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Liquid Crystals

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^a State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P.R. China ^b Department of Chemistry, Northeast Normal University, Changchun 130024, P.R. China

To cite this Article Zhang, Qixian , Jiao, Liansheng , Shan, Changsheng , Hou, Peng , Chen, Bin , Xu, Xiaoyu and Niu, Li(2008) 'Synthesis and characterisation of novel imidazolium-based ionic liquid crystals with a *p*-nitroazobenzene moiety', *Liquid Crystals*, 35: 6, 765 – 772

To link to this Article: DOI: 10.1080/02678290802130264

URL: <http://dx.doi.org/10.1080/02678290802130264>

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Synthesis and characterisation of novel imidazolium-based ionic liquid crystals with a *p*-nitroazobenzene moiety

Qixian Zhang^{ab}, Liansheng Jiao^a, Changsheng Shan^a, Peng Hou^a, Bin Chen^b, Xiaoyu Xu^a and Li Niu^{a*}

^aState Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P.R. China; ^bDepartment of Chemistry, Northeast Normal University, Changchun 130024, P.R. China

(Received 5 March 2008; final form 15 April 2008)

A novel series of compounds with different counter anions, i.e. 1-{{[4-(4-nitrophenylazo)phenoxy]}alkyl-3-methyl-1*H*-imidazol-3-ium bromide salts (**C_n**, *n*=3, 6, 10) and tetrafluoroborate salts (**D_n**, *n*=3, 6, 10), were synthesised by the incorporation of an imidazolium group into paraffin side chain-terminated 4-nitroazobenzene derivatives. Their chemical structures were determined by ¹H NMR, ¹³C NMR, UV spectroscopy and elemental analysis. The thermotropic liquid crystalline properties of these materials were further studied by polarising optical microscopy, wide-angle X-ray diffraction and differential scanning calorimetry. The results show that **C_n** and **D_n** (*n*=6, 10) exhibit smectic liquid crystalline phases. The ionic liquid groups play an important role in forming the smectic layer structure, via enhancement of the thermal stability of the smectic state.

Keywords: ionic liquid crystals; imidazolium derivatives; smectic phase enhancement

1. Introduction

Liquid crystalline materials are attracting increasing attention due to their extensive applications, such as in organic electronics (1), optoelectronic devices (2), biological medical fields (3), nonlinear optics (4), etc. Among liquid crystalline materials, ionic liquid crystalline materials based on imidazolium salts are some of the most important and the most interesting to investigate. Ionic liquid crystals (ILCs) are a class of liquid crystalline compounds containing anions and cations; they possess the properties of both ionic liquids and liquid crystals (LCs) (5). Ionic liquids exhibit many useful properties, such as a very low vapour pressure, high thermal stability, non-flammability, high chemical stability, high ionic conductivity and a wide electrochemical window (6, 7), which may enable them to serve widely as a new generation of solvents in synthesis, catalysis, separation and electrochemistry (8–10). Among the known ILCs, imidazolium salts are the most frequently studied. Imidazoles can form ionic liquids and ILCs by quaternisation (11–14). The ionic interaction of imidazolium tends to stabilise lamellar mesophases, which show great potential as ordered reaction media that can impart selectivity in reactions by ordering reactants (15). Incorporation of imidazolium ion functionalities into paraffin side chain-terminated 4-nitroazobenzene derivatives could lead to a new series of liquid crystalline materials for research and industrial applications. We expected that the ionic interaction of the imidazolium group could stabilise

the mesophase of the azobenzene moiety over a wide temperature range (16). Azobenzene derivatives with such a broad mesophase range are promising for use in high-density optical data storage and photochemical devices (17, 18). In this paper, the synthesis of these compounds is described together with the characterisation of their thermotropic liquid crystalline properties. The influence of the anion on mesomorphic properties was also explored.

2. Experimental

Synthesis of compounds **C_n**

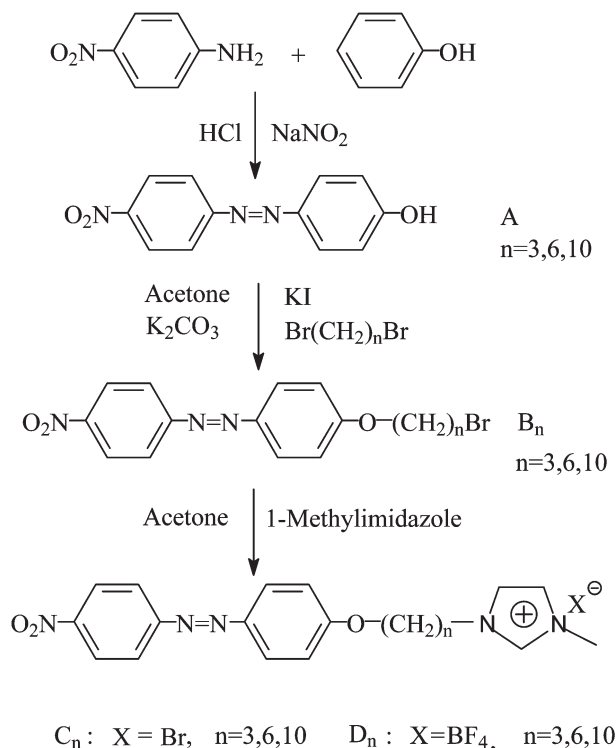
The synthetic strategy adopted is shown in Scheme 1. The intermediates **A** and **B_n** were first prepared as described in a previous report (19). Their structures were confirmed further by ¹H NMR.

