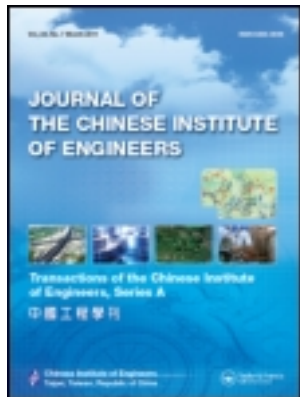


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## Improvement of fast responsive LC materials by bent-core dopants in optical compensated bend mode liquid crystal displays

Hong-Cheu Lin<sup>a\*</sup>, Ling-Yung Wang<sup>a</sup>, Meng-Dan Jiang<sup>a</sup>, Shin-Yi Tsai<sup>a</sup>,  
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Stabilization of bend configuration in optical compensated bend (OCB) mode cells by doping bent-core molecules was developed in this study. The values of response time ( $t$ ) and threshold voltage ( $V_{th}$ ) in OCB cells were dependent not only on the concentration but also on the shape, dipole direction, and flexible chain length of the doping molecules. Experimental results showed that the total response time ( $t_{total}$ ) and threshold voltage ( $V_{th}$ ) of OCB cells could be reduced by doping bent-core molecules, and smaller  $t$  values produced by reducing flexible chain lengths. In addition, attaining smaller  $V_{th}$  values could be achieved by reducing polarization of bent-core molecules. In general, higher concentrations of dopants normally induced shorter field-on response time ( $t_{on}$ ) and a minimum field-off response time ( $t_{off}$ ) occurred at 0.5% of doping concentration, where the fastest total response time ( $t_{total}$ ) values were achieved.

**Keywords:** fast response; OCB mode cell; bent-core dopant

### 1. Introduction

The technologies of liquid crystal displays (LCDs) have been well-developed in recent years. Optical compensated bend (OCB) mode LCDs were also been expanded into LCD panels to take advantage of fast response times and wide view angles. Bend state, which can be varied from the field-off state of splay arrangement (Figure 1), is a useful working condition (field-on state) for OCB cells under electric fields. Working conditions are switched between lower and higher applied voltages to form white and black states, respectively. Then, pre-transition state is defined as the white state with a lower applied voltage in the working region. Therefore, suppression or elimination of splay state to reduce response time and operating voltage is also necessary for the improvement of OCB mode. On the other hand, reducing the applied voltage of pre-transition state for OCB mode LCD's (the so-called pre-transition behavior) has been a major objective in recent research approaches. Various techniques using optical polymerization of ultraviolet curable LC monomers have been used to generate polymer walls so as to stabilize bend alignment (Kang *et al.* 2002, Kikuchi *et al.* 2005, Asakawa *et al.* 2007). In addition, nanoscaled dopants such as nanoparticles (Yoshikawa

*et al.* 2002, Shiraki *et al.* 2004, Miranda *et al.* 2006, Haraguchi *et al.* 2007, Rachtet *et al.* 2007) or carbon nanotubes (Huang *et al.* 2006) have been added to reduce the operating voltage and response time in twisted nematic mode cells. Also, polymer stabilized cholesteric texture cells with different chiral dopants and reactive monomers have been investigated (Huang *et al.* 2007) to survey the effect of doping concentration. Highly qualitative electro-optical properties (including fast response time and lower driving voltage) in OCB cells have also been instigated by the formation of pixel-isolating polymer wall and pre-tilt angle behavior in vertical alignment layers by ion beam exposure (Seo *et al.* 2007, Lee *et al.* 2008).

In this study, in order to improve the response time and threshold voltage properties (lower response time and pre-transition behavior), a new approach, of utilizing bent-core dopants in OCB cells, was developed for bent-core doped frameworks as shown in Figure 2. Novel bent-core materials, with three aromatic ring structures, containing polar ester linking groups and different flexible chain lengths, ( $n=3, 6,$  and  $12$ ) were synthesized (as shown in Figure 3, where CB1–CB4 are bent-core dopants and CB5 is a linear-shape dopant) and doped into

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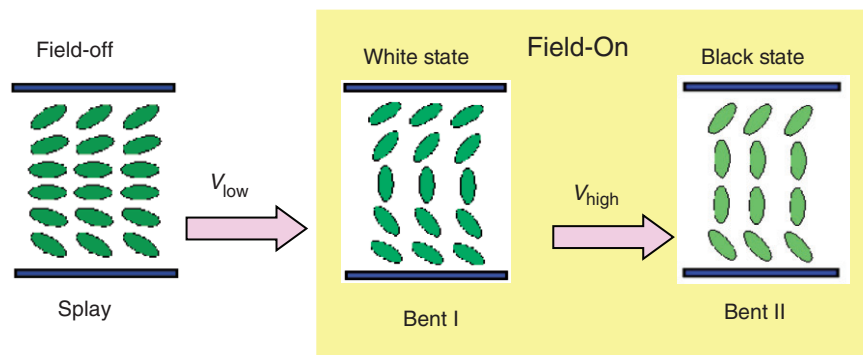


Figure 1. LC switching behavior of OCB cells in electric field-off (splay type) and field-on (bent types) states.

