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Qiang Wei^a; Lin Shi^a; Xiaotao Yuan^a; Lipei Zhang^a; Hui Cao^a; Huai Yang^a

^a Department of Materials Physics and Chemistry, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, PR China

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Synthesis and phase behaviour of hydrogen-bonded liquid crystalline complexes of allyloxybenzoic acid compounds with 4,4'-bipyridine

QIANG WEI, LIN SHI, XIAOTAO YUAN, LIPEI ZHANG, HUI CAO and HUAI YANG*

Department of Materials Physics and Chemistry, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, PR China

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Three kinds of benzoic acid compounds were synthesized and characterized; the corresponding symmetric hydrogen-bonded liquid crystalline complexes based on these benzoic acid compounds and 4,4'-bipyridine (BPy) were then prepared. The existence of the hydrogen bonds was verified by Fourier transform infrared spectroscopy. The liquid crystalline properties of the complexes were demonstrated by polarizing microscopy and differential scanning calorimetry. 4-Allyloxy-2-fluorobenzoic acid and two fluorinated hydrogen-bonded complexes exhibited only nematic phases, whereas the non-fluorinated complex showed both smectic and nematic phases. The clearing points and mesophase thermal range of the complexes decreased with increasing number of lateral fluorine atoms on the rigid core.

1. Introduction

Intermolecular hydrogen bonding has attracted much attention because it offers the possibility of incorporating diversified molecular designs. Novel liquid crystalline properties can be obtained from supramolecular architecture through hydrogen bonding between various proton donors and acceptors. In 1989, Kato and Frechet [1] were the first to show that hydrogen bonding between carboxyl and pyridyl moieties was useful for the formation of supramolecular hydrogen-bonded liquid crystals. Since then, many hydrogen-bonded liquid crystals based on carboxyl and pyridyl groups have been synthesized and investigated [2–6]. In recent years, quinoline, isoquinoline, 4,4'-bipyridine and 2,2'-bipyridine have been developed as new proton acceptors in order to obtain novel structures with different mesomorphic properties [7–12]. In most of these reported hydrogen-bonded complexes, 4-alkylbenzoic acids and 4-alkoxybenzoic acids were widely used as the most feasible proton donors. However, to our knowledge, no study on hydrogen-bonded liquid crystals with carboxylic acids containing allyloxy groups or fluorine atoms as proton donors has been reported.

In this paper we report the synthesis and characterization of three kinds of benzoic acid compounds

containing allyloxy groups. The corresponding symmetric hydrogen-bonded liquid crystalline complexes based on these benzoic acid compounds and 4,4'-bipyridine were then prepared, and the existence of the hydrogen bonds was verified by FTIR. The liquid crystalline properties of the complexes were demonstrated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC).

2. Experimental

2.1. Characterization

IR spectra were recorded on a Nicolet 510P instrument and ^1H NMR and ^{13}C NMR spectra on a Bruker AV400 instrument in CDCl_3 . The mesomorphic properties were studied using an Olympus BX-51 polarizing microscope equipped with a Linkam Scientific LTS 350 heating/freezing stage. For DSC, a Perkin-Elmer DSC 6 instrument was used, with scanning rates of $10^\circ\text{C min}^{-1}$ when heating and 5°C min^{-1} when cooling; the samples were sealed in aluminium capsules in the air and the holding atmosphere was dry nitrogen.

2.2. Synthesis

All the starting materials were commercially available and used without further purification. The synthetic route to these compounds is shown figure 1; procedures are summarized below.

