

A Liquid Crystal Material with High Negative Dielectric Anisotropy for Improving Response Time

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Abstract

Response time is one of the most important parameters to evaluate an LCD panel. To achieve faster response in LCDs, better liquid crystal monomers are needed while other parameters remain unchanged. For this purpose, liquid crystal monomers with higher dielectric anisotropy and lower rotational viscosity are urgently required. Herein, in this work, we reported a new liquid crystal material, named DBDF, that possessed highly negative dielectric anisotropy and relatively low viscosity. Utilizing a proper ratio in the liquid crystal mixtures, DBDF could maintain high reliability and stability before and after UV irradiation. Furthermore, compared to normal liquid crystal materials, the addition of DBDF enabled a shorter response time when keeping other parameters the same. Overall, DBDF will be a good candidate to improve the response of liquid crystals.

Author Keywords

liquid crystal, negative liquid crystal, dielectric anisotropy, response time.

1. Introduction

Liquid crystal displays (LCDs) have proceeded considerably since the 21st century.^[1,2] Nowadays, the LCD industry is developing in the direction of fast response time (RT), low power consumption, high resolution and high contrast.^[3,4] Such evolution directions raised requirements for new generations of LCD materials. Liquid crystal materials play a critical role in the fabrication of LCD panels and are closely related to the display properties such as response time, contrast ratios and driving voltages.^[4-6]

Liquid crystals (LCs) used in LCD panels usually consist of 10 to 20 different liquid crystal monomers and other additives.^[7] The monomers physically interact with each other and eventually form a steady state, exhibiting specific physical properties, such as clearing point (T_{ni}), optical anisotropy (Δn), dielectric anisotropy ($\Delta\epsilon$), elastic constant (K_{11} , K_{22} and K_{33}) and rotational viscosity (γ_1).^[8-10] Among all these parameters, response time is related to dielectric anisotropy, elastic constant and rotational viscosity of liquid crystals.^[11,12] High $\Delta\epsilon$ can decrease the driving voltage of LCs and thus reduce the response time compared to LCs with low $\Delta\epsilon$. However, conventional liquid crystal materials with negative dielectric anisotropy usually exhibit high rotational viscosity due to the existence of fluorine atoms on the edge of the core structure.^[13] Moreover, the ratio of γ_1/K_{eff} was usually used to estimate the response time. Increasing K value and decreasing γ_1 are the common strategies to decrease the response time of LCs. Nevertheless, increasing K and decreasing γ_1 are contradictory.

High K molecules generally possess more rigid rings in the structures, which will increase rotational viscosities and clearing points, leading to an even slower response. Utilizing low K monomers will cause the drop of T_{ni} of the final LC mixtures and is possibly not able to meet the industrial requirements.^[14] Therefore, further decreasing the response time based on traditional liquid crystal materials is becoming more and more difficult.

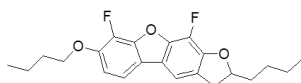
Ferroelectric liquid crystals perform much better than nematic liquid crystals at response time. Since spiral structures of ferroelectric liquid crystals in the SmC phase show spontaneous polarization and molecular conversion at the microsecond level, ferroelectric liquid crystals can reduce the response time to less than 1 millisecond.^[15-17] However, spiral structures and polarization characteristics of the SmC phase require extremely high surface anchoring force to promote uniform alignment over a large area, so the mass production of ferroelectric liquid crystals is still a challenge.^[18]

To break through the bottleneck and improve the response time of negative liquid crystals, new liquid crystal monomers are urgently required. Therefore, in this paper, we developed a new liquid crystal monomer based on the scaffold of dibenzodifuran with a high negative dielectric anisotropy, named DBDF (DiBenzoDiFuran). DBDF showed extraordinary absolute $\Delta\epsilon$ and relatively low rotational viscosity. Compared to normal liquid crystal materials, the addition of a proper amount of DBDF showed a negligible effect on reliability and stability before and after UV exposure. With the addition of DBDF, LC mixtures displayed faster response time in display panels without affecting reliability.