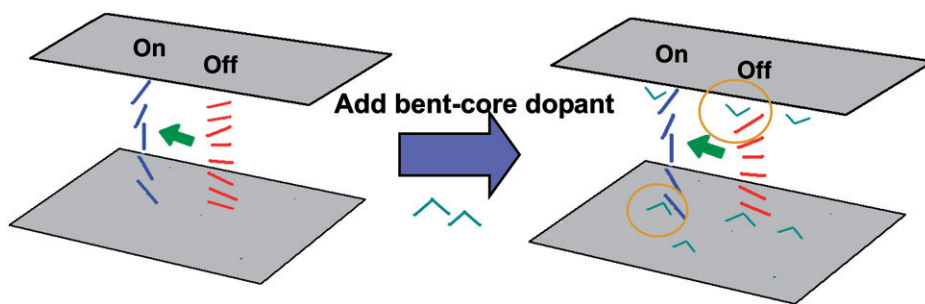


Figure 2. The bent-core doped framework in nematic liquid crystals (red and blue colors) with bent-core dopants (green color) in OCB cells.

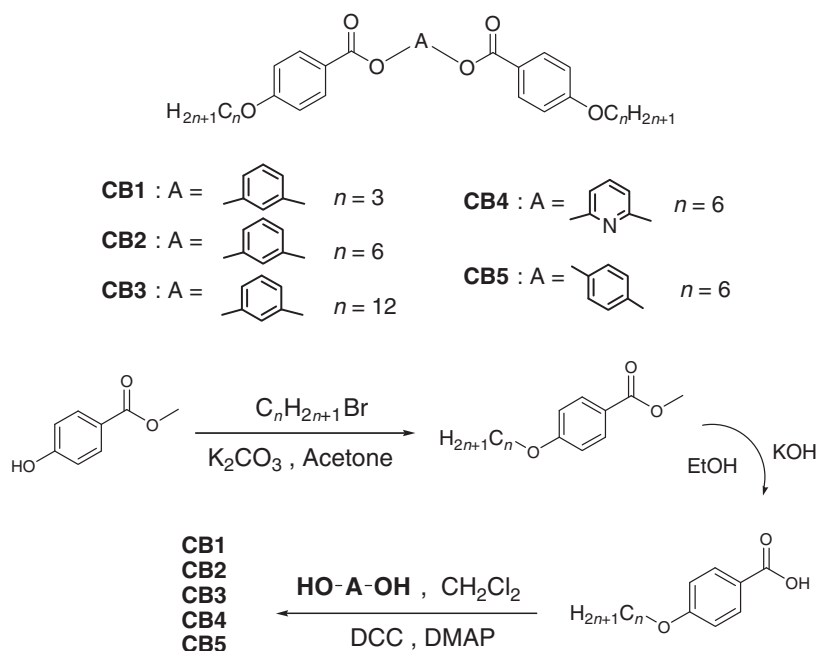


Figure 3. Molecular structures of bent-core (CB1–CB4) and linear-shaped (CB5) dopants.

commercial nematic LC host (ZCE-5096) with various doping ratios (0, 0.1, 0.5, 1, and 5 wt%) as guest-host LC mixtures to be utilized in the OCB mode LCDs. The doping effect of bent-core

materials on the electro-optical properties of these LC mixtures (LC host doped with different bent-core and linear-shaped materials) in OCB cells were surveyed.

## 2. Experimental

### 2.1. Analytical methods

The chemical structures of bent-core doping materials were well-characterized by  $^1\text{H-NMR}$  and elemental analyses (EA).  $^1\text{H-}$  and  $^{13}\text{C-NMR}$  spectra were recorded on a Varian Unity 300 MHz spectrometer using  $\text{DMSO-d}_6$  and  $\text{CDCl}_3$  as solvents, and EA were performed on a Heraeus CHN-OS RAPID elemental analyzer. The commercial nematic LC host (ZCE-5096) was purchased from Merck Chemical Co. The electro-optical properties of LC materials were determined in commercially available OCB cells (from Mesostate Corp., thickness =  $4.25\ \mu\text{m}$ , active area =  $1\ \text{cm}^2$ ) coated with rubbing polyimide alignment layers (parallel rubbing direction).  $V$ - $T$  measurements were performed under AC fields of square waveform from  $\pm 10\ \text{V}$  to  $\pm 0\ \text{V}$  decreasing gradually at a frequency of 60 Hz, and the threshold voltage ( $V_{\text{th}}$ ) was determined by the voltage with the highest transmittance. Switching time measurements were started with 3 min of holding at a square waveform of  $\pm 10\ \text{V}$  under a frequency of 60 Hz (from splay to bend), and followed by 3 min of holding at an arbitrary waveform of  $\pm 7$  and  $\pm 29.5\ \text{V}$  under a frequency of 60 Hz in order to avoid going back to the splay state. Then, the field-on response time ( $t_{\text{on}}$ ) was determined from an arbitrary waveform of voltages  $\pm 7\ \text{V}$  (in dark state) to  $\pm 2\ \text{V}$  (in bright state), and the field-off response time ( $t_{\text{off}}$ ) was decided by a reversed voltage process (from  $\pm 2$  to  $\pm 7\ \text{V}$ ), correspondingly. Switching time measurements were determined by the time period for 90% change of transmission. Finally, the value of total response time ( $t_{\text{total}}$ ) was determined by the summation of the field-on response time ( $t_{\text{on}}$ ) and the field-off response time ( $t_{\text{off}}$ ), i.e.,  $t_{\text{total}} = t_{\text{on}} + t_{\text{off}}$ . As shown in Figure 4(a) and (b), one set of example data regarding  $V$ - $T$  and switching time measurements of the pure LC host (ZCE-5096) were given values of  $1.93\ \text{V}$  ( $V_{\text{th}}$ ) and  $4.57\ \text{ms}$  ( $t_{\text{total}}$ ), respectively. The theoretical calculation of dipole moment values was roughly computed by the energy-minimized structures for compounds CB2 and CB4 using the MM2 method of Chem3D Ultra 8.0 (version: Chemoffice 2004).