For compound **A**, ¹H NMR (400 MHz, CDCl₃): 8.37 (2H, d, *J*=9.6 Hz, Ar–H), 7.96 (4H, t, *J*=9.0 Hz, Ar–H), 7.00 (2H, d, *J*=8.6 Hz, Ar–H), 5.36 (1H, s, Ar–OH).

For compound **B₃**, ¹H NMR (400 MHz, CDCl₃): 8.37 (2H, d, *J*=8.4 Hz, Ar–H), 7.96–8.00 (4H, m, Ar–H), 7.05 (2H, d, *J*=8.7 Hz, Ar–H), 4.23 (2H, t, *J*=11.7 Hz, OCH₂), 3.62–3.66 (2H, m, CH₂Br), 2.34–2.42 (2H, m, CH₂).

For compound **B₆**, ¹H NMR (400 MHz, CDCl₃): 8.36 (2H, d, *J*=8.1 Hz, Ar–H), 7.95–7.99 (4H, m, Ar–H), 7.02 (2H, d, *J*=8.4 Hz, Ar–H), 4.05–4.12 (2H, m, OCH₂), 3.44 (2H, m, CH₂Br), 1.83–1.89 (4H, m, CH₂), 1.43–1.56 (4H, m, CH₂).

*Corresponding author. Email: lniu@ciac.jl.cn



Scheme 1. Synthesis of imidazolium salt derivatives containing an azobenzene moiety.

For compound **B**₁₀, ¹H NMR (400 MHz, CDCl₃): 8.38 (2H, d, *J*=9.0 Hz, Ar-H), 7.96–8.01 (4H, m, Ar-H), 7.03 (2H, d, *J*=8.6 Hz, Ar-H), 4.06–4.10 (2H, m, OCH₂), 3.40–3.45 (2H, m, CH₂Br), 1.82–1.89 (4H, m, CH₂), 1.45–1.50 (4H, m, CH₂), 1.26–1.34 (8H, m, CH₂).

1-{[4-(4-nitrophenylazo)phenoxy]}propyl-3-methyl-1H-imidazol-3-ium bromide (**C**₃) and other **C**_{*n*} compounds.

B₃ (2.54 g, 0.02 mol) and 1-methylimidazole (1.64 g, 0.02 mol) were dissolved in 30 ml of dry acetone and the mixture vigorously stirred and refluxed for 24 h under a flow of dry nitrogen. After cooling to room temperature, excess acetone was evaporated in vacuum. The crude product was precipitated by addition of excess hexane, then recrystallised from ethanol and finally dried under vacuum giving pure **C**₃ as a brown-red solid. Yield 85%, m.p. 176°C. ¹H NMR (400 MHz, CDCl₃): 8.63 (1H, s, imidazolium ring), 8.09–8.12 (2H, m, Ar-H), 7.63–7.67 (4H, m, Ar-H), 7.40 (1H, s, imidazolium ring), 7.31 (1H, s, imidazolium ring), 6.84–6.87 (2H, m, Ar-H), 4.32 (2H, t, *J*=13.2 Hz, N-CH₂), 4.04 (2H, t, *J*=8.1 Hz, OCH₂), 3.72 (3H, s, N-CH₃), 2.23–2.29 (2H, m, CH₂). ¹³C NMR (100 MHz, DMSO-*d*₆): 29.41, 36.26, 46.81, 65.79, 115.79, 122.94, 123.64, 124.10, 125.54, 125.90, 137.28, 146.85, 148.50, 155.80, 162.50. Elemental analysis: calculated for C₁₉H₂₀N₅O₃Br, C

51.13, H 4.52, N 15.69%; found C 51.34, H 4.39, N 15.38%.

