Enhancement of electro-optical properties of twisted nematic liquid crystals by doping aromatic hydrocarbon liquids

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Abstract: In this paper, doping liquid materials to enhance the electro-optical (EO) properties of twisted nematic liquid crystals (NLCs) was presented. Two aromatic hydrocarbon (AH) liquids, toluene and 1-methylnaphthalene, were chosen as dopants in order to lower the driving voltage and response time of the NLCs. A 18% decrease in driving voltage and response time was achieved by doping 10 wt% toluene into NLCs. The main reason of this phenomenon is due to a large amount of reduction in the rotational viscosity of AH liquids doped NLCs. This method provides an easy and potential choice for applications in various LC display systems.

OCIS codes: (160.3710) Liquid crystals; (230.2090) Electro-optical devices.

References and links

1. K. C. Chu, C. Y. Chao, Y. F. Chen, Y. C. Wu, and C. C. Chen, "Electrically controlled surface plasmon resonance frequency of gold nanorods," Appl. Phys. Lett. **89**(10), 103107 (2006).
2. H. Qi, B. Kinkead, and T. Hegmann, "Unprecedented dual alignment mode and Freedericksz transition in planar nematic liquid crystal cells doped with gold nanoclusters," Adv. Funct. Mater. **18**(2), 212–221 (2008).
3. W. K. Lee, Y. S. Choi, Y. G. Kang, J. Sung, D. S. Seo, and C. Park, "Super-fast switching of twisted nematic liquid crystals on 2D single wall carbon nanotube networks," Adv. Funct. Mater. **21**(20), 3843–3850 (2011).
4. J. Liu, J. C. She, S. Z. Deng, J. Chen, and N. S. Xu, "Ultrathin seed-layer for tuning density of ZnO nanowire arrays and their field emission characteristics," J. Phys. Chem. C **112**(31), 11685–11690 (2008).
5. H. G. Walton, "Influence of TiO_2 nanoparticle doping on the splay and bend elastic constants of the nematic liquid crystal 4-butyl-4-heptyl-bicyclohexyl-4-carbononitrile, CCN47," Mol. Cryst. Liq. Cryst. (Phila. Pa.) **574**(1), 60–66 (2013).
6. H. K. Chung, H. G. Park, Y. S. Ha, J. M. Han, J. W. Lee, and D. S. Seo, "Superior electro-optic properties of liquid crystal system using cobalt oxide nanoparticle dispersion," Liq. Cryst. **40**(5), 632–638 (2013).
7. S. Torgova, E. Pozhidaev, A. Lobanov, M. Minchenko, and B. Khlebtsov, "Nanocomposites consisting of gold nanorods and nematic liquid crystals: optical properties," Mol. Cryst. Liq. Cryst. (Phila. Pa.) **525**(1), 176–183 (2010).
8. D. P. Singh, S. K. Gupta, and R. Manohar, "$ZnO_{1-x}S_x$ nanosphere in ferroelectric liquid crystal matrix: the effect of aggregation and defects on the dielectric and electro-optical properties," Adv. Condens. Matter Phys. **2013**, 250301 (2013).
9. K. Araya, D. A. Dunmur, M. C. Grossel, G. R. Luckhurst, S. E. Marchant-Lane, and A. Sugimura, "Flexible dimers as dopants for liquid crystal display mixtures with faster relaxation times," J. Mater. Chem. **16**(48), 4675–4689 (2006).
10. P. Kilickiran, A. Masutani, N. Hollfelder, G. Nelles, and A. Yasuda, "Halogenated non-planar dopants for fast response liquid crystals," SID Symposium Digest **38**, 999–1002 (2007).
11. P. Kilickiran, A. Masutani, T. Roberts, N. Hollfelder, B. Schüller, G. Nelles, and A. Yasuda, "Towards faster liquid crystals at lower driving voltages," J. SID **16**, 63–70 (2008).
12. M. R. Cargill, G. Sandford, A. J. Tadeusiak, G. D. Love, N. Hollfelder, F. Pleis, G. Nelles, and P. Kilickiran, "Highly fluorinated biphenyl ether systems as dopants for fast-response liquid crystal display applications," Liq. Cryst. **38**(8), 1069–1078 (2011).
13. S. T. Wu, A. M. Lackner, and U. Efron, "Optimal operation temperature of liquid crystal modulators," Appl. Opt. **26**(16), 3441–3445 (1987).
14. S. Gauza, H. Y. Wang, C. H. Wen, S. T. Wu, A. J. Seed, and R. Dabrowski, "High birefringence isothiocyanato tolane liquid crystals," Jpn. J. Appl. Phys. **42**(1), 3463–3466 (2003).
15. P. R. Gerber, "Measurement of the rotational viscosity of nematic liquid-crystals," Appl. Phys., A Mater. Sci. Process. **26**(3), 139–142 (1981).

