Supplementary Information

Laterally substituted ionic liquid crystals and the resulting rheology behavior

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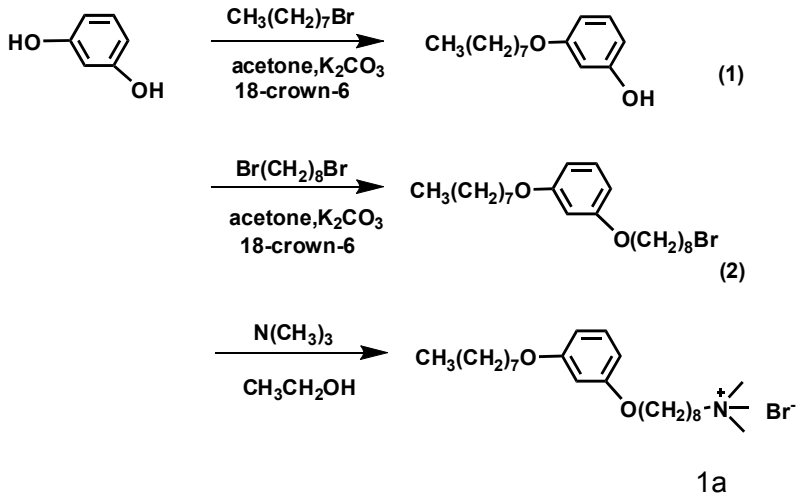
Experimental Section

1. Synthesis of quaternary ammoniums 1a.



Scheme S1. Synthetic procedures of 1a.

The followings are detailed synthetic processes:

Synthesis of 3-(octyloxy)phenol (compound 1)

Benzene-1,3-diol (5.00 g, 0.0454 mol), 1-bromooctane (7.30 g, 0.0378 mol), anhydrous K_2CO_3 (7.85 g, 0.0568 mol) and several small grains of 18-crown-6 were dissolved in acetone (100 mL), the mixture was stirred under refluxing and a nitrogen atmosphere for 24 hours. The product was filtered to remove K_2CO_3, and then acidified by diluted hydrochloric acid to pH = 2. After rotary evaporation, the residue was treated with water and extracted with chloroform. The organic layer was collected and dried over anhydrous $MgSO_4$, and then concentrated. The product was purified by column chromatography on silica gel with a mixture of dichloromethane/petroleum ether (v/v, 1/8) as eluent. The pure compound was obtained as a light yellow liquid. Yield: 37.6% (3.16 g).

Synthesis of 1-(8-bromooctyloxy)-3-(octyloxy)benzene (compound 2)

Compound 1 (3.16 g, 0.0142 mol), 1, 8-dibromohexane (4.17 g, 0.0171 mol) and anhydrous K_2CO_3 (2.94 g, 0.0213 mol) and several small grains of 18-crown-6 were dissolved in acetone (100 mL), the mixture was stirred under refluxing and a nitrogen atmosphere for 24 hours. The product was filtered to remove K_2CO_3, and then acidified by diluted hydrochloric acid to pH = 2. After rotary evaporation, the residue was treated with water and extracted with chloroform. The organic layer was dried over anhydrous $MgSO_4$, and then concentrated. The product was purified by column chromatography on silica gel with a mixture of dichloromethane/petroleum ether (v/v, 1/20) as eluent. The pure compound was obtained as a colorless liquid. Yield: 46.2% (2.7 g).

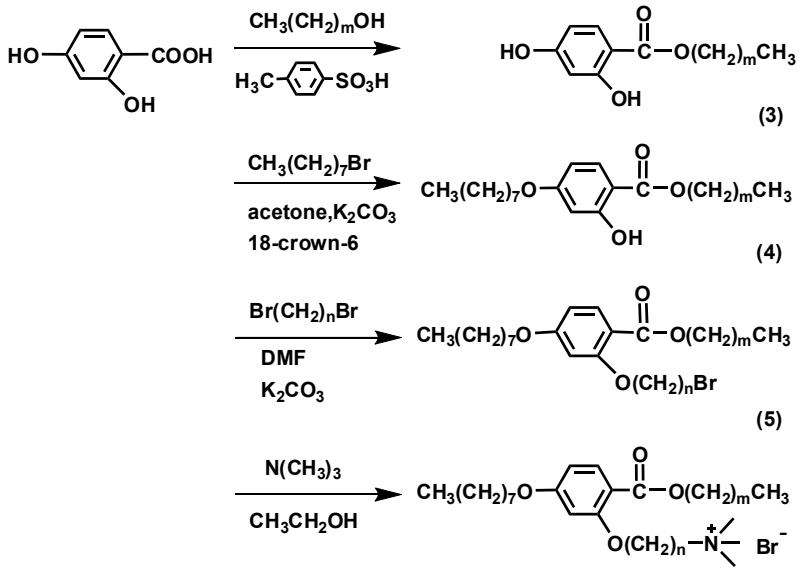
Synthesis of N,N,N- trimethyl-8-[3-(octyloxy)phenoxy]octan-1-aminium bromide (1a)

Compound 2 (2.70 g, 0.00655 mol) and trimethylamine (30% aqueous solution, 12.9 g, 0.0655 mol) were dissolved in ethanol (50 mL), the mixture was stirred under refluxing for 24 hours. After removal of water and ethanol by rotary evaporation, the product was vacuumized to remove the excess trimethylamine. The residue was purified by column chromatography on silica gel with a mixture of dichloromethane/methanol (v/v, 8:1) as eluent. The crude product was recrystallized from chloroform/ethyl ether (v/v, 1/20); the pure product was isolated as a white

solid. Yield: 65.2% (2.01 g).

For 1a: ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.139 (t, J = 8.0 Hz, 1 H), 6.477–6.433 (m, 3 H), 3.918 (t, J = 6.5 Hz, 4 H), 3.576 (t, J = 8.5 Hz, 2 H), 3.456 (s, 9 H), 1.779–1.726 (m, 6 H), 1.474–1.275 (m, 18 H), 0.877 (t, J = 7.0 Hz, 3 H). Anal. Calcd for 1a ($C_{25}H_{46}NO_2Br$): C, 63.54; H, 9.81; N, 2.96. Found: C, 63.52; H, 10.12; N, 2.60. MALDI-TOF MS: *m/z*: 392.3, corresponding to $[C_{25}H_{46}NO_2]^+$ ion.