*Corresponding author. Email: yanghuai@mater.ustb.edu.cn

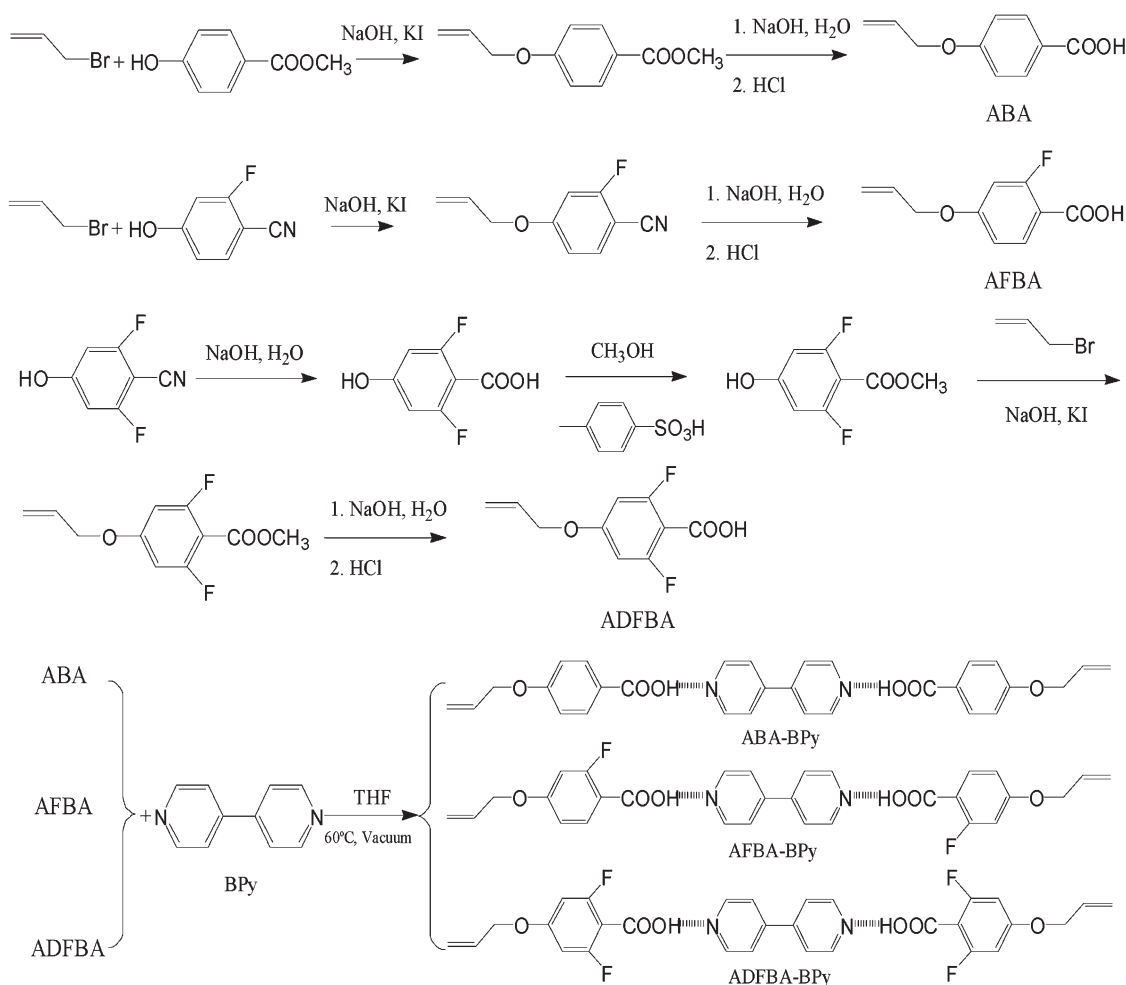


Figure 1. Synthetic route for the hydrogen-bonded liquid crystalline complexes.

2.2.1. 4-Allyloxybenzoic acid (ABA). A literature method [13] was used to prepare 4-allyloxybenzoic acid (ABA) in the yield of 85%. IR, ν/cm^{-1} : 2560–3088 (acidic $-\text{OH}$ stretching), 1680 ($\text{C}=\text{O}$ stretching), 1605, 1508 (aromatic $\text{C}=\text{C}$), 1251 ($\text{C}-\text{O}$ stretching). ^1H NMR (400 MHz, CDCl_3): δ 5.44 (d, H, $\text{HCH}=\text{CH}$), 5.33 (d, H, $\text{HCH}=\text{CH}$), 6.07 (m, H, $\text{CH}_2=\text{CH}-\text{CH}_2$), 4.62 (d, 2H, $\text{CH}-\text{CH}_2-\text{O}$), 6.96 (d, 2H, Ar-3, Ar-5), 8.06 (d, 2H, Ar-2, Ar-6). ^{13}C NMR (100 MHz, CDCl_3): 68.81, 114.35, 118.15, 121.59, 132.24, 132.34, 162.95, 171.30.