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16. H. Kneppe, F. Schneider, and N. K. Sharma, "Rotational viscosity -gamma-1 of nematic liquid-crystals," J. Chem. Phys. **77**(6), 3203–3208 (1982).
17. H. Schad and H. R. Zeller, "Universal law for the rotational viscosity of nematic liquid-crystals," Phys. Rev. A **26**(5), 2940–2945 (1982).
18. S. T. Wu and C. S. Wu, "Experimental confirmation of the osipov-terentjev theory on the viscosity of nematic liquid crystals," Phys. Rev. A **42**(4), 2219–2227 (1990).
19. G. Christoph, W. Stille, and G. Strobl, "Dependence of the rotational viscosity of nematic mixtures on the rotational diffusion constants of their components," J. Chem. Phys. **99**(4), 3075–3081 (1993).
20. M. Imai, H. Naito, M. Okuda, and A. Sugimura, "Determination of rotational viscosity and pretilt angle in nematic liquid crystals from transient current: Influence of ionic conduction," Mol. Cryst. Liq. Cryst. A **259**(1), 37–46 (1995).
21. E. Jakeman and E. P. Raynes, "Electrooptic response times in liquid-crystals," Phys. Lett. A **39**(1), 69–70 (1972).

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1. Introduction

Liquid crystals (LCs) are currently one of the most employed materials for electro-optical (EO) applications. A wide range of commercialized display devices, such as cell phones, monitors, or touching panels, are utilizing the techniques of liquid crystal displays (LCDs). In order to enhance the EO characteristic of LCDs, it is a quite important task to decrease the response time and lower the driving voltage in LCD applications. Recent years, doping nanoparticles into NLCs has been of magnificent interest to improve the EO properties of NLC devices. Many kinds of conducting nanomaterials, such as gold nanorods [1], gold nanoclusters [2], carbon nanotubes [3] etc., were dispersed into NLCs. Besides, many researchers developed insulating nanoparticles such as diamond powders, ZnO [4], TiO2 [5], and Ce3O4 [6] etc. to mix with LCs. A variety of valuable effects has been observed including maintaining the voltage holding ratio, lowering the threshold voltage, suppressing the screen effect, or reducing the transient current [1–6]. However, these nanoparticles might precipitate or aggregate to cause topological defects and to increase the response time and break the phase of LCs [7, 8]. In order to avoid these drawbacks of using nanoparticles, liquid materials might be an alternative choice to be as dopants. Previously, some flexible dimers were used to improve the relaxation times of LCDs [9]. Diaryl-ether derivatives or fluorinated biphenyl ethers also successfully improved the switching time on both positive and negative LCs [10–12], and the enhanced EO properties are mostly attributed to the reduced rotational viscosity. Therefore, we consider that doping liquid materials to decrease viscosity might be a better way to improve the LCD performances.

In this study, two aromatic hydrocarbon (AH) liquids, toluene and 1-methylnaphthalene (the chemical structures are shown in Fig. 1), were doped into NLCs for properties modification. The AH liquids are completely miscible with NLCs because they are comprised of simple aromatic rings. After the AH liquids were doped into NLCs, lower driving voltage and faster response time were observed in twisted nematic (TN) cells. Since toluene and 1-methylnaphthalene are both low-viscosity liquids (0.59 cP and 3.26 cP at 20°C, respectively) relative to NLCs, the viscosity of NLCs reduced by doping these two AH liquids were expected. We measured the rotational viscosity and demonstrated the relationship between the viscosity change and enhanced EO properties of doped NLC mixtures. Based on the aromatic dopants which researchers had utilized [9–12], our results demonstrate a much simpler and more common choice of doping AH liquid materials into NLCs. The AH liquids are potentially used in different LC systems that open a simple and efficient way to enhance the performance of LC electro-optical devices for display applications.

