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Li-Rong Zhu[ab]; Fei Yao[a]; Jie Han[a]; Mei-Li Pang[a]; Ji-Ben Meng[a]
[a] Department of Chemistry, Nankai University, Tianjin, China [b] Key Laboratory of Functional Polymer Materials of Ministry of Education, Nankai University, Tianjin, China

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Synthesis, single crystal structure and liquid crystalline properties of bent-shaped 2,5-diaryl 1,3,4-oxadiazoles

Li-Rong Zhu[a,b], Fei Yao[a], Jie Han[a]*, Mei-Li Pang[a] and Ji-Ben Meng[a]

[a]*Department of Chemistry, Nankai University, Tianjin, 300071, China;* [b]*Key Laboratory of Functional Polymer Materials of Ministry of Education, Nankai University, Tianjin 300071, China*

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Two bent-shaped 1,3,4-oxadiazole-based compounds, namely 2-[4-(2-(4-methylphenyl)-(E)-1-ethenyl)]phenyl-5-(4-pentyloxyphenyl)-1,3,4-oxadiazole **5a** and 2-[4-(2-(4-fluorophenyl)-(E)- ethenyl-5-(4-pentyloxyphenyl)-1,3,4-oxadiazole **5b**, were synthesised and their liquid crystalline properties were studied in this paper. Compound **5a** exhibited an enantiotropic nematic mesophase, while **5b** displayed an enantiotropic smectic A phase. No banana-shaped mesophases were found in these mesogens, although they adopt a bent-shaped molecular structure as confirmed by the single X-ray diffraction crystallography.

Keywords: heterocyclic liquid crystals; stilbene; single X-ray crystallography; synthesis

1. Introduction

Ever since Niori *et al.* (*1*) reported the unusual ferroelectric properties of liquid crystals derived from achiral bent-core molecules in 1996, banana-shaped mesogens have received much attention from the viewpoints of both basic science and practical application (*2*, *3*). Generally, the banana-shaped liquid crystals have a bent angle of about 120°C, which often results from a central 1,3-phenylene (*4–6*). 2,5-Diaryl-1,3,4-oxadiazole-based liquid crystals have been studied intensively by different research groups; these mesogens may exhibit rich mesophases such as nematic, smectic and columnar phases via rational molecule modifications (*7–12*). From structural analysis, such compounds have a bent angle of ca. 134° (*13–16*), which should be sufficient to form banana-shaped phases in theory (*17*). Recently, Cristiano *et al.* have tried to devise banana-shaped liquid crystals based on the 1,3,4-oxadiazole ring; however, replacement of the central phenyl ring by a heterocyclic 1,3,4-oxadiazole ring often results in formation of nematic or smectic mesophase, which are typical for rod-like mesogens (*18*). Then, Kang *et al.* (*19*) reported the first example of a 1,3,4-oxadiazole-based mesogen exhibiting banana mesophase. In this regard, it is possible to devise and synthesise novel banana-shaped liquid crystallines derived from the 1,3,4-oxadiazoles. Herein, we report the synthesis and liquid crystalline behaviours of two 1,3,4-oxadiazole-based derivatives containing a stilbene moiety. The stilbene moiety was introduced to the target compounds as it was often used as a structural unit to form banana phases due to the bent-shaped structure (*20*, *21*).

2. Results and discussion

2.1 Synthesis and characterisation

The final compounds **5a** and **5b** were prepared successfully via the multi-step synthetic route shown in Scheme 1. The structures were fully characterised by means of ^{1}H NMR, ^{13}C NMR, MS and elemental analysis. The absolute conformation of **5a** was further confirmed by single X-ray crystallographic analysis. Colourless needle crystals of **5a** suitable for X-ray diffraction determination were obtained by slow evaporation of its CH_2Cl_2 solution at room temperature. Notably, although a few single crystal structures of 1,3,4-oxadiazaole-based compounds have been reported in the literature (*13–16*), mesogenic examples are still lacking. To our knowledge, **5a** is the first example of a mesogenic 1,3,4-oxadiazole compound determined by means of single X-ray crystallography.

