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COMMUNICATION

Design of an extremely high birefringence nematic liquid crystal based on a dinaphthyl-diacetylene mesogen[†]

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We designed dinaphthyl-diacetylene-based nematic liquid crystals with alkoxy tails (DNDA–OC*m*) and evaluated their birefringence (Δn). Actual measurements of pure target compounds showed that DNDA–OC2 had the highest value of 0.62 at 550 nm at T_c + 10 °C.

Recently, high-birefringence (Δn) liquid crystalline (LC) materials have been increasingly used in various optical devices such as organic light-emitting diodes (OLEDs),¹ photostorage devices,² laser-emitting films,³ and telecommunication devices,⁴ and such materials are being extensively investigated from the viewpoint of finding even more applications. These materials have a small cell gap and small film thickness, leading to a short response time that proves advantageous in applications such as those mentioned above. Among LC compounds with high Δn values, those with conjugation along the long molecular axis are preferred. Multiple bonds or unsaturated rings are mainly employed for increasing the conjugation length. For example, LC compounds containing biphenyl,⁵ tolane,⁶ bistolane,⁷ heterocycle-tolane,⁸ and diphenyl-diacetylene (DPDA)⁹ moieties have been reported thus far.

Very recently, we have also reported on the birefringence of DPDA derivatives containing alkoxy tails (DPDA–OC*m*), as measured by considering specific compounds.¹⁰ We have established a method for the direct evaluation of Δn of nematic LC compounds. Our results show the great potential of these derivatives as compounds that do not suffer from host liquid crystal effects. This method is a strong tool for screening high Δn nematic LC compounds.

The naphthalene skeleton has emerged as a candidate for high- Δn LC compounds, especially 2,6-disubstitution products because of the almost linear structure of naphthalene.¹¹ In addition, dinaphthyl-diacetylene (DNDA) with alkoxy tails (DNDA–OC*m*), *e.g.* 1,4-bis(2-naphthyl)buta-1,3-diyne, has also been reported.^{11d} However, the optical properties—*e.g.* refractive index and birefringence—of these compounds have not yet been reported.

In this paper, we report the Δn values of compounds of the DNDA–OC*m* series by employing our method. We find that these compounds show extremely high Δn values and a nematic phase over

a wide temperature range. By examining the wavelength and temperature dependence of Δn for various alkoxy tail lengths, we then discuss their optical properties in detail.

The synthesis of dialkoxy-dinaphthyl-diacetylene (DNDA–OC*m*) (Fig. 1) was performed with the literature method.^{11d} The structures of the obtained compounds were confirmed by ¹H-NMR, ¹³C-NMR and high-resolution mass spectrometry (see ESI[†]).

The thermal properties of DNDA-OC*m* were investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). Representative DSC curves, and all the phase transition temperatures and enthalpy changes were measured during the cooling scan, the results of which are shown in the ESI[†]. As might have been expected, all the compounds were observed to exhibit nematic behaviour. However, all compounds in the DNDA-OC*m* series had a high transition temperature. In particular, DNDA-OC1-3 was observed to gradually decompose at ~260 °C. Therefore, we could not observe a clearing point with respect to DNDA-OC1-3. On the other hand, DNDA-OC5, 6, 8, and 9, which have tails of a certain length, showed a relatively reasonable melting point of 120–130 °C, similar to those reported in the literature.^{11d}

In the UV-visible spectra, the absorption edge of DNDA–OC6 was approximately 375 nm because of the naphthalene backbone. Other compounds of the DNDA–OC*m* series also exhibited similar absorption tails and waveforms. Because these compounds do not exhibit absorption in the visible regions, the DNDA moiety should serve as an appropriate mesogen for optical films. The representative UV-vis spectrum of DNDA–OC6 is shown in the ESI[†].

The Δn values of LC compounds were obtained by extrapolating the values measured by using a eutectic mixture that served as an LC phase at room temperature.^{2,5-9} It should be noted that we have only measured the values of the target LC compounds. The measurement method of Δn is described in the literature.¹⁰⁶

The wavelength-dependent Δn values of DNDA–OCm are plotted in Fig. 2 as respective maximum values before they are crystallized in a cooling process. All the compounds showed extremely high values of Δn . To the best of our knowledge, no





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Fig. 2 Wavelength dependence on birefringence of DNDA–OC*m* series at T_c + 10 °C.

other compounds have been measured to show such high values among the actual values of pure compounds. In particular, Δn is considerably higher in the blue region than in the near infrared region, because the former is closer to the absorption wavelength of the compounds of the DNDA–OC*m* series.^{7c} Moreover, by increasing the number of alkoxy tails from 2 to 9, the value of Δn at 550 nm for DNDA–OC*m* reduces from 0.62 to 0.37, with an average of approximately 0.2, which can be explained on the basis of the dilution effect, molecular packing density effect, decreased optical anisotropy, and order parameter effects.^{5a,12}

