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Calorimetric study on two biphenyl liquid crystals

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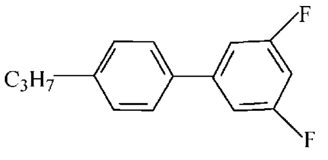
Abstract

The molar heat capacities of the two biphenyl liquid crystals, 3BmFF and 3BmFFXF3, with a purity of 99.7 mol% have been precisely measured by a fully automated precision adiabatic calorimeter in the temperature range between $T = 80$ and 350 K. Nematic phase–liquid phase transitions were found between $T = 297$ K and 300 K with a peak temperature of $T_{\text{peak}} = (298.071 \pm 0.089)$ K for 3BmFF, and between $T = 316$ and 319 K with a peak temperature of $T_{\text{peak}} = (315.543 \pm 0.043)$ K for 3BmFFXF3. The molar enthalpy ($\Delta_{\text{trs}}H_{\text{m}}$) and entropy ($\Delta_{\text{trs}}S_{\text{m}}$) corresponding to these phase transitions have been determined by means of the analysis of the heat capacity curves, which are (15.261 ± 0.023) kJ mol^{-1} and (51.202 ± 0.076) J K^{-1} mol^{-1} for 3BmFF, (31.624 ± 0.066) kJ mol^{-1} and (100.249 ± 0.212) J K^{-1} mol^{-1} for 3BmFFXF3, respectively. The real melting points (T_1) and the ideal melting points (T_0) with no impurities of the two compounds have been obtained from the fractional melting method to be (298.056 ± 0.018) K and (298.165 ± 0.038) K for 3BmFF, (315.585 ± 0.043) K and (315.661 ± 0.044) K for 3BmFFXF3, respectively. In addition, the transitions of these two biphenyl liquid crystals from nematic phase to liquid phase have further been investigated by differential scanning calorimeter (DSC) technique; the repeatability and reliability for these phase transitions were verified.

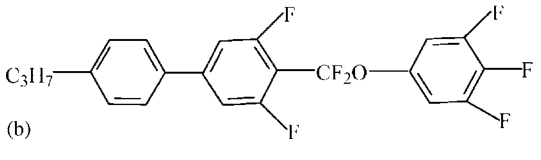
Keywords: Adiabatic calorimetry; Heat capacity; Liquid crystal; 3BmFF; 3BmFFXF3; DSC; Phase transition

1. Introduction

Recently many efforts were made due to liquid crystal's fascinated state of aggregation that exhibits a molecular order in a size range similar to that of a crystal but acts more or less as a viscous liquid. Much attention was paid to it due to its ubiquitous application in active matrix mode-liquid crystal display devices (AM-LCD) as it enable to display with extreme precision. The structures of the two liquid crystal compounds applied to display constituent are as follows:



(a)



(b)

in which, (a) is named as: 3,5-difluoro-4′-propyl-1,1′-biphenyl, its CA registry: 137528-87-1, its abbreviation: 3BmFF, its molecular formula: $C_{15}H_{14}F_2$; (b) is named as: 4-[difluoro (3,4,5-trifluorophenoxy)-methyl]-3,5-difluoro-4′-propyl-1,1′-biphenyl, its CA registry: 303186-20-1, its abbreviation: 3BmFFXF3, its molecular formula: $C_{22}H_{15}F_7O$. The two liquid-crystal compounds aforementioned exhibit high voltage retention and low threshold voltage, very small dependency upon the temperature, a large refractive-index anisotropy and have excellent compatibility with other liquid crystal materials at low temperature. Therefore, the two compounds are shown as good candidates for liquid crystal display element.

Comprehensive understanding of materials will be achieved only when both their microscopic structural aspects and macroscopic energetic and/or entropic aspects are revealed. Although thermodynamic quantities principally reflect macroscopic aspects of materials, they are closely related statistically to the microscopic energy schemes of all kinds of molecular degrees of freedom. One can, therefore, gain detailed knowledge about the microscopic level on the basis of precise calorimetry. Among various thermodynamic measurements, heat capacity calorimetry is extremely useful tool for investigating thermal properties.