### 2.2. Synthesis

The synthetic procedures were followed according to three routes as shown in Figure 3. The flexible chains with three various lengths of alkyl chains (3, 6, and 12) were attached to both sides of the bent-core dopants to acquire related products. De-protecting actions were executed by the procedures to eliminate the methyl-protecting groups. Finally, the rigid-core connections

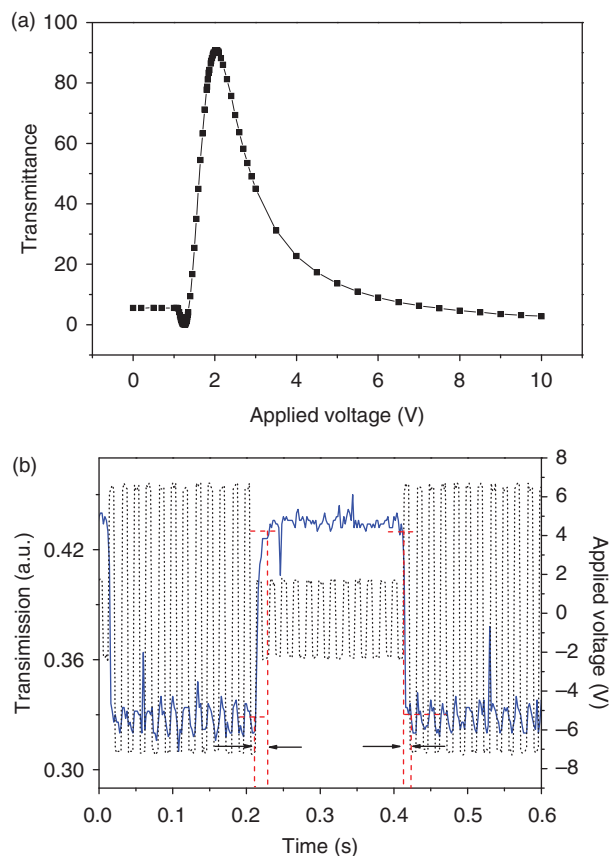


Figure 4. Electric-optical measurements of the pure LC host (ZCE-5096): (a)  $V$ - $T$  measurements and (b) switching time measurements of the field-on response time ( $t_{\text{on}}$ ) and the field-off response time ( $t_{\text{off}}$ ).

were proceeded to yield five different benzene derivatives (CB1–CB5).

#### 2.2.1. Synthesis of compounds 1–3, 1–6, and 1–12

Reagent methyl 4-hydroxybenzoate (1 equivalent),  $\text{K}_2\text{CO}_3$  (1.5 equivalents), and various 1-bromoalkanes (1-bromo-propane, 1-bromo-hexane, and 1-bromo-dodecane, 1.1 equivalents) were dissolved in acetone solvent and stirred for 15 h at reflux temperature. After reaction, acetone was removed by evaporation under reduced pressure, and residue was extracted with water/dichloromethane (DCM). Then, organic liquid layer was dried over anhydrous magnesium sulfate. After removal of the solvent by evaporation under reduced pressure, the crude product was purified by column chromatography to get white solids. **1–3**: Yield: 91%,  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ): 7.56 (d,  $J=9.0\ \text{Hz}$ , 2H, Ar-H), 7.03 (d,  $J=9.0\ \text{Hz}$ , 2H, Ar-H), 4.18 (t,  $J=6.0\ \text{Hz}$ , 2H,  $\text{OCH}_2$ ), 3.89 (s, 3H,  $\text{OCH}_3$ ), 1.44–1.24 (m, 2H,  $\text{CH}_2$ ),

