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Novel asymmetrical single- and double-chiral liquid crystal diads with wide blue phase ranges

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In this study, two series of novel asymmetrical single- and double-chiral liquid crystal diads using a central linker to link two different mesogenic cores were successfully synthesized. The effects of the position of chiral centers and the number of aromatic rings on the mesomorphic and electro-optical properties were investigated. We found that diads III-N (where N = A, B, C and D) have better mesophasic properties than II-N (where N = A, B, C, D and E). Compared with III-C with a chiral center at the terminal alkoxyl chain, diad III-D exhibited the widest temperature range of BPI (ca. 31°C) as the chiral center was introduced to the central linker. Besides III-D, BPs were also observed in diads II-B and III-B with a chiral center at the central spacer. According to our experimental results and molecular modeling, the mesomorphic properties and temperature ranges of BPs will be affected by the values of biaxiality and dipole moment, along with the bent shape of molecular geometry. Therefore, we demonstrated the first example of asymmetrical single- and double-chiral liquid crystal diads involved chiral centers located at the central linker to exhibit BPs, including the mesophases of BPI and BPIII, which might offer new BP single-components to the future applications of eutectic liquid crystal mixtures with wide BP ranges.

Introduction

It is well known that liquid crystal molecules may reveal many different mesophases, including nematic,1 smectic,2 cholesteric,3 and blue phases, are attributed to their chemical structures, such as molecular configurations with specific shapes and dipole moments. Among these mesophases, blue phase liquid crystals (BPLCs) are observed between isotropic phase and chiral nematic (N*) phase during cooling process, which have less applications due to their narrow mesophasic ranges (usually about 1 K).4 It has been reported that BPLCs aggregate into internal helical alignments called “double twist cylinders (DTC)”,5,6 where are three types of BPLCs: blue phase I (BPI), blue phase II (BPII) and blue phase III (BPIII). The packing structures of these three BPLCs are described as follows: BP I is a body-center cubic structure, BP II is a simple cubic structure,7,8 and BP III is the same symmetry as the isotropic phase with arbitrary orientation.9,10 BPLCs have different performances in the field of optoelectronics: Among all BPs, BP III has the fastest response speed,11 and BP II shows smaller hysteresis and faster response time than BP I.12 Though very narrow ranges of BPLCs were observed, polymer stabilized BPLCs was first discovered by Kikuchi et al. to extend the temperature range of BPs phase over 60°C.13 Since BPLC arrangements were stabilized by the polymer network design to enlarge the BPLC ranges, general interests have been attracted to develop BPLCs recently. Some advantages in the fields of optoelectronics and photonics are listed as follows:14,15 fast response time (about sub-millisecond), no alignment layer required,16 and free of typical birefringence.17

Nowadays, several research groups have reported numerous methods to induce the blue phase and enlarge the temperature range of blue phase, which were accomplished either by structural modifications or mixture optimizations. For example, Yang et al. utilized hydrogen bonds to stabilized BPLCs, where two complimentary hydrogen-bonded moieties were self-assembled by hydrogen bonds to form a BP complex with a wide temperature range about 23°C.18 In addition, they also tried to dope hydrogen-bonded bent-shaped and T-shaped molecules to stabilize BPs.19 Pivenenko et al. synthesized bimesogens structures to induce BPLCs with a BP temperature range ca. 44°C.20 Besides, U-shaped molecules have also been doped with a chiral additive to extend the BP range successfully.21 There are some reports demonstrated that several biaxial nematic LCs doped with certain amounts of chiral materials can enhance the temperature range of BPs.22–24 Although BPLCs have so many benefits, very limited single-component BPLC molecules with wide BPLC ranges have been developed so far. Lately, many experts have designed special molecular structures with different shapes to exhibit or stabilize BPLC mesophases: rod-like,25 bent-core,26 T-shape,27 discotic28 and (asymmetrical or symmetrical) diad29 architectures. Yoshizawa et al. used a binaphthyl structure to stabilize the blue phase with a temperature range of 30°C approximately.30 Interestingly, various structures of liquid crystal diads have been reported,31,32 but the mesophasic behavior of liquid
crystals almost only showed the nematic or smectic phases. However, Takezoe et al. linked a flexible spacer between a rod and a cholesterol mesogenic unit which exhibited a wide range of BPs.13 Our previous research also reported a bent-core oxadiazole-based liquid crystal to possess a blue phase with a wide range of ca. 30°C.36