2. Synthesis of quaternary ammoniums 1b-1e and 2a-2c.



1b-1d

1b m = 0, n = 8
1c m = 1, n = 8
1d m = 2, n = 8
1e m = 3, n = 8

2a-2c

2a m = 1, n = 6
2b m = 1, n = 10
2c m = 1, n = 12

Scheme S2. Synthetic procedures of 2a-2c and 1b-1e.

Taking 2a as a representative compound, the followings are detailed synthetic processes (1b-1d, and 2b, 2c were synthesized with similar procedures).

Synthesis of Ethyl 2,4-dihydroxybenzoate (Compound 3)

2.4-dihydroxybenzoic acid (7.00 g, 0.0455 mol), p-toluene sulfonic acid (2.10 g, 0.0122 mol) were dissolved in anhydrous ethanol (100 mL), which had been dehydrated with sodium. The mixture was stirred under refluxing and a nitrogen

atmosphere for 20 hours. After rotary evaporation, the residue was treated with water and extracted with chloroform. The organic layer was dried over anhydrous MgSO4, and then concentrated. The product was purified by column chromatography on silica gel with a mixture of dichloromethane /methanol (v/v, 20/1) as eluent. The pure compound was obtained as a white powder. Yield: 24.2% (2.0 g).

Synthesis of Ethyl 2-hydroxy-4-(octyloxy)benzoate (Compound 4)

Compound 3 (2.72 g, 0.0149 mol), 1-bromooctane (3.46 g, 0.0179 mol), anhydrous K_2CO_3 (3.09 g, 0.0224 mol) and several small grains of 18-crown-6 were dissolved in acetone (100 mL), the mixture was stirred under refluxing and a nitrogen atmosphere for 24 hours. The product was filtered to remove K_2CO_3, and then acidified by diluted hydrochloric acid to pH = 2. After rotary evaporation, the residue was treated with water and extracted with chloroform. The organic layer was dried over anhydrous $MgSO_4$, and then concentrated. The product was purified by column chromatography on silica gel with a mixture of dichloromethane/petroleum ether (v/v, 1/10) as eluent. The pure compound was obtained as a white powder. Yield: 77.6% (3.4 g).

Synthesis of Ethyl 2-(6-bromohexyloxy)-4-(octyloxy)benzoate (Compound 5)

Compound 4 (1.70 g, 0.00577 mol), 1,6-dibromohexane (1.83 g, 0.00750 mol) and anhydrous K_2CO_3 (1.20 g, 0.00866 mol) were dissolved in DMF (the less the better), the mixture was stirred in dark at room temperature for 24 hours. The product was mixed with water (V_{water}:V_{DMF} = 8:1), and then acidified by diluted hydrochloric acid to pH = 2. The mixture was frozen in refrigerator until some light yellow oil was observed at the bottom. The oil was washed with water three times; all of the water phase was collected together, and then extracted with ethyl ether. All of the organic phase was dried over anhydrous $MgSO_4$. After rotary evaporation, the residue was purified by column chromatography on silica gel with a mixture of dichloromethane/petroleum ether (v/v, 1/1) as eluent. The pure compound was obtained as a light yellow liquid. Yield: 62.9% (1.66 g).

Synthesis of 6-[(2-ethoxycarbonyl)-5-(octyloxy)phenoxy]-N,N,N-trimethylhexan-1-aminium bromide (2a***)***

Compound 5 (n = 6, 1.66 g, 0.00363 mol) and trimethylamine (30% aqueous solution,

7.13 g, 0.0362 mol) were dissolved in ethanol (50 mL), the mixture was stirred under refluxing for 24 hours. After removal of water and ethanol by rotary evaporation, the product was vacuumized to remove the excess trimethylamine. The residue was purified by column chromatography on silica gel with a mixture of dichloromethane/methanol (v/v, 8/1) as eluent. The pure compound was obtained as a white solid. Yield: 88.7% (1.66 g).

All the other compounds were synthesized following the similar procedures to 2a.

For 1b: ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.815–7.784 (d, J = 15.5 Hz, 1 H), 6.478–6.446 (m, 2 H), 4.010–3.955 (m, 4 H), 3.833 (s, 3 H), 3.587–3.530 (m, 2 H), 3.440 (s, 9 H),1.868–1.732 (m, 6 H), 1.543–1.258 (m, 18 H), 0.885–0.862 (t, J = 11.5 Hz, 3 H). Anal. Calcd for 1b ($C_{27}H_{48}NO_4Br\cdot H_2O$): C, 59.11; H, 9.19; N, 2.55. Found: C, 58.98; H, 9.31; N, 2.73. MALDI-TOF MS: *m/z*: 450.3, corresponding to $[C_{27}H_{48}NO_4]^+$ ion.

For 1c: ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.802–7.785 (d, J = 8.5 Hz, 1 H), 6.463–6.438 (m, 2 H), 4.313–4.270 (m, 2 H), 3.994–3.958 (m, 4 H), 3.572 (t, J = 8.5 Hz, 2 H), 3.455 (s, 9 H), 1.846–1.744 (m, 6 H), 1.512–1.248 (m, 21 H), 0.879 (t, J = 7.0 Hz, 3 H). Anal. Calcd for 1b ($C_{28}H_{50}NO_4Br\cdot 2H_2O$): C, 57.92; H, 9.37; N, 2.41. Found: C, 58.38; H, 9.81; N, 1.99. MALDI-TOF MS: *m/z*: 464.3, corresponding to $[C_{28}H_{50}NO_4]^+$ ion.

For 1d: ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.815–7.798 (d, J = 8.5 Hz, 1 H), 6.470–6.451 (m, 2 H), 4.201 (t, J = 7 Hz, 2 H), 4.007–3.969 (m, 4 H), 3.576 (t, J = 8.5 Hz, 2 H), 3.445 (s, 9 H), 1.843–1.735 (m, 8 H), 1.521–1.256 (m, 18 H), 1.015 (t, J = 7.5 Hz, 3 H), 0.888 (t, J = 7Hz, 3 H). Anal. Calcd for 1c ($C_{29}H_{52}NO_4Br\cdot 1.6H_2O$): C, 59.29; H, 9.47; N, 2.38. Found: C, 58.86; H, 9.00; N, 2.73. MALDI-TOF MS: *m/z*: 478.3, corresponding to $[C_{29}H_{52}NO_4]^+$ ion.