0.84 (t,  $J=5.4$  Hz, 3 H, CH<sub>3</sub>). **1-6**: Yield: 95%, <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.57 (d,  $J=9.0$  Hz, 2 H, Ar-H), 7.10 (d,  $J=9.0$  Hz, 2 H, Ar-H), 4.09 (t,  $J=6.3$  Hz, 2 H, OCH<sub>2</sub>), 3.91 (s, 3 H, OCH<sub>3</sub>), 1.45–1.29 (m, 8 H, CH<sub>2</sub>), 0.86 (t,  $J=5.4$  Hz, 3 H, CH<sub>3</sub>). **1-12**: Yield: 94%, <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): 7.61 (d,  $J=9.0$  Hz, 2 H, Ar-H), 7.12 (d,  $J=9.0$  Hz, 2 H, Ar-H), 4.12 (t,  $J=6.30$  Hz, 2 H, OCH<sub>2</sub>), 3.93 (s, 3 H, OCH<sub>3</sub>), 1.74 (t,  $J=6.3$  Hz, 2 H, OCH<sub>2</sub>CH<sub>2</sub>), 1.42–1.24 (m, 18 H, CH<sub>2</sub>), 0.84 (t,  $J=6.3$  Hz, 3 H, CH<sub>3</sub>).

### 2.2.2. Synthesis of compounds **2-3**, **2-6**, and **2-12**

These compounds were obtained from the reaction of compounds **1-*n*** ( $n=3, 6,$  and  $12$ , 1 equivalent) and KOH (4 equivalents) in ethanol at reflux temperature for 10 h. Water was added to produce the precipitate, and the crude product was recrystallized from ethanol/hexane to give a white solid. **2-3**: Yield: 95%, <sup>1</sup>H-NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  12.51 (s, 1 H, COOH), 7.87 (d,  $J=8.7$  Hz, 2 H, Ar-H), 7.05 (d,  $J=8.7$  Hz, 2 H, Ar-H), 4.10 (t,  $J=6.3$  Hz, 2 H, OCH<sub>2</sub>), 1.44–1.21 (m, 2 H, CH<sub>2</sub>), 0.88 (t,  $J=6.0$  Hz, 3 H, CH<sub>3</sub>). **2-6**: Yield: 95%, <sup>1</sup>H-NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  12.59 (s, 1 H, COOH), 7.85 (d,  $J=8.7$  Hz, 2 H, Ar-H), 6.98 (d,  $J=8.7$  Hz, 2 H, Ar-H), 4.05 (t,  $J=6.3$  Hz, 2 H, OCH<sub>2</sub>), 1.72–1.65 (m, 2 H, OCH<sub>2</sub>CH<sub>2</sub>), 1.39–1.15 (m, 6 H, CH<sub>2</sub>), 0.84 (t,  $J=6.0$  Hz, 3 H, CH<sub>3</sub>). **2-12**: Yield: 92%, <sup>1</sup>H-NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  12.53 (s, 1 H, COOH), 7.81 (d,  $J=8.7$  Hz, 2 H, Ar-H), 6.95 (d,  $J=8.7$  Hz, 2 H, Ar-H), 4.01 (t,  $J=6.3$  Hz, 2 H, OCH<sub>2</sub>), 1.74–1.66 (m, 2 H, OCH<sub>2</sub>CH<sub>2</sub>), 1.34–1.16 (m, 18 H, CH<sub>2</sub>), 0.84 (t,  $J=6.3$  Hz, 3 H, CH<sub>3</sub>).

### 2.2.3. Synthesis of compounds **CB1**–**CB4**, and **CB5**

Compound **2-*n*** ( $n=3, 6,$  and  $12$ , 2 equivalents), dihydroxyl-benzene derivatives (1 equivalent), *N,N*-dicyclohexylcarbodiimide (1.2 equivalents) and a catalytic amount of 4-(*N,N*-dimethylamino) pyridine were dissolved in dry DCM under nitrogen for 15 h at room temperature. The precipitated dicyclohexylurea was filtered off and washed with an excess of DCM (20 mL). The filtrate was extracted with water/DCM and organic liquid layer was dried over anhydrous magnesium sulfate. After removal of the solvent by evaporation under reduced pressure, the residue was recrystallized from ethanol to give a white solid. **CB1**: Yield: 70%, <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.98 (d,  $J=9.0$  Hz, 4 H, Ar-H), 7.51 (t,  $J=7.5$  Hz, 1 H, Ar-H), 7.06 (d,  $J=7.5$  Hz, 2 H, Ar-H), 7.03 (s, 1 H, Ar-H), 6.92 (d,  $J=9.0$  Hz, 4 H, Ar-H), 4.06 (t,  $J=6.0$  Hz, 2 H, OCH<sub>2</sub>), 1.42–1.27 (m, 2 H, CH<sub>2</sub>), 0.85 (t,  $J=6.0$  Hz, 3 H, CH<sub>3</sub>); <sup>13</sup>C-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  164.51,