In this study, we synthesized two series of novel asymmetrical single- and double-chiral liquid crystal diads with an odd-number spacer to link two different mesogenic rods and introduced chiral centers into the central linker and/or flexible terminus of the diads. We demonstrated the effects of the number of aromatic rings and the central linker and/or flexible terminus of the diads. The phase transition behaviors of the central linker and/or flexible terminus of the diads. Moreover, the phase transition sequences, electric-optical properties, Kerr constants and theoretical calculations of molecular modeling were investigated in this report.

Experimental

Spectroscopic analysis.

$^1$H NMR spectra were recorded on a Bruker Unity 300 MHz spectrometer using DMSO-d$_6$, CDCl$_3$ and THF-d$_8$ as solvents. Elemental analyses (EA) were performed on a Heraeus CHN-OES RAPID elemental analyzer. Synchrotron powder X-ray diffraction (XRD) measurements were performed at beam-line BL17A equipped with magnetic of the National Synchrotron Radiation Research Center (NSRRC), Taiwan, where the wavelength of X-ray was 1.33336 Å. The powder samples were packed in a capillary tube and heated by a heat gun, for which the temperature controller is programmable by a PC with a PID feedback system. The scattering angle theta was calibrated by a mixture of silver behenate and silicon.

Molecular simulation method.

The gas phase optimization of all asymmetrical structures of liquid crystal diads II-N (N = A, B, C, D and E) and III-N (where N = A, B, C and D) was carried out with the generalized gradient approximation (GGA) density functional B97D along with dispersion correction$^{37}$ using the standard 6-31G(d,p) basis set. The predicted minima were further confirmed by frequency calculations at the same level. Only the lowest energy conformations are reported here. The electrostatic potential derived charges (ESP) were calculated according to Merz–Singh–Kollman (MK) scheme$^{38}$ at the B97D/6-31G(d,p) level of theory, ESP results were used to compute maps of electrostatic potential. The results of all the calculations reported in this work were obtained using the Gaussian 09 ab initio/DFT quantum chemical package.$^{39}$

Liquid-crystalline and physical properties.

The phase transition behaviors of all final asymmetrical diads were characterized by polarizing optical microscopy (POM) using a Leica DMLP equipped with a temperature control hot stage (Mettler Toledo FP82HT). Temperatures and enthalpies of phase transitions were determined by differential scanning calorimetry (DSC, model: Perkin Elmer Pyris 7) under N$_2$ at a heating and cooling rate of 1 °C/min$^{-1}$. The performance of optical properties was determined in the range of blue phase temperature and the optical transmittance was studied with a function of applied electric AC field at 2 kHz. The transmittance with 100 % and 0 % were calibrated by that the cell under parallel polarizers. The distance between electrodes was 10 μm and the cell gap was maintained at 7.5 μm by spacers.

Preparation of materials.

(S)-6-((4’-cyano-[1,1’-biphenyl]-4-yl)oxy)-4-methylhexyl 4-((4-((4-( (R)-octan-2-yl)oxy)benzoyl)oxy)benzoyl)oxy)benzoate. (III-D). The synthesis of compound III-D was shown in Scheme 1. To a stirred solution of M1 (3.0 g, 9.7 mmol), M2 (2.42 g, 4.9 mmol) and 4-(N,N-dimethylamino)pyridine (DMAP) (0.13 g, 1.06 mmol) in dry dichloromethane (100 mL), N,N-dicyclohexylcarbodiimide (DCC) (2.35 g, 11.6 mmol) was added and the reaction mixture stirred at room temperature overnight under nitrogen. The resulting precipitate of dicyclohexylurea (DCU) was filtered off and washed with an excess of dichloromethane (20 mL). The solvent was evaporated and the crude product was purified by silica gel chromatography (n-hexane/dichloromethane = 1:1 v/v) and then recrystallized from methanol/dichloromethane (5:1 v/v) to afford compound III-D as a white solid in 78 % yield. $^1$H NMR (300 MHz, CDCl$_3$): δ (ppm) 8.27 (d, J = 8.7 Hz, 2H), 8.17 (d, J = 8.7 Hz, 2H), 8.14 (d, J = 9.0 Hz, 2H),
Table 1  Phase transition temperatures (°C) and enthalpies (J/g) of asymmetrical liquid crystal diads.*