For 1e: ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.813–7.796 (d, J = 8.5 Hz, 1 H), 6.476–6.451 (m, 2 H), 4.246 (t, J = 6.5 Hz, 2 H), 4.009–3.972 (m, 4 H), 3.575 (t, J = 8.5 Hz, 2 H), 3.453 (s, 9 H), 1.860–1.690 (m, 8 H), 1.539–1.259 (m, 20 H), 0.967 (t, J = 7.5 Hz, 3 H), 0.892 (t, J = 7.0 Hz, 3 H). Anal. Calcd for 1d ($C_{30}H_{54}NO_4Br\cdot H_2O$): C, 61.00; H, 9.56; N, 2.37. Found: C, 60.99; H, 9.10; N, 2.18. MALDI-TOF MS: *m/z*: 492.4, corresponding to $[C_{30}H_{54}NO_4]^+$ ion.

For 2a: ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.828–7.810 (d, J = 9.0 Hz, 1 H), 6.468–6.441 (m, 2 H), 4.279–4.237 (m, 2 H), 4.018–3.971 (m, 4 H), 3.616 (t, J = 8.5 Hz, 2 H), 3.471 (s, 9 H), 1.842–1.755 (m, 6 H), 1.675–1.619 (m, 2 H), 1.555–1.499 (m, 2 H), 1.480–1.424 (m, 2 H), 1.371–1.261 (m, 11 H), 0.888 (t, J = 7 Hz, 3 H).

Anal. Calcd for 2a ($C_{26}H_{46}NO_4Br{\cdot}2H_2O$): C, 56.51; H, 9.12; N, 2.53. Found: C, 56.95; H, 9.55; N, 2.09. MALDI-TOF MS: *m/z*: 436.3, corresponding to $[C_{26}H_{46}NO_4]^+$ ion.

For 2b: ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.807–7.790 (d, J = 8.5 Hz, 1 H), 6.457–6.438 (m, 2 H), 4.320–4.277 (m, 2 H), 3.990–3.955 (m, 4 H), 3.562 (t, J = 6.5 Hz, 2 H), 3.466 (s, 9 H)，1.846–1.742 (m, 6 H), 1.491–1.251 (m, 25 H), 0.878 (t, J = 7.0 Hz, 3 H). Anal. Calcd for 2b ($C_{30}H_{54}NO_4Br{\cdot}H_2O$): C, 61.00; H, 9.56; N, 2.37. Found: C, 61.44 ; H, 9.97; N, 1.94. MALDI-TOF MS: *m/z*: 492.4, corresponding to $[C_{30}H_{54}NO_4]^+$ ion.

For 2c: ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.813–7.796 (d, J = 8.5 Hz, 1 H), 6.463–6.439 (m, 2 H), 4.325–4.283 (m, 2 H), 3.992–3.957 (m, 4 H), 3.565 (t, J = 8.5 Hz, 2 H), 3.470 (s, 9 H), 1.850–1.744 (m, 6 H), 1.510–1.266 (m, 29 H), 0.881 (t, J = 7.0 Hz, 3 H). Anal. Calcd for 2c ($C_{32}H_{58}NO_4Br{\cdot}H_2O$): C, 62.12; H, 9.77; N, 2.26. Found: C, 62.53; H, 10.17; N, 1.82. MALDI-TOF MS: *m/z*: 520.4, corresponding to $[C_{32}H_{58}NO_4]^+$ ion.

Compounds 3a and 3b were synthesized according to previous report. [1]

For 3a: ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.540 (s, 1 H), 7.261–7.223 (m, 2 H), 4.138–4.123 (t, J = 7.5 Hz, 2 H), 3.924 (s, 3 H), 1.879–1.852 (m, 2 H), 1.321-1.129 (m, 30 H), 0.879–0.865 (t, J = 7.0 Hz, 3 H), Anal. Calcd for 2c ($C_{22}H_{43}N_2PF_6$): C, 55.12; H, 8.80; N, 5.84. Found: C, 54.99; H, 9.02; N, 5.83. MALDI-TOF MS: *m/z*: positive spectrum, 335.3, corresponding to $[C_{22}H_{43}N_2]^+$ ion; negative spectrum, 144.8, corresponding to $[PF_6]^+$

For 3b: ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.212–7.208 (d, J = 2.0 Hz, 1 H), 7.144–7.140 (d, J = 2.0 Hz, 1 H), 4.031–4.016 (t, J = 7.5 Hz, 2 H), 3.805 (s, 3 H), 2.605 (s, 3 H), 1.830–1.772 (m, 2 H), 1.337-1.259 (m, 30 H), 0.886–0.872 (t, J = 7.0 Hz, 3 H). Anal. Calcd for 2c ($C_{23}H_{45}N_2PF_6$): C, 55.85; H, 9.17; N, 5.66. Found: C, 56.01; H, 8.96; N, 5.73. MALDI-TOF MS: *m/z*: positive spectrum, 349.5, corresponding to $[C_{21}H_{41}N_2]^+$ ion

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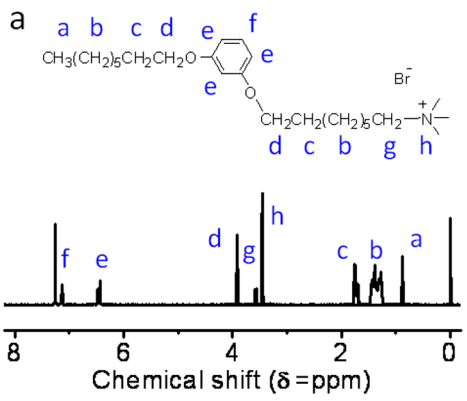
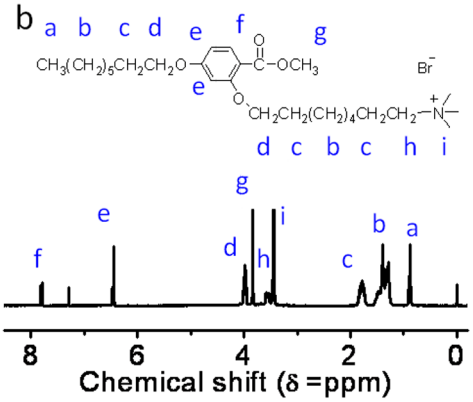
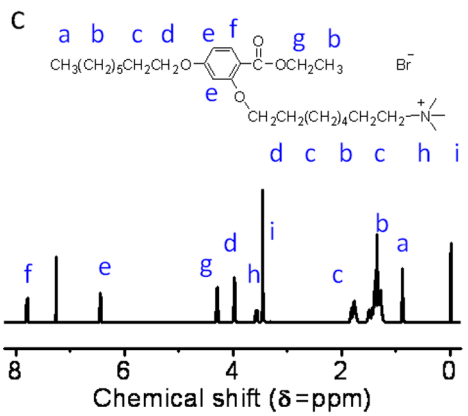
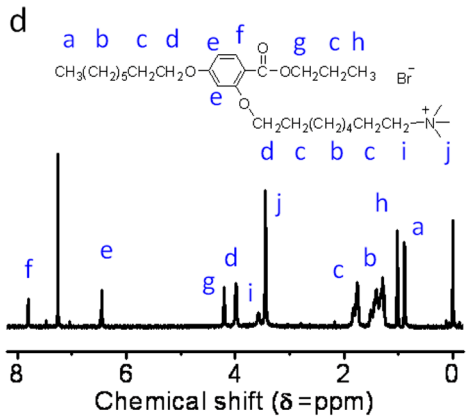
Reference:

