Low mid-infrared absorption tolane liquid crystals terminated by 2,2-difluorovinyloxy: synthesis, characterization and properties

Electronic supplementary information

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1. Syntheses and characterization

1.1 Syntheses

1.1.1 Synthesis of trimethyl ((4-(2,2,2-trifluoroethoxy)phenyl)ethynyl)silane (**2**)

Under nitrogen protection, 1-bromo-4-(2,2,2-trifluoroethoxy)benzene (25.5 g, 100 mmol), ethynyltrimethylsilane(16.7 g, 170 mmol), triethylamine(100 mL), $Pd(PPh_3)_2Cl_2$ (1.1 g, 1.5 mmol) and CuI (0.9 g, 5 mmol)were added to a three-necked flask. The mixture was stirred and heated at 70°C for 3 h. After cooling the mixture to room temperature, the reaction mixture was filtered through Celite, then the filtrate was extracted with hexane and washed three times with ammonium chloride solution. The combined organic layers were dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by column chromatography on silica gel to obtain a colorless oil (23.4 g, 86%).

1.1.2 Synthesis of 1-ethynyl-4-(2,2,2-trifluoroethoxy)benzene(**3**)

Trimethyl((4-(2,2,2-trifluoroethoxy)phenyl)ethynyl)silane(21.8 g, 80 mmol), KOH (2.2 g, 40 mmol) and EtOH (100 mL) were added to a three-necked flask under nitrogen protection. The mixture was stirred for 2 h at room temperature and then poured into water. After extracted with hexane and washed three times with water, the organic layer was dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by column chromatography on silica gel to a obtain colorless oil(13.8 g, 86%).

1.1.3 Synthesis of **5**

1-ethynyl-4-(2,2,2-trifluoroethoxy)benzene (11.2 g, 60 mmol), triethylamine (70 mL), $Pd(PPh_3)_2Cl_2$ (0.63 g, 0.9 mmol), and CuI (0.57 g, 3 mmol) were added to a three-necked flask under nitrogen protection. After cooling to 0°C, a solution of 1-bromo-2(3)-fluoro-4-iodobenzene (18.1 g, 60 mmol) in triethylamine (20 mL)was added over 1 h, then the mixture was stirred for 3 h at 0°C. The reaction solution was filtered through Celite and the filtrate was extracted with hexane. After washed three times with ammonium chloride solution, the combined organic layers were dried over $MgSO_4$. The solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel to obtain white crystals (19.3 g, 86%).

1.1.4 Synthesis of **7**

Under nitrogen protection, a mixture of **5** (4.7 g, 10 mmol), arylboronic acid **6** (2.9 g, 11 mmol), K_2CO_3(4.1 g, 30 mmol) and $Pd(PPh_3)_4$ (0.12 g, 0.1 mmol) in 30 mL of THF and 30 mL water was stirred and heated to reflux for 8 h. After cooling the mixture to room temperature, the mixture was diluted with water and extracted three times with toluene. The combined organic layers were dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by column chromatography on silica gel using n-heptane as eluent. After evaporation the solvent, it was recrystallized from ethanol to obtain a white crystals 4.8 g (yield 75%) with GC purity of 99.6%.

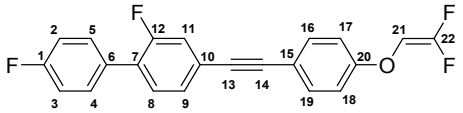
1.1.5 Synthesis of final products

Under nitrogen protection, 2.0 M LDA (30 mmol) was injected into a cooled -80°C stirred solution of **7** (10 mmol) in dried THF (100 mL). After addition, the reaction temperature was maintained at -80°C for 3 h. The solution was poured into a mixture of 10% aqueous NH_4Cl (50 mL) and ice (50 g). The aqueous layer was extracted with n-pentane, and the combined organic extracts were washed with 10% aqueous NH_4Cl, and dried with anhydrous sodium sulfate. The solvent was removed under vacuum. The residue was first chromatographed with n-heptane on silica gel, then by crystallization from n-heptane to yield final products as white crystals.