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In this paper, two nematic-liquid-crystals were investigated using adiabatic calorimetry and thermal analysis. Along with observations with the polarizing microscope, calorimetric measurements are best suitable for the recognition of phase transitions and the determination of their temperature. Elucidation of their structures is basically important from the viewpoint of condensed states of matter. Thermodynamic studies provide us with knowledge about the molecular motions closely related to a given structure. In order to elucidate the difference between these two mesomorphic states from a thermodynamic viewpoint, we report here the first precise heat capacity measurements for two biphenyl liquid crystals based on adiabatic calorimetry.

2. Experimental

2.1. Samples

3BmFF and 3BmFFXF3 compounds were synthesized according to the method reported in the literature [1] and purified by repeated recrystallization from acetic acid. The structures of two liquid crystals compounds were confirmed by ^{1}H NMR and element analysis. The purities of the compounds were determined to be 99.7 mol% on the basis of the fractional melting method. The optical textures of the mesophases of two samples were observed using a polarizing microscope (XST-2 Shanghai automation instrument Co., China) equipped with a heating stage.

2.2. Adiabatic calorimetry

Heat capacities were measured with an adiabatic calorimeter [2] in the 78–350 K range by using a sample cell having inner volume of 6 cm^3. The air in the sample cell was pumped out and a small amount of helium gas was sealed in the cell to aid heat transfer. The temperature and energy data for heat capacity measurements were automatically collected by use of the Data Acquisition/Switch unit (Model: 34970 A, Agilent, USA) and processed online by a computer. The sample weight of 3BmFF and 3BmFFXF3 used for the heat capacity measurements are 1.9497 and 1.8573 g, which are equivalent to 8.3775 and 4.3359 mmol, based on their corresponding molar mass of 232.73 g mol^{-1} and 428.35 g mol^{-1}, respectively. Prior to the heat capacity measurements of the samples, the reliability of the calorimetric apparatus was verified by heat capacity measurements of the reference standard material-alumina (SRM720). The deviations of our calibration results from the recommended values reported by Archer [3] are within ± 0.20% in the temperature range of 80–400 K.

2.3. DSC measurement

To establish the temperature dependence of the heat capacity above the transition to the isotropic liquid, a commercial differential scanning calorimeter (DSC141 Setaram France) was employed to determine the thermal properties of the samples. The sample masses are 5.8 mg for 3BmFF and 4.0 mg for 3BmFFXF3. The flow rate of N_2 with a high purity was 30 mL min^{-1}, the scanning rate 5 K min^{-1}.

3. Results and discussion

3.1. Heat capacity

The low-temperature experimental molar heat capacities of 3BmFF and 3BmFFXF3 are shown in Fig. 1 and tabulated in Table 1 and Table 2, respectively. The enduring time needed for thermal equilibration was 15 min outside the transition region. These are typical for this adiabatic calorimeter independently of samples. In the transition region, however, the thermal relaxation time was significantly and abruptly prolonged when the transition temperature was approached. This truncation obviously has an influence on the resulting data for apparent heat capacity, but no effect on the integrated enthalpy change because of the first law of the thermodynamics [4]. From Fig. 1, it can be seen that heat capacities of these two biphenyl liquid crystals increase with increasing temperature in a smooth and continuous manner in the temperature range prior to phase transitions, which implies that the two compounds are stable in the temperature range interested. At the same time, two nematic phases–liquid phase transition were observed in the range of temperature studied. The experimental molar heat capacities have been fitted to the following polynomials in reduced temperature (X) by the least square fitting.