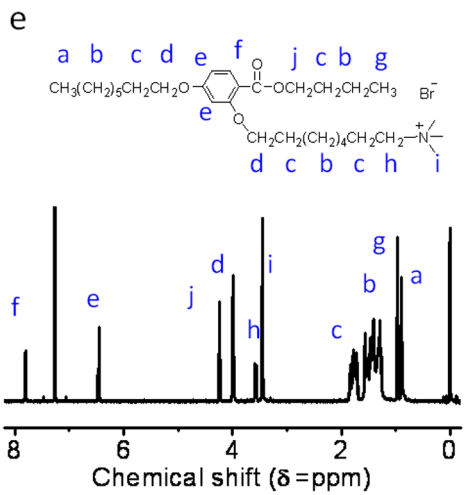
1. C. M. Gordon, J. D. Holbrey, A. R. Kennedy and K. R. Seddon, *J. Mater. Chem.*, 1998, **8**, 2627-2636.

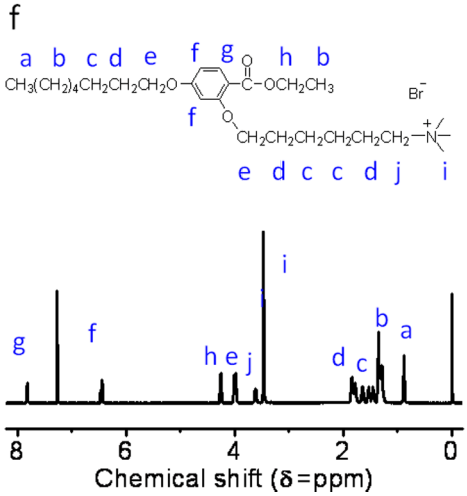












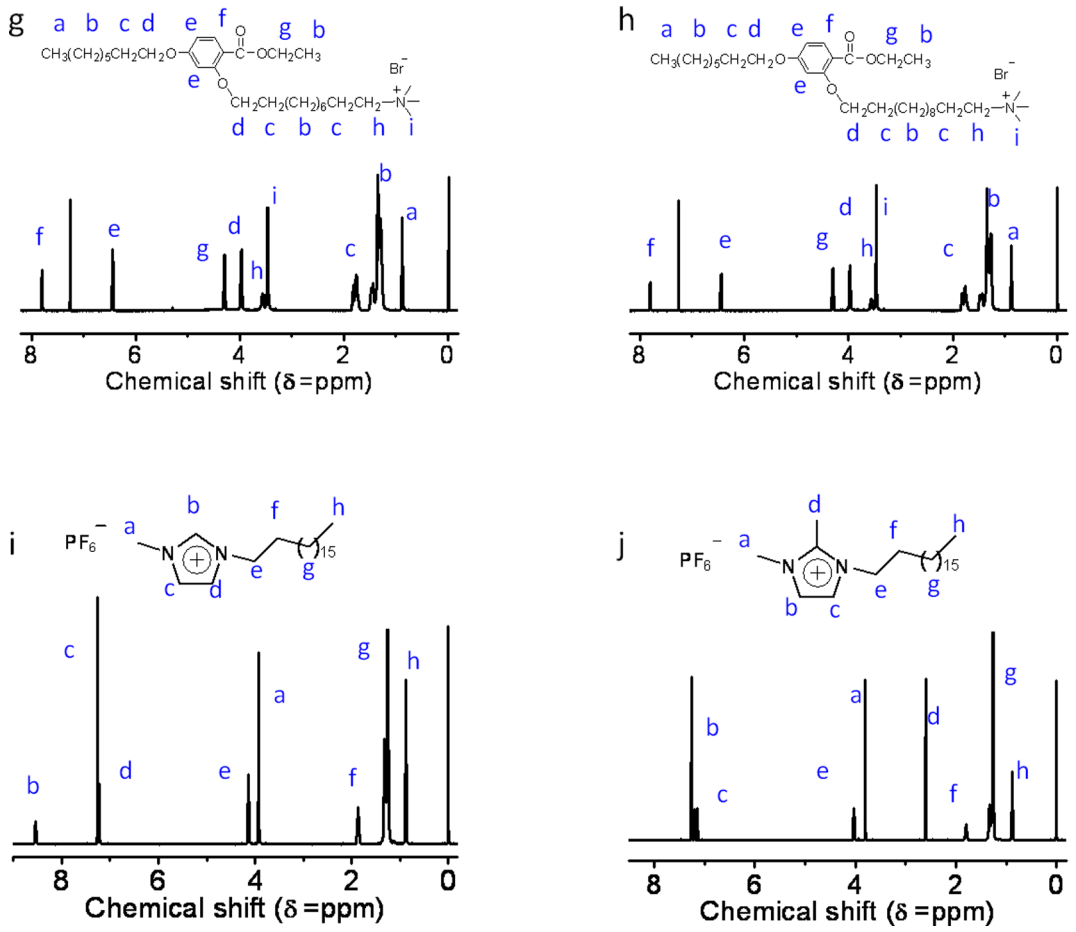


Fig. S1 ^{1}H NMR spectra of 1a (a), 1b (b), 1c (c), 1d (d), 1e (e), 2a (f), 2b (g), 2c (h), 3a (i), and 3b (j) in $CDCl_3$.