Compound **C**₆ was synthesised according to **C**₃ and obtained as brown-red solid. Yield 81%, m.p. 153°C. ¹H NMR (400 MHz, CDCl₃): 10.61 (s, 1H, imidazolium ring), 8.37–8.34 (2H, m, Ar-H), 7.96–7.99 (4H, m, Ar-H), 7.33–7.36 (2H, m, imidazolium ring), 7.03–7.04 (2H, m, Ar-H), 4.38 (2H, t, *J*=15.3 Hz, N-CH₂), 4.12 (3H, s, N-CH₃), 4.07 (2H, t, *J*=12.3 Hz, OCH₂), 1.45–2.03 (8H, m, CH₂). ¹³C NMR (100 MHz, CDCl₃): 25.85, 26.34, 29.24, 30.62, 37.18, 50.45, 68.47, 115.32, 122.19, 123.50, 123.69, 125.09, 126.03, 138.33, 147.22, 148.58, 156.41, 163.12. Elemental analysis: calculated for C₂₂H₂₆N₅O₃Br, C 54.11, H 5.37, N 14.34%; found C 53.96, H 5.41, N 13.98%.

Compound **C**₁₀ was synthesised following a procedure similar to that described above using **B**₁₀ and 1-methylimidazole; the target material was obtained as a brown-red solid. Yield 84%, m.p. 110°C. ¹H NMR (400 MHz, CDCl₃): 10.92 (1H, s, imidazolium ring), 8.35–8.38 (2H, m, Ar-H), 7.95–7.97 (4H, m, Ar-H), 7.17–7.19 (2H, m, imidazolium ring), 7.01–7.04 (2H, d, Ar-H), 4.32 (2H, t, *J*=15.0 Hz, N-CH₂), 4.12 (3H, s, N-CH₃), 4.06 (2H, t, *J*=13.5 Hz, OCH₂), 1.33–1.90 (16H, m, CH₂). ¹³C NMR (100 MHz, CDCl₃): 26.33, 26.63, 29.34, 29.49, 29.65, 29.75, 30.70, 37.14, 50.55, 68.88, 115.32, 122.27, 123.48, 123.98, 125.07, 126.01, 138.00,

147.14, 148.53, 156.45, 163.33. Elemental analysis: calculated for $C_{26}H_{34}N_5O_3Br$, C 57.35, H 6.29, N 12.86%; found C 57.64, H 6.49, N 12.57%.

1-{\{4-(4-nitrophenylazo)phenoxy\}}propyl-3-methyl-1H-imidazol-3-ium tetrafluoroborate (D_3) and other D_n compounds.

C_3 (24 mmol) was dissolved in 30 ml of H_2O , and then a solution of 6 mmol of Na_2BF_4 in 20 ml of H_2O was added dropwise. The mixture was stirred for 1 h at $80^\circ C$ under nitrogen; the precipitate that came out from the solution in the procedure was filtered and washed with water several times. The crude product was recrystallised from ethanol and dried in vacuum for 24 h to give pure D_3 as a brown-red solid. Yield 85%, m.p. $169^\circ C$. 1H NMR (400 MHz, acetone- d_6): 9.27 (1H, s, imidazolium ring), 8.55–8.57 (2H, m, Ar–H), 8.11–8.21 (4H, m, Ar–H), 7.99 (1H, s, imidazolium ring), 7.89 (1H, s, imidazolium ring), 7.25–7.27 (2H, m, Ar–H), 4.80 (2H, t, $J=10.5$ Hz, N– CH_2), 4.44 (2H, t, $J=9.0$ Hz, OCH_2), 4.20 (3H, s, N– CH_3), 2.64–2.70 (2H, m, CH_2). ^{13}C NMR (100 MHz, acetone- d_6): 29.20, 36.08, 47.33, 65.46, 115.43, 123.12, 123.42, 125.09, 125.73, 137.31, 147.34, 149.00, 156.24, 162.65. Elemental analysis: calculated for $C_{19}H_{20}N_5O_3BF_4$, C 50.35, H 4.45%, N 15.45%; found C 50.14, H 4.31, N 15.72%.

Compound D_6 , synthesised using the procedure for D_3 , was obtained as a brown-red solid. Yield 81%, m.p. $115^\circ C$. 1H NMR (400 MHz, $CDCl_3$): 9.08 (1H, s, imidazolium ring), 8.35–8.37 (2H, m, Ar–H), 7.94–7.99 (4H, m, Ar–H), 7.20 (2H, s, imidazolium ring), 7.00–7.03 (2H, m, Ar–H), 4.24 (2H, t, $J=14.7$ Hz, N– CH_2), 4.07 (2H, t, $J=12.3$ Hz, OCH_2), 3.99 (3H, s, N– CH_3), 1.46–2.01 (8H, m, CH_2). ^{13}C NMR (100 MHz, acetone- d_6): 24.26, 25.64, 29.45, 29.89, 36.24, 47.13, 65.32, 115.32, 123.23, 123.52, 124.31, 125.12, 125.53, 137.44, 147.14, 149.08, 156.14, 162.45. Elemental analysis: calculated for $C_{26}H_{34}N_5O_3BF_4$, C 53.35, H 5.29, N 14.14%; found C 53.67, H 5.52, N 14.53%.