2.2.2. 4-Allyloxy-2-fluorobenzoic acid (AFBA). A mixture of 2-fluoro-4-hydroxybenzonitrile (13.7 g, 0.1 mol), NaOH (4.4 g, 0.11 mol), allyl bromide (0.11 mol) and butanone (100 ml) was heated to 60°C and stirred for 10 h. After cooling, the mixture was washed 2–3 times with 20 ml of 10% aqueous NaOH and the butanone removed by evaporation. The residues were mixed with 80 ml of 10% aqueous NaOH, heated under reflux for 24 h, then acidified with hydrochloric

acid after cooling. The precipitate was filtered off and recrystallized from 95% ethanol; yield 72%. IR, ν/cm^{-1} : 2556–3083 (acidic $-\text{OH}$ stretching), 1688 ($\text{C}=\text{O}$ stretching), 1630 ($\text{C}=\text{C}$ stretching), 1508 (aromatic $\text{C}=\text{C}$ stretching), 1242 ($\text{C}-\text{O}$ stretching), 1019 ($\text{C}-\text{F}$ stretching). ^1H NMR (400 MHz, CDCl_3): δ 5.44 (d, H, $\text{HCH}=\text{CH}$), 5.34 (d, H, $\text{HCH}=\text{CH}$), 6.04 (m, H, $\text{CH}_2=\text{CH}-\text{CH}_2$), 4.60 (d, 2H, $\text{CH}-\text{CH}_2-\text{O}$), 6.67 (d, H, Ar-3), 6.76 (d, H, Ar-5), 7.98 (m, H, Ar-6). ^{13}C NMR (100 MHz, CDCl_3): 68.92, 102.87 (d, $^2J_{\text{CF}}=25.6$ Hz), 109.52, 110.53, 118.20, 131.46, 133.70, 164.07, 165.10 (d, $^1J_{\text{CF}}=260.05$ Hz), 169.45.

2.2.3. 2,6-Difluoro-4-allyloxybenzoic acid (ADFBA). 2,6-difluoro-4-hydroxybenzonitrile (15.5 g, 0.1 mol) was added to 100 ml of 10% aqueous NaOH; the mixture was heated under reflux for 24 h, then acidified with hydrochloric acid. The precipitate was collected and recrystallized from alcohol. The resulting crystals, together with 4 g of toluene-4-sulfonic acid, 60 ml of

