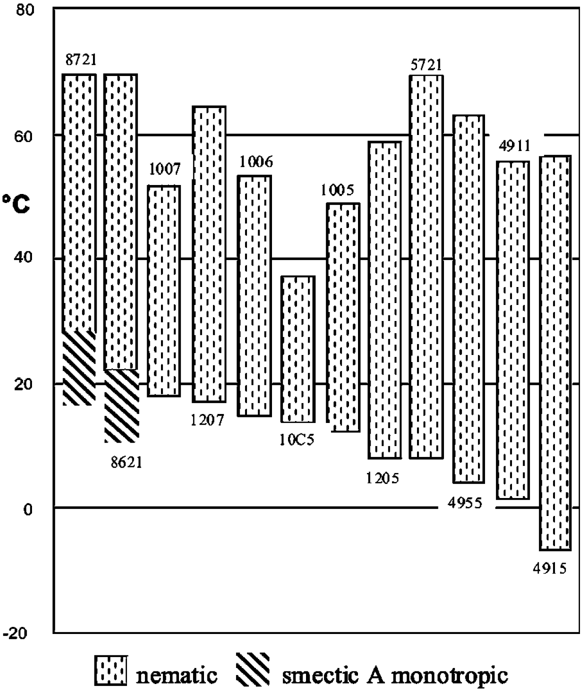

FIGURE 1 Mesophase ranges of several room temperature azo LC compositions. Numbers near the bars identify the compositions.

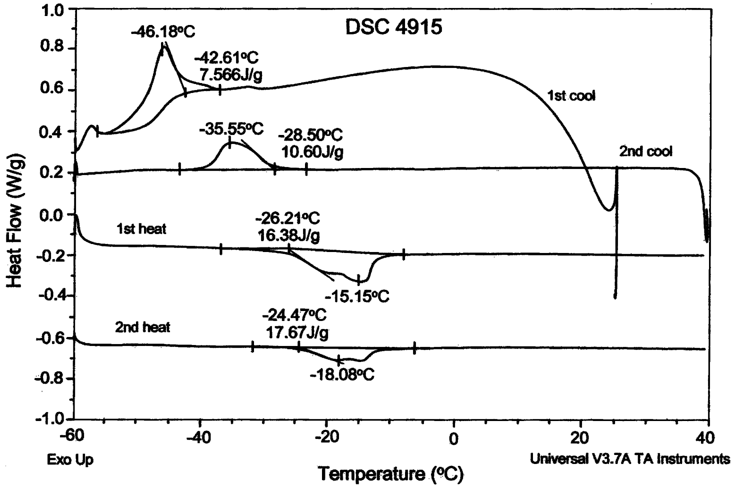

FIGURE 2 DSC curves of composition 4915.

the LC has to be exposed to in order to start the photoinduced mesophase-isotropic phase transition. The "transition energy E_{iso}" determines the amount of light energy that the LC has to be exposed to in order for the material to be transformed into an isotropic phase. Both the transition and incubation energies are measured for a laser beam of $\lambda = 409\,\text{nm}$ wavelength and $I = 6.2 \cdot 10^{-3}\,\text{W/cm}^2$ power density, polarized parallel to the planar orientation of $10\,\mu\text{m}$ thick LC layers. The "optical anisotropy Δn" is defined as the difference between the principal values of the refractive indices of LC. It was measured for the wavelength $\lambda = 633\,\text{nm}$ at $T = 23^\circ\text{C}$. The constant of "orientation diffusion D" allows an evaluation of the free relaxation time τ of the LC director reorientation in cells of thickness L with hard anchoring boundary conditions using the formula $\tau = L^2/D$. This is related to the orientational viscosity γ and the elastic constant K_1 of the liquid crystal by the expression $D = \pi^2 K_1/\gamma$.

The smectic A phases of the compositions 8621 and 8721 are monotropic, however, they are stable at the room temperature forming giant (several millimeter thick), highly transparent, smectic monodomains. A photo of such a monodomain is shown in Figure 3.

SINGLE COMPONENT ROOM TEMPERATURE AZO LCS

As mentioned above, symmetrical 4,4′-dialkyl azobenzenes have no mesophase or show monotropic nematic or smectic phases only. We synthesized nonsymmetrical 4,4′-di-n-alkylazobenzenes with the