163.55, 151.52, 132.24, 129.62, 121.22, 119.06, 115.90, 114.25, 69.70, 22.37, 10.40. EA: Calcd for C<sub>26</sub>H<sub>26</sub>O<sub>6</sub>: C, 71.87; H, 6.03. Found: C, 71.80; H, 6.09. **CB2**: Yield: 64%, <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.92 (d,  $J=9.0$  Hz, 4 H, Ar-H), 7.60 (t,  $J=8.1$  Hz, 1 H, Ar-H), 7.12 (d,  $J=8.1$  Hz, 2 H, Ar-H), 7.05 (s, 1 H, Ar-H), 6.98 (d,  $J=9.0$  Hz, 4 H, Ar-H), 4.07 (t,  $J=6.0$  Hz, 2 H, OCH<sub>2</sub>), 1.75–1.63 (m, 2 H, OCH<sub>2</sub>CH<sub>2</sub>), 1.41–1.26 (m, 6 H, CH<sub>2</sub>), 0.86 (t,  $J=6.0$  Hz, 3 H, CH<sub>3</sub>); <sup>13</sup>C-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  164.51, 163.55, 151.52, 132.24, 129.62, 121.20, 119.05, 115.90, 114.25, 68.25, 31.48, 28.98, 25.59, 22.51, 13.96. EA: Calcd for C<sub>32</sub>H<sub>38</sub>O<sub>6</sub>: C, 74.11; H, 7.39. Found: C, 74.51; H, 7.12. **CB3**: Yield: 75%, <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.85 (d,  $J=9.0$  Hz, 4 H, Ar-H), 7.46 (t,  $J=8.7$  Hz, 1 H, Ar-H), 6.99 (d,  $J=8.7$  Hz, 2 H, Ar-H), 6.85 (s, 1 H, Ar-H), 6.63 (d,  $J=9.0$  Hz, 4 H, Ar-H), 4.02 (t,  $J=6.3$  Hz, 2 H, OCH<sub>2</sub>), 1.66–1.60 (m, 2 H, OCH<sub>2</sub>CH<sub>2</sub>), 1.29–1.08 (m, 18 H, CH<sub>2</sub>), 0.80 (t,  $J=6.3$  Hz, 3 H, CH<sub>3</sub>); <sup>13</sup>C-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  164.53, 163.54, 151.51, 132.24, 129.62, 121.20, 119.05, 115.90, 114.25, 68.25, 31.84, 29.58, 29.56, 29.51, 29.48, 29.28, 29.01, 25.90, 22.61, 14.05. EA: Calcd for C<sub>44</sub>H<sub>62</sub>O<sub>6</sub>: C, 76.93; H, 9.10. Found: C, 76.46; H, 9.39. **CB4**: Yield: 33%, <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.02 (d,  $J=9.0$  Hz, 4 H, Ar-H), 7.75 (t,  $J=7.5$  Hz, 1 H, Ar-H), 6.98 (d,  $J=7.5$  Hz, 2 H, Ar-H), 5.68 (d,  $J=9.0$  Hz, 4 H, Ar-H), 3.96 (t,  $J=6.3$  Hz, 2 H, OCH<sub>2</sub>), 1.71 (m, 2 H, OCH<sub>2</sub>CH<sub>2</sub>), 1.34–1.27 (m, 6 H, CH<sub>2</sub>), 0.92 (t,  $J=6.0$  Hz, 3 H, CH<sub>3</sub>); <sup>13</sup>C-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  164.04, 163.78, 156.93, 141.98, 132.55, 120.63, 114.33, 114.23, 68.25, 31.46, 28.96, 25.57, 22.50, 13.94. EA: Calcd for C<sub>31</sub>H<sub>37</sub>NO<sub>6</sub>: C, 71.65; H, 7.18. Found: C, 71.58; H, 7.32. **CB5**: Yield: 69%, <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.03 (d,  $J=9.0$  Hz, 4 H, Ar-H), 7.25 (d,  $J=9.0$  Hz, 4 H, Ar-H), 7.03 (d,  $J=9.0$  Hz, 4 H, Ar-H), 3.99 (t,  $J=6.0$  Hz, 2 H, OCH<sub>2</sub>), 1.75 (m, 2 H, OCH<sub>2</sub>CH<sub>2</sub>), 1.33–1.25 (m, 6 H, CH<sub>2</sub>), 0.92 (t,  $J=6.0$  Hz, 3 H, CH<sub>3</sub>); <sup>13</sup>C-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  164.79, 163.52, 148.33, 132.27, 122.58, 121.31, 114.24, 68.26, 31.48, 28.98, 25.59, 22.51, 13.96. EA: Calcd for C<sub>32</sub>H<sub>38</sub>O<sub>6</sub>: C, 74.11; H, 7.39. Found: C, 74.41; H, 7.32.

## 3. Results

In this study, five doping materials composed of three aromatic ring structures (as illustrated in Figure 3) were synthesized and provided as the guest system (doping ratio = 0, 0.1, 0.5, 1, and 5 wt%) to mix with the nematic LC host (ZCE-5096) in OCB mode cells with a cell gap of 4.25  $\mu$ m. The influence of molecular shape, polar direction, and flexible chain length on the



response time ( $t_{on}$ ,  $t_{off}$ , and  $t_{total}$ ) and threshold voltage ( $V_{th}$ ) were investigated.