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase transition temperature (°C) [enthalpies (J/g)]</th>
<th>ΔTbp (°C)</th>
<th>ΔTn (°C)</th>
<th>ΔTc (°C)</th>
<th>ΔTnas (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>II-A</td>
<td>Iso 99.2 [0.41] N 68.7 [1.89] SmA 36.6 [2.03] Cr</td>
<td>30.5</td>
<td>32.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II-B</td>
<td>Iso 93.8 [0.54] BPIII 90.4° N* 70.4 [2.31] SmA 44.3 [2.11] Cr</td>
<td>3.4</td>
<td>20.0</td>
<td>26.1</td>
<td></td>
</tr>
<tr>
<td>II-C</td>
<td>Iso 23.8 [3.57] Cr</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II-D</td>
<td>Iso 24.9 [16.11] Cr</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II-E</td>
<td>Iso 41.8 [0.10] N* 30.9 [0.83] Cr</td>
<td>10.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III-A</td>
<td>Iso 195.0 [1.12] N 119.1 [2.99] SmA 63.0 [1.51] Cr</td>
<td></td>
<td>75.9</td>
<td>56.1</td>
<td></td>
</tr>
<tr>
<td>III-B</td>
<td>Iso 182.2 [0.94] BPI 180.7° N* 106.2 [2.44] SmA 72.5 [1.22] Cr</td>
<td>1.5</td>
<td>74.5</td>
<td>33.7</td>
<td></td>
</tr>
<tr>
<td>III-C</td>
<td>Iso 109.5 [11.76] N˚ 87.6 [5.43] SmA 79.7 [2.03] Cr</td>
<td>21.9</td>
<td></td>
<td>7.9</td>
<td></td>
</tr>
<tr>
<td>III-D</td>
<td>Iso 108.0 [0.36] BPI 76.6° N˚ 51.9 [1.63] Cr</td>
<td>31.4</td>
<td></td>
<td>24.7</td>
<td></td>
</tr>
</tbody>
</table>

* Peak temperatures in the DSC profiles obtained during the first heating and cooling cycles at a rate of 1 °C/min. ** Iso = isotropic phase; BPIII = blue phase III; BPI = blue phase I; N = nematic phase; N˚ = chiral nematic phase; SmA = smectic A phase; Cr = crystal; * The transition to this phase was observed under the polarizing optical microscope and it was too weak to be recognized by the DSC. (Phase transition temperatures and enthalpies of heating process are shown in Table S1.)

Mesophase and thermal properties

As shown in Table 1, the phase transition temperatures, enthalpies and mesophase ranges of the asymmetrical liquid crystal diads were determined by differential scanning calorimetry (DSC) and polarizer optical microscope (POM). The transition temperature of BP-Chiral nematic (N˚) was determined by POM (at a cooling rate of 0.5 °C/min) due to their undetectable enthalpy changes by DSC. To realize the effect of various asymmetrical configurations, including different numbers (or positions) of chiral centers and aromatic rings, on mesophase and thermal properties of these asymmetrical single- and double-chiral liquid crystal diads, the comparison of all compounds is described as follows:

(i) Compounds II-N (where N = A, B, C, D and E).