Compound D_{10} was synthesised following a procedure similar to that described above; the target material was obtained as a brown-red solid. Yield 84%, m.p. $104^\circ C$. 1H NMR (400 MHz, $CDCl_3$): 9.04 (1H, s, imidazolium ring), 8.35–8.38 (2H, m, Ar–H), 7.94–7.99 (4H, m, Ar–H), 7.20 (2H, m, imidazolium ring), 7.01–7.04 (2H, m, Ar–H), 4.20 (2H, t, $J=15.3$ Hz, N– CH_2), 4.06 (2H, t, $J=12.9$ Hz, OCH_2), 3.99 (3H, s, N– CH_3), 1.33–1.90 (16H, m, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): 26.33, 26.58, 29.27, 29.50, 29.63, 29.74, 30.41, 36.79, 50.61, 68.89, 115.33, 122.21, 123.48, 123.86, 125.10, 126.02, 137.19, 147.19, 148.61, 156.47, 163.34. Elemental analysis: calculated for $C_{26}H_{34}N_5O_3Br$, C 56.64, H 6.22, N 12.70%; found C 57.02, H 6.46, N 12.34%.

Characterisations

1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained using a Varian Unity 400 spectrometer (400 MHz) and tetramethylsilane (TMS) as an internal reference. Elemental analyses were carried out on a Thermo Quest Italia S.P.A. FlashEA1112 apparatus. UV–visible spectra were measured with a Cary 500 UV–visible–NIR (Varian Co, USA) spectrophotometer. Photoluminescence (PL) spectra were measured with a Shimadzu RF-5301 PC spectrofluorometer. Morphologies as well as changes in birefringence were observed by polarising optical microscopy (POM) using a Leica DMLP microscope equipped with a Leitz 350 heating stage. Differential scanning calorimetry (DSC) was carried out on Perkin-Elmer DSC-7 with a scan rate on heating and cooling of $10^\circ C\ min^{-1}$. Wide-angle X-ray diffraction (WAXD) experiments were performed on a Philips X-ray generator (PW 1700), and a flat plate camera using nickel-filtered Cu K_α radiation.

3. Results and discussion

Synthesis

As shown in Scheme 1, the intermediates **A** and **B_n** were first prepared according to literature methods (19) and their structures confirmed by NMR. **C_n** were prepared by the addition reaction of 1-methylimidazole and **B_n**. The imidazolium derivatives **D_n** with BF_4 anion were prepared by the exchange reaction of Br anion to BF_4 anion in the imidazolium derivatives **C_n**.

Liquid crystalline properties

The phase behaviour of **C_n** and **D_n** compounds was examined by DSC, POM and WAXD. Figure 1 shows POM photomicrographs of compounds **C_n** and **D_n** ($n=6, 10$) in their mesophases. A focal-conic fan-shaped texture was observed for the higher homologues of both **C_n** and **D_n** ($n=6, 10$) in their mesophases, indicating the formation of a smectic phase. In contrast, due to their high crystalline temperature, **C₃** and **D₃** were non-mesomorphic. Moreover, a pseudo-homeotropic area coexisted with focal-conic fan-shaped texture in both heating and cooling runs. Under shearing, only pseudo-homeotropic texture appeared, indicating smectic A (SmA) behaviour. A SmA phase was assigned to all four compounds shown in Figure 1.

Generally, ionic liquids based on imidazolium salts are difficult to crystallise from the liquid state or a mesophase (20). A supercooled state with partial