In order to realize the molecular configuration effect on the mesomorphic properties and phase transition temperatures, bent-core and linear compounds CB1–CB4 and CB5 were investigated by POM and DSC measurements as shown in Figure 5 and Table 1. The bent-core compounds CB1–CB4 did not reveal any mesophase, but the enantiotropic nematic phase of the linear compound CB5 was obtained, which was verified by POM to show the enantiotropic Schlieren texture as shown in Figure 5. Compared with the linear compound CB5 possessing the nematic phase, the shape-isomeric compound CB2 (as well as the other bent-core compounds CB1–CB4) did not reveal any mesophase. These results also proved the linear shape of compound CB5 and the bent-core shape of compounds CB1–CB4 due to their different preferences in formation of the mesophase, which are well-known from the basic principles of liquid crystalline molecules. Besides, Okamoto's group has shown that the rod-like molecules with three aromatic rings and two ester linkages, which have exactly the same rigid core as compound CB5 (Tasaka *et al.* 2006), have the linear molecular shape. Hence, compounds CB1–CB4, (synthesized by the meta-substituted central core rings of compound CB5) should generate the bent-core molecular shape. Similar to the bent-core molecular shape of compounds CB1–CB4, the analogous bent-core five-ring molecules (resorcinol derivatives), which bear the same central aromatic ring with 1,3-substituted ester linkages, have also been proven to possess the bent-core molecular shape by the molecular modeling (Wang *et al.* 2009).

In order to compare the molecular shape effect, linear dopant CB5 (Tasaka *et al.* 2006) and bent-core molecules CB1–CB4 were doped into LC host (ZCE-5096) with various doping ratios and their threshold voltages ( $V_{th}$ ) were demonstrated in Table 2. The threshold voltages ( $V_{th}$ ) of the LC mixtures containing bent-core molecules CB1–CB4 were effectively reduced in contrast to that of pure LC host (ZCE-5096). The  $V_{th}$  value of the LC mixture containing dopant CB2 (i.e., LC + CB2) was decreased the most as the weight ratio of dopant CB2 is equal to 0.5 wt%; however, the  $V_{th}$  values were slightly increased by, between 1 and 5 wt%. For the LC mixture containing the linear-shaped molecule CB5 (i.e., LC + CB5), larger  $V_{th}$  values than that of pure LC (without any dopants) were obtained by increasing the weight ratio of dopant CB5. Therefore, the bent-shaped configurations of dopants CB1–CB4 were more useful to substantially reduce the threshold voltages ( $V_{th}$ ) of OCB mode LCDs than linear dopant CB5. This result suggested

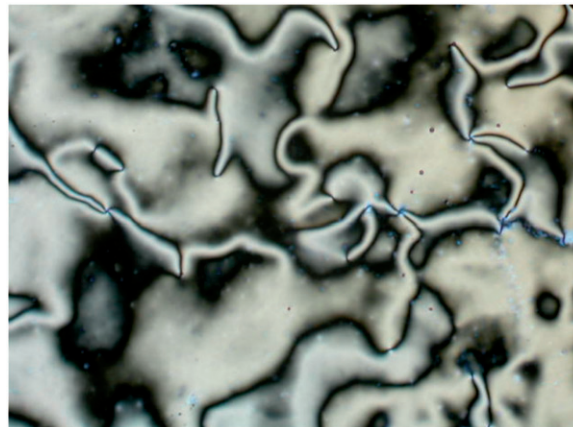


Figure 5. POM texture during the cooling process: the nematic phase with the Schlieren texture of linear compound CB5 at 200°C.

Table 1. Phase transition temperatures and enthalpies of bent-core and linear compounds CB1–CB4 and CB5.

Compound	Phase transition temperature/°C (enthalpy/kJ/g)
CB1	Cr 90.9 (23.8) Iso
	Iso 76.9 (26.4) Cr
CB2	Cr 71.4 (21.6) Iso
	Iso 28.9 <sup>a</sup> Cr
CB3	Cr 60.6 (20.4) Iso
	Iso 39.9 <sup>a</sup> Cr
CB4	Cr 60.6 (23.8) Iso
	Iso 27.0 <sup>a</sup> Cr
CB5	Cr 123.7 (25.6) N 208.6 (5.2) Iso
	Iso 206.0 (5.9) N 116.8 (29.5) Cr

Notes: Cr and Cr' = crystalline phase; N = nematic phase; Iso = isotropic phase.

<sup>a</sup>The phase transition temperature was obtained by POM only. The phase transitions were measured by DSC at the second cooling scan with a cooling rate of 5°C/min.

that the bent-shaped molecules might provide bent prominences to unstabilize their splay arrangements so as to reduce the  $V_{th}$  values. However, dopant CB5 was unable to contribute bent protrusions due to the linear shape of CB5, so ineffective  $V$ – $T$  improvement happened in this case.

With respect to the different flexible chain lengths ( $n = 3, 6,$  and  $9$ ) of dopants CB1–CB3 (with the same bent-shaped phenyl center) doped into LC host, their effects on threshold voltages ( $V_{th}$ ) are compared in Table 2. For all doping ratios of LC mixtures with bent-core dopants, lower  $V_{th}$  values than that of pure LC were observed. Moreover, the LC mixture containing dopant CB2 (i.e., LC + CB2) has the smallest

Table 2. Threshold voltages ( $V_{th}$ ) of LC mixtures in OCB cells where the nematic host (ZCE-5096) were doped with various concentrations of dopants (CB1–CB5).