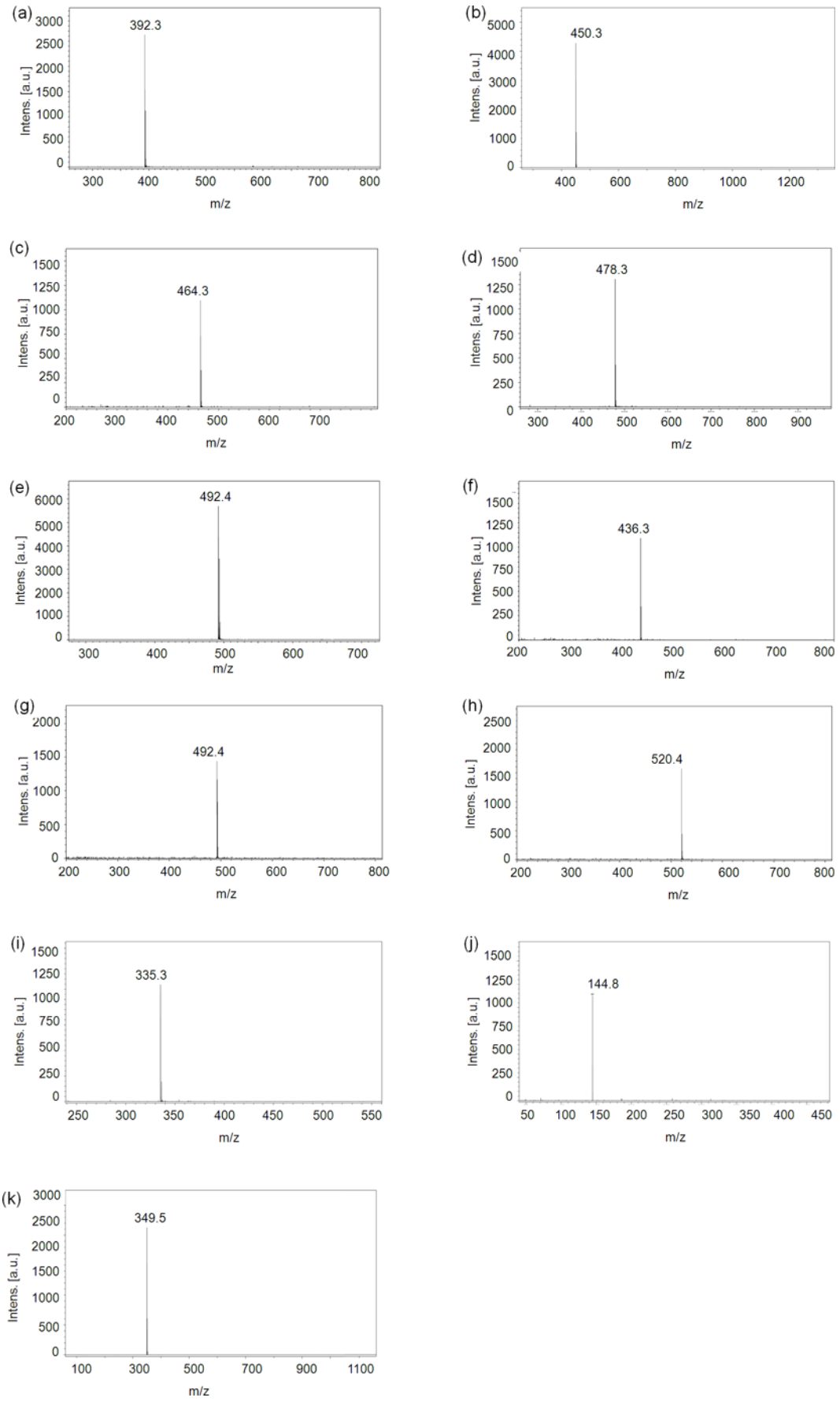


Fig.S2 MALDI-TOF MS spectra of 1a-1e, 2a-2c and 3a, 3b: (a) $[1a]^+$, (b) $[1b]^+$, (c)

$[1c]^+$, (d) $[1d]^+$, (e) $[1e]^+$, (f) $[2a]^+$, (g) $[2b]^+$, (h) $[2c]^+$, (i) $[3a]^+$, (j) the negative spectrum of 3a (the value 144.5 corresponds to the molecular weight of $[PF_6]^-$, indicating the successful metathesis reaction), (k) $[3b]^+$.