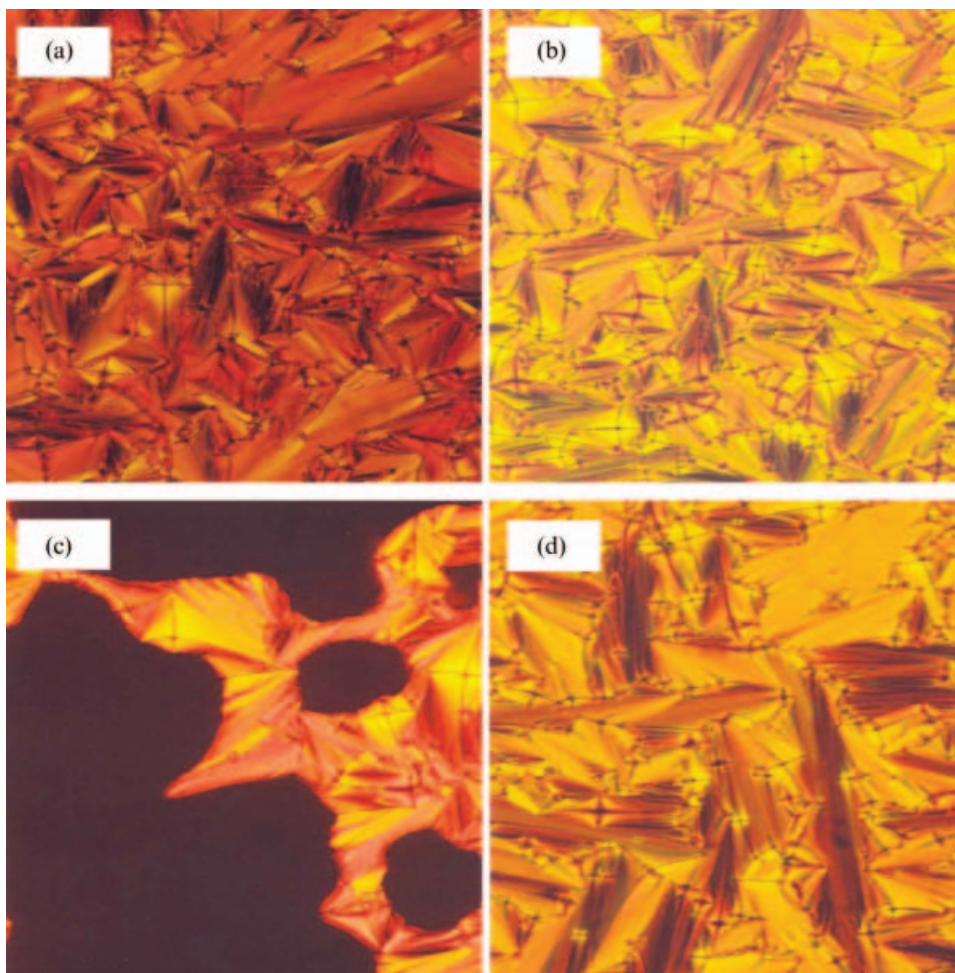


Figure 1. Photomicrographs ($\times 200$) of C_n and D_n . The fan texture of the mesophases of (a) C_6 at 130°C on cooling; (b) D_6 at 110°C on cooling; (c) C_{10} at 154°C on heating; (d) D_{10} at 131°C on cooling.

crystallisation, which is characteristic of polymer materials, can be often observed in the case of the low molar mass imidazolium salt derivatives (5).

The crystallisation could not be easily observed for both D_6 and D_{10} on cooling run at a rate of $10^\circ\text{C min}^{-1}$, and the focal-conic fan texture was preserved down to room temperature. A similar observation was also reported for ILCs with imidazolium moieties (21), which mainly originated from insertion of imidazolium ion moieties.

The results for D_n were further confirmed by DSC and XRD measurements. Figure 2 shows the DSC curves of D_n compounds. In the DSC measurements of D_{10} , an exothermic peak appeared at 161°C when the compound was cooled from the molten state, confirming a phase transition from the isotropic phase to a smectic phase. Another exothermic peak at 51°C is assigned to crystallisation. An exothermic peak at 53°C can be observed in the second heating run, although there is no exothermic peak on the first heating run, which is due to the recrystallisation of

the sample. Other two peaks at 104 and 165°C on the second heating run were attributed to crystal–SmA and SmA–isotropic transitions, respectively.

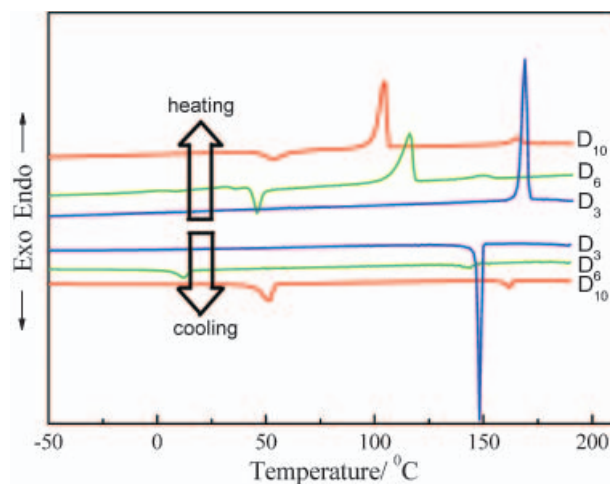
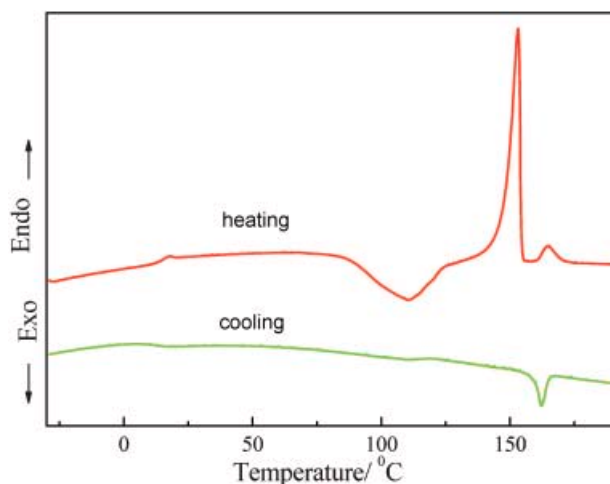


Figure 2. DSC curves of D_n .