Compound II-A (no chiral center) exhibits a phase transition sequence of Iso–Nematic (N)–Smectic A (SmA)–Crystal. We tried to introduce a single chiral center to the central linker and flexible terminus of diads II-B and II-C, respectively. In contrast to II-C, diad II-B revealed BPIII (ranging 3.4 °C) due to the chiral center located at the central spacer, which induced twisting power but didn’t diminish the interactions of mesogenic cores. However, as the chiral center was shifted to the terminal alkoxy chains, the mesophases were totally vanished in II-C due to a stronger chiral twisting of the chiral center closer to the rigid core. Moreover, we also introduced double chiral centers to both central linker and flexible terminus of diad II-D, which do not have any mesophases due to even a stronger chiral twisting than II-C to further eliminate mesogenic interactions of mesophases. The strongest chiral twisting of both diads II-C and II-D to reduce the mesogenic interactions of rigid cores were also evidenced by their lowest crystallization (as well as isotropization) temperatures among all diads. Among these described chiral diads (II-B, II-C and II-D), only diad II-B with a single chiral center at the central spacer displayed mesophases, including BPIII. Hence, another single chiral diad II-E was introduced to investigate the effects of chiral center position at the central spacer, which showed a phase transition sequence of Iso-N˚-Crystal. Diad II-E with a chiral center at the central spacer possessed a mesophase of N˚, but BPIII was absence in II-E due to the different location of chiral center in contrast to II-B. Accordingly, a single chiral center located at the appropriate position of the central linker was required for diad II-B to obtain BPIII.

Fig. 1 Chemical structures of compounds II-N (where N = A, B, C, D and E) and III-N (where N = A, B, C and D).
(ii) Compounds III-N (where N = A, B, C and D).

The phase transition sequence of compound III-A is similar to II-A, i.e., Iso-N-SmA-Crystal, but III-A has higher transition temperatures and wider mesoscopic ranges (i.e., N and SmA) than II-A due to the longer rigid core of III-A with a stronger π-π interaction. Similar to II-B and II-C, a single chiral center was introduced to the central spacer and flexible terminus of diads III-B and III-C, respectively. In comparison with III-C, single-chiral diad III-B exhibited BPI (ranging 1.5°C) due to the chiral center located at the central spacer. Nevertheless, as the chiral center was shifted to the terminal alkoxyl chain, III-C had similar mesophases of III-B, i.e., N’ and SmA, but BPI was totally disappeared in III-C due to a stronger chiral twisting of the chiral center closer to the rigid core. Because of the same reason, compared with III-B, most transition temperatures and both mesoscopic ranges of N’ and SmA were reduced in III-C. Accordingly, SmA was totally removed and BPI (ranging 31°C) was induced in double-chiral diad III-D owing to the introduction of double chiral centers to both central spacer and flexible terminus. Similarly, the strongest chiral twisting of diad III-D to decrease the mesogenic interactions of rigid cores was also evidenced by its lowest phase transition temperatures among all diads in series III.

(iii) Comparison of series II and III.

All phase transition temperatures of the corresponding phases in compounds III-N were higher than those of compounds II-N (where N = A, B, C and E) because of the longer rigid core of series III-N (where N = A, B, C and D) with stronger π-π interactions. Among all diads, only diads II-C and II-D did not have any mesophases owing to their strongest chiral twisting with less mesogenic interactions of shorter rigid cores. In contrast to II-C and II-D, compounds III-C and III-D with a longer rigid core possessed stronger π-π interactions to compensate the chiral twisting thus to preserve the molecular assembly of mesophases. Interestingly, among all asymmetrical diads, BPIs only exited in single-chiral diads II-B, III-B and double-chiral diad III-D, which all possessed chiral centers at central spacer. Compared with BPII of II-B, the other diads III-B and III-D possessed BPI owing to their longer rigid core. Above all, double-chiral diad III-D was discovered to possess the widest BP temperature range among all diads, which is the first molecular design of liquid crystal diad with double-chiral centers (at both central spacer and flexible terminus) in the literature.

Optical and XRD investigations

Regarding the blue phases of diads II-B, III-B and III-D, we investigated the phase transitions by POM on cooling process (cooling rate 0.5 °C min⁻¹). Fig. 2(a)-2(d) show the phase transitions of Iso-BPIII-N’-SmA in II-B, respectively. In addition, the POM texture of III-B at 181.0°C upon cooling (0.5 °C min⁻¹) is also illustrated in Fig. S1. Meanwhile, the phase transitions of Iso-BPII-N’ in III-D are shown in Fig. 3(a)-3(c), respectively. All phase transitions were investigated by XRD measurements and their related data are shown in Fig. S2 and Table S2 of the supporting information. Generally, sharp reflection peaks of XRD patterns (representing layer d-spacings) were observed in the small angle area of the smectic phase (including SmA), but only broad peaks were revealed in the wide angle area of the N and N’ phases. As shown in Table S2 (see the supporting information), II-A and II-B processed d-spacing values of 41.8 Å and 43.4 Å, respectively. In addition, III-A, III-B and III-C also exhibited d-spacing values of 49.7 Å, 50.1 Å and 45.7 Å, respectively. Their d-spacing values (d) were a little larger than their corresponding molecular lengths (L) by the theoretical simulation (shown below), which suggested the d-spacing values of SmA phase in these diads are interdigitated layer arrangements (i.e., L<d<2L). Therefore, the SmA phase was verified not only by the focal-conic fan texture of POM photo-images but also by the d-spacing values of sharp reflection peaks.