ZCE-5096	LC + CB1 (V)	LC + CB2 (V)	LC + CB3 (V)	LC + CB4 (V)	LC + CB5 (V)
0 wt%	1.93	1.93	1.93	1.93	1.93
0.1 wt%	1.83	1.85	1.79	1.72	1.91
0.5 wt%	1.78	1.38	1.78	1.6	1.97
1 wt%	1.73	1.48	1.87	1.79	2.32
5 wt%	1.65	1.72	1.76	1.65	2.35

Table 3. Total response time ( $t_{total}$ ) of  $R$ – $T$  measurements.

ZCE-5096	$t_{total}$ (ms)				
	LC + CB1	LC + CB2	LC + CB3	LC + CB4	LC + CB5
0 wt%	4.57	4.57	4.57	4.57	4.57
0.1 wt%	3.95	3.62	4.23	4.23	5.97
0.5 wt%	3.35	3.47	3.70	3.71	6.01
1 wt%	4.28	4.22	4.33	4.14	7.09
5 wt%	3.96	4.5	3.69	6.96	7.58

Table 4. Field-on response time ( $t_{on}$ ) of  $R$ – $T$  measurements.

ZCE-5096	$t_{on}$ (ms)				
	LC + CB1	LC + CB2	LC + CB3	LC + CB4	LC + CB5
0 wt%	1.45	1.45	1.45	1.45	1.45
0.1 wt%	1.47	1.38	1.69	1.43	1.14
0.5 wt%	1.28	1.56	1.20	1.36	1.44
1 wt%	1.54	1.26	1.04	1.61	1.77
5 wt%	1.18	1.4	0.73	1.76	1.85

$V_{th}$  values of 1.38 and 1.48 V at doping ratios of 0.05 and 1 wt%, respectively. This indicated that bent molecules may contribute to a useful pre-transition situation by their bent skeletons, and the lowest driving voltage might be required by the suitable chain length of  $n=6$  for the optimal bent protrusions.

To compare the effect of polar direction, LC mixtures consisting of bent-core dopants CB4 and CB2 with the same flexible chain length ( $n=6$ ) were compared. In the investigation of dipole moment values, the total dipole value of CB4 (11.6 debye) was slightly larger than that of CB2 (8.3 debye). It seems that the LC mixture containing dopant CB4 (i.e., LC + CB4) with opposite polar direction contributed from bent-shaped pyridyl center has less reduction of  $V_{th}$  values than that containing less polar dopant CB2 (at doping ratios of 0.5 and 1 wt%). However, the polar effect in different directions is still not clear for

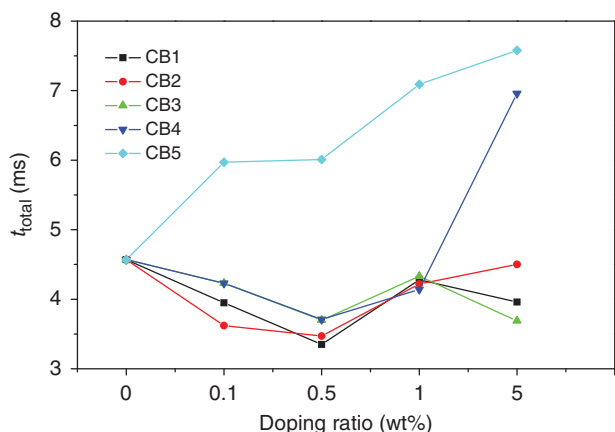
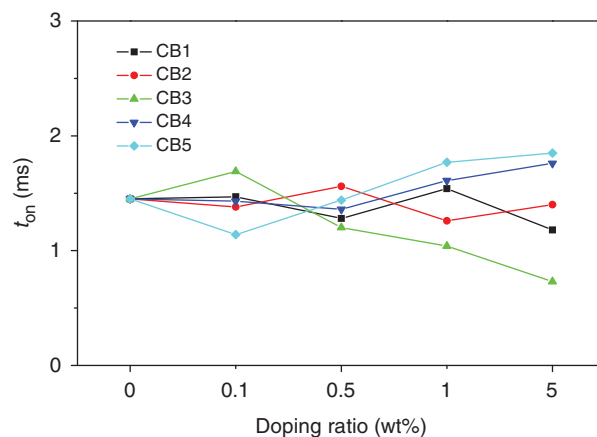
$V$ – $T$  measurements due to insufficient bent-core dopants.

The data of  $R$ – $T$  (transmittance vs. response time) measurements in OCB cells are shown in Tables 3–5 and Figures 6–8. The LC mixture containing the linear-shaped dopant CB5 (i.e., LC + CB5) did not show any improvements in  $t_{on}$  and  $t_{off}$  values, and even caused worse  $t_{on}$  and  $t_{off}$  values than pure LC host. This might be attributed to high viscosity originating from the stiffness of linear-shaped CB5, which restricted the fluidity of the LC host, so that a longer time would be needed for switching between field-on and field-off states.