Figure 3. DSC curves of C_6 .

Figures 1a and 1c show, respectively, the optical textures of C_6 at 130°C and C_{10} at 154°C. The liquid crystalline properties of C_n ($n=6, 10$) are quite similar to those of D_6 and D_{10} , and their mesomorphic structures can also be retained at room temperature. However, C_n have a stronger tendency to supercool to a solid state than the D_n compounds. Figure 3 shows the DSC curves of compound C_6 ; the exothermic peak of crystallisation for C_6 can not be observed in the DSC measurements during the cooling run. As shown in Figure 3, an exothermic peak at 110°C was also found in the second heating run. All the results indicate that imidazolium salts with fluorinated anions tend to have lower melting points than compounds with non-fluorinated anions, and the ionic interaction of imidazolium salts with BF_4 anions is much stronger than that with Br anions (22). All the compounds show only one transitional peak in their mesogenic phase, which also indicated that all four compounds exhibit SmA liquid crystalline behaviour. Combined with the results of DSC and POM, we can conclude that their mesomorphic structures are SmA. The thermal properties of the imidazolium salt derivatives are summarised in Table 1.

The liquid crystalline phases of B_n can not be observed without the insertion of imidazolium salt because the crystalline temperature is much higher than the mesophase temperature, whereas both C_n and D_n easily exhibit smectic phases over a wide temperature range by the covalent incorporation of imidazolium ion groups into B_n . Thus the ionic interaction between imidazolium salts can induce and stabilise the smectic phases (16). It can also be seen that the mesomorphic temperature ranges of C_{10} and D_{10} compounds ($n=10$) with a longer alkyl spacer are

Table 1. Phase transition temperatures (°C) and enthalpies (kJ mol^{-1} , in parentheses) of C_n and D_n determined by DSC (on second heating at $10^\circ\text{C min}^{-1}$).

Compound	Transition	T (ΔH) (heating)	T (ΔH) (cooling)
C_3	Cr-I	177 (97.0)	135 (64.4)
C_6	Cr-SmA	153 (61.9)	–
	SmA-I	165 (4.8)	162 (5.2)
C_{10}	Cr-SmA	110 (2.7)	–
	SmA-I	170 (8.6)	166 (8.6)
D_3	Cr-I	169 (54.6)	147 (51.6)
D_6	Cr-SmA	115 (56.1)	12 (10.0)
	SmA-I	149 (5.2)	143 (5.1)
D_{10}	Cr-SmA	104 (68.1)	51 (31.3)
	SmA-I	165 (8.3)	161 (5.4)

(Cr=crystal; SmA=smectic A phase; I=isotropic phase).

somewhat wider than those of C_6 and D_6 compounds. Moreover, no liquid crystalline phases can be observed in C_3 and D_3 with lower flexible group, suggesting that the length of the flexible chain also plays an important role for the stabilisation of the smectic phases for the novel imidazolium-based ILCs with a nitroazobenzene moiety.

The mesomorphic structure of the imidazolium salt derivatives was further examined by X-ray diffraction (XRD). Figure 4 shows the XRD pattern of D_{10} at various temperatures during the cooling scan. The XRD pattern of D_{10} at 140°C has two sharp diffraction peaks in the small-angle region, implying the formation of a layered structure. On the other hand, a broad diffraction peak in the wide-angle region indicates liquid-like arrangement of the molecules within the layers. The d -spacing based upon the sharp peak ($\sim 2.7^\circ$) is estimated to be about 32.70 Å, which is roughly 10 Å longer than the calculated molecular lengths. The d -spacing values and the observation of focal-conic fan texture indicated that the molecules of D_{10} would have a smectic A_d (SmA_d) arrangement in their liquid crystalline phases. The d -spacing (17.3 Å) corresponding to the sharp peak near 5.1° is associated with the length between the azobenzene group and the imidazolium ion group. However, at present details of the diffraction peak near 5.1° have not been clarified (21). Very weak crystallisation peaks could be found in the XRD patterns of D_{10} in the crystalline state (at 20°C and 60°C) during cooling, indicating that the compound did not crystallise easily, which agrees well with microscopic observations. X-ray diffraction patterns of D_6 were similar to those of D_{10} .

The layer spacing values (d) of C_{10} , C_6 , D_{10} and D_6 are collected in Table 2.

