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## Liquid Crystals

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### Synthesis, characterisation and liquid crystal properties of 2,5-bis[5-alkyl(alkoxy)phenyl-1,3,4-oxadiazole]bromobenzenes

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## Synthesis, characterisation and liquid crystal properties of 2,5-bis[5-alkyl(alkoxy)phenyl-1,3,4-oxadiazole]bromobenzenes

Chunpeng Chai<sup>ab</sup>, Qian Yang<sup>a</sup>, Xinghe Fan<sup>a\*</sup>, Xiaofang Chen<sup>a</sup>, Zhihao Shen<sup>a</sup> and Qifeng Zhou<sup>a</sup>

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A series of new thermal bilateral liquid crystal compounds with the phenylenebis-1,3,4-oxadiazole structure was synthesised. The molecular structures of the oxadiazole compounds were confirmed by FT-IR and <sup>1</sup>H NMR spectroscopy, elemental analysis and mass spectrometry. Thermogravimetric analysis indicates that the compounds in an atmosphere of nitrogen have good thermal stability. Measurements using differential scanning calorimetry, polarising optical microscopy and temperature-dependent wide-angle X-ray diffraction indicated that the liquid crystalline properties are related to the length of the end groups. When the end group was *tert*-butyl or alkoxy with four and six carbons, the compounds exhibit no liquid crystal phase. However, compounds with end groups containing more than eight carbons show significant bidirectional thermally-induced liquid crystal properties and the structure of the liquid crystal phase is the lamellar smectic A phase. All the compounds exhibit blue fluorescence.

**Keywords:** liquid crystals; 3,4-oxadiazole; OLEDs

### 1. Introduction

Organic light-emitting diodes (OLEDs) have attracted much attention during the past decade due to their potential application in flexible flat-panel displays as well as electroluminescent devices (1–5). As the study of electroluminescent materials became more detailed, researchers realised that high-efficiency carriers are critical to the improvement of device performance (6–9). In particular, high electron-transfer efficiency is believed to be a critical factor in the achievement of a further increase of device performance. The study of electron-transfer materials was carried out somewhat later than that of hole-transfer materials (10, 11). The transfer of the carriers in organic materials depends on the intermolecular gap, and the relative overlap of molecular orbitals between amorphous molecules always present a random distribution. However, the self-organisation character of the liquid crystal molecule can help this overlap to become ordered, which is advantageous for the transfer of carriers. Electroluminescent materials that exhibit liquid crystalline properties can help the carrier transfer efficiency increase by several orders in the liquid crystal phase (12).

1,3,4-oxadiazole derivatives are the most commonly used electron-transporting chromophore because of their electron-deficient nature (13–16).

The 1,3,4-oxadiazole fragment is one of the best structural units for the synthesis of electron-transfer organic electroluminescence molecules, and the compounds with such a structure always exhibit good electron-transfer properties as well as good thermal and chemical stability (2, 4, 17–22).

According to the general character of the liquid crystal structure, we know that phenyl-1,3,4-oxadiazole groups can be used as the rigid structural unit to form the base for liquid crystal molecule. If an alkyl group of a certain length is added to such a structural unit, it is possible to design an electroluminescent molecule that possesses liquid crystalline properties.

In this paper, we report the design and synthesis of a new series of compounds with the phenylenebis-1,3,4-oxadiazole structure, the 2,5-bis[5-alkyl(alkoxy)phenyl-1,3,4-oxadiazole] bromobenzenes. Differential scanning calorimetry (DSC), polarising optical microscopy (POM) and temperature-dependent wide-angle X-ray diffraction (WAXD) measurements indicate that the liquid crystalline properties are related to the length of the end groups. The compounds are important intermediates for the synthesis of derivatives with the 1,3,4-oxadiazole molecular group. The compounds studied have better chemical, optical and thermal stabilities compared with conventional liquid crystals that combine two or more phenyl rings by several ester and carboxyl amide groups.

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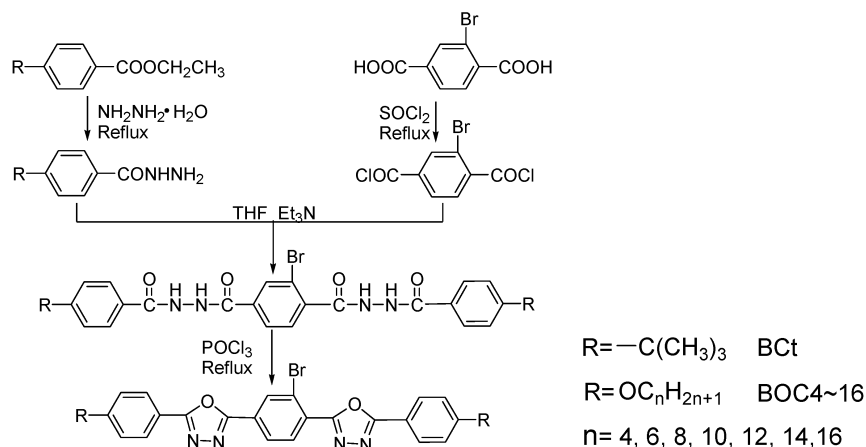


Figure 1. Synthetic route for the target compounds.