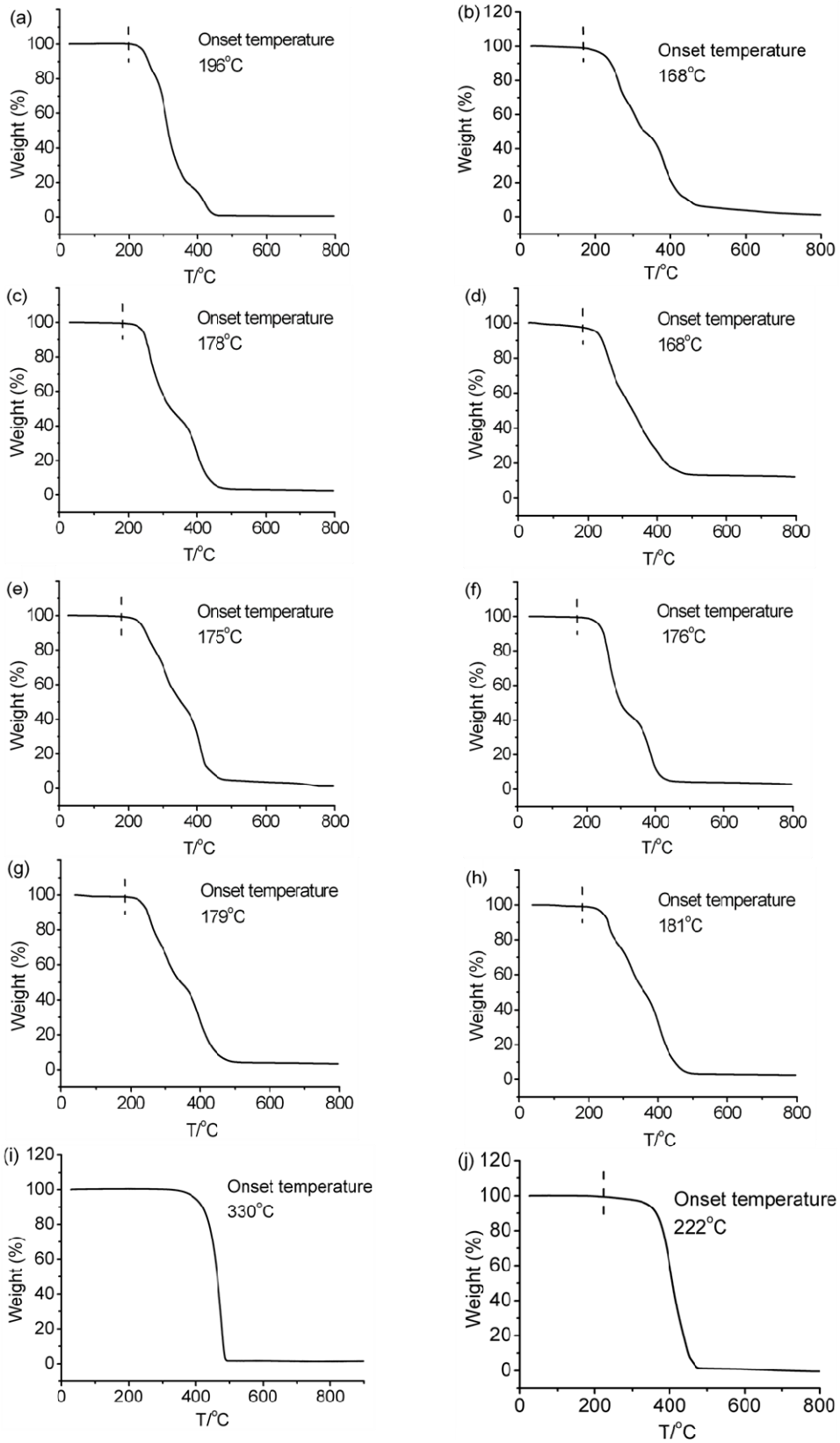


Fig. S3 TGA thermograms of 1a (a), 1b (b), 1c (c), 1d (d), 1e (e), 2a (f), 2b (g), 2c (h), 3a (i), and 3b (j).

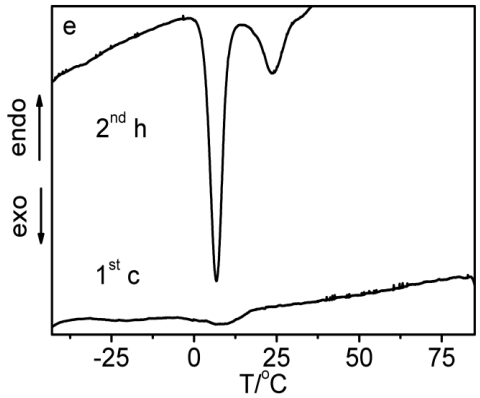


Fig. S4 Magnified DSC thermogram of compound 1e (h and c represent the heating and cooling scan).

Table S1. Bragg diffractions and the diffraction planes collected from the X-ray diffractograms for 1a-1e.

Compounds	T/°C	*d*/Å	*hkl**
1a	25	22.1	001
	145	38.4	001
		18.8	002
		12.6	003
		7.5	005
		6.3	006
		5.4	007
		4.7	008
		4.2	009
		3.8	0010
		4.6	100
		3.3	110
		2.3	200
1b	70	35.3	001
1c	25	41.1	001
1c	25	33.3	001
1e	25	35.3	001

* *hkl* are the Miller indices of the diffractions

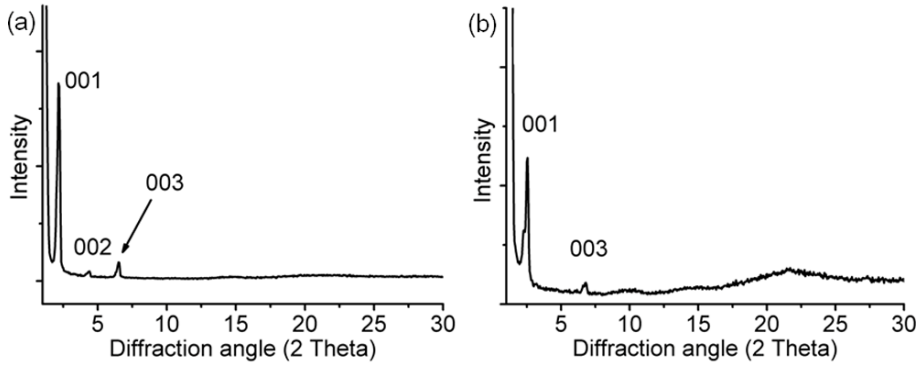


Fig. S5 Variable-temperature XRD patterns of 1c (a) and 1d (b) at room temperature.

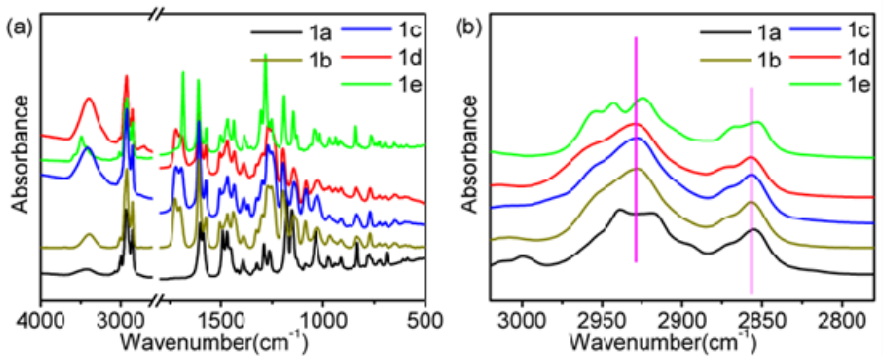


Fig. S6 FT-IR spectra of 1a-1e at room temperature.

Table S2. FT-IR assignments of 1a-1e and 2a-2c.