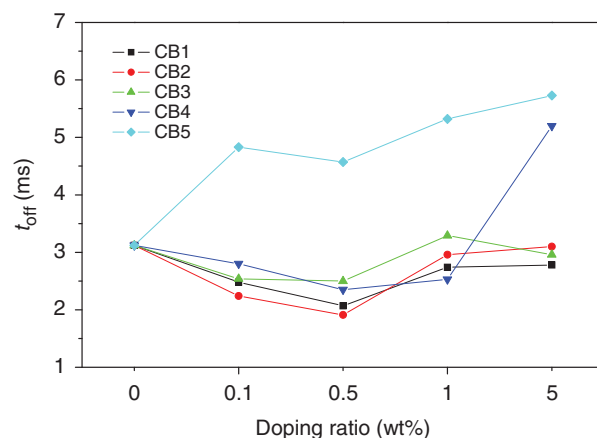
Comparing the LC mixtures containing bent-core dopants CB1–CB3 in Table 3 and Figure 6, all  $t_{total}$  values were reduced at doping ratios lower than 1 wt%, and the lowest  $t_{total}$  values were obtained at the doping ratio of 0.5 wt% in all of these LC mixtures.

Table 5. Field-off response time ( $t_{\text{off}}$ ) of  $R$ - $T$  measurements.

ZCE-5096	$t_{\text{off}}$ (ms)				
	LC + CB1	LC + CB2	LC + CB3	LC + CB4	LC + CB5
0 wt%	3.12	3.12	3.12	3.12	3.12
0.1 wt%	2.48	2.24	2.54	2.8	4.83
0.5 wt%	2.07	1.91	2.50	2.35	4.57
1 wt%	2.74	2.96	3.29	2.53	5.32
5 wt%	2.78	3.1	2.96	5.2	5.73

Figure 6. Total response time ( $t_{\text{total}}$ ) of  $R$ - $T$  measurements with different doping ratios.Figure 7. Field-on response time ( $t_{\text{on}}$ ) of  $R$ - $T$  measurements with different doping ratios.

Nevertheless, slight increase in  $t_{\text{total}}$  values over pure LC host was acquired at the highest doping ratio of 5 wt%. Furthermore, even though almost all  $t_{\text{on}}$  values (in Table 4 and Figure 7) were reduced by increasing the doping ratios, increase in  $t_{\text{off}}$  values (in Table 5 and Figure 8) occurred at more doping ratios (1 and 5 wt%) to cause slight increase in  $t_{\text{total}}$  values. This was because the pre-transition behavior from the bent frameworks of the doped materials conflicted with each other. When enough voltage was applied for OCB mode to switch from bend bright state to bend dark state, LC would stand nearly perpendicular to the cell surface, as would the electric field. However, LC molecules would lie down without any additional driving force as the electric field was removed at switching-off time. Therefore,  $t_{\text{off}}$  values would increase if the dopant ratio was excessively high, and  $t_{\text{total}}$  values would also be increased. This phenomenon indicated that a moderate dopant concentration of 0.5 wt% would be appropriate for the induction of pre-transition, and an excess of bent dopants had no advantage in reducing switching times. In these three cases, the influence of the flexible chain length on  $R$ - $T$

Figure 8. Field-off response time ( $t_{\text{off}}$ ) of  $R$ - $T$  measurements with different doping ratios.

measurements was also contrasted. Less reduction of  $t_{\text{total}}$  values was observed in the LC mixture containing bent-core dopant CB1 in contrast to those containing bent-core dopants CB2 and CB3, which meant that shorter flexible chain structure should be useful to promote lower switching time.



It is interesting to compare the  $R$ - $T$  results of LC mixtures containing dopants CB2 and CB4. Higher  $t_{\text{total}}$  values were observed for the LC mixture containing dopant CB4, especially in the highest doping ratio of 5 wt%, which indicated that the opposite polar direction would diminish pre-transition behavior due to the prohibition against polar contribution from ester groups. The phenomenon demonstrated that the low pre-transition behavior was shown not only by the bent-shaped framework but also by the intermolecular polar direction, which suggested that a polar effect could be acquired where higher  $t_{\text{total}}$  values were provided because a higher polar direction in molecule would be helpful in reducing response time. Overall, almost a 25% reduction in  $t_{\text{total}}$  values was obtained in all bent-core doped LC mixtures.

#### 4. Conclusion

We successfully developed a series of new LC mixtures containing bent-core dopants with different flexible chain lengths in several doping ratios for OCB mode LCDs. The effects of the shape, dipole direction, flexible chain length, and doping ratio of the doping molecules on the values of response time and threshold voltage were analyzed. All bent-core dopants did effectively reduce threshold voltages and switching time values, and higher efficiency of switching time reduction was acquired for the dopant structure with shorter flexible chains such as the best sample of dopant CB1. The optimal electro-optical properties of LC mixtures by doping 0.5 wt% of bent-core dopants yielded almost 25% reduction in  $t_{\text{total}}$  values. In summary, the values of response time and threshold voltage in OCB mode cells can be reduced by doping bent-core molecules into LC hosts, and the values of  $t_{\text{total}}$  and  $V_{\text{th}}$  can be tuned by the flexible chain lengths and polarization directions of bent-core molecules.

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