The structure of D_{10} in the mesophase was determined on the basis of X-ray diffraction measurements. A model for the arrangement of the

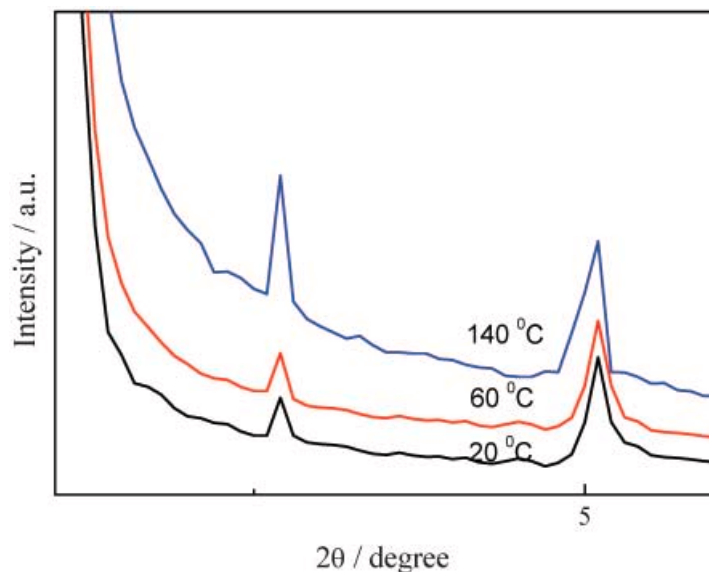


Figure 4. X-ray diffraction patterns of D_{10} at different temperatures upon cooling from the isotropic phase.

mesogenic groups of D_{10} in the smectic layers is shown in Scheme 2. In this model, D_{10} neighbouring mesogenic groups overlap each other and the azobenzene groups face each other in the lateral direction. The interaction of the azobenzene groups keeps the orientation order of liquid crystal molecules in the layer. The imidazolium salt parts became associated to form a smectic layer (SmA_d) and all the layers are further linked with the imidazolium ions through electrostatic interactions (23). We consider that the organisation of the imidazolium salt parts contributes to the formation of the smectic layer structure through electrostatic interactions.

UV-visible and PL spectra

The optical properties of B_n and C_n were also investigated. Typical UV-visible and PL spectra in $CHCl_3$ solution are shown in Figure 5 (the concentrations were ca. $10^{-4}M$). The compounds all exhibit an absorption maximum at ca. 378 nm and weak shoulders at ca. 448 nm, which are related to $\pi-\pi^*$ and $n-\pi^*$ transitions of the azobenzene trans-cis

configuration, respectively (as shown in Figure 5A and 5B). PL spectra of B_n and C_n excited at 378 nm in $CHCl_3$ solution are shown in Figures 5C and 5D. The spectra of B_3 , B_6 and B_{10} exhibit maxima at 437, 438 and 439 nm, respectively, and the PL spectra of C_n are similar to those of B_n . These results suggest that the imidazolium salts have no influence on the arrangement of the azobenzene groups in solution.

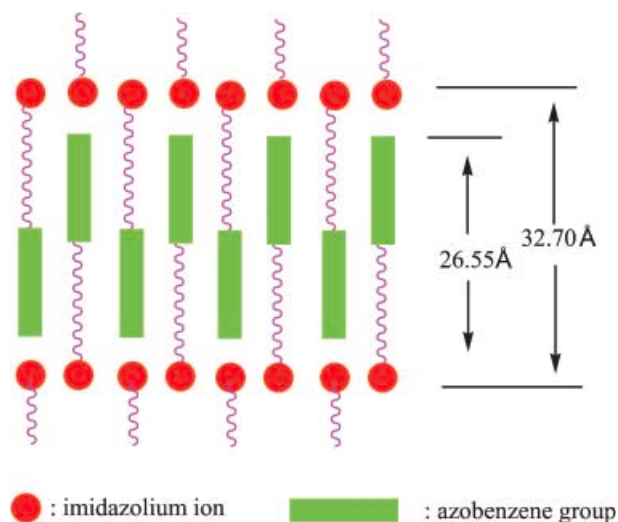
4. Conclusions

In summary, a series of monomers C_n and D_n have been synthesised and characterised by DSC, POM,

Table 2. XRD data for C_{10} , C_6 , D_{10} and D_6 .

Compound	Molecular length ^a (<i>l</i>)/Å	Temperature ^b /°C	Layer spacing (<i>d</i>)/Å	Phase
C_6	22.18	130	27.63	SmA
C_{10}	26.55	145	34.30	SmA
D_6	22.18	75	24.06, 12.45	SmA
D_{10}	26.55	140	32.70, 17.30	SmA

^aMolecular length calculated using ChemDraw; ^bMeasured temperatures.



Scheme 2. Schematic model of interdigitated structure for D_{10} in smectic A phase.