## 2. Results and discussion

### Synthesis and characterisation of structure

The target products and their syntheses are shown in Figure 1. In the synthesis of dialkoxybenzoyl hydrazide, the dialkoxybenzoic acetates with end groups of more than 10 carbons were synthesised according to methods reported previously (23, 24). The reactants were dissolved in hydrazine hydrate, which is both a reactant and solvent, and were heated for 24 h under reflux. After vacuum vaporisation of the excess hydrazine hydrate, only a limited amount of solid product precipitated and most of the residue is viscous fluid that is difficult to treat. In this study, we added the correct quantity of ethanol as solvent in this step, and as soon as the reactant mixture was kept still and cooled, needle-like or sheet-like crystals precipitated. The addition of ethanol simplified the treatment of the reactant mixture and also helped to obtain purer product.

In the synthesis of the dihydrazide, it was very important to keep the system dry, which restrained the decomposition of the acyl chloride added into the system. So triethylamine and tetrahydrofuran, which were both used as acid-combination agent in the reaction, were dried and refined. As the addition of acyl chloride can release a large amount of heat, the temperature of the system was kept below 0°C and the speed of addition was rather slow. Dropping too fast can make some part of the system overheat to induce many side reactions, which leads to the inhibition of the formation of dihydrazide and the thermal polymerisation of the ethyl group, which both reduce the product yield. The post treatment in this step is to pour the resulting solution into water to precipitate, and then filter the solid. However, in the synthesis of dihydrazide a viscous colloid was obtained instead of a solid precipitate, which made

the post treatment very difficult. Such a phenomenon may be caused by solvent remaining along with the product, so we vacuum vaporised the resultant solution to almost dry and then added water to disperse the solid; dilute hydrochloric acid was then added to neutralise any unreacted triethylamine to ease vacuum filtration. The solubility of the target compound is relatively weak, so the crude product had to be recrystallised directly in tetrahydrofuran or 1,4-dioxane, and the pure product obtained usually after two or three recrystallisations.

The structure of the products was consistent with that designed previously, based on the results of  $^1H$  NMR, mass and IR spectroscopy and elemental analysis. The elemental analysis data of physical properties of the target compounds are shown in Table 1.

Figure 2a shows the IR spectra of the target compound BOC14 and its corresponding precursor dihydrazide (DOC14). From the IR spectra, it can be seen that the  $-NH$  stretching vibration peak of the dihydrazide precursor at  $3220\text{ cm}^{-1}$  and the  $-C=O$  stretching vibration peak at  $1643\text{ cm}^{-1}$  disappeared, whereas a  $C=N$  stretching vibration peak at  $1610\text{ cm}^{-1}$  appeared, all of which indicates that the dihydrazide precursor cyclised into an oxadiazole ring in the presence of phosphorus oxychloride. Figure 2b shows the IR spectra of the target compounds BCt, BOC6, BOC10 and BOC14. The band at  $1610\text{--}1620\text{ cm}^{-1}$  is ascribed to the specific band of 1,3,4-oxadiazole ring; the band at  $1493\text{--}1560\text{ cm}^{-1}$  corresponds to the stretching vibration band of the aromatic ring; the peak at  $840\text{ cm}^{-1}$  corresponds to the  $C-H$  bending vibration peak of the 2,5-disubstituted benzene.

Using chloroform-*d* as solvent, the  $^1H$  NMR spectra of the target compounds were obtained. Figure 3 shows the NMR spectra of products with

Table 1. Physical properties and elementary analysis data for the target compounds.

Compd.	Formula	Yield/%	MS (m/e)	M.p./°C <sup>a</sup>	Elements analysis found (calcd.)		
					C%	H%	N%
BCt	C <sub>30</sub> H <sub>29</sub> BrN <sub>4</sub> O <sub>2</sub>	72	556	245	64.63 (64.53)	5.24 (5.44)	10.05 (9.86)
BOC4	C <sub>30</sub> H <sub>29</sub> BrN <sub>4</sub> O <sub>4</sub>	61	589	227	61.52 (61.13)	4.83 (4.96)	9.88 (9.50)
BOC6	C <sub>34</sub> H <sub>37</sub> BrN <sub>4</sub> O <sub>4</sub>	64	646	200	63.18 (63.25)	5.83 (5.98)	8.71 (8.68)
BOC8	C <sub>38</sub> H <sub>45</sub> BrN <sub>4</sub> O <sub>4</sub>	67	702	195	65.04 (65.04)	6.52 (6.46)	7.84 (7.98)
BOC10	C <sub>42</sub> H <sub>53</sub> BrN <sub>4</sub> O <sub>4</sub>	73	758	190	66.18 (66.57)	7.03 (7.05)	7.42 (7.39)
BOC12	C <sub>46</sub> H <sub>61</sub> BrN <sub>4</sub> O <sub>4</sub>	65	813	185	68.05 (67.88)	7.82 (7.55)	6.75 (6.88)
BOC14	C <sub>50</sub> H <sub>69</sub> BrN <sub>4</sub> O <sub>4</sub>	66	870	182	68.72 (69.03)	7.93 (7.99)	7.42 (7.39)
BOC16	C <sub>54</sub> H <sub>77</sub> BrN <sub>4</sub> O <sub>4</sub>	70	926	179	69.66 (70.03)	8.29 (8.38)	5.96 (6.05)

<sup>a</sup>Determined by DSC measurement on the second heating.

–C(CH<sub>3</sub>)<sub>3</sub> and –OC<sub>16</sub>H<sub>33</sub> as end groups as examples to show the chemical shifts and the labels for the different hydrogen atoms.