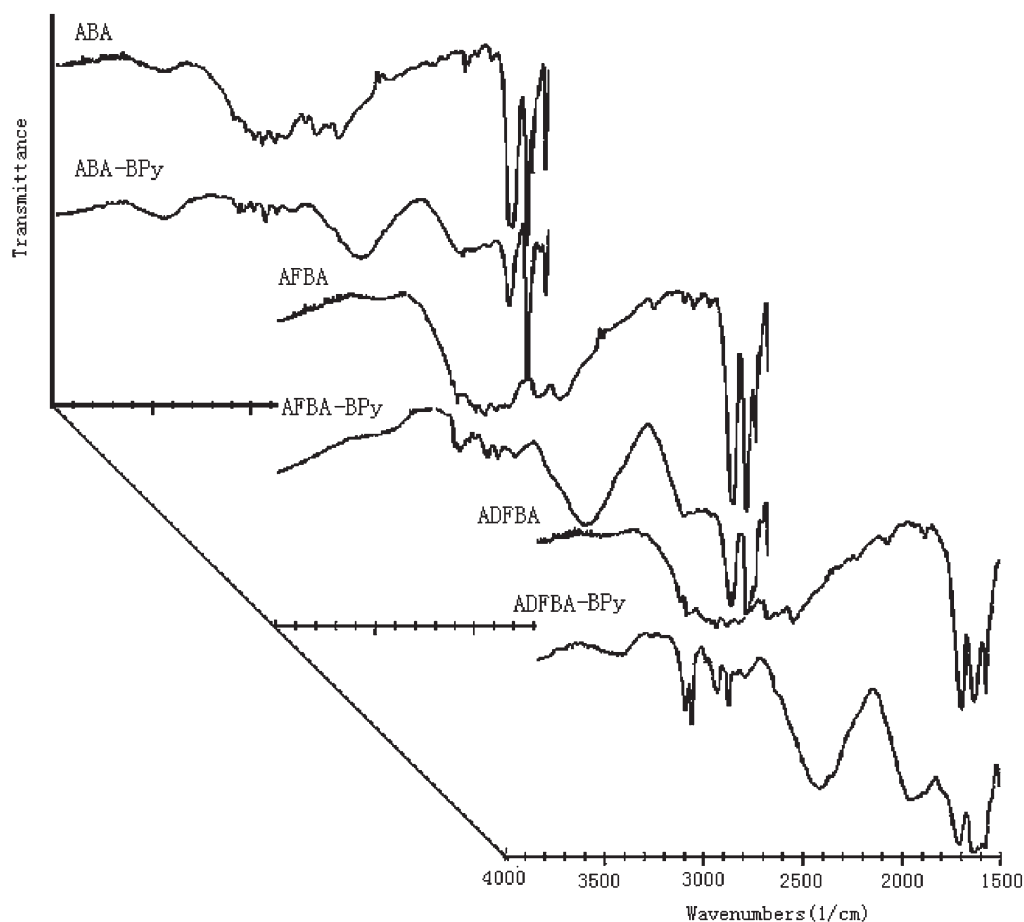


Figure 2. FTIR spectra of 4-allyloxybenzoic acid compounds and their corresponding hydrogen-bonded complexes.

alcohol and 20 ml of benzene, were added to a flask with a Dean–Stark trap and heated under reflux for 10 h. The reaction mixture was then poured into water and the precipitate collected and washed with water. The remaining powder was mixed with NaOH (4.4 g, 0.11 mol), allyl bromide (0.11 mol) and butanone (100 ml). The subsequent steps were the same as for the synthesis of ABA; yield 58%. IR, ν/cm^{-1} : 2552–3118 (acidic $-\text{OH}$ stretching), 1692 ($\text{C}=\text{O}$ stretching), 1632 ($\text{C}=\text{C}$ stretching), 1580 (aromatic $\text{C}=\text{C}$ stretching), 1247 ($\text{C}-\text{O}$ stretching), 1052 ($\text{C}-\text{F}$ stretching). ^1H NMR (400 MHz, CDCl_3): δ 5.44 (d, H, $\text{HCH}=\text{CH}$), 5.37 (d, H, $\text{HCH}=\text{CH}$), 6.03 (m, H, $\text{CH}_2=\text{CH}-\text{CH}_2$), 4.59 (d, 2H, $\text{CH}-\text{CH}_2-\text{O}$), 6.54 (d, H, Ar-3, Ar-5). ^{13}C NMR (100 MHz, CDCl_3): 69.62, 99.45 (d, $^2J_{\text{CF}}=18.5$ Hz), 101.73 (t, $^2J_{\text{CF}}=10.2$ Hz), 118.94, 131.43, 163.24, 164.17 (t, $^1J_{\text{CF}}=177.1$ Hz), 166.64.

2.2.4. Synthesis of the hydrogen bonded complexes. The benzoic acid compound (0.002 mol) and 4,4'-bipyridine (BPy) (0.001 mol) were dissolved in THF (5 ml) and heated to 60°C for several minutes. The THF was

removed under reduced pressure and the resulting solid complex dried under vacuum at 60°C for 12 h.