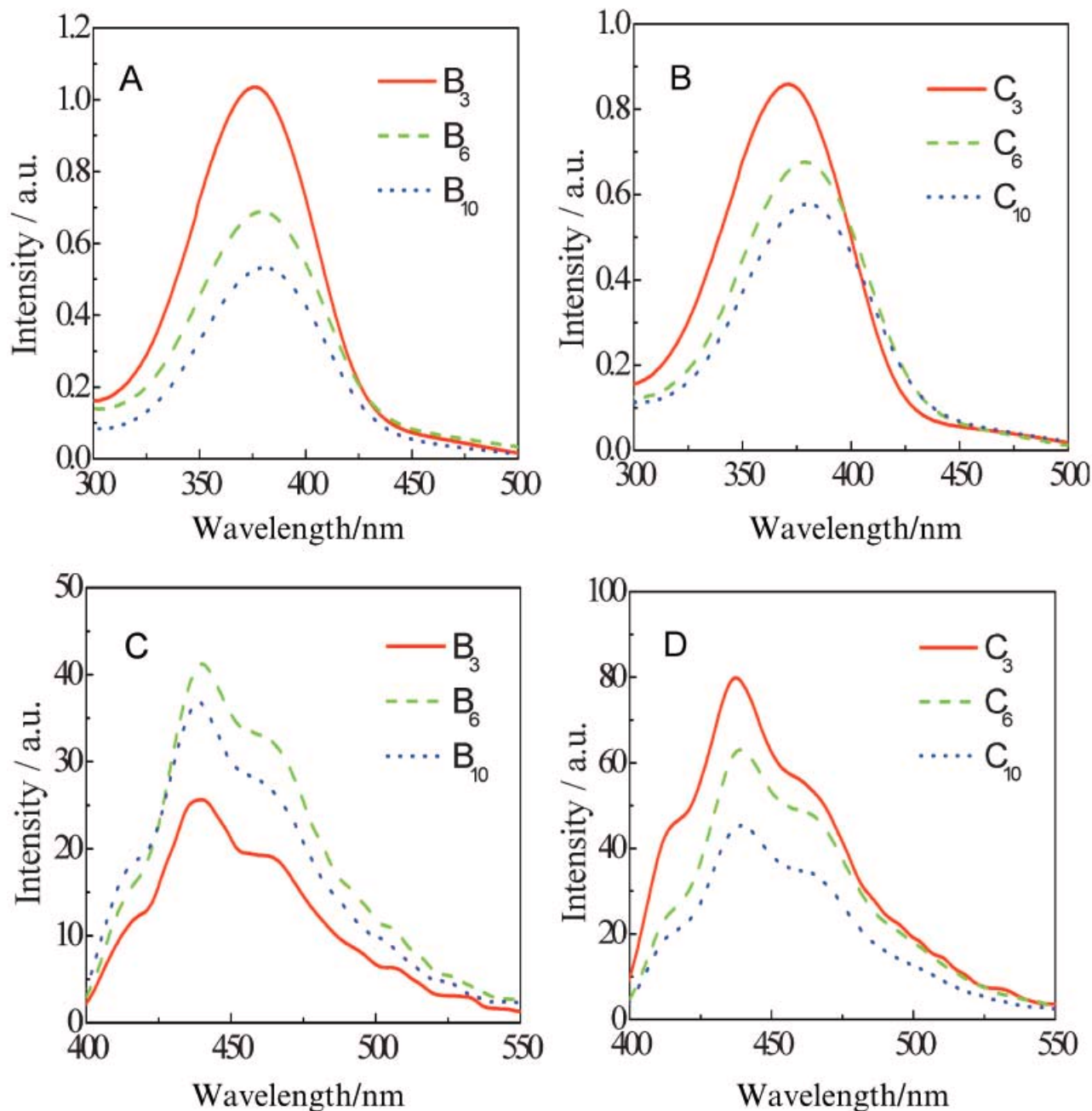


Figure 5. UV-visible and PL spectra of B_n and C_n in chloroform. UV-visible spectra of (A) B_n and (B) C_n compounds. Fluorescence spectra of (C) B_n and (D) C_n compounds.

WAXD, UV-visible and PL measurements. C_n and D_n ($n=6, 10$) exhibit SmA phase textures. Ionic interaction between imidazolium salts and the flexible chain plays an important role for the stabilisation of the smectic phases. They all are hard to crystallise from the mesophase during the cooling scan and their SmA mesophases can be maintained even down to room temperature. This finding may contribute to the development of novel anisotropic materials for high-density optical data storage (24, 25).

Acknowledgements

The authors are most grateful to the National Science Foundation of China (No.20475053 and No.20673109), Department of Science and Technology of Jilin Province (No.20050102) and Ministry of Science and Technology of China (No.2006BAKB05).

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