1a	1b	1c	1d	1e	2a	2b	2c	Assignments
3012	3007	3010	3014	3018	3008	3012	3012	CH_3–N^+ asymmetric stretching
2939	2954	2954	2956	2954	2952	2954	2956	CH_3 asymmetric stretching
2939	—	—	—	2943	—	—	—	Fermi resonance[2, 3]
2917	2928	2929	2929	2926	2929	2927	2925	CH_2 asymmetric stretching
2871	2872	2870	2872	2866	2870	2870	2869	CH_3 symmetric stretching
2854	2856	2856	2856	2852	2856	2856	2854	CH_2 symmetric stretching
—	1722	1718	1718	1721	1712	1722	1724	∅-C=O stretching
1603	1609	1608	1608	1610	1608	1608	1608	C – C framework stretching
1587	1574	1574	1574	1572	1574	1574	1574	C – C framework stretching

1491	1504	1504	1504	1502	1504	1504	1504	C – C framework stretching
—	1479	1479	1478	1476	1479	1479	1479	CH_2–N scissor stretching
1470	1468	1468	1468	1468	1468	1468	1468	CH_2 scissoring
1452	1441	1435	1435	1437	1437	1437	1435	N^+–CH_2 symmetric stretching
1390	1389	1388	1389	1387	1387	1387	1390	CH_3 scissoring
1290	1298	1296	1296	1303	1298	1296	1296	CH_2 wagging modes
1263	1273	1271	1269	1282	1269	1271	1271	∅ – O – C asymmetric stretching
1151	1142	1142	1144	1146	1142	1142	1142	C–N stretching

Reference:

2. J.-F. Bardeau, A. N. Parikh, J. D. Beers and B. I. Swanson, *J. Phys. Chem. B*, 1999, **104**, 627-635.
3. W. Li, S. Yi, Y. Wu and L. Wu, *J. Phys. Chem. B*, 2006, **110**, 16961-16966.

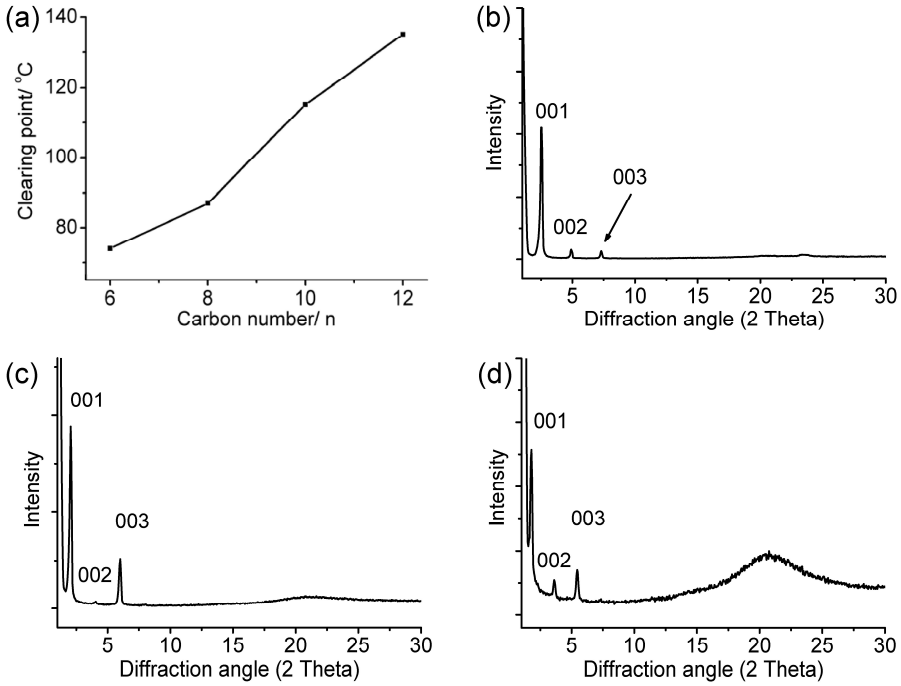


Fig. S7 Plot of clearing point with the length of hydrophobic chains from 2a, through 1b, 2b to 2c (a); Variable-temperature XRD patterns of 2a (a), 2b (b), 2c (c) at room temperature.

Table S3. The N values and the corresponding temperatures of all of the compounds.

	1b	1c	1d	2a	2b	2c	3a	3b
T/°C	100	80	80	70	100	125	150	160
N	0.855	0.803	0.835	0.671	0.812	0.632	0.191	0.312

Table S4. The activation energy of all compounds at liquid crystalline isotropic states.

ΔE（KJ mol^{-1} K^{-1}）	1b	1c	1d	2a	2b	2c	3a	3b
Sm A	106.34	175.32	81.78	276.69	266.21	64.97	14.88	30.01
Iso	70.94	66.07	65.52	53.24	54.96	44.53	9.75	22.56

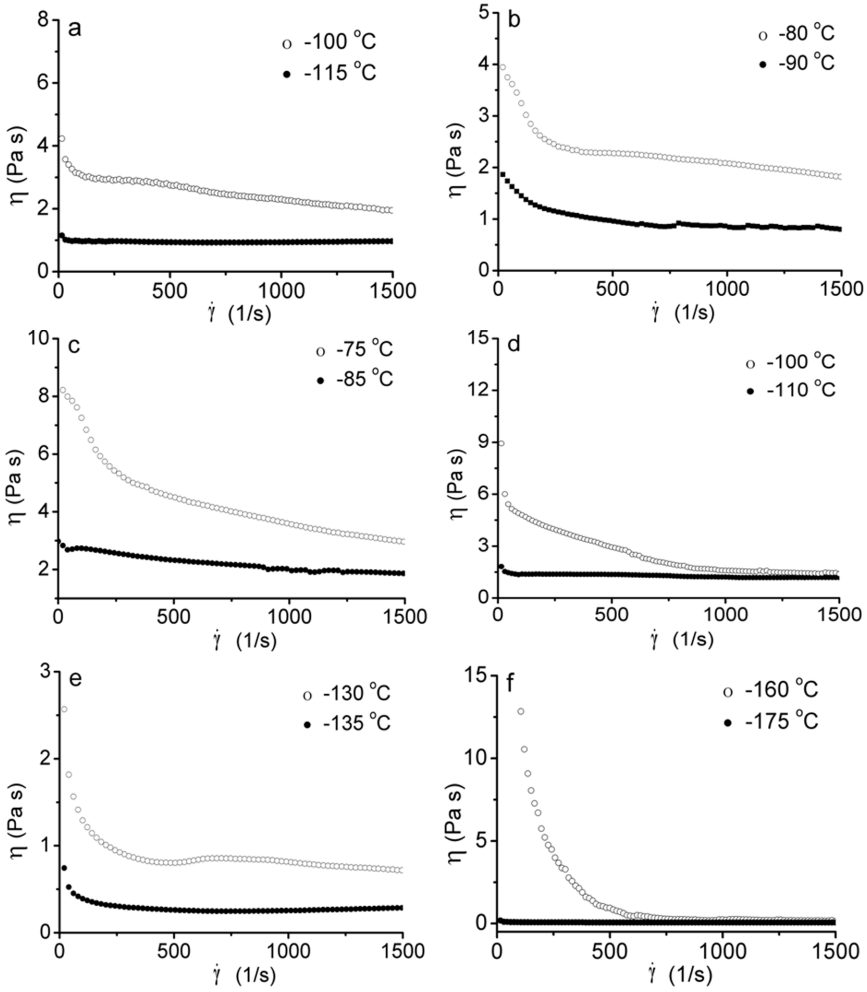


Fig. S8 The viscosity-shear rate plots of 1b (a), 1c (b), 2a (c), 2b (d), 2c (e), and 3b (f).