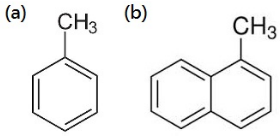

Fig. 1. Chemical structures of (a) toluene and (b) 1-methylnaphthalene.

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2. Experimental

Toluene (purity 99.8%, TEDIA) and 1-methylnaphthalene (purity > 94%, Merck) were doped into commercialized NLC (DF-7538A, Daily Polymer Corp.) separately with doping concentrations at weight ratios of 2.5, 5.0, 7.5, and 10.0 wt.%. The mixtures were then stirred at room temperature for one day. After the solutions were well-mixed, the mixtures with various doping concentrations were injected into empty cells of glass substrates coated with indium tin oxide (ITO) electrodes. On the top of ITO, the surfaces were covered with rubbed polyimide alignment layer. The unidirectional aligned substrates were fabricated in antiparallel direction with cell gap 15 μm and in twisted 90° direction with cell gap 4 μm for the measurement of phase retardation and EO properties, respectively. After the mixtures were injected, all cells were sealed with UV-curing adhesives to prevent the leakage of NLC mixtures.

The normally-white TN NLC cells were set up for the EO measurement of voltage-transmittance (V-T) curve and response time characteristics under room temperature. NLC cells were placed between mutually perpendicular polarizer and analyzer. A square wave voltage (1 kHz) with amplitude from 0 V to 8 V was applied to NLC cells. A He-Ne laser (λ = 632.8 nm) provided the incident laser light which was directed into the NLC cells, and the transmitted light intensity was measured through a photodiode. The NLC cells were also observed by a polarizing optical microscope (POM) and its charge-coupled device (CCD) camera to verify whether there were local defects generated by the doped liquid materials in NLC mixtures.

3. Results and discussions

The POM images of NLC mixtures are shown in Fig. 2. Figure 2(a) is the result of pure undoped NLCs and Figs. 2(b)-2(c) are the results of NLCs doped with 10 wt.% toluene and 1-methylnaphthalene, respectively. Each set of pictures contains the bright states (voltage off) on the left side and dark states (voltage applied) on the right. From these pictures, there were no noticeable defects in the AH liquids doped NLCs. Only the mixture with 10 wt.% 1-methylnaphthalene presents a little weak dark state compared with the undoped NLCs. As the doping concentration raises to 12 wt.%, the dark states shown in Figs. 2(d)-2(e) are too weak, which degrades the contrast ratio obviously. Therefore, we did not proceed the following experiments at AH liquids doping concentrations beyond 10 wt.%.

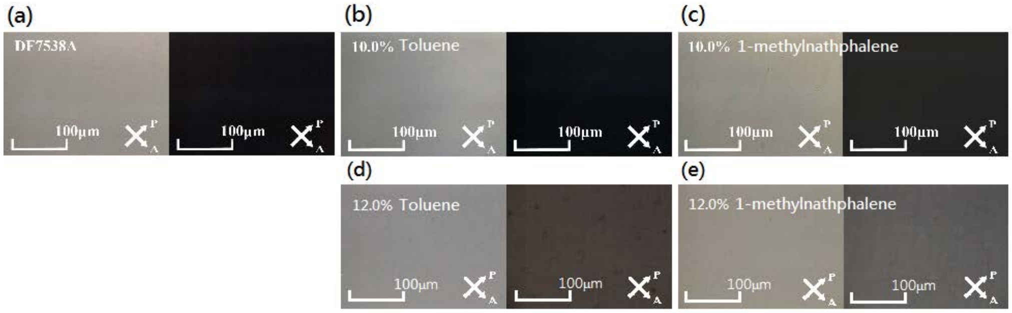

Fig. 2. Polarizing optical microscopy (POM) pictures of (a) NLCs, (b) doping 10 wt.% toluene, and (c) doping 10 wt.% 1-methylnaphthalene, (d) doping 12 wt.% toluene, and (e) doping 12 wt.% 1-methylnaphthalene. POM images show the bright states (voltage off) on the left side and dark states (voltage applied) on the right side for each group of pictures. A and P show the directions of analyzer and polarizer.