2. Evaluation of the physical properties of DBDF

Every single component in liquid crystals is able to affect the mixture properties significantly. By adjusting the types and ratios of monomers, liquid crystal materials can behave quite different physical properties with various potential applications. Therefore, evaluating the physical properties of DBDF monomer could accelerate the understanding of this new liquid crystal material and the development of new liquid crystals (Scheme 1). The physical properties of monomers are usually measured in known liquid crystal hosts with the addition of the proper amount. The addition of too little amount may generate unstable data because of the weighing errors, while adding an excess amount possibly displays solubility problems. Therefore, to compare the properties of the DBDF monomer with a common negative LC monomer, DBDF and one reference monomer were added with a ratio of 4 %

(w/w) into a liquid crystal host, respectively. As shown in Table 1, the addition of DBDF dramatically enhanced the negative dielectric anisotropy of the mixture from -3.86 to -4.50, while adding reference only changed $\Delta\epsilon$ slightly to around -4.05, demonstrating the high negative $\Delta\epsilon$ of DBDF. In terms of Tni, the reference exhibited a negative effect on the host. Moreover, Δn and the viscosity of Host-DBDF and Host-reference were increased. The properties of DBDF and reference were estimated in Table 2. Compared to the reference, DBDF displayed extraordinarily negative dielectric anisotropy ($\Delta\epsilon = -19.9$), which was much higher than that of the reference. Even though DBDF exhibited a relatively low Tni value, the lower rotational viscosity of DBDF indicated a faster response. In addition, DBDF showed a similar Δn with reference, which could be possibly employed to decrease the cell gap and response time. In general, DBDF exhibited quite fascinating physical properties and potentially could be used to decrease the response time when fabricated into panels.



DBDF

Scheme 1. The chemical structure of DBDF.**Table 1.** The properties of liquid crystals.

Name	Host	Host-DBDF	Host-ref
Components	100% host	96% host 4% DBDF	96% host 4% ref
Tni (°C)	79.6	78.0	82.9
Δn (589 nm)	0.1153	0.1185	0.1193
$\Delta\epsilon$ (1 kHz)	-3.86	-4.50	-4.05
K_{11} (pN)	13.6	13.4	14.1
K_{33} (pN)	14.6	14.0	15.4
γ_1 (mPa·s)	75.0	80.1	80.9

Table 2. The estimated properties of DBDF and reference monomers.

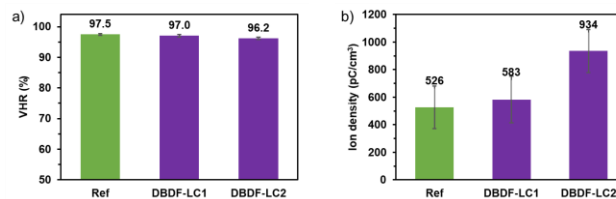
Name	DBDF	Reference
Tni (°C)	39.6	162.1
Δn (589 nm)	0.1953	0.2153
$\Delta\epsilon$ (1 kHz)	-19.9	-8.6
γ_1 (mPa·s)	384.8	502.7

3. Evaluation of the reliabilities of DBDF

The reliability of liquid crystal monomers determines whether a monomer can be applied to produce mature liquid crystal materials. To evaluate the reliability of liquid crystal materials, voltage holding ratio (VHR) and ion density are the most fundamental parameters to check. High VHR and low ion density usually indicate relatively good reliability and allow the material to be tested on the production line. To fairly compare the VHR and ion density of DBDF and mature liquid crystal samples, reference and two DBDF-containing LCs were prepared with commonly used liquid crystal monomers and DBDF. In general, Tni and $\Delta\epsilon$ can affect the VHR value. High Tni and low absolute $\Delta\epsilon$ are usually associated with high VHR values. Low absolute $\Delta\epsilon$ can decrease the adsorption of ionic impurities in LC mixtures and thus show higher VHR value than LCs with high absolute $\Delta\epsilon$. Therefore, during the preparation of samples, the Tni of the three samples was maintained at a similar level (Table 3). Due to the nature of high negative dielectric anisotropy, higher amounts of DBDF in liquid crystals could greatly increase the absolute $\Delta\epsilon$ of liquid crystal mixtures, which might lead to a low VHR value. As shown in Figure 1, with increased absolute $\Delta\epsilon$, the VHR value slightly decreased while the ion density increased as the amount of DBDF increased, which was consistent with the expectation. Though $\Delta\epsilon$ of DBDF-LC1 and DBDF-LC2 were much more negative than Ref, they showed only a slightly lower VHR value (97.0% and 96.2%, respectively) compared to Ref (97.5%), indicating quite good reliability.