### Thermal stability

The thermogravimetric analysis (TGA) curves of the target compounds in air and nitrogen are shown in Figure 4, from which it can be concluded that all the compounds have excellent thermal stability in a

nitrogen atmosphere, and 5% of them have thermogravimetric temperature above 380°C. From Figure 4 it can be seen that the thermal stability of the compounds is worse in air than in nitrogen.

### Liquid crystalline properties

The DSC curves of the compounds are shown in Figure 5 and the associated data are listed in Table 2.

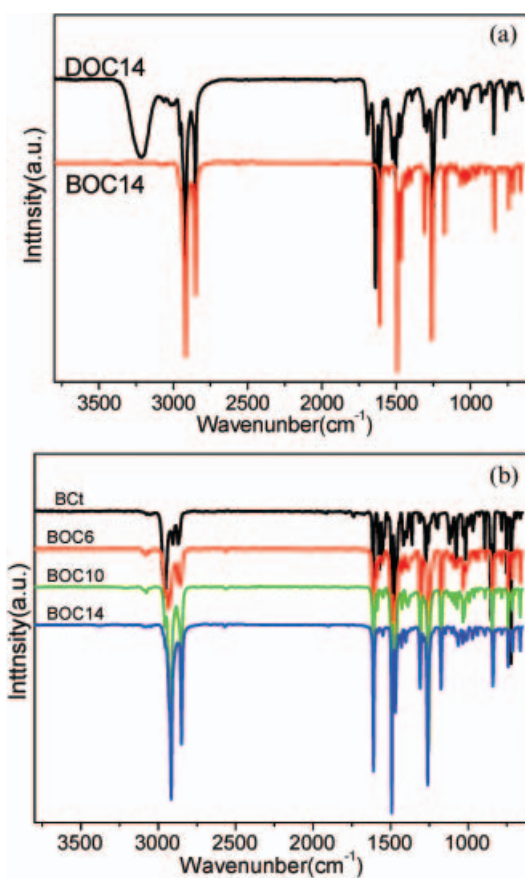


Figure 2. FT-IR spectra of (a) BOC14 and its dihydrazide (DOC14) and of (b) BCt, BOC6, BOC10 and BOC14.

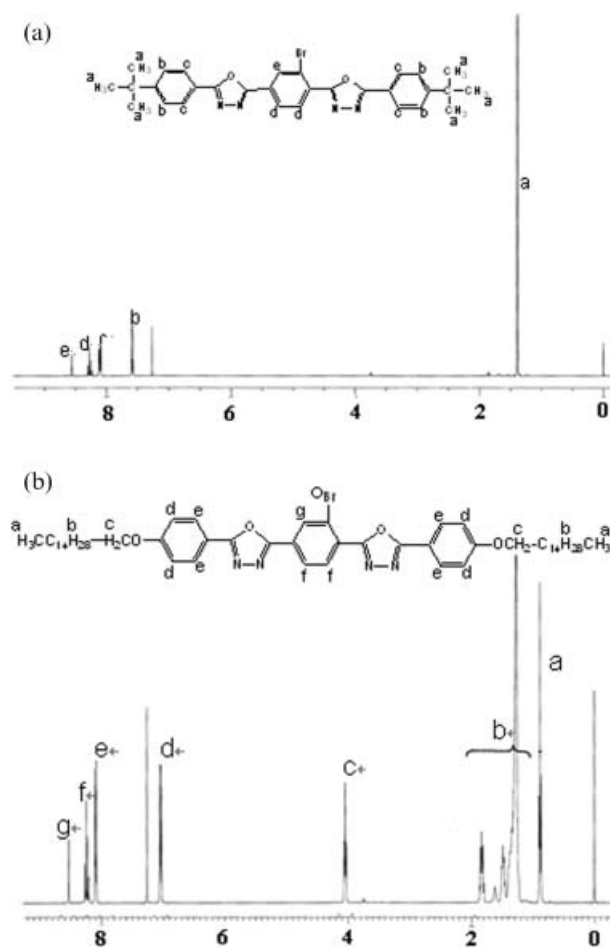


Figure 3. <sup>1</sup>H NMR spectra of BCt and BOC16.

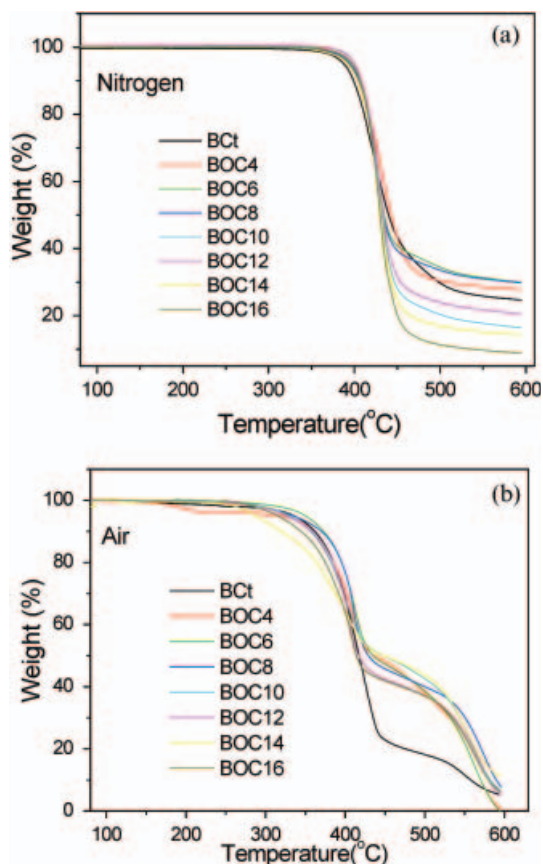


Figure 4. TGA curves of target compounds (a) under a nitrogen atmosphere and (b) under air at a heating rate of  $10^{\circ}\text{C min}^{-1}$ .