Figure 1 depicts the crystal structure of **5a**, and the crystallographic data are summarised in Table 1. These X-ray data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (CCDC 696794). The asymmetric unit of structure **5a** comprises two symmetrically inequivalent molecules with an average molecular length of *ca* 25.4 Å. Both molecules adopt a bent, 'banana-like' shape with an average exocyclic angle C–O–C of 134°, as reported in other 1,3,4-oxadiazole-based derivatives with an azo linkage group (*22*). The molecules are piled in a layered structure as seen in Figure 2. Within each layer molecules are placed with an anti-parallel orientation of their mean planes. There are weak non-covalent C–H·π interactions between neighbouring molecules.

*Corresponding author. Email: hanjie@nankai.edu.cn

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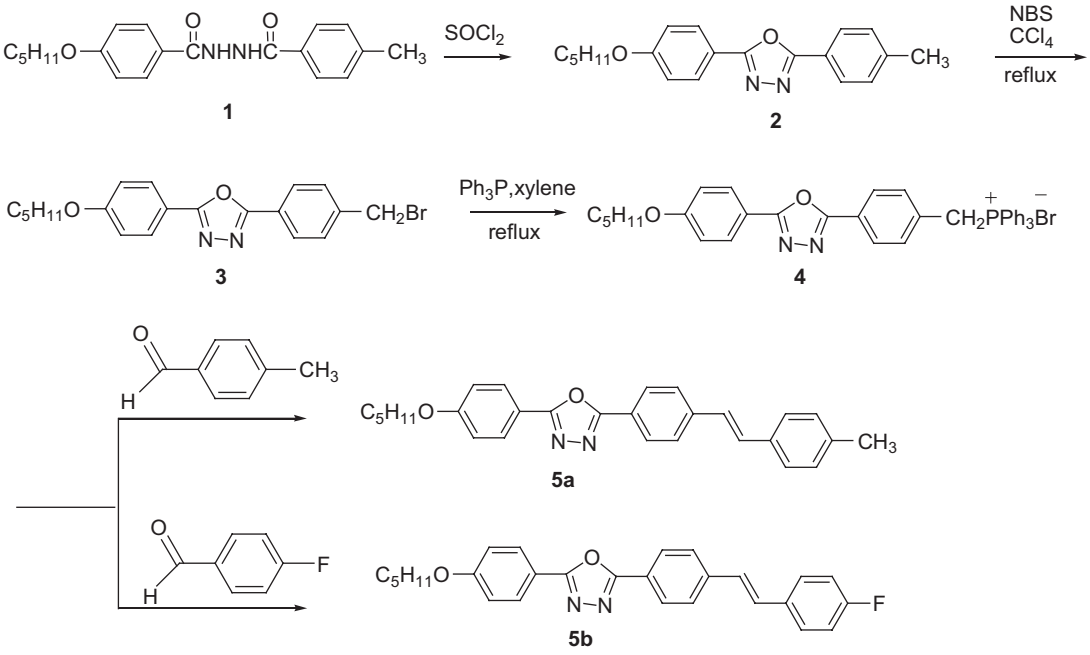

Scheme 1. The synthetic route and reaction conditions to **5a** and **5b**.

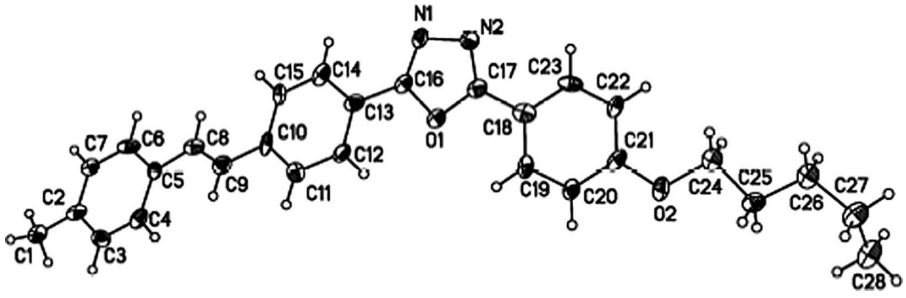

Figure 1. X-ray crystallographic structure of **5a**.