TABLE 3 The properties of Ref, DBDF-LC1, DBDF-LC2 and Ref-RT.

Name	Ref	DBDF-LC1	DBDF-LC2	Ref-RT
Tni (°C)	77.4	77.8	78.0	78.0
Δn (589 nm)	0.0966	0.1006	0.1058	0.0991
$\Delta\epsilon$ (1 kHz)	-2.98	-3.57	-4.24	-3.56
K_{11} (pN)	13.1	13.4	13.3	13.3
K_{33} (pN)	15.5	15.2	15.0	15.3
γ_1 (mPa·s)	66.9	73.5	82.1	78.3
γ_1/K_{11}	5.11	5.49	6.17	5.89

**Figure 1.** The reliability tests of reference, DBDF-LC1 and DBDF-LC2. (a) The VHR value and (b) ion density of Ref, DBDF-LC1 (3 w/w%) and DBDF-LC2 (6 w/w%).

Ultraviolet irradiation sometimes can significantly affect the stability and reliability of liquid crystal samples, causing a dramatic VHR decline.^[19] To examine the UV effect on DBDF-containing LCs, VHR values of Ref, DBDF-LC1 and DBDF-LC2 were measured after different doses of UV exposure (Figure 2). Ref and DBDF-LC1 displayed minimal VHR changes before and after 8J and 16J UV exposure. The VHR of DBDF-2 exhibited a slight VHR decline with higher doses of UV irradiation, demonstrating that high amounts of DBDF in liquid crystal mixtures showed some negative effect on its anti-UV ability. It is worth noting that Ref mainly consists of normal liquid crystal monomers, which commonly exhibit fairly good reliability before and after UV irradiation. DBDF-LC1 with 3% (w/w) DBDF displayed negligible VHR change compared with Ref, indicating a comparable UV-resistant ability with Ref. Though DBDF-2 with 6% (w/w) displayed a small decrease in VHR value, which is 1.1% and 3.6% after 8J and 16J of UV irradiation, respectively, the resulting DBDF-LC2 after UV irradiation still exhibited high VHR value (91.8%). The results suggested that the addition of 6% DBDF displayed relatively good reliabilities and reasonable UV resistance ability. Therefore, the addition of a proper amount of DBDF does not affect the stability and reliability of liquid crystal mixtures.

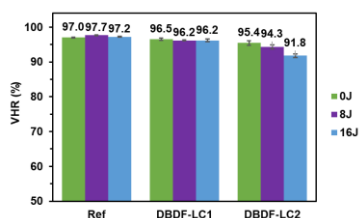


Figure 2. The VHR changes of Ref, DBDF-LC1 and DBDF-LC2 after different doses of UV exposure.

4. The effect of DBDF on response time

The response time is one of the dominant parameters to assess a liquid crystal material. The pursuit of a shorter response time is one of the main targets in the LCD industry. The response time for FFS liquid crystal materials can be estimated by γ_1/K_{11} .^[20, 21] Smaller γ_1/K_{11} indicates a shorter response time. Beyond that, absolute $\Delta\epsilon$ is relevant to the threshold voltage, which can affect the turn-on response time under the same driving voltage. Therefore, to evaluate the contribution of DBDF to response time and eliminate the influence of factors, Ref-RT without DBDF inside, was prepared as a reference (Table 3). Ref-RT and DBDF-LC1 exhibited very similar photophysical properties, including T_{ni} , $\Delta\epsilon$ and K values. The reliabilities of Ref-RT and DBDF-LC1 were first compared. Various conditions were conducted on LC samples to accelerate the aging of liquid crystal materials under natural conditions (Figure 3). Before aging, DBDF-LC1 exhibited similar VHR and ion density values with Ref-RT. UV exposure of 8J slightly decreased the VHR of DBDF-LC1 (1.2%). However, UV displayed almost no effect on Ref-RT. Even though DBDF-LC1 behaved a mild loss in VHR after UV, the sample itself still showed quite high VHR, indicating negligible impact

on its behavior in real panels. Meanwhile, 7-day aging by the backlight and 20-day aging by heat barely generated changes in the VHR value of the two samples. Surprisingly, backlight and heat aging significantly reduced the ion densities of Ref-RT and DBDF-LC1, and VHR values of two liquid crystals were measured. In general, DBDF-LC1 exhibited quite good reliabilities.