Figures 5a and 5b show, respectively, the second heating curve and the first cooling curve. There is only one endothermic peak while heating and only one exothermic peak while cooling for the compounds BCt, BOC4 and BOC6, which indicates that the only processes are melting and crystallisation, with no other phase transformation. However, two endothermic peaks appear when the compounds BOC8, BOC10, BOC12, BOC14 and BOC16 are heated, which correspond to the transformation from the crystalline (Cr) phase to a liquid crystalline phase and the transformation from liquid crystal to isotropic (I) liquid. There are two exothermic peaks in the cooling DSC curves, which correspond to the transformation from isotropic state to liquid crystal state and the transformation from liquid crystal state to crystalline state. The results of DSC analysis indicate that BCt, BOC4 and BOC6 exhibit no liquid crystalline phase, whereas BOC8, BOC10, BOC12, BOC14 and BOC16 are bidirectional thermally-induced liquid crystals with only one liquid crystal phase.

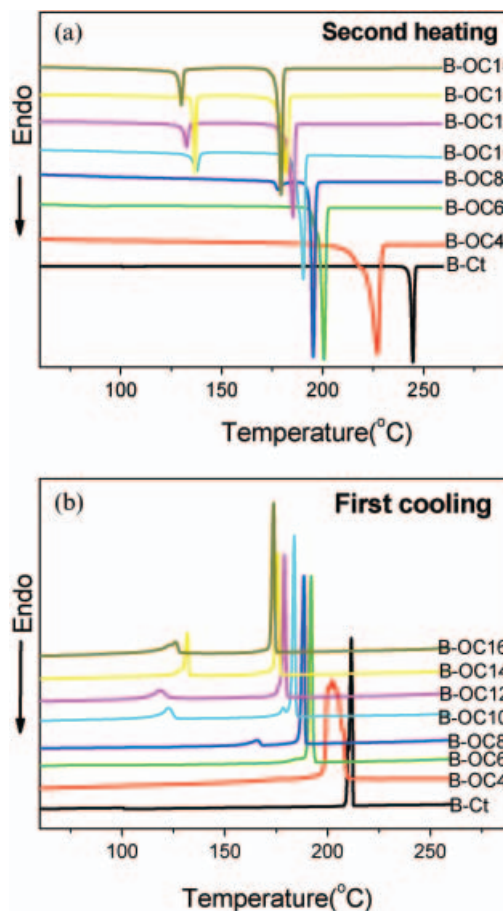


Figure 5. DSC curves of (a) compounds on heating and (b) scan at  $5^{\circ}\text{C min}^{-1}$  under  $\text{N}_2$  atmosphere.

In order to study the characteristics of the liquid crystal phase of the compounds, BOC8, BOC10, BOC12, BOC14 and BOC16 were observed using POM. The five compounds all enter the liquid crystal state at the first phase-transfer temperature in the DSC curve, when a bright-field, colourful birefringent texture can be observed. Upon further heating, the compounds enter an isotropic state and the field of view turns black. When cooling from isotropic state, the compounds all enter the liquid crystal state first and then begin to crystallise. The above observations indicate that they are enantiotropic liquid crystals. Using this process, the polarised light observation of the liquid crystal texture was recorded. As shown in Figure 6, the texture is mainly of the sector type, which is characteristic of the texture of a smectic phase.

In order to examine the structure of the liquid crystalline state further, temperature-dependent X-ray powder diffraction was utilized to study compounds BOC14 and BOC16. Figure 7 shows the X-ray diffraction patterns of the compounds at three different temperatures. From Figure 7, it can be seen

Table 2. Liquid crystalline properties of the target compounds.

Monomer	Phase transitions ( $^{\circ}\text{C}$ ) and corresponding enthalpy changes ( $\text{kJ mol}^{-1}$ )	
	Heating	Cooling
BCt	Cr 245 (40.38) I	I 212 (38.33) Cr
BOC4	Cr 227 (37.09) I	I 202 (34.04) Cr
BOC6	Cr 200 (49.28) I	I 192 (45.34) Cr
BOC8	Cr 195 (47.27) S 178 (2.70) I	I 189 (46.74) S 165 (4.08) Cr
BOC10	Cr 190 (47.86) S 138 (7.11) I	I 184 (41.66) S 122 (9.07) Cr
BOC12	Cr 185 (45.84) S 133 (10.14) I	I 179 (46.51) S 118 (10.56) Cr
BOC14	Cr 182 (45.21) S 137 (18.35) I	I 176 (48.14) S 132 (19.38) Cr
BOC16	Cr 179 (48.0) S 130 (11.89) I	I 174 (48.83) S 126 (16.43) Cr

Cr=crystal; S=smectic phase; I=isotropic liquid.