For the solid phase of 3BmFF over the temperature range of $T = 78$–289 K:

$$C_{\mathrm{p,m}}(\mathrm{J\,K^{-1}\,mol^{-1}}) = 183.50 + 105.50X + (-5.4411\mathrm{E}-14)X^2 + (4.9741\mathrm{E}-14)X^3$$

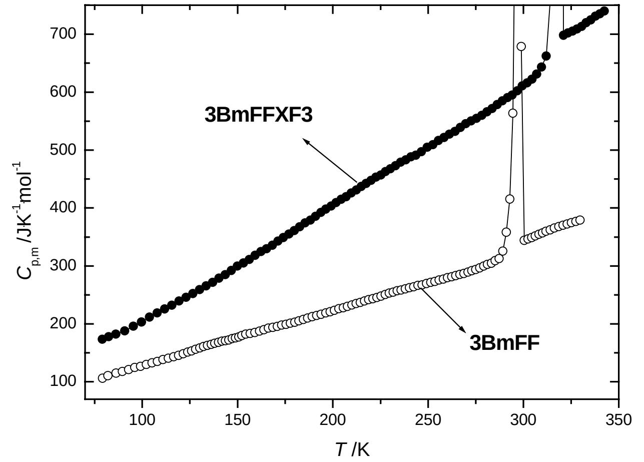

Fig. 1. The plot of experimental molar heat capacities ($C_{\mathrm{p,m}}$) of 3,5-difluoro-4′-propyl-1,1′-biphenyl (3BmFF) and 4-[difluoro (3,4,5-trifluorophenoxy)-methyl]-3,5-difluoro-4′-propyl-1,1′-biphenyl (3BmFFXF3) for the whole temperature region studied against the temperature (T).

Table 1
The experimental molar heat capacities of 3,5-difluoro-4′-propyl-1,1′-biphenyl (3BmFF) (Relative molecular mass $M = 232.73\,\mathrm{g\,mol^{-1}}$)

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})	T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})
79.235	106.41	177.752	201.30	268.798	287.05
82.040	110.55	180.018	202.95	270.951	289.41
86.254	114.92	182.257	205.13	272.842	291.65
89.622	118.02	184.487	207.63	274.929	294.01
92.878	121.14	186.779	210.23	277.017	296.48
96.043	124.66	189.172	212.55	279.104	300.02
99.130	126.93	191.542	214.59	281.127	302.73
102.131	129.96	193.890	216.63	283.171	304.91
105.066	132.98	196.239	219.07	285.172	309.19
107.937	135.21	198.565	221.05	287.202	312.91
110.872	138.47	200.869	223.38	289.151	325.73
113.677	141.02	203.163	226.21	291.038	358.08
116.547	143.24	205.436	227.96	292.818	415.32
119.101	145.62	207.719	230.42	294.453	563.64
121.505	148.57	209.959	232.63	295.768	989.56
123.853	151.52	212.201	235.03	296.651	1987.1
125.941	153.51	214.416	237.02	297.166	3712.2
128.028	156.05	216.634	239.48	297.647	8314.4
130.181	158.68	218.822	241.76	297.778	10368
132.199	160.89	221.005	243.65	297.872	12236
134.198	163.08	223.136	245.71	297.945	13068
136.182	164.48	225.288	247.85	298.011	13750
138.074	166.55	227.441	250.88	298.101	10132
139.965	168.14	229.528	253.26	298.837	678.79
141.857	170.21	231.616	254.86	300.479	343.98
143.618	171.25	233.703	257.24	302.392	346.39
145.445	172.44	235.856	258.59	304.306	349.10
147.206	174.51	238.009	260.50	306.197	351.64
148.902	175.78	240.226	262.49	308.089	354.65
150.663	177.61	242.379	264.16	309.981	357.11
152.294	179.92	244.597	266.31	311.851	359.95
154.301	182.22	246.877	267.12	314.047	362.30
156.665	183.74	249.119	269.58	316.218	365.71
159.101	185.29	251.350	271.67	318.553	367.91
161.492	187.42	253.577	273.15	320.774	370.22
163.864	190.12	255.773	275.74	322.924	372.36
166.222	192.66	257.969	277.45	325.135	374.66
168.563	194.10	260.144	279.69	327.479	376.90
170.884	195.68	262.339	281.39	329.719	379.09
173.189	197.99	264.493	283.40		
175.478	199.36	266.645	285.23		

where, $X = [T\,(\mathrm{K}) - 183.5]/105.5$, T is the absolute temperature. $R^2 = 0.9997$, where R^2 is the correlation coefficient of the fitted polynomial. Relative deviations of the experimental heat capacity values from the fitting heat-capacity values are within ± 0.30% except for several points around upper and lower limits of temperature range in the solid phase