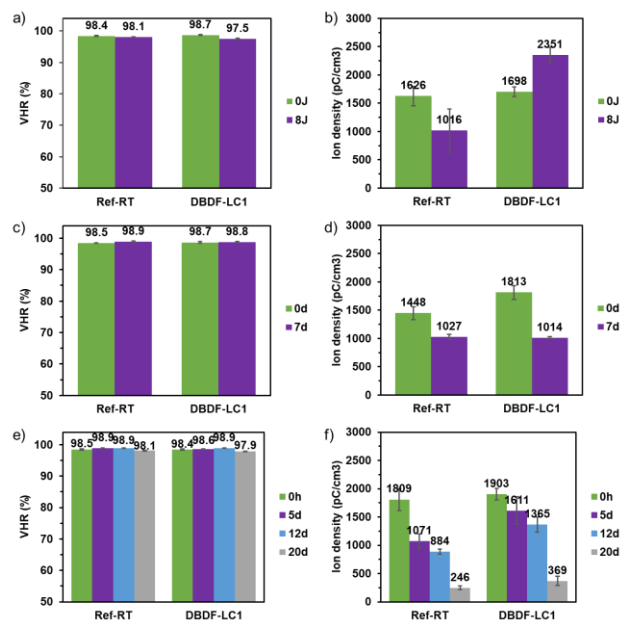


Figure 3. Reliability test of Ref-RT and DBDF-LC1. (a) VHR and (b) ion density of Ref-RT and DBDF-LC1 before and after 8J UV irradiation. (c) VHR and (d) ion density of Ref-RT and DBDF-LC1 before and after aging by backlight for 7 days. (e) VHR and (f) ion density of Ref-RT and DBDF-LC1 during heat aging at 60°C.

The rotational viscosity γ_1 of Ref-RT was larger than DBDF-LC1 (Table 3). Since K_{11} values of Ref-RT and DBDF-LC1 were almost the same, DBDF-LC1 displayed a 6.8% smaller γ_1/K_{11} than Ref-RT, suggesting that the response time of Ref-RT was slower than DBDF-LC1. To validate the expectation, DBDF-LC1 and Ref-RT were fabricated into panels, which could be utilized to measure the response time of liquid crystals (Figure 4a and b). Because cell gaps are one of the essential parameters that influence the response time, it is of primary importance to measure the cell gap of two sample cells. The cell gaps of Ref-RT and DBDF-LC1 were 2.99 μm and 2.95 μm , respectively, suggesting a minimal effect on their voltage-transmittance (V-T) curve and response time measurement (Figure 4c). Voltage-transmittance curves were then tested (Figure 4d). The V-T curve of Ref-RT and DBDF-LC1 overlapped well, demonstrating that two samples could be driven by the same voltage. The driving voltage was usually determined as the voltage at 97% transmittance, which was 6.4V for these two samples. Therefore, 6.4V driving voltage was exploited for measuring response time. As shown in Figure 4e, DBDF-LC1 displayed shorter T_{on} , T_{off} and RT than Ref-RT. With the addition of 3% DBDF towards

DBDF-LC1, the response time was 4.7% shorter than that of Ref-RT, which was consistent with the variation trend of γ_1/K_{11} values. Response time can also be reduced by decreasing the cell gaps. Therefore, by adding more amount of DBDF into the LC host, the response time is able to be further decreased. Overall, DBDF was an excellent liquid crystal monomer candidate that could significantly improve the response time of LCD panels without affecting the optical properties and reliabilities.