that there is almost no peak in the X-ray pattern above the clearing point ( $180^{\circ}\text{C}$ ), with only a wide dispersion peak at  $2\theta=20^{\circ}$ , which indicates that it is in the isotropic state with no long-range order. At room temperature, there are several diffraction peaks, which indicate that BOC14 and BOC16 are crystalline at room temperature. In the diffraction curve at  $160^{\circ}\text{C}$ , there is no peak at the wide-angle area, and the curve is very flat at  $2\theta=20^{\circ}$  even after zooming in, which indicates that no long-range order exists. At the same time, three sharp peaks appear at the small-angle area, so it can be judged that the

liquid crystal phase of BOC14 and BOC16 at this temperature is probably a smectic A (SmA) or smectic C phase. It is impossible to be any other smectic phase, because other smectic phase will cause relatively sharp diffraction peak at the wide-angle area, which correspond to small intermolecular distances. The interlamellar spacing of the three diffraction peaks in the small-angle area are  $d_1=3.85\text{ nm}$ ,  $d_2=1.83\text{ nm}$  and  $d_3=0.9\text{ nm}$  for BOC14 and  $d_1=3.78\text{ nm}$ ,  $d_2=1.983\text{ nm}$ ,  $d_3=1.34\text{ nm}$  for BOC16, with a ratio of 1:1/2:1/4. The interlamellar spacing of the first diffraction calculated from the

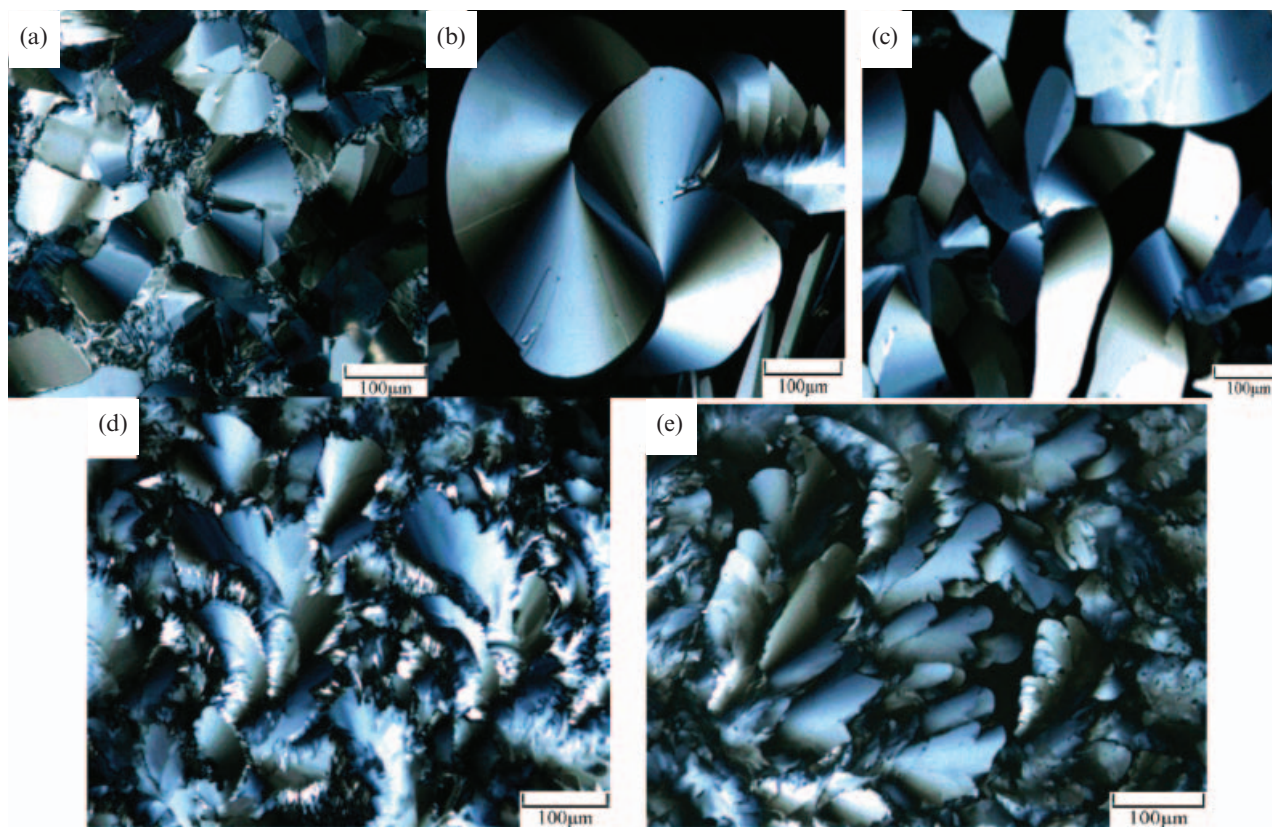


Figure 6. Typical textures of (a) BOC8 at  $186^{\circ}\text{C}$ , (b) BOC10 at  $182^{\circ}\text{C}$ , (c) BOC12 at  $175^{\circ}\text{C}$ , (d) BOC12 at  $172^{\circ}\text{C}$  and (e) BOC16 at  $170^{\circ}\text{C}$ .