On the other hand, the Δn value of DNDA–OC2 is greater than that of DPDA–OC1. This is due to DNDA–OC2 is highly oriented than DPDA–OC1 in this measurement temperature. Compared with DNDA–OC2, the measurement temperature region of DNDA–OC1 is narrower, because DNDA–OC1 shows a higher crystallization temperature (T_c) than that of DNDA–OC2. Essentially, in increased nematic phase region, an order parameter is a larger value.^{7b} Therefore, DNDA–OC2 is highly oriented and shows higher Δn value than DPDA–OC1. Haller's approximation¹³ is usually employed to describe the temperature dependence of birefringence:

$$\Delta n = \Delta n_0 S \tag{1}$$

$$\Delta n = \Delta n_0 \left(1 - T/T_{\rm i}\right)^{\beta} \tag{2}$$

Here, *S* is the order parameter; Δn_0 , the perfectly oriented birefringence (*S* = 1); β , the material constant; and *T*_i, the isotropic point of the LC phase. The values of n_0 and β were obtained by fitting the experimental data using eqn (1) and (2), respectively. The temperature-dependent Δn values for the compounds of the DNDA–OC*m* series (see ESI†) were found to exhibit a good curvilinear relationship. However, DNDA–OC1 was considered as an exception because its temperature span in which Δn was measurable is too small. Further, all the compounds were fitted to eqn (1) and (2) with the Δn_0 , β , and T_i values listed in Table 1. As expected, all the values of Δn_0 were high, and the β values were constant at approximately 0.2 (for a more detailed calculation of β , see ESI†).

First, the results showed that the compounds of the DNDA–OC*m* series had a high potential when they were perfectly oriented; in particular, the potential of DNDA–OC2 was approximately 0.78 at 550 nm. This implied that if the orientation degree was the same (S = 1), Δn_0 decreased when the length of the alkoxy tails increased as well as the wavelength dependence of birefringence.

Table 1 Δn_0 and β values of DNDA–OCm at 550 nm

Sample	Δn_0	β	T_{i}^{a}	$T_{\rm i}$
DNDA-OC2	0.78	0.14	319.8	b
DNDA-OC3	0.74	0.18	290.0	b
DNDA-OC5	0.64	0.19	246.0	243.2^{c}
DNDA-OC6	0.64	0.19	239.0	236.1^{c}
DNDA-OC8	0.59	0.20	208.4	210.2^{d}
DNDA-OC9	0.53	0.17	192.0	197.8 ^d
DPDA-OC2	0.68	0.17	212.2	208.8^{d}
DPDA-OC3	0.60	0.18	178.1	175.2^{d}
DPDA-OC5	0.50	0.15	154.9	153.1 ^d
DPDA-OC6	0.46	0.16	151.0	147.5 ^d

^{*a*} Associated with the fitting plot. ^{*b*} We could not confirm their T_i because of their decomposition at ~260 °C. ^{*c*} Observed by POM. ^{*d*} Measured by DSC (heating).

Next, we compared the T_i values obtained from the fitting of the experimental data with those measured by DSC under heating for DNDA–OC8 and 9. These two sets of T_i values were similar. Although the fitted values were slightly different from those measured by DSC, they were in good agreement.

Recently, we have reported that diphenyl-diacetylene with alkoxy tails (DPDA–OCm) exhibited high Δn values. Therefore, in this study, we carried out a relative comparison of DNDA-OC6 with DPDA-OC6 at 550 nm at a standardized temperature $(T_i - T)$, and we found that these compounds showed a wavelength-dependent birefringence. Therefore, it is observed that at the same standardized temperature, the Δn value of DNDA-OC6 is greater than that of DPDA–OC6 by ~ 0.1 (Fig. 3). This difference is attributed to the longer conjugation length of DNDA-OC6, which is caused by the conversion of benzene rings to naphthalene rings. Moreover, we also compared the Δn_0 values with those of DPDA–OCm at 550 nm for the same alkoxy tails. The Δn_0 values of DPDA–OC2, 3, 5, and 6 are shown in Table 1. The Δn_0 values of DNDA–OCm are found to be greater than those of DPDA-OCm by 0.12 or more. These results indicate that converting a benzene ring into a naphthalene ring dramatically increases the birefringence.

Moreover, we carried out a comparison of the Δn_0 value of DNDA–OC*m* with that of DPDA–OC*m*, and approximated Δn_0 of O–DNDA–O by the following equation:^{10b}

$$\Delta n_0 = (\Delta n_1 + 2m\nu\Delta n_2)/(1 + 2m\nu) \tag{3}$$



Fig. 3 Comparison of Δn value of DNDA–OC6 with that of DPDA–OC6 at the same standardized temperature.

where Δn_1 is Δn of a O–DNDA–O moiety; Δn_2 , Δn of the alkyl tails; *m*, carbon number of alkoxy tails; ν , a volume fraction of a methylene unit of alkoxy tails, respectively. As a result, Δn_0 of O–DNDA–O moiety is approximated as 0.91, it is hardly different from that of O– DPDA–O moiety, 0.90.¹⁰⁶ On the other hand, in a relation of alkoxy tail lengths and Δn_0 values, it is revealed that DNDA–OC*m* maintains higher Δn_0 values than that of DPDA–OC*m* on increasing alkoxy tail lengths. It is thought to be due to decreased influence of the dilution effect by the alkoxy tails, with respect to DNDA–OC*m* having a larger mesogen.

In conclusion, we have synthesized compounds of the DNDA– OCm series and measured their birefringence in the nematic phase as well as the wavelength and temperature dependence of the birefringence. Our results showed that this series exhibited extremely high birefringence, with DNDA–OC2 showing the highest value of 0.62 at 550 nm. The nematic birefringence decreased with an increase in the alkoxy tail length of m because of the dilution effect. The birefringence of DNDA–OC6 was found to be higher than that of DPDA– OC6 at 550 nm at standardized temperature. In addition, with respect to Δn_0 values, that is, the case of perfectly oriented birefringence (S =1), those of DNDA–OCm are greater compared to DPDA–OCm because of the longer π -conjugation of the naphthalene skeleton. Thus, our investigations show that the DNDA–OCm series of compounds has great potential for use as high- Δn materials.

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