The V-T characteristics of various doping concentrations were measured and shown in Fig. 3. The driving voltage (V_d) is defined as the voltage required to achieve 10% of the maximum transmittance. The driving voltage of undoped NLC was 2.46 V, and it decreased as AH liquids doping concentration increased. Toluene doped NLCs exhibited a larger impact on the descending of the driving voltage, as shown in Fig. 3(a). It was reduced by 18% to 2.02

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V at 10 wt.% toluene doped in NLCs. The driving voltage of 1-methylnaphthlene doped NLCs (Fig. 3(b)) was also reduced by 12% to 2.17 V at the concentration of 10 wt.%. All the measurements were reproduced and yielded similar results after several weeks, showing the stability of doping these two AH liquids into NLCs.

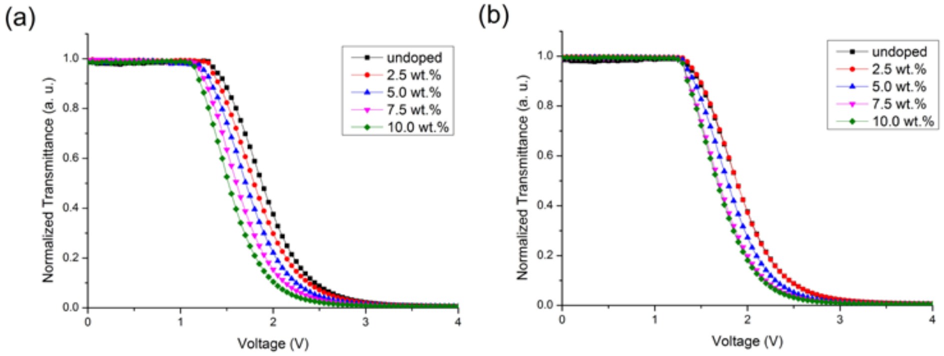

Fig. 3. Voltage-transmittance curves with various doping concentrations of (a) toluene and (b) 1-methylnaphthalene.

The results of response time measurements were shown in Fig. 4. Response time is defined as the addition of rise time and decay time. Rise time and decay time are evaluated as the time intervals required to reach 10% and 90% of the transmittance by the application and removal of external voltage (8 V), respectively. Figures 4(a)-4(b) show the performances of rise time and decay time of NLCs doped with toluene and 1-methylnaphthalene, respectively. Rise time was decreased with doping toluene into NLCs, but showed no dependence on the doping concentrations. 1-methylnaphthalene, on the other hand, had no noticeable effects on reducing the rise time. However, both toluene and 1-methylnaphthalene dopants were capable to reduce the decay time of NLCs. As the results, the response time (rise time + decay time) of NLCs was ultimately decreased by 18% and 15% from 22.8 ms to 18.6 ms and 19.4 ms by doping 10 wt.% toluene and 1-methylnaphthalene, respectively.

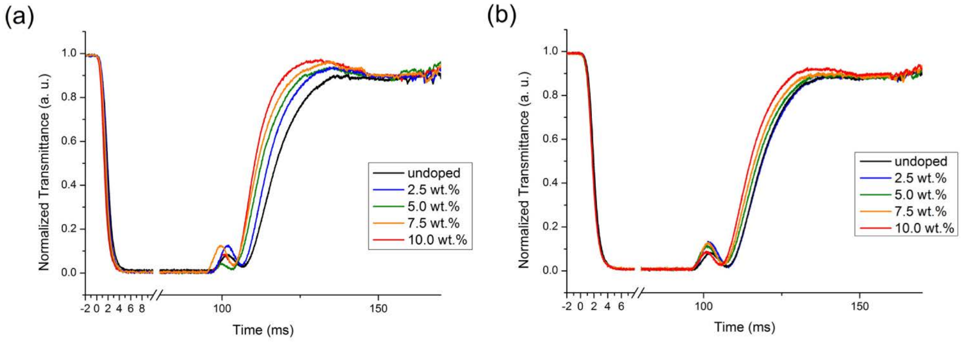

Fig. 4. (a) & (b) The performances of rise time and decay time of doping toluene and 1-methylnaphthalene into NLCs, respectively.