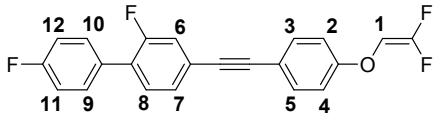
1.2 Characterization

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a spectrometer operating at 500 and 126 MHz. The mass spectra (MS) were obtained by GC/MS Thermo DSQ II with m/z 35–500.

Compound **A1**: The yield was 81% of white crystals with GC purity of 99.7%.



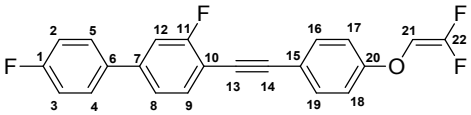
^{13}C NMR(126 MHz, $CDCl_3$)δ (ppm): C_1(163.61, 161.64), C_{12}(160.18, 158.21), C_{22}(159.07, 156.85, 156.75, 154.53), C_{20}(157.24), $C_{16,19}$(133.34), C_6(131.17, 131.13), C_5(130.67, 130.65), C_4(130.61, 130.58), C_7(130.47, 130.43), C_8(128.21, 128.10), C_9(127.72, 127.70), C_{10}(124.15, 124.07), C_{11}(119.13, 118.93), C_{15}(117.48), $C_{2,3}$(115.63, 115.46), $C_{17,18}$(115.42), C_{21}(104.42, 104.29, 103.97, 103.85), C_{14}(90.12), C_{13}(87.58, 87.56).



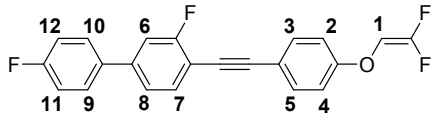
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): $H_{(3,5,7,8)}$7.57 – 7.48 (m, 4H), $H_{(9,10)}$7.41 – 7.33 (m, 2H), H_6 7.30 (d, J = 11.5 Hz, 1H), $H_{(11,12)}$ 7.18 – 7.10 (m, 2H), $H_{2,4}$ 7.01 (d, J = 9.0 Hz, 2H), H_1 6.09 (dd, J = 15.0, 3.5 Hz, 1H).

EI-MS m/z (rel. int.%): 367.9(M^+, 100), 338.9(23), 287.9(29), 267.9(9), 184.0(6), 144.0(5).

Compound **B1:** The yield was 83% of white crystals with GC purity of 99.8%.



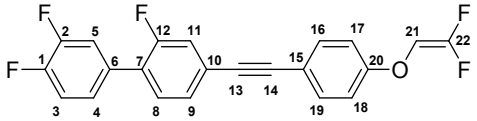
^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm): C_1(163.92, 161.95), C_{11}(163.84, 161.84), C_{22}(159.06, 156.84, 156.74, 154.52), C_{20}(157.24), C_7(142.16, 142.10), C_6(135.36), C_9(133.62, 133.61), $C_{16,19}$(133.35), $C_{4,5}$(128.67, 128.60), C_8(122.43, 122.40), C_{15}(117.61), $C_{2,3}$(116.04, 115.86), $C_{17,18}$(115.38), C_{12}(113.95, 113.78), C_{10}(11074, 110.61), C_{21}(104.43, 104.31, 103.99, 103.87), C_{13}(94.44, 94.41), C_{14}(82.15).



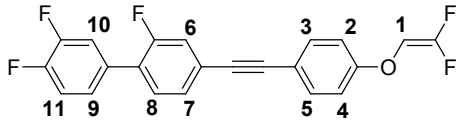
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): $H_{(3,5,6,7,8)}$7.58 – 7.51 (m, 5 H), $H_{(9,10)}$7.34 – 7.27 (m, 2 H), $H_{(11,12)}$7.19 – 7.11 (m, 2H), $H_{2,4}$ 7.01 (d, J = 9.0 Hz, 2H), H_1 6.10 (dd, J = 15.0, 3.5 Hz, 1H).

EI-MS m/z (rel. int.%): 367.9(M^+, 100), 338.9(23), 287.9(28), 267.9(8), 184.0(6), 144.0(6).

Compound **A2:** The yield was 82% of white crystals with GC purity of 99.7%.