2.2 Liquid crystal properties

The LC properties of compounds **5a** and **5b** were investigated by differential scanning calorimetry (DSC) and polarised optical microscopy (POM). The mesophases were identified according to the classification system reported by Dierking (*23*). The phase transition temperatures and associated enthalpy changes derived from DSC measurements are listed in Table 2. Compound **5a** exhibited an enantiotropic nematic mesophase, which was identified by the typical schlieren texture (Figure 3(a)) observed under POM, while **5b** displayed a fan-shaped and focal conic texture (Figure 3(b)) charactistic for smectic A mesophase. The identity of the mesophases was also consistent with the transition enthalpy of the clearing point of these compounds. The nematic–isotropic phase transition enthalpy for **3a** is 0.2 kJ mol^{-1}, which is much lower than that (6.5 kJ mol^{-1}) for the smectic A to isotropic phase transition for **3b**. The only difference in molecular structures of **5a** and **5b** is they have different terminal groups. Compound **5a**, with an end methyl group, tends to form nematic phase, while **5b** exhibits a smectic A phase due to the terminal fluorine atom. The effect of the terminal groups on liquid crystalline properties is consistent with the results reported in the literature (*24*, *25*). According to the single crystal structure shown in Figure 1, although compounds **5a** and **5b** adopt a bent-shape structure, both of them only exhibited mesophases typical for calamitic liquid crystals, and no B-phase was found in these mesogenic compounds. From a search of the literature, the banana-shaped liquid crystals usually contain five or more benzene

Table 1. Selected crystallographic data for **5a**.

Compound	**5a**
Formula	$C_{28}H_{28}N_2O_2$
Formula weight	424.52
T (K)	113(2)
Space group	Triclinic, P-1
a (Å)	5.8209(12)
b (Å)	17.824(4)
c (Å)	23.085(5)
α (°)	74.58(3)
β (°)	89.49(3)
γ (°)	87.85(3)
V (Å^{-3})	2307.3(8)
Z	4
μ (mm^{-1})	0.077
F (000)	904
Crystal size (mm)	0.16 × 0.12 × 0.08
θ, range for data (deg)	1.68–25.02
Reflns collected/unique	13305/8026
$R[F^2 > 2\sigma(F^2)]$	R_1 = 0.2616
$wR(F2)$, all data	wR_2 = 0.5531

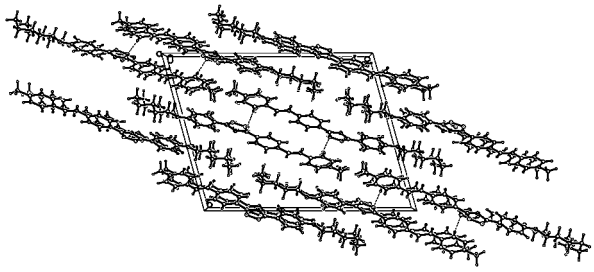

Figure 2. The packing diagram of **5a**.

Table 2. Phase transition temperatures (T/°C) and the associated enthalpy values (in parentheses) of **5a** and **5b**.

Compound	Phase transitions[a] T[°C] (ΔH [kJ mol^{-1}])[b]
5a	Cr 177.8 (29.6) N 190.9 (0.2) Iso Iso 186.9 (–0.3) N 138.0 (–19.2)
5b	Cr 134.5 (23.5) SmA 201.5 (6.5) Iso Iso 200.2 (–2.3) SmA 112.9 (–8.3) Cr

[a] Cr = crystal phase; SmA = smectic A mesophase; N = nematic mesophase; Iso = isotropic liquid, [b] determined by DSC.

and heterocyclic rings connected by different linkage groups, which is a crucial factor leading to polar packing and producing B-phases (*12*). However, compounds **5a** and **5b** in this work contain only four rings, which is not enough to result in B-phases. In the literature, Cristiano *et al.* reported a series of 1,3,4-oxadiazole-based mesogens containing five rings and also did not find B-phases. They suggested that the mesophases were determined by the both the geometric and eletrostatic factors of the oxadiazole moity; however, the definitive reason for the lack of B-phases in these liquid crystal materials is still not very clear (*18*).