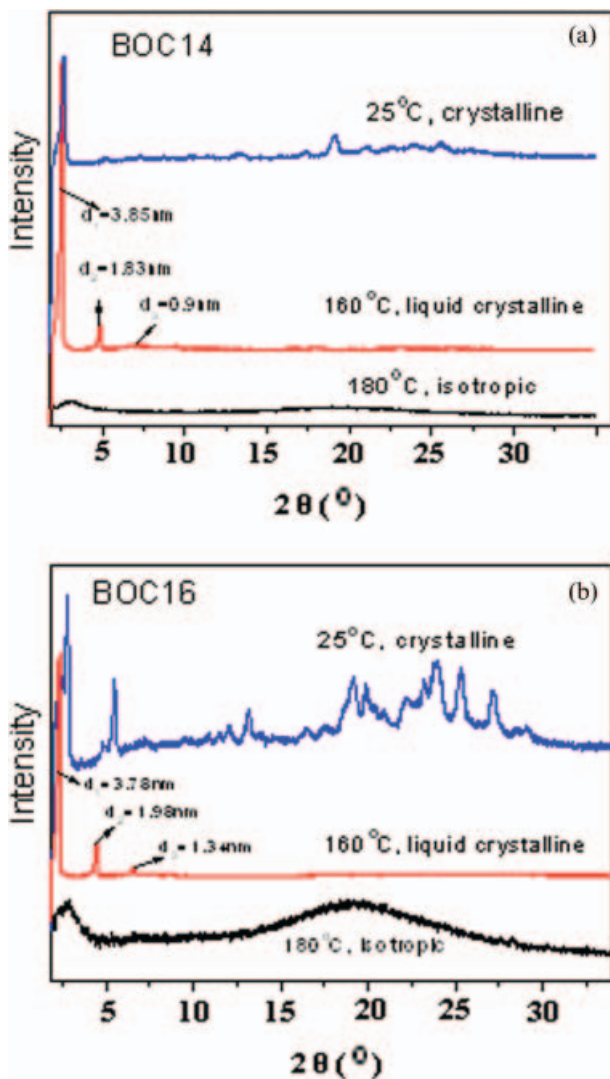


Figure 7. Powder WAXD patterns of BOC14 and BOC16.

spectrum is close to the result of a theoretical calculation, which shows that the stretched length is 3.59 nm for BOC14 and 3.8 nm for BOC14, when the alkyl end group takes the zigzag conformation. So we conclude that the liquid crystalline phases of BOC14 and BOC16 are lamellar SmA phases.

Form the results of DSC, POM and temperature-dependent WAXD measurements it is concluded that the liquid crystalline properties of this series of monomers are related to the length of the end groups. When the end group is relatively short, i.e. *tert*-butyl or alkoxy with four or six carbons, the monomers exhibit no liquid crystalline properties. When the alkoxy end group contains more than eight carbons, the monomers exhibit liquid crystalline properties. Because there are five aromatic rings in the liquid crystal mesogen, which causes strong rigidity, the aliphatic end group needs to be rather long to exhibit

liquid crystalline property. The liquid crystal monomers are all bidirectional liquid crystals, and the structure of the liquid crystalline phase is a lamellar SmA phase.

### Optical properties

Figure 8 shows to the UV–visible absorption and photoluminescence (PL) spectra of the compounds. The maximum absorption wavelength, the maximum transmitting wavelength in solution and solid state, as well as the fluorescence quantum yield in solution are listed in Table 3.

From the UV–visible absorption spectrum of the dilute solution of the compounds in tetrahydrofuran, we can see there are two absorption bands corresponding to the BCt monomer, whereas the other monomers with alkoxy end groups all have three absorption bands; the bands of the lowest energy correspond to the  $\pi$ – $\pi^*$  transition. There is strong  $\pi$ – $\pi^*$  interaction in the target molecules and their main absorption lies in the UV region. Compared with other compounds with alkoxy end groups, the  $\lambda_{\text{max}}$  has a blue shift of 14 nm, which is caused by the P– $\pi$  conjugation and the stronger electron-donating capability of the alkoxy group than the *tert*-butyl group in BCt. Among the series of the monomers with alkoxy end groups, the length of the alkyl group has no influence on the absorption band and the maximum absorption wavelength,  $\lambda_{\text{max}}$ .

From the fluorescence spectrum, it can be seen that the maximum transmitting wavelength,  $\lambda_{\text{max}}$ , of the monomers dissolved in THF are 390 nm and 409 nm, respectively. As shown in Figure 9, the maximum transmitting wavelength,  $\lambda_{\text{max}}$ , of the compounds in the solid state all exhibit a red shift of 50 nm compared with their solution behaviour,

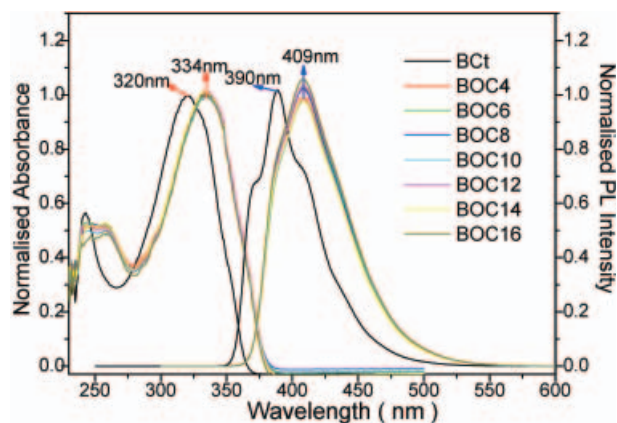


Figure 8. UV–visible absorption and PL spectra of compounds in  $10^{-6}\text{ M}$  THF solution.

and a shoulder-peak appears, which both indicate that the molecules in the solid state aggregate compactly and that maybe the excimer state recombination occurs. Among the series of compounds with alkoxy end groups, the length of the alkyl group has no influence on the fluorescence emitting spectrum of their solution state, while has some effect on the fluorescence emitting spectrum of solid state. The data listed in Table 3 show that all the compounds have blue fluorescence.