For the liquid phase of 3BmFF over the temperature range from $T = 300$ to 330 K:

$$C_{p,m}(\mathrm{J\,K^{-1}\,mol^{-1}}) = 315.01 + 15.011X + (4.4411E - 15)X^2$$

where, $X = [T\,(\mathrm{K}) - 315]/15$. $R^2 = 0.9999$. Relative deviations of the experimental heat capacity values from the fitting heat-capacity values are within ± 0.20%.

For the solid phase of 3BmFFXF3 over the temperature range of $T = 78$–307 K:

$$C_{p,m}(\mathrm{J\,K^{-1}\,mol^{-1}}) = 389.87 + 237.46X - 21.074X^2 - 8.4311X^3 + 33.511X^4$$

where, $X = [T\,(\mathrm{K}) - 192.5]/114.5$. $R^2 = 0.9994$. Relative deviations of the experimental heat capacity values from the fitting heat-capacity values are within ± 0.30%.

For the liquid phase of 3BmFFXF3 over the temperature range of $T = 317$–340 K:

$$C_{p,m}(\mathrm{J\,K^{-1}\,mol^{-1}}) = 709.81 + 25.255X + 2.9241X^2 - 3.2641X^3$$

where, $X = [T\,(\mathrm{K}) - 328.5]/11.5$. $R^2 = 0.9984$. Relative deviations of the experimental heat capacity values from the fitting heat-capacity values are within ± 0.30%.

Table 2
The experimental molar heat capacities of 4-[difluoro (3,4,5-trifluorophenoxy)-methyl]-3,5-difluoro-4′-propyl-1,1′-biphenyl (3BmFFXF3) (relative molecular mass $M = 428.349\ \mathrm{g\,mol^{-1}}$

T (K)	$C_{\mathrm{p,m}}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	T (K)	$C_{\mathrm{p,m}}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)	T (K)	$C_{\mathrm{p,m}}$ ($\mathrm{J\,K^{-1}\,mol^{-1}}$)
78.205	171.89	189.001	381.91	278.048	560.45
81.476	175.94	191.726	388.42	280.713	566.08
85.232	180.34	194.391	394.05	283.379	572.76
89.879	186.15	197.057	399.15	286.044	579.09
94.324	194.18	199.707	405.18	288.649	584.55
98.604	201.29	202.338	410.94	291.193	588.94
102.732	209.47	204.932	415.33	293.738	596.16
106.738	216.84	207.537	421.49	296.342	604.59
110.625	223.36	210.141	426.94	298.887	609.88
114.413	230.12	212.746	432.75	301.431	616.21
118.109	237.17	215.290	438.02	303.914	625.01
121.727	243.67	217.835	443.13	306.398	636.96
125.271	249.99	220.379	448.75	308.863	655.42
128.745	256.81	222.863	452.27	311.205	765.07
132.160	262.93	225.346	458.43	313.161	1420.2
135.513	269.09	227.890	463.01	314.394	3806.4
138.813	276.19	230.556	468.45	314.989	9182.7
142.067	282.29	233.221	474.26	315.259	16619
145.265	289.41	235.887	478.13	315.409	24017
148.419	296.93	238.491	483.23	315.510	28869
151.537	302.24	241.157	486.39	315.596	27813
154.607	308.01	244.064	492.38	316.124	3141.2
157.644	315.25	247.033	499.76	317.787	691.04
160.647	321.53	249.940	504.34	320.149	694.97
163.609	326.53	252.848	511.37	322.512	698.11
166.541	332.38	255.695	516.47	324.813	701.84
169.441	339.42	258.542	522.28	327.237	706.36
172.315	345.52	261.389	526.68	329.599	712.65
175.158	351.53	264.237	533.71	331.962	717.36
177.977	357.66	267.023	539.87	334.324	723.64
180.769	363.75	269.809	544.97	336.626	727.57
183.536	370.58	272.536	549.19	338.928	732.68
186.274	375.41	275.322	554.29		