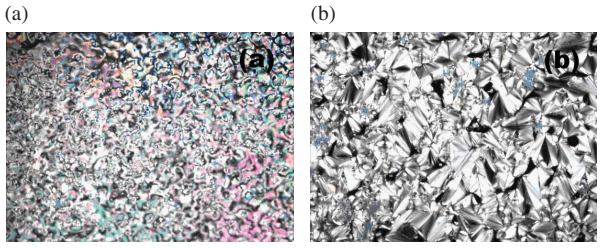

Figure 3. Optical photomicrographs (magnification 200×) of (a) nematic mesophase with schlieren texture for **5a** at 160°C in the cooling cycle; (b) smectic A mesophase with fan-shaped and focal conic texture for **5b** at 130°C in the cooling cycle.

3. Conclusions

We report the synthesis, structure and liquid crystalline properties of new 1,3,4-oxadiazole-based compounds containing a stilbene unit. All of the final compounds exhibit enantiotropic nematic or smectic mesophases, which are determined by the nature of the terminal groups. Although these compounds adopt a bent-shape structure, none of them displayed banana-shaped mesophases due to the short mesogenic core.

4. Experimental section

4.1 Equipment and techniques

The starting compound **1** was prepared according to the method in literature (*26*). All other chemicals were commercially available and used as received. Solution ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV300 (300M) spectrometer. Chemical shifts are reported in ppm downfield of TMS. Proton decoupled ^{13}C NMR spectra were recorded at 101 MHz on the same NMR spectrometer. Elemental analyses were performed on a YANACO CHN CORDER MT-3 apparatus. Electrospray-ionisation (ESI) mass spectra were recorded on a Finnigan LCQ Advantage spectrometer. Intensity data of a single crystal of **5a** were collected using a Bruker SMART 1000 diffractometer with graphite-monochromatised MoK_α X-ray radiation (λ = 0.71073 Å) and Saturn CCD area detector. The X-ray crystal structure was solved by the direct method and expanded using Fourier syntheses technique. All the non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were calculated from idealised geometry of the attached parent atoms and the positions and thermal parameters were refined using a riding model. Structural

refinement based on the full-matrix least-squares refinement on $|F|^2$ values was performed by using CrystalStructure or SHELXL97 suite program (*27*).

Thermal properties were measured with differential scanning calorimetry (NETZSCH DSC 204) under a nitrogen atomosphere at a heating and cooling rate of 5°C min^{-1} and calibrated with a pure indium sample. Mesophases in the melt were identified with a polarising optical microscope (OLYMPUS BX51) under a crossed polariser equipped with a control unit and a hot stage, and the samples were placed between two pieces of untreated glass slides using heating and cooling rates of 5°C min^{-1}.

4.2 Synthesis

4.2.1 Synthesis of 2-(4-pentyloxyphenyl)-5-p-tolyl-1, 3, 4-oxadiazole ***2***

Compound 4-methylbenzoic acid N′-(4-pentyloxybenzoyl)hydrazide **1** (5 mmol) was added to $SOCl_2$ (5 mL) in dried benzene (20 mL). The reaction mixture was refluxed for 7 h and the excessive thionyl chloride and solvent were removed by vacuum distillation. The crude solid was collected and washed several times with distilled water and was further purified by silica gel column chromatography using ethyl acetate/petroleum ether (*v*/*v* = 1:3) as an eluent. The reaction products were obtained as off-white solids in 87.3% yield. m.p.128–130°C; ^{1}H NMR (300 MHz, $CDCl_3$) *δ*:0.95 (t, 3H, ^3J = 6.6 Hz, **CH_3**CH_2-), 1.44–1.63 (m, 4H, CH_3(C**H_2**)$_2CH_2CH_2O$-), 1.78–1.89 (m, 2H, -C**H_2**CH_2O-), 2.44 (s, 3H, Ar-C**H_3**), 4.04 (t, 2H, ^3J = 6.6 Hz, -CH_2O-), 7.01 (d, 2H, ^3J = 8.4 Hz, Ar-H), 7.32 (d, 2H, ^3J = 7.8 Hz, Ar-H), 8.03 (d, 2H, ^3J = 7.8 Hz, Ar-H), 8.06 (d, 2H, ^3J = 8.4 Hz, Ar-H); MS (+cESI): m/z: 323.30 $[M+1]^+$; Anal. calculated for $C_{20}H_{22}N_2O_2$: C 74.51, H 6.88, N 8.69; found C 74.37, H 6.63, N 8.84.