TABLE 1 Characterization of Room Temperature Azo-LC Compositions

LC	T [°C]	n_2 [cm^2/W]	E_{inc} [J/cm^2]	E_{iso} [J/cm^2]	Δn	D [cm^2/s]	$\varepsilon_\perp$	$\varepsilon_\parallel$	U_{Fr} [Volts] 1 kHz
1005	12.5 N 49 I	$2.0 \cdot 10^{-1}$	0.073	0.39	0.18	$5.3 \cdot 10^{-6}$	3.0	3.4	8.2
1006	15 N 53 I	$2.1 \cdot 10^{-1}$	0.074	0.39	0.18	$5.2 \cdot 10^{-6}$	3.2	3.6	9.7
1007	17.5 N 52 I	$2.4 \cdot 10^{-1}$	0.077	0.51	0.18	$5 \cdot 10^{-6}$	3.2	3.7	9.9
1205	8 N 59 I	$2.1 \cdot 10^{-1}$	0.13	0.73	0.21	$6.3 \cdot 10^{-6}$	3.2	4.0	9.5
1207	16.5 N 63.5 I	$1.9 \cdot 10^{-1}$	0.14	0.82	0.20	$6.2 \cdot 10^{-6}$	3.2	3.9	9.8
5721	8 N 70 I	$1.2 \cdot 10^{-1}$	0.19	1.35	0.23	$3.6 \cdot 10^{-6}$	2.6	3.3	15
8721*	SmA 28 N 71.5 I	$1.1 \cdot 10^{-1}$	0.16	1.68	0.21	$8.7 \cdot 10^{-6}$	3.1	3.2	22.8
8621*	SmA 22 N 72 I	$1.1 \cdot 10^{-1}$	0.16	1.64	0.20	$6.1 \cdot 10^{-6}$	3.0	3.3	19.6
3178	18 N 41.5 I	$1.8 \cdot 10^{-1}$	0.058	0.28	0.14	$5.5 \cdot 10^{-6}$	2.4	3.2	8.5
3155	3 N 48 I	$2.2 \cdot 10^{-1}$	0.11	0.43	0.20	$5.1 \cdot 10^{-6}$	2.6	3.3	7.5
10C5	13.5 N 37 I	$3.5 \cdot 10^{-1}$	0.023	0.2	0.16	$3.6 \cdot 10^{-6}$	2.7	3.4	7.2
4911	2 N 56 I	$1.9 \cdot 10^{-1}$	0.075	0.52	0.18	$4.7 \cdot 10^{-6}$	3.3	3.9	20.5
4955	2 N 63 I	$2.1 \cdot 10^{-1}$	0.13	0.93	0.20	$4.4 \cdot 10^{-6}$	3.0	3.7	19.8
4915	−7 N 57 I	$2.1 \cdot 10^{-1}$	0.067	0.47	0.18	$4.1 \cdot 10^{-6}$	3.1	3.7	17
4913	3 N 52 I	$2.0 \cdot 10^{-1}$	0.076	0.60	0.20	$4.2 \cdot 10^{-6}$	3.0	3.6	18
4153	4 N 57 I	$2.0 \cdot 10^{-1}$	0.10	0.79	0.21	$4 \cdot 10^{-6}$	3.0	3.5	16.3

*Smectic A phases are monotropic. The crystal-smectic phase transition temperature depends on cooling rate.

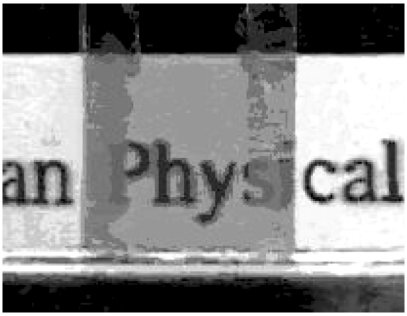

FIGURE 3 Highly transparent monodomain of smectic 8621 in a 4 mm thick cell.

number of carbon atoms (n) 1 to 5 on one end and (m) 2 to 8 on the other end of the azobenzene molecule. Insertion of two different alkyl pendants into the molecule of azobenzene drastically changes its mesogenic properties compared with the combination of alkyl-alkoxy substituents or combination of two symmetrical alkyl pendants. Phase transition temperature of these synthesized nonsymmetrical 4,4′-di-*n*-alkylazobenzenes are listed in Table 2. A sharp decrease in the yields of intermediate nitroso compounds obtained from 4-alkylanilines did not allow us to study compounds with the number of carbons atoms in the alkyl chain larger than 6.

The appearance of the nematic phase in nonsymmetrical 4,4′-di-*n*-alkylazobenzenes is observed starting from the second carbon atom in the shorter of the two pendants. Increasing the number of carbon atoms lowers the phase transition temperature driving the melting points of some individual compounds below 0°C. The widest enantiotropic nematic phase, 3 to 34°C, is obtained for 4-*n*-propyl-4′-*n*-heptylazobenzene ($n = 3$, $m = 7$ in Table 2). The nematic-smectic phase transition point is –16°C for 4-*n*-propyl-4′-*n* octylazobenzene ($n = 3$, $m = 8$ in Table 2); the smectic phase is monotropic in this case but its existence means that the lifetime of the supercooled nematic phase of this compound should be very long (the nematic range in this case should be -16 to 25°C).