### 3. Conclusion

We have designed and synthesised a series of 2,5-bis[5-alkyl(alkoxy)phenyl -1,3,4-oxadiazole] bromobenzenes, which are very important derivatives of 1,3,4-oxadiazole. Elemental analysis and mass, IR and  $^1\text{H}$  NMR spectroscopies have been used to characterise their structure. Thermogravimetric analysis indicates that the compounds in an atmosphere of nitrogen have good thermal stability. DSC, POM and temperature-dependent WAXD measurements indicate that their liquid crystalline properties are related to the length of the end group. When the end groups are *tert*-butyl or alkoxy with four or six carbons, the compounds show no liquid crystal properties, whereas compounds with end groups of more than eight carbons show significant bidirectional thermally-induced liquid crystalline properties and the structure of the liquid crystal phase is a lamellar SmA phase. All the compounds exhibit blue fluorescence.

### 4. Experimental

#### Materials and measurements

Organic solvents were chemically pure or analytically pure, except that THF was refluxed in calcium hydride under nitrogen and evaporated before using.

Table 3. The UV-visible and PL spectral data of the target compounds (wavelengths in nm).

Monomer	UV-vis		PL		Fluorescence quantum yield $\Phi/\%$
	$\lambda_{\text{max}}$ (Soln.)	$\lambda_{\text{max}}$ (Soln.)	$\lambda_{\text{max}}$ (Solid)	$\lambda_{\text{max}}$ (Solid)	
BCt	320	390	413	33.02	
BOC4	334	409	457	45.38	
BOC6	334	409	435	52.37	
BOC8	335	409	436	46.17	
BOC10	334	409	443	57.51	
BOC12	335	409	444	49.09	
BOC14	334	409	439	51.99	
BOC16	334	409	440	46.56	

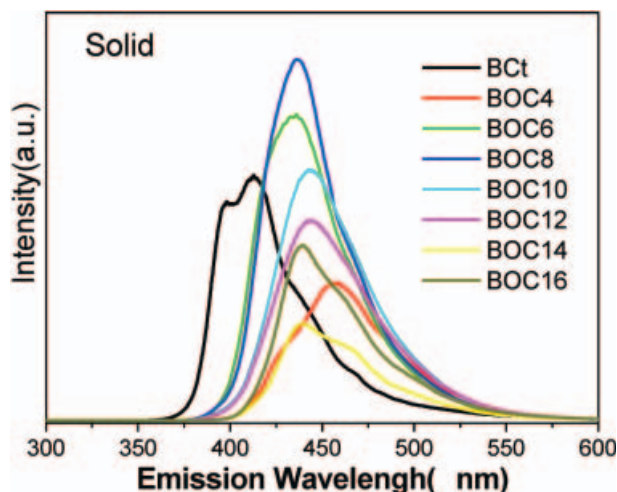


Figure 9. Photoluminescence of solid compounds.

Phosphorus oxychloride was redistilled before use. Triethylamine was refluxed in KOH for 24 h and evaporated under dry conditions. DMF was dried with magnesium sulfate overnight and evaporated under reduced pressure. Thionyl chloride was redistilled before use. All other reagents were used as received from commercial sources.

$^1\text{H}$  NMR spectra were recorded using a Bruker 400 MHz instrument with tetramethylsilane as the internal standard at room temperature in  $\text{CDCl}_3$  or  $\text{DMSO}-d_6$ . FTIR spectra were recorded in KBr discs with a Bruker Vector22, with the wavenumber between  $4000\text{--}400\text{ cm}^{-1}$  and a resolution of  $1\text{ cm}^{-1}$ . Mass spectra were recorded with Finnigan-MAT ZAB-HS mass spectrometer, with EI or CI as ionization resource. Elemental analyses were made on an Elementar Vario EL instrument. TGA was performed on a TA SDT 2960 instrument at a heating rate of  $10^\circ\text{C min}^{-1}$  in a nitrogen and air atmosphere. DSC examination was carried out using a TA DSC Q100 calorimeter at a heating rate of  $10^\circ\text{C min}^{-1}$  under continuous nitrogen flow. The sample size was about 4 mg and the data were based on the second heating process. POM observations were conducted on a Leitz Laborlux 12 microscope with a Leitz 350 hot stage. One-dimensional WAXD powder experiments were performed on a Philips X'Pert Pro diffractometer with a 3 kW ceramic tube as the X-ray source (Cu KR) and an X'celerator detector. The sample stage was set horizontally. The reflection peak positions were calibrated with silicon powder ( $2\theta > 15^\circ$ ) and silver behenate ( $2\theta < 10^\circ$ ). Background scattering was recorded and subtracted from the sample patterns. A temperature control unit (Paar Physica TCU 100) in conjunction with the diffractometer was utilized to study the structure evolutions



as a function of temperature. The heating and cooling rates in the WAXD experiments were  $1.5^{\circ}\text{C min}^{-1}$ . UV-visible absorption spectra were recorded on a Varian Cary 50 spectrophotometer (Varian, Australia), with the wavelength between 200–800 nm and the width of the spectral band between 0.2 and 4.0 nm. Fluorescence measurements were carried out on a Spex Fluorolog-3 spectrophotometer, with the exciting and emitting slit width of 5.0 nm, electron-multiplier phototube voltage of 400 V, scanning rate of  $240\text{ nm min}^{-1}$  and determined with correction spectroscopy. Fluorescence quantum yields were determined by comparing the integrated PL density of a reference 9,10-diphenylanthracene in toluene with a known quantum yield (ca.  $5 \times 10^{-6}\text{M}$ , quantum yield =  $1.00 \pm 0.05$ ). The fluorescence quantum yield,  $\phi$ , was calculated using the formula (25–27):

$$\phi = \phi_r \left( \frac{A}{A_r} \right) \left( \frac{OD_r}{OD} \right) \left( \frac{n}{n_r} \right)^2, \quad (1)$$

where  $A$  is the fluorescence integral area,  $OD$  is the absorbance,  $n$  is the refraction index and the subscript  $r$  stands for the reference substance for which the fluorescence quantum yield is already known.