4.2.2 Synthesis of 2-(4-pentyloxyphenyl)-5-(4-bromomethylphenyl)-1,3,4-oxadiazole ***3***

Compound **2** (0.5 mmol), dry carbon tetrachloride (15 mL), *N*-bromosuccinimide (0.55 mmol), and catalyst amount of dibenzoyl peroxide were added to a 100 mL round-bottom flask fitted with a reflux condense. The reaction mixture was refluxed under a nitrogen atmosphere for 5 min, and initiated with visible light. The resulting mixture was refluxed for 5 h, then the reaction mixture was cooled to room temperature and filtered to remove the succinimide. The filtrate was evaporated and the residue was column chromatographed (silica, dichlomethane-ethyl acetate, 25:1 v/v) to afford the respective compound **3** as white solids in 78%. White solid; m.p: 134–136°C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*:0.94 (t, 3H, ^3J = 6.6 Hz, C**H_3**CH_2-), 1.39–1.49 (m, 4H, CH_3(C**H_2**)$_2CH_2CH_2O$-), 1.81–1.85 (m, 2H, -C**H_2**CH_2O-), 4.04 (t, 2H, ^3J = 6.6 Hz, -C**H_2**O-), 4.54 (s, 2H, -C**H_2**Br), 7.02 (d, 2H, ^3J = 8.8 Hz, Ar-**H**), 7.55 (d, 2H, ^3J = 8.4 Hz, Ar-**H**), 8.06 (d, 2H, ^3J = 8.8 Hz, Ar-**H**), 8.10 (d, 2H, ^3J = 8.4 Hz, Ar-**H**). MS: 401.1 (M^+).

4.2.3 Synthesis of compound 2-[4-(2-(4-methylphenyl)-(E)-1-ethenyl)]phenyl-5-(4-pentyloxyphenyl)- 1,3,4-oxadiazole ***5a***

To a round-bottom flask were added were added the intermediate compounds **3** (0.5 mmol), and triphenylphosphine (0.8 mmol) in dry xylene (25 mL). The flask was purged with nitrogen, and the reaction mixture was refluxed overnight. The Wittig salt formed was filtered to afford the crude products of **4** as white solids, which were used in the next step reaction directly. The wittig salt **4** (0.3 mmol) was dissolved in 20 mL of dry tetrahydrofuran and 15 mL of methylene chloride. The resultant solution was added anhydrous potassium carbonate (1 mmol) and 18-crown-6 (ca. 5 mg). After stirring this mixture for 15 min, *p*-tolualdehyde (0.45 mmol) was added slowly. The reaction mixture was refluxed overnight. The excessive K_2CO_3 was removed by filtration and the solvent was removed from the filtrate by rotary evaporation. The crude product was purified by silica gel column chromatography using dichloromethane/ethyl acetate (25:1) as eluent to give **5a** as white solids in 75%. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*:0.94 (t, 3H, ^3J = 6.6 Hz, C**H_3**CH_2-), 1.39–1.46 (m, 4H, CH_3(C**H_2**)$_2CH_2CH_2O$-), 1.79–1.85 (m, 2H, -C**H_2**CH_2O-), 2.38 (s, 3H, Ar-C**H_3**), 4.04 (t, 2H, ^3J = 6.6 Hz, -C**H_2**O-), 7.02 (d, 2H, ^3J = 8.7 Hz, Ar-H), 7.09 (d, 1H, $^3J_{trans}$ = 16.2 Hz, -C**H** = CH-), 7.19–7.26 (m, 3H, Ar-H and -CH = C**H**-), 7.45 (d, 2H, ^3J = 8.1 Hz, Ar-**H**), 7.64 (d, 2H, ^3J = 8.1 Hz, Ar-**H**), 8.07 (d, 2H, ^3J = 8.7 Hz, Ar-**H**), 8.10 (d, 2H, ^3J = 8.4 Hz, Ar-**H**); ^{13}C NMR (75MHz, $CDCl_3$) *δ*:14.0, 21.3, 22.5, 28.2, 28.9, 68.3, 115.0, 116.2, 122.6, 126.5, 126.7, 126.8, 127.1, 128.7, 129.5, 130.8, 134.0, 138.2, 140.7, 161.9, 164.3, 164.5; MS(+cESI): m/z: 425.4 $[M+1]^+$; Anal. calculated for $C_{28}H_{28}N_2O_2$: C 79.22, H 6.65, N 6.60; found C 79.34, H 6.41, N 6.46.