3.2. The temperature, molar enthalpy and entropy of phase transitions

Pre-melting occurred owing to the presence of impurities in the sample. The measurements of the melting point and the molar entropy of fusion of the sample were done as follows: the temperatures for the start of the pre-melting and for complete melting were determined. Between these two temperatures the melting point was determined by successive approximation through stepwise heating. Then, by heating the sample from a temperature slightly lower than the initial melting temperature to a temperature slightly higher than the final melting temperature, the enthalpy of the sample was evaluated. The enthalpy used to heat the empty sample container and the sample itself (solid or liquid) was subtracted from the total amount of heat introduced to the sample and container during the whole fusion, the melting enthalpy of the sample can be obtained, as described in the literature [5,6].

Three series of heat-capacity experiments in the phase-transition regions of the two compounds were carried out so that the reversibility and repeatability of the fusion region were verified. Before each series of measurements, the sample was cooled from $T = 350\ \mathrm{K}$ to $T < 275\ \mathrm{K}$ using different cooling rates. In the first series, the sample was quenched into liquid nitrogen (about $20\ \mathrm{K\,min^{-1}}$); in the second series, the sample was naturally cooled (about $0.5\ \mathrm{K\,min^{-1}}$); and in the third series, the ice water was used as coolant (about $5\ \mathrm{K\,min^{-1}}$). The results of the three series of repeated experiments are plotted in the Figs. 2 and 3, and also given in Table 3. It can be seen from these results that the phase transition is reversible and repeatable, no supercooling and other thermal anomaly were caused by the different cooling rates.

The melting temperature T_{trs} of the sample was calculated from an equation according to the fractional melting method based on the heat capacity in the fusion region, as described in the literature [5,6]. The molar enthalpy of fusion $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$ was determined following the Eq. (1), as described in the literature [5,6]. The molar entropy of fusion, using the Eq. (2), was calculated.

$$\Delta H_{\mathrm{m}} = \frac{\left[Q - \int_{T_{\mathrm{i}}}^{T_{\mathrm{m}}} C_{\mathrm{P},1}\mathrm{d}T - n\int_{T_{\mathrm{m}}}^{T_{\mathrm{f}}} C_{\mathrm{P},2}\mathrm{d}T - \int_{T_{\mathrm{i}}}^{T_{\mathrm{f}}} \bar{H}_0\mathrm{d}T\right]}{n} \quad (1)$$

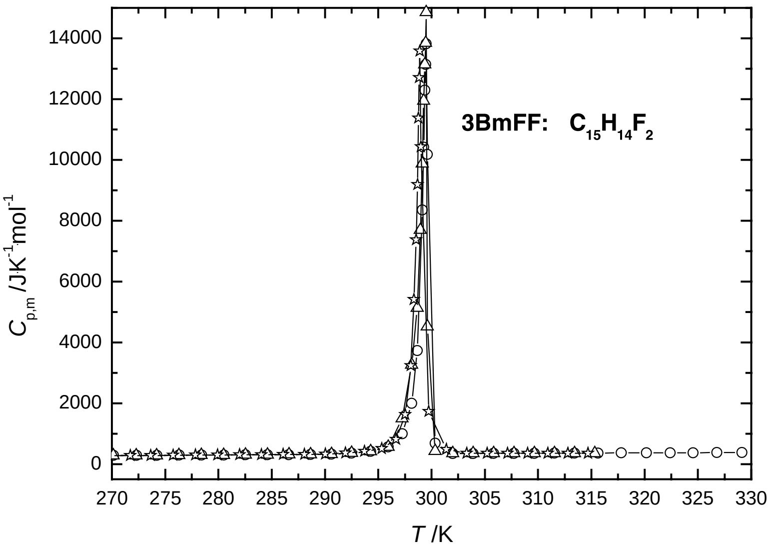

Fig. 2. The experimental molar heat capacities ($C_{p,m}$) of 3,5-difluoro -4′-propyl-1,1′-biphenyl (3BmFF) in the phase-transition region. ("○" = The first series of heat capacity measurements; "△" = the second series of heat capacity measurements; "☆" = the third series of heat capacity measurements).