## Synthesis

### Dialkoxybenzoic acetate (1)

Dihydroxybenzoic acetate (16.26 g, 0.1 mol), dry potassium carbonate (69.11 g, 0.5 mol), bromoalkane (0.15 mol) and a small amount of potassium iodide dissolved in 250 ml acetone were added to a 500 ml flask. The reaction mixture was stirred and heated under reflux. The system becomes a white suspension. The reaction time required increases as the end chain becomes longer. Thin-layer chromatography was used to decide whether the reaction is complete. After cooling the resultant mixture, vacuum distillation, and filtration to remove potassium carbonate, and the filtered solid was washed using acetone. The filtrate was collected, the acetone removed by rotatory vaporisation and the residue recrystallised in dry methanol or ethanol and then dried under vacuum. The yields of the dialkoxybenzoic acetates with different length of alkoxy group are all above 90%, of which the products for  $n \leq 8$  are colourless transparent fluids, where those for  $n \leq 10$  are white crystals at room temperature.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.0 (s, 2H,  $-\text{OCH}_2-$ ), 0.99 (s, 3H,  $-\text{CH}_3$ ), 6.90, 7.95 (m, 4H,  $-\text{Ar}-\text{H}$ ), 4.3 (s, 2H,  $-\text{COOCH}_2-$ ).

### Dialkoxybenzoyl hydrazide (2)

For  $n \leq 10$ , 0.10 mol **1** and 80 ml hydrazine hydrate were stirred 24 h under reflux. After cooling the colourless mixture, vacuum distillation removed most of the hydrazine hydrate until a large amount of white solid was precipitated. The solid was filtered and washed three times before finally washing with petroleum ether until the filtrate became colourless. The white solid obtained was dried under vacuum. For  $n > 10$ , 0.10 mol **1**, 40 ml hydrazine hydrate and 80 ml dry ethanol were stirred for 24 h under reflux to obtain a colourless transparent solution. After cooling, crystals were precipitated in 12 h then washed with a large amount of water, vacuum filtered and washed with petroleum ether until the filtrate became colourless. Finally, white needle-like or sheet-like crystals were obtained and dried under vacuum. The yields were all above 80%.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.0 (s, 2H,  $-\text{OCH}_2-$ ), 0.98 (s, 3H,  $-\text{CH}_3$ ), 6.93, 7.98 (m, 4H,  $-\text{Ar}-\text{H}$ ). Compared with **1**, there is no chemical shift of H in the ester group ( $-\text{COOCH}_2-$ ).

### 2-Bromoterephthalic chloride (3)

Redistilled thionyl chloride (30 ml) and one drop of dimethylformamide were added to 2-bromoterephthalic acid (2.45 g, 0.01 mol). The reaction was performed for 2 h under reflux. Excess thionyl chloride was removed by rotatory vaporisation before washing the filtered product three times with petroleum ether. The residual pale yellow fluid was dissolved in 50 ml of tetrahydrofuran.

### Dihydrazide (4)

Dialkoxybenzoyl hydrazide (20 mmol) was dissolved in 100 ml of tetrahydrofuran in an ice bath, and then 10 ml triethylamine added. When a solution of 2-bromoterephthalic chloride in tetrahydrofuran was added dropwise, a white precipitate appeared at once. After the dropwise addition, the mixture was stirred for 24 h at room temperature. Excess tetrahydrofuran was removed by vacuum distillation, and the resulting solid dispersed in water. Dilute hydrochloric acid was added to neutralize the unreacted triethylamine until the solution is neutral. A white solid was obtained after vacuum filtration, washing with water and tetrahydrofuran and drying under vacuum. The yield is about 60%.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 10.49 (m, 4H,  $-\text{NH}-$ ), 8.31, 7.89, 7.56, 7.05 (m, 11H,  $-\text{Ar}-\text{H}$ ), 7.21 (1H,  $-\text{CH}=\text{}$ ), 6.01, 5.48 (2H,  $=\text{CH}_2$ ), 4.03 (s, 4H,  $-\text{OCH}_2-$ ), 0.91 (s, 6H,  $-\text{CH}_3$ ).

*2,5-Bis[5-alkyl(alkoxy)]phenyl-1,3,4-oxadiazole]bromobenzene*

A solution of 5 mmol **4** in 30 ml phosphorus oxychloride was stirred under reflux for 14 h. After cooling, the solution poured slowly while stirring into an ice–water mixture. A yellow-green solid appeared at once and aqueous sodium hydroxide solution added to neutralise the mixture. After filtration, washing with water and drying under vacuum, the products were separated and purified through a silica gel column with the mixed solvent of dichloromethane and ethyl acetate (8:1) as the eluent. The product after separation using silica gel column was dried by rotatory evaporation and vacuum filtered using methanol. After drying under vacuum, recrystallization in tetrahydrofuran was performed and pure product obtained. The structure of the products agreed with that of our design, according to <sup>1</sup>H NMR, mass spectra, elemental analysis and infrared spectra results (see Table 1).

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