Within all the parameters that influence the response time and driving voltage, rotational viscosity (γ_1) and elastic constant (K_{eff}) are significant intrinsic parameters of NLCs. Rotational viscosity is proportional to response time and the driving voltage while the elastic constant is inversely proportional to them. In some previous studies, the doped nanoparticles tended to enlarge the elastic constant by raising the dielectric anisotropy ($\Delta\varepsilon$) of NLCs [6]. Although the rotational viscosity of NLCs might increase slightly, the visco-elastic coefficient (γ_1/K_{eff}) was decreased. Therefore, the slight increase of rotational viscosity could be negligible to treat it as a constant during doping nanoparticles. In our work, we consider

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rotational viscosity should be the main reason to improve the EO properties of NLCs since toluene and 1-methylnaphthalene are both extremely low-viscosity materials compared with NLCs. Although elastic constant might decrease at the same time, the EO properties are still improved as long as the visco-elastic coefficient decreases [13, 14].

Several experimental methods had been developed to measure the rotational viscosity [15–20], and the phase decay time measurement [18] was used in this work. Antiparallel aligned cells were used to measure the phase retardation and the birefringence. A small bias voltage (V_b), which was usually chosen at the first maximum or minimum transmittance occurred in the phase retardation figure, was applied to cells so that the LC directors were deformed by a small angle. After the bias voltage was cut off, the phase decay time $\delta(t)$ and the intensity of transmittance $I(t)$ can be expressed as [18]

$$\delta(t) = \delta_0 \exp(-\frac{2t}{\tau_0}) \tag{1}$$

$$I(t) = I_0 \sin^2(\frac{\Delta_{tot} - \delta(t)}{2}) \tag{2}$$

where δ_0 represents the initial relative phase retardation; I_0 is the initial transmittance at $t = 0$; Δ_{tot} and τ_0 are the total phase retardation and the phase relaxation time, respectively. τ_0 is determined from the slope of the curve of $\ln(\delta(t)/\delta_0)$ versus time t. As shown in Fig. 5(a), the phase relaxation time of NLCs was lowered by doping the AH liquids, which implies that AH liquids doped NLCs need less time to return the original phase compared with undoped NLCs. After the derivation of τ_0, the following Eqs. express the rotational viscosity:

$$\gamma_1 = \frac{\tau_0 K_{11} \pi^2}{d^2} \tag{3}$$

$$K_{eff} = (\frac{V_{th}}{\pi})^2 \varepsilon_0 \Delta\varepsilon \tag{4}$$

where d is the cell gap, V_{th} is the Fréedericksz threshold voltage, which was determined from the phase retardation curve, $\Delta\varepsilon = \varepsilon_{/\!/} - \varepsilon_{\perp}$ is the dielectric anisotropy.

The birefringence and dielectric anisotropy of the NLC mixtures are showed in Table 1. Since the AH liquids do not have optical and dielectric anisotropy, both Δn and $\Delta\varepsilon$ decrease after doping, which lowers the elastic constant. The orientation order of LC molecules would be disadvantageously impeded if the elastic constant decreases in large scale, which is observed by the weak dark state of high doping concentration in Fig. 2. However, as shown in Fig. 5(b), the rotational viscosity of NLCs decreased to nearly half of its original value when 10 wt.% toluene were doped, so the visco-elastic coefficient still decreased with the rise of doping concentrations. Moreover, the Eq. (3) shows that the visco-elastic coefficient is just proportional to the phase relaxation time, so the descending of τ_0 already implies the higher response speed of NLCs. Since 1-methylnaphthalene has higher viscosity than toluene, it is less effective to decrease the viscosity of NLCs compared with toluene. From the above derivations and calculations, we unambiguously proved the viscosity was the main role to decrease the visco-elastic coefficient in this study.