3. Results and discussion

3.1. FTIR spectra

The IR spectra of the benzoic acid compounds and their corresponding hydrogen-bonded complexes were recorded at room temperature in the solid state. The formation of hydrogen bonds in the complexes, as shown in figure 2, was confirmed by IR. The IR spectra of the benzoic acid compounds showed the characteristic stretching band (approximately from 2500 to 3200 cm^{-1}) resulting from dimerized carboxylic acid. In the IR spectra of ABA-BPy, AFBA-BPy and ADFBA-BPy, the broad band disappeared and characteristic bands (at 2445 and 1933, 2440 and 1939, 2413 and 1957 cm^{-1} , respectively) resulting from the hydrogen bond between carboxylic acid and pyridyl group appeared. The $\text{C}=\text{O}$ stretching bands of ABA, AFBA and ADFBA were centred at 1680, 1688 and 1692 cm^{-1} , respectively, but in their corresponding hydrogen-

Table 1. Phase transition temperatures ($^{\circ}\text{C}$) of benzoic acid compounds and 4,4'-bipyridine (Cr=crystal, N=nematic, I=isotropic).

Compound	Phase transition temperature
ABA	Cr $\xrightleftharpoons[164]{}$ I
AFBA	Cr $\xrightleftharpoons[115]{}$ N $\xrightleftharpoons[117]{}$ I
ADFBA	Cr $\xrightleftharpoons[126]{}$ I
BPy	Cr $\xrightleftharpoons[113]{}$ I

bonded complexes, they shifted to 1694, 1697 and 1708 cm^{-1} , respectively. These shifts also identified the presence of the hydrogen bonds [2].

3.2. Thermal and phase behaviour

By using DSC and POM, the phase transition temperatures of BPy, ABA, AFBA and ADFBA were recorded and are summarized in table 1. The POM observations showed an interesting phenomenon: although the introduction of a lateral fluorine atom widened the AFBA molecule, monotropic nematic properties could still be observed when cooling the melt of AFBA. In the case of ABA, a narrower molecule, no mesomorphic properties was observed when cooling its melt.