$$\Delta S_m = \frac{\Delta H_m}{T_m} \tag{2}$$

where T_i is temperature slightly lower than the initial transition temperature, T_f is a temperature slightly higher than the final transition temperature, Q the total energy introduced into the sample cell from T_i to T_f, H_0 the heat capacity of the sample cell from T_i to T_f, $C_{p,1}$ the heat capacity of the sample in solid phase from T_i to T_m, $C_{p,2}$ the heat capacity of the sample in liquid phase from T_m to T_f and n is molar amount of the sample. When a transition is first order, the normal heat capacity may jump at the transition temperature. A jump in the heat capacity is clearly recognized between nematic phase and isotropic liquid.

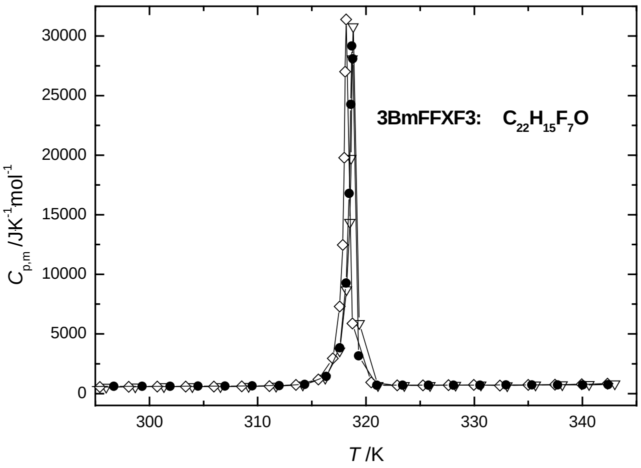

Fig. 3. The experimental molar heat capacities ($C_{p,m}$) of 4-[difluoro (3, 4, 5 - trifluorophenoxy)- methyl] -3,5- difluoro- 4′- propyl-1, 1′- biphenyl (3BmFFXF3) in the phase-transition region. ("●" = The first series of heat capacity measurements; "▽" = the second series of heat capacity measurements; "◇" = the third series of heat capacity measurements).

The results of T_{trs}, $\Delta_{trs}H_m$ and $\Delta_{trs}S_m$ of the sample obtained from the three series of repeated heat-capacity measurements are listed in Table 3.

The enthalpies and entropies of the phase transition for 3BmFFXF3 are almost two times as those of 3BmFF. This may be attributed to the different molecular weight of the two liquid crystal compounds in spite of having similar biphenyl group. So it can be concluded that molecular weight has primary impact on thermodynamic functions in the present research.

3.3. *Purity determination of the sample*

The purity of the sample is evaluated from a set of equilibrium melting temperature (T) and melting fractions (F) corresponding to these temperatures [5,6]. The experimental results, which include T_{trs} or T_1, T_0 and (1–N), obtained from the fractional melting method in the fusion region are also listed in the Table 3. The plot of the equilibrium melting temperature (T) versus the reciprocal of the melting fractions ($1/F$) is a straight line, as shown in the literatures [5,6]. Extrapolation of the straight line to $1/F = 0$ and $1/F = 1$ gives T_0 and T_1. Here, T_1 is the melting temperature (T_{trs}) of the impure compound obtained form fractional fusion experiment and T_0 is the melting temperature of a theoretically or absolutely pure sample. The melting point (T_1) obtained from the fractional melting agrees basically with the peak temperature (T_{peak}) obtained from the heat capacity measurements. The purity of the sample (1–N) can be calculated from the Van't Hoff equation, as described in the literatures [5,6], in agreement with the result of gas chromatograph analysis (more than 99.40% for the two samples).