Compound **5b** was prepared according to the same procedure as that of **5a**. The spectroscopic data and elemental analysis data are collected as follows:

2-[4-(2-(4-fluorophenyl)-(E)-ethenyl-5-(4-pentyloxyphenyl) -1,3,4-oxadiazole **5b**: White solid. Yield: 78%. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*:0.94 (t, 3H,

^3J = 6.6 Hz, C**H**$_3$CH$_2$-), 1.39–1.47 (m, 4H, CH$_3$(C**H**$_2$)$_2$CH$_2$CH$_2$O-), 1.79–1.85 (m, 2H, -C**H**$_2$ CH$_2$O-), 4.03 (t, 2H, ^3J = 6.6 Hz, -C**H**$_2$O), 7.01–7.10 (m, 5H, Ar-H and -C**H** = CH-), 7.21 (d, 1H, $^3J_{trans}$ = 15.9 Hz, -CH = C**H**-), 7.50-7.53 (m, 2H, Ar-**H**), 7.63 (d, 2H, ^3J = 8.0 Hz, Ar-**H**), 8.07 (d, 2H, ^3J = 8.7 Hz, Ar-**H**), 8.09 (d, 2H, ^3J = 8.4 Hz, Ar-**H**); ^{13}C NMR (75 MHz, CDCl$_3$) δ:14.0, 22.3, 28.2, 28.9, 68.3, 115.0, 116.2, 122.6, 126.5, 126.7, 126.8, 127.1, 128.7, 129.5, 130.8, 134.0, 138.2, 140.7, 161.9, 164.3, 164.5; MS(+cESI): m/z: 429.4[M+1]$^+$; Anal. calculated for $C_{27}H_{25}FN_2O_2$: C 75.68, H 5.88, N 6.54; found C 75.57, H 6.03, N 6.39.