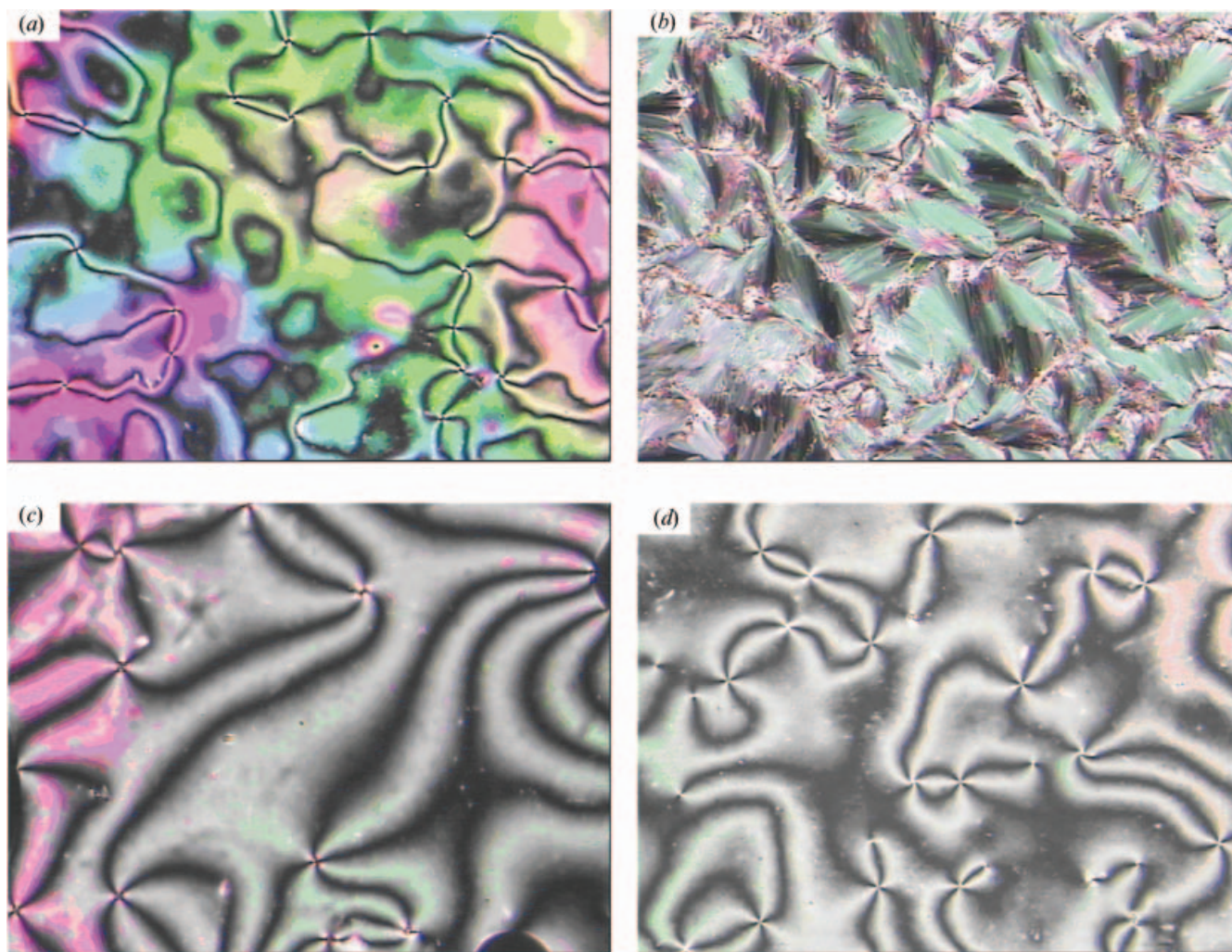


Figure 3. Optical textures of the hydrogen-bonded complexes on cooling. (a) Schlieren texture of ABA-BPy at 156°C ($\times 100$). (b) Fan-shaped texture of ABA-BPy at 123°C ($\times 200$). (c) Schlieren texture of AFBA-BPy at 119°C ($\times 100$). (d) Schlieren texture of ADFBA-BPy at 119°C ($\times 100$).