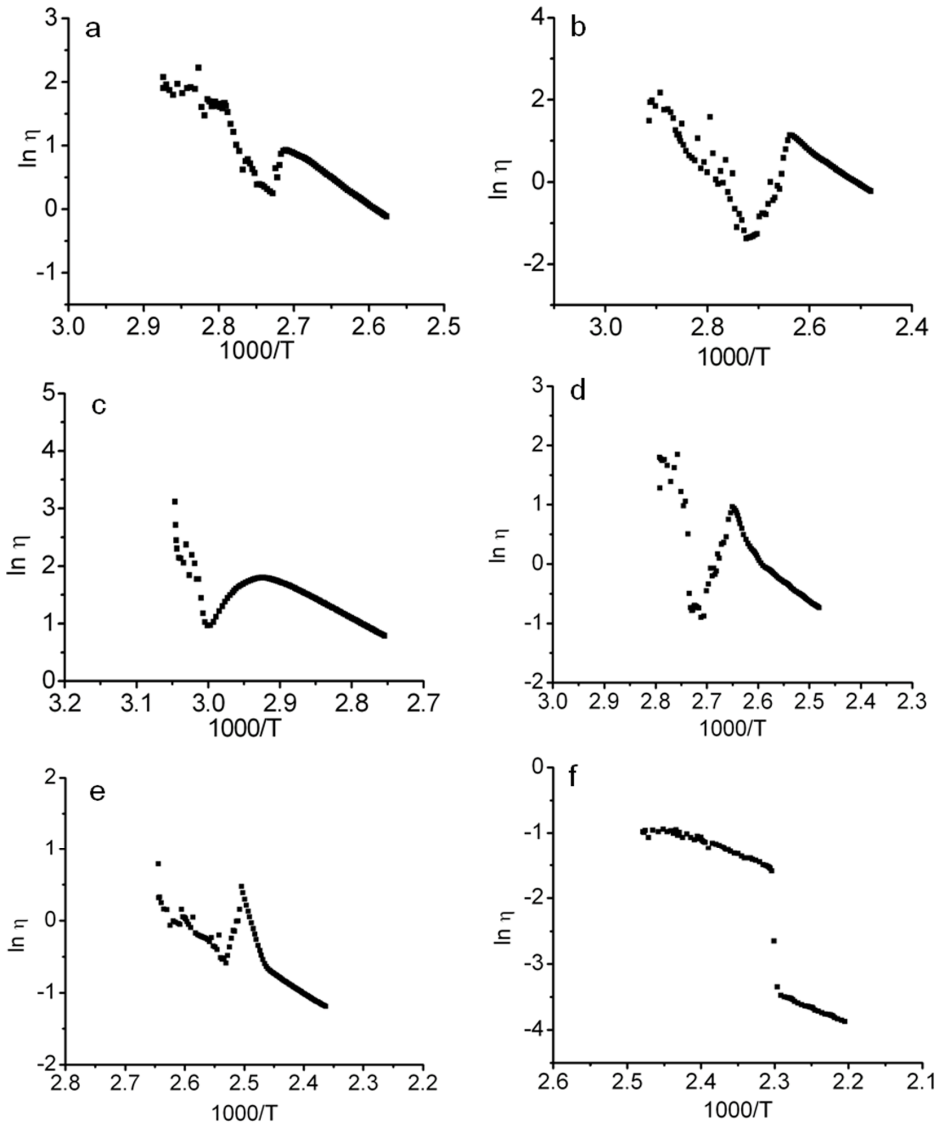


Fig. S9 The viscosity vs. temperature curves of 1b (a), 1c (b), 2a (c), 2b (d), 2c (e), and 3b (f).

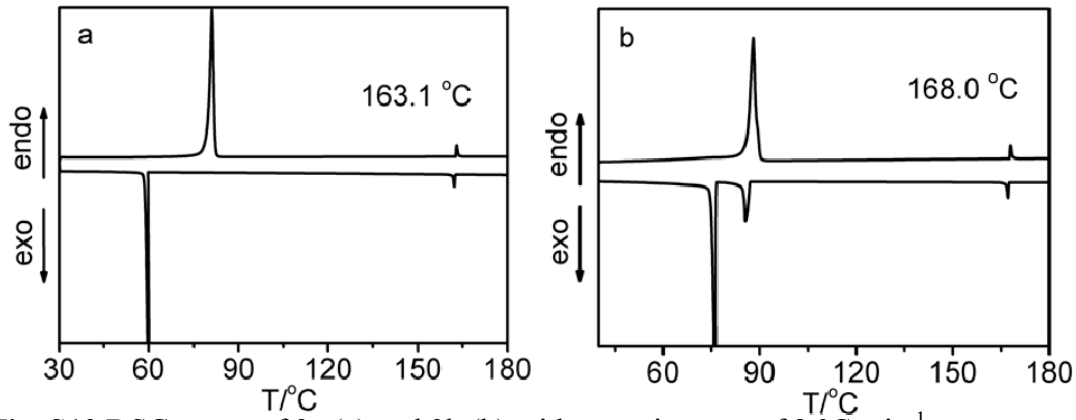


Fig. S10 DSC traces of 3a (a) and 3b (b) with scanning rate of 2 °C min^{-1}.

Table S5 The DSC breadth of the S-I transitions for all the ILCs with heating rate of 2 ^{o}C min^{-1}.

Compounds	1b	1c	1d	2a	2b	2c	3a	3b
Breadth (ΔT/°C)	20.6	19.0	7.9	11.0	29.0	16.3	1.7	2.7