Table 3
The results of melting of the two compounds obtained from three series of heat capacity measurements

Compounds	Thermodynamic quantities	Series 1, x_1	Series 2, x_2	Series 3, x_3	$(\bar{x} \pm \sigma_a)$[a]
3BmFF	Total energy Q (J)	208.643	208.728	208.599	208.657 ± 0.038
	T_{peak} (K)	298.011	298.199	297.905	298.071 ± 0.089
	$\Delta_{trs}H_m$(kJ mol^{-1})	15.215	15.279	15.286	15.261 ± 0.023
	$\Delta_{trs}S_m$ (J K^{-1} mol^{-1})	51.06	51.24	51.31	51.20 ± 0.08
	T_1 or T_{trs} (K)	298.055	298.089	298.026	298.056 ± 0.018
	T_0 (K)	298.176	298.224	298.095	298.165 ± 0.038
	(1−N) (%)	99.75	99.72	99.85	99.77 ± 0.04
3BmFFXF3	Total energy Q (J)	210.926	210.793	211.129	210.949 ± 0.098
	T_{peak} (K)	315.510	315.626	315.493	315.543 ± 0.043
	$\Delta_{trs}H_m$(kJ mol^{-1})	31.751	31.629	31.526	31.624 ± 0.066
	$\Delta_{trs}S_m$ (J K^{-1} mol^{-1})	100.63	100.21	99.90	100.25 ± 0.21
	T_1 or T_{trs} (K)	315.561	315.669	315.525	315.585 ± 0.043
	T_0 (K)	315.642	315.745	315.596	315.661 ± 0.044
	(1−N) (%)	99.69	99.71	99.73	99.71 ± 0.01

[a] $\sigma_a = \sqrt{\sum_{i=1}^{3}(x_i - \bar{x})^2/n(n-1)}$, in which n is the experimental number; x_i, a single value in a set of dissolution measurements; $\bar{x}$, the mean value of a set of measurement results.

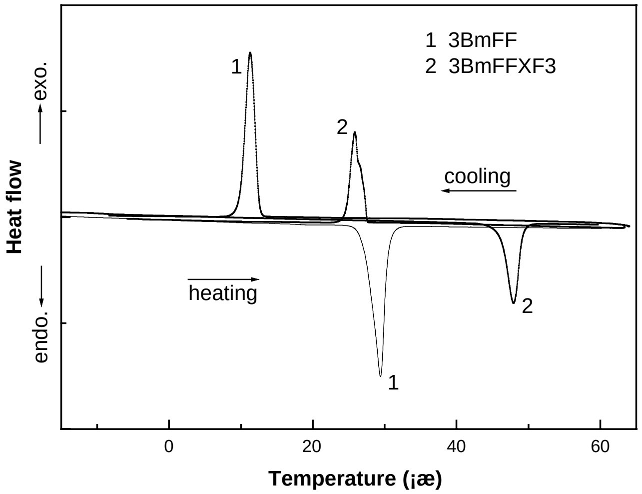

Fig. 4. Heating and cooling DSC runs at a scan rate of 5 K min^{-1} for 3BmFF and 3BmFFXF3.

3.4. DSC analysis

Fig. 4 illustrates the heating and cooling DSC runs recorded at a scan rate of 5 K min^{-1}. All the compounds exhibited a nematic phase–liquid phase transition during programmed scanning and gave completely reproducible thermograms, implying no decomposition. No other thermal anomaly was found. Large supercooling and large superheating amounting to 10 K were observed in the DSC experiments for the phase transitions from/to the nematic. Supercooling and superheating phenomena are rarely observed in ordinary liquid crystalline substances except for the transition from mesophase to crystal. This may be attributed to the molecular structure have no enough time to relax. The results gained from DSC are in agreement with those obtained by adiabatic calorimetry.

Acknowledgements

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