Optical and XRD investigations

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![Optical and XRD images](image_url)

**Cooling Process**

Fig. 2 POM textures of II-B upon cooling (0.5 °C min⁻¹). (a) isotropic state at 100°C. (b) blue phase III at 92.1°C. (c) chiral nematic phase at 80.2°C. (d) smectic A phase at 60.1°C. (Scale bar: 40μm. White arrows are the directions of polarizers and analyzers.)

The II-B behavior of BPIII could be verified by the rotation of the analyzer (see Fig. 4). As the analyzer was rotated clockwise by a small angle of 10° from the crossed position, the color was changed from blue to light blue (Fig. 4(a)). Upon rotating the analyzer counterclockwise by the same angle (10°) from the crossed position, the color was changed from blue to red (Fig. 4(c)). The POM observations also indicated that the phase of BPIII has selective reflection colors according to their pitch lengths, which were examined by changing the cross angles in the polarizer and analyzer of POM

![Electro-optical images](image_url)

**Electro-optical studies**

In order to investigate the electro-optical switching behavior in the blue phase of diads II-B and III-D, a rectangular wave function of the AC field at a frequency of 2 kHz was applied to measure the optical transmittance. Fig. 5 shows the voltage-transmittance curve at $T-T_{BP}=-2^\circ C$, where the black lines with solid squares and circle squares represent the transmittance of compound II-B upon increasing and decreasing voltages, respectively. The red lines with

![Electro-optical images](image_url)
solid dots and circle dots stand for the transmittance of III-D upon increasing and decreasing voltages, respectively. Both II-B and III-D showed enhanced transmittance by increasing the electric field. As transmittance reached 10 % and 90 % in the V-T curve, we found that III-D had higher respective electrical fields (11.5 and 17.2 V μm⁻¹) than II-B (10.2 and 15.6 V μm⁻¹). In addition, in-plane-switching (IPS) cells were utilized to realize the V-T hysteresis by increasing the voltage to saturation. Because hysteresis will influence the grayscale of liquid crystal device, the hysteresis should be minimized for real applications.²⁶ The definition of hysteresis is ∆V/Von (ΔV is the voltage difference between the forward and backward directions at half of the peak transmittance and Von is the driving voltage).²³ The electro-optical switching exhibited that II-B did not have any hysteresis (~0 %), but III-D was observed to have a large hysteresis (~27 %). Compared with II-B, the higher applied voltages (10 % and 90 % transmittance in the V-T curve) and hysteresis of III-D were due to a larger number of aromatic rings in III-D with stronger π-π interactions.

![Graph showing optical transmittance of diads II-B and III-D in BPs (at T-T_{BP} = -2°C).](image)

The values of response time for diads II-B and III-D were obtained from the electro-optical response curves of Fig. S3(a) and S3(b), respectively (see the supporting information). As summarized in Fig. 6, their values of response time were measured with a rectangular wave of the AC field (at a frequency of 2 kHz) for the rise and decay processes at T-T_{BP} = -2°C. The definitions of the rise time (τ_{on}) and decay time (τ_{off}) are the response time values for 90% transmittance change by increasing and decreasing voltage, respectively.⁴² Forty Both τ_{on} values of II-B and III-D in Fig. 6(a) were found to be reduced concomitantly by increasing voltage, but their τ_{off} values in Fig. 6(c) are enhanced by increasing voltage. The behaviour of increasing τ_{off} values with higher voltages can be explained by the unwinding helix mode of BPLCs stabilized by a higher voltage which is more difficult to relax back easily via the removal of electric fields.⁴¹ In the meanwhile, we found that the rise time τ_{on} of III-D is smaller than II-B, but the decay time τ_{off} of III-D is larger than II-B. Thus, the values of rise time (τ_{on}) and decay time (τ_{off}) have opposite trends for diads II-B and III-D. As a result, the values of total response time (τ_{total}=τ_{on}+τ_{off}) in Fig. 6(c) are enhanced by increasing voltage, which has the same trend as the decay time (τ_{off}) due to the larger values of τ_{off} with more contributions to τ_{total} compared with those of τ_{on}. According to Table S3, the average values of total response time (τ_{total}=τ_{on}+τ_{off}) for II-B and III-D are 2.74 and 3.56 ms, respectively, where II-B has the fastest total response time.