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References

(1) Niori, T.; Sekine, T.; Watanbe, J.; Furukawa, T.; Takezoe, H. *J. Mater. Chem.* **1996**, *6*, 1231–1233.
(2) Pelzl, G.; Diele, S.; Weissflog, W. *Adv. Mater.* **1999**, *11*, 707–724.
(3) Ros, M.B.; Serrano, J.L.; Fuente, M.R. De la; Folcil, C.L. *J. Mater. Chem.* **2005**, *15*, 5093–5098.
(4) Pelzl, G.; Tamba, M.T.; Findeisen-Tandel, S.; Schröder, M.W.; Baumeister, U.; Diele, S.; Weissflog, W. *J. Mater. Chem.* **2008**, *18*, 3017–3031.
(5) Yu, F.C.; Yu, L.J. *Chem. Mater.* **2006**, *18*, 5410–5420.
(6) Folcia, C.L.; Ortega, J.; Etxebarria, J. Pintre, I.; Ros, M.B. *Chem. Mater.* **2006**, *18*, 4617–4626.
(7) Srivastava R.M.; Neves Filho R.A.W.; Schneider R.; Vieira A.A.; Gallardo H. *Liq. Cryst.* **2008**, *35*, 737–742.
(8) Chai C.; Yang Q.; Fan X.; Chen X.; Shen Z.; Zhou Q. *Liq. Cryst.* **2008**, *35*, 133–141.
(9) Han, J.; Wang, J.-Y.; Zhang, F.-Y.; Zhu, L.-R.; Pang, M.-L.; Meng, J.-B. *Liq. Cryst.* **2008**, *35*, 1205–1214.
(10) Para, M.L.; Hidalgo, P.I.; Soto-Bustamante, E.A.; Barberá, E.Y.; Trujillo-Rojo, V.-H. *Liq. Cryst.* **2008**, 35, 1251–1262.
(11) Qu S.; Li M. *Tetrahedron*, **2007**, *63*, 12429–12436.
(12) Wen C.-R.; Wang Y.-J.; Wang H.-C.; Sheu H.-S.; Lee G.-H.; Lai C.-K. *Chem. Mater.* **2005**, *17*, 1646–1654.
(13) Han, J.; Zhang, F.-Y.; Chen, Z.; Wang, J.-Y.; Zhu, L.-R.; Pang, M.-L.; Meng, J.-B. *Liq. Cryst.* **2008**, *35*, 1359–1365.
(14) Wang, C.; Pälsson, L.-O.; Batsanov, A.S.; Bryce, M.R. *J. Am. Chem. Soc.* **2006**, *128*, 3789–3799.
(15) Han, J.; Chui, S.S.-X.; Che, C.M. *Chem. Asian. J.* **2006**, *1*, 814–825.
(16) Hughes, G.; Kreher, D.; Wang, C; Batsanov, A.S.; Bryce, M. *Org. Biomol. Chem.* **2004**, *2*, 3363–3367.
(17) Weissflog, W.; Nádasi, H.; Dunemann, U.; Pelzl, G.; Diele, S.; Eremin, A.; Kresse, H. *J. Mater. Chem.* **2001**, *11*, 2748–2758.
(18) Cristiano, R.; Ely, F. Gallardo, H. *Liq. Cryst.* **2005**, *32*, 15–25.
(19) Kang, S.; Saito, Y.; Watanabe, N.; Tokita, M.; Takanishi, Y.; Takezoe, H.; Watanabe, J. *J.Phys. Chem. B* **2006**, *110*, 5205–5214.
(20) Mieczkowski, J.; Gomola, K.; Koseska, J.; Pociecha, D.; Szydlowska, J.; Gorecka, E. *J. Mater. Chem.* **2003**, *13*, 2132–2137.
(21) Mieczkowski, J.; Szydlowska, J.; Matraszek, J.; Pociecha, D.; Gorecka, E.; Donnio, B.; Guillon, D. *J. Mater. Chem.* **2002**, *12*, 3392–3399.
(22) Carella, A.; Castaldo, A.; Centore, R.; Fort, A.; Sirigu, A.; Tuzi, A. *J. Chem. Soc. Perkin Trans. 2*, **2002**, 1791–1795.
(23) Dierking I. *Texture of Liquid Crystals* [M]. WILEY-VCH Vrlag, GmbH & Co. KGaA: Weinheim, 2003.
(24) Sung, H.-H.; Lin, H.-C. *Liq. Cryst.* **2004**, *31*, 831–841.
(25) Han, J.; Chang, X.-Y.; Zhu, L.-R.; Wang, Y.-M.; Meng, J.-B.; Lai, S.-W.; Chui, S.S.-Y. *Liq. Cryst.* **2008**, *35*, 1379–1394.
(26) Han, J.; Chang, X.-Y.; Wang, X.-G.; Zhu, L.-R.; Pang, M.-L.; Meng, J.-B. *Liq. Cryst.* **2009**, *36*, 157–163.
(27) Sheldrick G.M. *SHELXS97 and SHELXL97*. University of Goettingen: Germany, 1997.