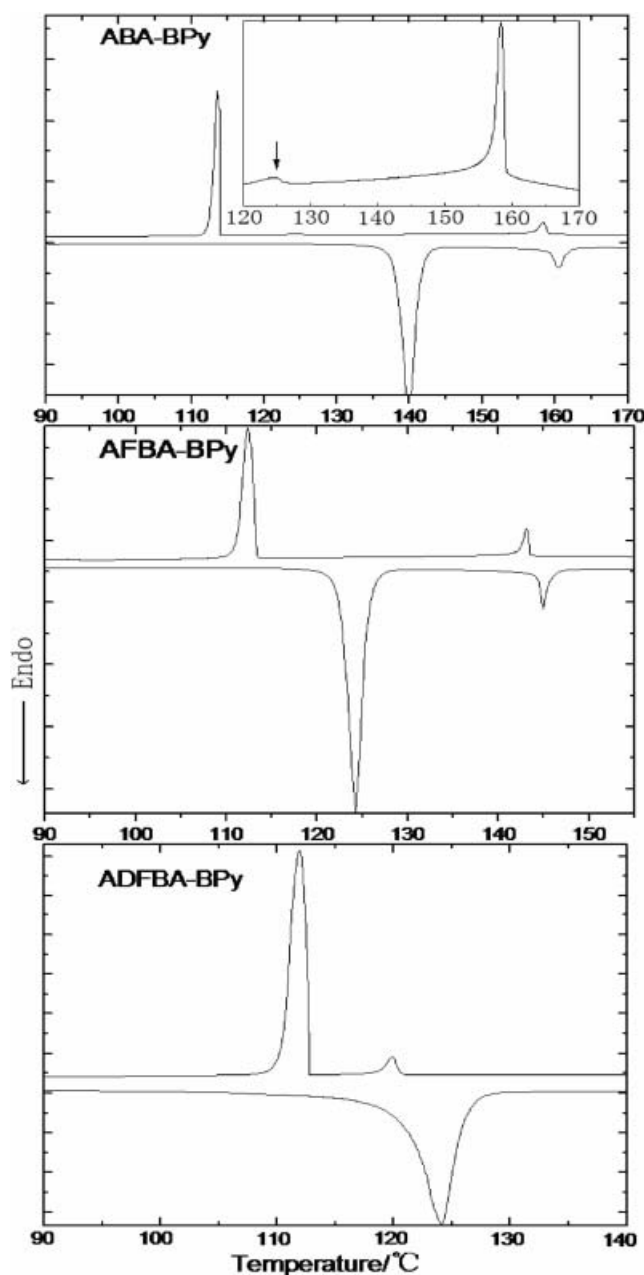


Figure 4. DSC spectra of the hydrogen-bonded complexes.

On heating, POM observation indicated that ABA-BPy and AFBA-BPy showed only nematic (N) properties, whereas ADFBA-BPy showed no liquid crystalline properties. During cooling, all three complexes exhibited nematic phase formation, beginning as small droplets, followed by the formation of a schlieren texture (see figure 3). In the case of the ABA-BPy complex, in addition to the isotropic–nematic (I–N) transition, nematic–smectic (N–S) transition indicated by the formation of fan-shaped texture (figure 3 b) was also observed on further cooling. In AFBA-BPy and

ADFBA-BPy, only the I–N and N–Cr transitions were observed.

The DSC spectra scanned during heating and cooling cycles of ABA-BPy, AFBA-BPy and ADFBA-BPy are shown in figure 4; the results agree well with POM observations. Detailed phase transition data obtained from DSC curves are summarized in table 2.

It may be concluded from table 2 that complexes ABA-BPy and AFBA-BPy are enantiotropic liquid crystals and both act as single molecules; however, although the ADFBA-BPy complex also acts as a single molecule, it is obviously a monotropic liquid crystal. The clearing point temperature and thermal range of the mesophase of these complexes decreased with the quantity of fluorine atoms on the proton donor. This can be explained by the reduced length-to-breadth ratio of the complexes, which depends mainly on the width of the proton donors. With the data for bond lengths and bond angles of the C–C, C=C, C–H and C–F bonds, we can determine the width of the proton donors as 0.437 nm for ABA, 0.456 nm for AFBA and 0.475 nm for ADFBA. Clearly, the increased width of the proton donors decreased the length-to-breadth ratio of the complexes, which is usually considered a disadvantageous factor for the formation of a mesophase.

4. Conclusion

We have successfully synthesized and characterized three kinds of symmetric hydrogen-bonded liquid crystals based on benzoic acid compounds and 4,4'-bipyridine. It is found that 4-allyloxy-2-fluorobenzoic acid and two fluorinated hydrogen bonded liquid crystal complexes exhibit only nematic phases, whereas the non-fluorinated complex shows both smectic and nematic phases. The clearing points and thermal range of the mesophases of the complexes decreased with increasing number of lateral fluorine atoms on the rigid core.

Table 2. Phase transition temperatures (°C) of the hydrogen-bonded complexes (Cr=crystal, N=nematic, S=smectic, I=isotropic).

Complex	Phase transition temperature
ABA-BPy	Cr $\xrightleftharpoons[113]{140}$ N $\xrightleftharpoons[125]{160}$ S $\xrightleftharpoons[158]{160}$ I
AFBA-BPy	Cr $\xrightleftharpoons[113]{124}$ N $\xrightleftharpoons[143]{145}$ I
ADFBA-BPy	Cr $\xrightleftharpoons[113]{124}$ N $\xrightleftharpoons[119]{124}$ I

Acknowledgements

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