![Graph showing response time of diads II-B and III-D in the BP at T-T_{BP} = -2°C.](image)

According to the definition of the Kerr effect,⁴⁵,⁴⁶ the formula: Δn_{induced} = λKE², where Δn is the electric field-induced birefringence, λ is the wavelength of light, K is the Kerr constant and E is the electric-field. The Kerr constants of II-B and III-D in their corresponding BPs were 2.2x10⁻¹¹ and 2.7x10⁻¹¹ mV⁻², respectively, where BPI of III-D demonstrated the largest Kerr constant. The BPs with large field-induced birefringences would cause the orientation changes of the ordered molecules easily. In contrast to nitrobenzene with a well-known and large Kerr constant 2.2x10⁻¹²mV⁻², II-B and III-D possessed Kerr constants 10 times larger than nitrobenzene might have useful applications in the future.

### Theoretical simulation

As alluded to above, we carried out geometry optimization at the B97D/6-31G(d,p) level for all asymmetrical liquid crystal diads II-N (N = A, B, C and D) and III-N (N = A, B, C and D) to analyze the structural variations. The main geometric parameters for the ground states of lowest energy conformations of II-B, III-B and III-D bearing chiral centers at the central linker and/or terminal alkyl chain are summarized in Table 2 with molecule length, breadth, bent angle and dipole moment, which can influence the temperature range and stabilization of blue phases (BP). In addition, the related data of the other compounds without BPs are shown in Tables S3-S5 (see the supporting information).

#### Table 2 Calculated lengths, breadths, bent angles and dipole moments of molecular structures in optimized asymmetrical liquid crystal diads at the B97D level with the 6-31G(d,p) basis set.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Length (Å)</th>
<th>Breadth</th>
<th>Breadth</th>
<th>Biaxial parameter</th>
<th>Bent angle (deg)</th>
<th>Dipole moment (Debye)</th>
</tr>
</thead>
<tbody>
<tr>
<td>II-B</td>
<td>39.5</td>
<td>8.8</td>
<td>6.0</td>
<td>1.47</td>
<td>139.4</td>
<td>10.9</td>
</tr>
<tr>
<td>III-B</td>
<td>45.0</td>
<td>10.8</td>
<td>6.4</td>
<td>1.69</td>
<td>141.1</td>
<td>13.1</td>
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<tr>
<td>III-D</td>
<td>43.2</td>
<td>12.1</td>
<td>6.5</td>
<td>1.86</td>
<td>132.1</td>
<td>13.2</td>
</tr>
</tbody>
</table>

"Bent angle (°) measured as the angle between the first, central and final benzene rings' centers of the bent-core structures. The dipole moments of the lowest energy structures are given (see supporting information Tables S4-S6)."
The front and side views of efficient molecular structures, III-D, III-B and II-B are shown in Fig. 7 and remaining other geometries are shown in the supporting information Fig. S4. The biaxiality, bent angle and dipole moment of molecular geometry play a very important role in widening and stabilizing the BP temperature range. The biaxiality is defined as the ratio of two distinguishable short axes ($W_1, W_2$) of the molecule with a flat shape (i.e., possessing a more non-circular cross section), which is different from the uniaxiality with two identical short axes ($W$). Hence, a similar molecular structure with a more bent shape (i.e., a smaller bent angle in Fig. 7) should have a larger biaxiality (i.e., a larger difference between $W_1$ and $W_2$). These parameters are defined as following: $L$ (length along the long axis), biaxiality equals $W_1/W_2$, $W_2$: width along the short axis normal to the benzene plane and $W_2$: width along the short axis parallel to the benzene plane) and bent angles are measured as the angles between the centers of the first, central and final benzene rings of the bent-core structures (see Fig. 7 and Table 2).