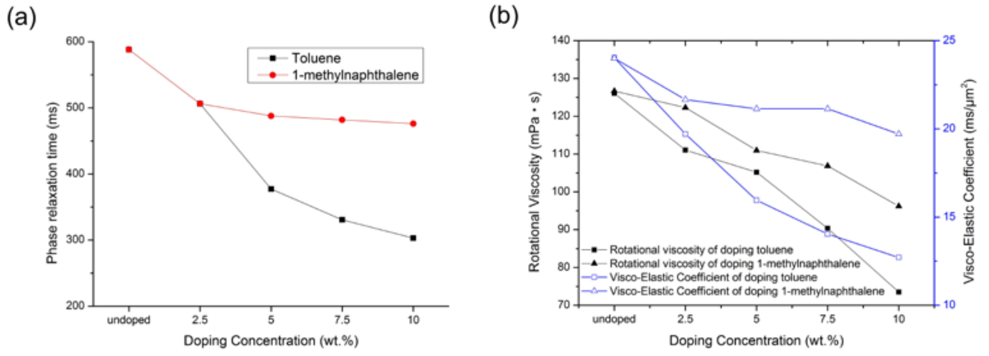

Fig. 5. (a) The phase relaxation time of NLCs doped with AH liquids at various concentrations. (b) The improvements of rotational viscosity and visco-elastic coefficient by doping AH liquids.

Table 1. The birefringence and dielectric anisotropy characteristics of AH doped NLCs.

	NLCs	Doping toluene (wt.%)				Doping 1-methylnaphthalene (wt.%)			
		2.5	5.0	7.5	10.0	2.5	5.0	7.5	10.0
Δn	0.092	0.088	0.083	0.080	0.078	0.091	0.090	0.089	0.086
Δε	7.22	6.98	6.82	6.51	6.45	6.98	6.63	6.38	6.03

Through Fig. 5 and Table 1, the improvement of driving voltage and response time could be explained. At low doping concentration, $\Delta\varepsilon$ does not change much compared with pure NLCs, which implies elastic constant does not decrease much, so rotational viscosity is the main parameter to influence EO properties. Since toluene helps NLCs to decrease the rotational viscosity more than 1-methylnaphthalene, 2.5 wt.% toluene could reduce the driving voltage obviously while 2.5 wt.% 1-methylnaphthalene has only subtle decrease on driving voltage. At high doping concentration, the elastic constant should be considered, so the visco-elastic coefficient has more influence on EO properties rather than rotational viscosity. Despite the rotational viscosity decreases drastically at high toluene doping concentration, driving voltage doesnot show the same tendency due to the visco-elastic coefficient. Likewise, visco-elastic coefficient decreases in a small amount at high 1-methylnaphthalene doping concentration, so the driving voltage also deceases very little at high doping concentration. For response time dynamics, it is referred to the following Eqs [21],

$$T_{rise} = \frac{\gamma_1 d^2}{K_{eff}\pi^2 \left|V^2 - V_d^{\ 2}\right|} \tag{5}$$

$$T_{decay} = \frac{\gamma_1 d^2}{K_{eff}\pi^2} \tag{6}$$

where T_{rise} and T_{decay} are the rise and decay time constants, respectively. Though the time constants are defined differently with the experimental results of response time, Eqs. (5) and (6) can show the tendency between Fig. 4 and Fig. 5(b). In Eq. (5), rotational viscosity does influence on the rise time, however, voltage also influences on the rise time. As the results of these two parameters, rise time of doped NLCs either decreases only a small amount, which barely figured out the concentration dependence (Fig. 4(a)), or seems no variation with the undoped rise time (Fig. 4(b)). It depends on how much viscosity decreases. Toluene helps

NLCs to decrease viscosity much more than 1-methylnaphthalene, so the small decrease of rise time could be observed in Fig. 4(a). For decay time, since there is no voltage dependence in Eq. (6), the decrease of decay time followed the similar mechanism with the decrease of driving voltage.

4. Conclusions

In this study, a simple and efficient way to improve the performance of TN LC devices by doping a small amount of AH liquids into LCs was presented. The electro-optical properties of TN LC devices can be optimized by adjusting the AH doping concentrations. When doping concentrations were increased, the AH liquids doped NLCs exhibited the lower driving voltage and faster response time. The main reason of this phenomenon is due to the low viscosity of AH liquids which lowers the rotational viscosity of NLC mixtures. Based on the aromatic dopants which researchers had utilized [9–12], our results demonstrate a much simpler and more common choice of doping AH liquid materials into NLCs. To sum up, without the drawbacks that doping solid nanoparticles could have, the AH liquid doping method provides a more promising opportunity for applications not only in various LC display systems but also other fields in similar aspect in the future.

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