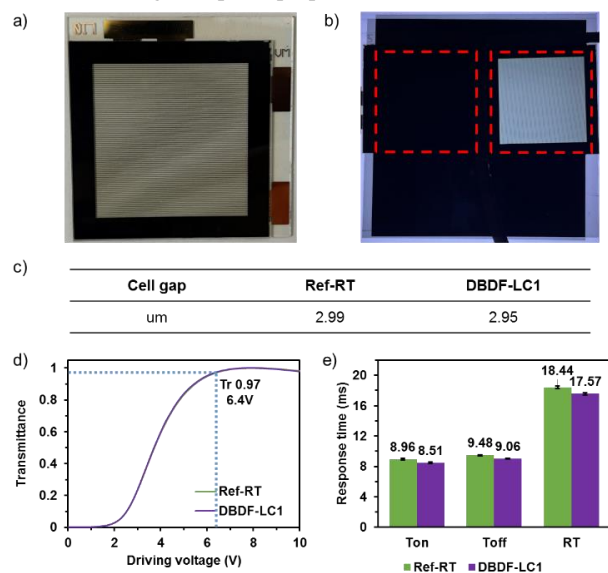


Figure 4. Response time test of Ref-RT and DBDF-LC1. (a) Test cell used for response time test. (b) Test cells at off-state and on-state. (c) The cell gaps selected for the response time test. (d) Voltage-transmittance curve of Ref-RT and DBDF-LC1. (e) Response time of Ref-RT and DBDF-LC1. The test cells were lit up with a 6.4V driving voltage.

5. Conclusion

The LCD industries are developing towards faster response, low power consumption, high contrast and high resolution. New liquid crystal materials are required to achieve these goals.^[22, 23] To improve the response time of existing liquid crystal materials, liquid crystal monomers with high K value, high absolute $\Delta\epsilon$ and low γ_1 are critical. The high K value and low γ_1 result in a small γ_1/K_{11} value, which can be used to reflect the response time in FFS panels. In terms of $\Delta\epsilon$, high absolute $\Delta\epsilon$ can decrease the usage of other monomers with negative dielectric anisotropy and high rotational viscosity, and replace them with less viscous monomers such as 4-propyl-4'-vinyl-bicyclohexyl, indirectly reducing the rotational viscosity of liquid crystal mixtures and their response time.

DBDF is one of such compounds that possess high absolute $\Delta\epsilon$ (-19.9) and relatively low γ_1 (384.8 mPa·s). The addition of a proper amount of DBDF in liquid crystals could maintain reliability after aging under different conditions. Furthermore, with similar T_{ni} , $\Delta\epsilon$ and K values, DBDF-LC1 displayed a shorter response time in test cells than Ref-RT, which was consistent with the γ_1/K_{11} trend. It should be noted that with the addition of only 3% DBDF, the response time was improved by 4.7%. By adding

more amount of DBDF and decreasing the cell gap, the response time could be further optimized. Therefore, DBDF is possibly an excellent material that can improve the response time of liquid crystals in LCD panels with a proper amount of addition.

Beyond that, the property of highly negative dielectric anisotropy makes DBDF a good candidate for the development of low-power consumption liquid crystals. The high absolute $\Delta\epsilon$ value of DBDF can increase the $\Delta\epsilon$ of liquid crystal mixtures and thus reduce the required driving voltage.^[24] The adding amount of DBDF without affecting the reliability might be improved by applying stabilizing reagents in LC mixtures. These possibilities might be explored in future work.

In this work, we explored the properties and applications of a new liquid crystal monomer, DBDF, which possessed high negative dielectric anisotropy and had the potential to improve the response time of liquid crystal mixtures. DBDF showed extraordinary absolute $\Delta\epsilon$ and relatively low γ_1 . The addition of a proper amount of DBDF in liquid crystal mixtures could maintain reliability to a similar extent with normal liquid crystal materials under various aging conditions. In addition, when meeting the same requirements on T_{ni} , Δn , $\Delta\epsilon$ and K values, samples containing a small amount of DBDF displayed significant improvement in the response time. Therefore, DBDF can be possibly exploited to develop new liquid crystals with faster response.

6. Acknowledgements

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7. References

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