Comparing the BP temperature range of compound II-B and III-B, diad II-B ($\sim$3.4°C) has a little wider BP range than III-B ($\sim$1.5°C), but diad III-B has one more aromatic ring than II-B. To explain this result, the difference of biaxiality, dipole moment and bent angle are further investigated between II-B and III-B. Although the values of biaxiality and dipole moment for diad III-B (biaxiality parameter $\sim$1.69 and dipole moment $\sim$13.1 D) are larger than those of II-B (biaxiality parameter $\sim$1.47 and dipole moment $\sim$10.9 D), diad II-B (139.4°) has a more bent shape than III-B (141.1°). In this study, we found that the bent shape of molecular geometry is useful to stabilize the BP range of diad II-B ($\sim$3.4°C) is wider than III-B ($\sim$1.5°C). On the other hand, diad III-D has one more chiral center at the terminal alkoxyxyl chain than III-B but the BP temperature range of III-D ($\sim$31.4°C) is much wider than that of III-B ($\sim$1.5°C). In order to explain this phenomenon, the differences of biaxiality, dipole moment and bent angle were studied between III-D and III-B. As shown in Table 2, diad III-D (biaxiality parameter $\sim$1.86 and dipole moment $\sim$13.2 D) has larger values of biaxiality and dipole moment than III-B (biaxiality parameter $\sim$1.69 and dipole moment $\sim$13.1 D). Besides, the molecular geometry of III-D (132.1°) is more bent than that of III-B (141.1°) so that diad III-D ($\sim$31.4°C) with a more bent shape (i.e., a larger biaxiality) is observed to have a wide temperature range of BP. In the investigation of biaxiality, bent angle and dipole moment effects on widening and stabilizing the BP temperature range, the large values of biaxiality and dipole moment, along with the bent shape of molecular geometry are found to be useful to extend and stabilize the temperature range of BP.

The electrostatic potential maps of all diads III-D, III-B and II-B calculated at the B97D/6-31G(d,p) level are shown in Fig. 8. The results reveal that the red color refers to the electron-rich and the blue color refers to more positive charge and thus the green color signifies the zero electrostatic potential. The highest negative potential (red) is always located at the C(O)=O and C=N functionalities. In addition, the remaining electrostatic potential maps of the other diads are also shown in the supporting information Fig. S5.

**Fig. 7** Molecular models of the lowest energy conformations for single molecules of diads (a) III-D (b) III-B and (c) II-B.

**Fig. 8** Molecular electrostatic potentials mapped on the electron densities of the lowest energy structures for the three asymmetrical liquid crystal diads: (a) III-D, (b) III-B and (c) II-B.

**Conclusions**

Two series of novel asymmetrical chiral liquid crystal diads II-N (where N = A, B, C, D and E) and III-N (where N = A, B, C and D) were synthesized to possess two different mesogenic units which were linked together by an odd-number spacer. The effects of the position of chiral centers and the number of aromatic rings on the mesophase properties (especially for BPs) were investigated. Among these diads, II-B exhibited blue phase III (BPIII) and diads III-B and III-D revealed blue phase I (BPI), where III-D showed the widest temperature of BPI ($\sim$31°C). The effects of the number of aromatic rings and the position of chiral centers on the behavior of mesophases, electric-optical properties and Kerr constants were...
systemically investigated. Based on the molecular modeling, we found that the large values of biaxiality and dipole moment, along with the bent shape of molecular geometry are useful to extend and stabilize the temperature range of BP's. Consequently, the first report of asymmetrical single- and double-chiral liquid crystal diads containing a chiral center at the central linker is illustrated to exhibit BP's, including the mesophases of BPI and BPIII. The single-component discoveries of novel liquid crystal diads with wide BP ranges will pave a new way to optimize BP ranges in the eutectic mixtures for future applications.

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Notes and references

† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/