Very weak but still anisotropic interactions of practically nonpolar molecules of nonsymmetrical 4,4′-di-*n*-alkylazobenzenes lead to unique mesogenic properties of these azo compounds. Some of these compounds, for example 4-*n*-butyl-4′-*n*-hexylazobenzene ($n = 4$, $m = 6$ in Table 2), are isotropic liquids having very low melting temperatures. They could serve as highly effective dopants for depression of the clearing temperature in the azo LC compositions. From a

TABLE 2 Phase Transitions Temperatures of Nonsymmetric Dialkyl Azobenzenes

Compound	Phase transitions, °C
n = 1	
m = 2	Cr 75 I
m = 3	Cr 59 I
m = 4	Cr 52 I
m = 5	Cr 64 I
m = 6	Cr 58.5 I
m = 7	Cr 51 I
m = 8	Cr 52 I
n = 2	
m = 3	Cr 42.5 I
m = 4	Cr 6 N 20 I
m = 5	Cr 25 I [3] N monotr
m = 6	Cr 19 I
m = 7	Cr 14 I [13] N monotr
m = 8	Cr 16 I [11.5] N monotr
n = 3	
m = 4	Cr 11.5 I [3] N monotr
m = 5	Cr 11 N 27 I
m = 6	Cr −22 I [11] N monotr
m = 7	Cr 3 N 34 I
m = 8	SmA monotr [−16] Cr12 N 25.5 I
n = 4	
m = 5	Cr 3 N 13.5 I
m = 6	Cr −2 N 7 I
m = 7	Cr 1 N 24 I
m = 8	SmA monotr [−11] Cr 11 N 21 I
n = 5	
m = 6	Cr 20 N 26 I
m = 7	Cr 10 N 40 I
m = 8	SmA monotr [4] Cr 15 N 35.5 I

practical point of view, in the case of nonsymmetrical 4,4′-di-*n*-alkylazobenzenes, we encountered the opposite problem, too low clearing temperatures. Their mixtures with the higher melting 4-*n*-alkyl-4′-*n* alkoxyazobenzenes may combine advantages of both series of homologous making feasible development of materials with even wider mesophase range.

CYANO-AZOBENZENES (PUSH-PULL STRUCTURES)

Inserting alkoxy or alkyl chains in the *para*-position of highly polar structure of 4-cyanoazobenzene leads to compounds with high melting points. Phase transition temperatures of 11 cyano azocompounds we

TABLE 3 Phase Transition Temperatures of Several Cyano Azocompounds

Compounds	Phase transitions, °C
4-*n*-alkoxy-4′-cyanoazobenzenes	
hexyloxy	Cr 99 N 116.5 I
heptyloxy	Cr 91 N 110 I
octyloxy	Cr 102 N 111 I
4-*n*-alkyl-4′-cyanoazobenzenes	
methyl	Cr 169 I
ethyl	Cr 118 I
propyl	Cr 90 N 91.5 I
butyl	Cr 100 I [76] N monotr
pentyl	Cr 91 I [86] N monotr
hexyl	Cr 89 I [72.5] N monotr
heptyl	Cr 76 N 80 I
octyl	Cr 85 I [74] N monotr

have synthesized are given in Table 3. Individual compounds of the series 4-*n*-alkoxy-4′-cyanoazobenzenes do not show practical nematic ranges. Although replacement of alkoxy groups by alkyl pendants leads to some decrease of melting points (10 to 17°C), the results are still far from being as impressive as in case of nonsymmetrical 4,4′-dialkylazobenzenes. Most of 4-*n*-alkyl-4′-cyanoazobenzenes have high transition temperatures dominated by monotropic nematic phases. Apparently, the high dipole moment associated with the cyano group enhances the tendency for crystallization. In principle, lowering of the melting temperatures of these, so-called "push-pull," azo structures could be achieved by inserting lateral substituents into their molecules in order to enhance molecular asymmetry.

SUMMARY

We have developed a large series of azo compounds, both multicomponent as well as single component, that possess room temperature nematic and smectic phases. Some of those materials have a wide mesophase temperature range, which makes them useful for a variety of practical applications. In addition, we have synthesized a series of high temperature azo LCs and isotropic azo compounds with very low melting points. Combination of those materials will allow the development of azo LC materials with custom phase transition temperatures. Physical, electro- and nonlinear-optical parameters of many of those materials have been characterized in detail. These materials are highly photosensitive exhibiting nonlinear refraction and transmission at nanowatt/microwatt power levels. They can be used for developing optically active complex material systems such as polymer dispersed liquid crystals, holographic PDLCs [10], and POLICRYPs [11], as well as for developing optically controlled cholesteric liquid crystals [12].

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