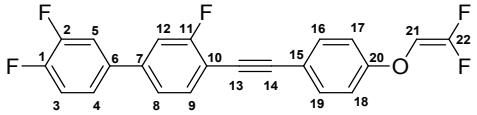
^{13}C NMR (126 MHz, $CDCl_3$)δ (ppm): C_{12}(160.11, 158.13), C_{22}(159.07, 156.85, 156.75, 154.53), C_{20}(157.24), C_2(151.28, 151.23, 149.31, 149.25), C_1(151.18, 151.13, 149.21, 149.15), $C_{16,19}$(133.36), C_6(132.03, 132.00, 131.99, 131.96), C_7(130.30, 130.27), C_8(127.82, 127.79), C_9(127.05, 126.94), C_5(m, 125.06), C_{10}(124.78, 124.70), C_{11}(119.22, 119.03), C_3(119.22, 119.03), C_{15}(117.48), C_4(117.35), $C_{17,18}$(115.43), C_{21}(104.40, 104.27, 103.95, 103.83), C_{14}(90.49), C_{13}(87.39, 87.36).



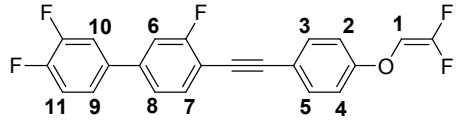
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): $H_{(8,10)}$ 7.55 – 7.48 (m, 2H), $H_{(2,3,7)}$ 7.43 – 7.33 (m, 3H), $H_{(6,9,11)}$ 7.33 – 7.20 (m, 3H), $H_{(2,4)}$ 7.01 (d, J = 9.0 Hz, 2H), H_1 6.10 (dd, J = 15.0, 3.5 Hz, 1H).

EI-MS m/z (rel. int.%): 385.9(M^+, 77), 356.9(26), 305.9(30), 280.9(38), 206.9(100), 44.0 (32).

Compound **B2:** The yield was 86% of white crystals with GC purity of 99.8%.



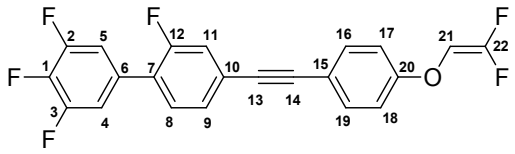
^{13}C NMR (126 MHz, $CDCl_3$)δ (ppm): C_1(163.92, 161.95), C_{11}(163.84, 161.84), C_{22}(159.06, 156.84, 156.74, 154.52), C_{20}(157.24), C_7(142.16, 142.10), C_6(135.36), C_9(133.62, 133.61), $C_{16,19}$(133.35), $C_{4,5}$(128.67, 128.60), C_8(122.43, 122.40), C_{15}(117.61), $C_{2,3}$(116.04, 115.86), $C_{17,18}$(115.38), C_{12}(113.95, 113.78), C_{10}(110.74, 110.61), C_{21}(104.43, 104.31, 103.99, 103.87), C_{13}(94.44, 94.41), C_{14}(82.15).



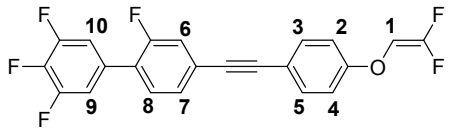
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): $H_{(6,7,10)}$ 7.59 – 7.51 (m, 3 H), $H_{(11)}$7.38 (ddd, J = 11.3, 7.5, 2.2 Hz, 1 H), $H_{(3,5,8,9)}$ 7.33 – 7.20 (m, 4 H), $H_{2,4}$ 7.01 (d, J = 8.8 Hz, 2H), H_1 6.10 (dd, J = 15.0, 3.5 Hz, 1H).

EI-MS m/z (rel. int.%): 385.9(M^+, 77), 356.9(26), 305.9(30), 280.9(38), 206.9(100), 44.0 (32).

Compound **A3:** The yield was 79% of white crystals with GC purity of 99.8%.



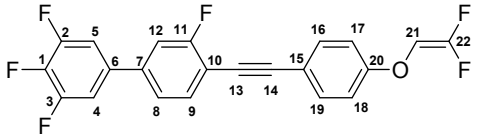
^{13}C NMR (126 MHz, $CDCl_3$)δ (ppm): C_{12}(160.05, 158.06), C_{22}(159.07, 156.85, 156.75, 154.53), C_{20}(157.37), C_2(152.24, 152.21, 150.26, 150.22), C_3(152.16, 152.13, 150.18, 150.14), C_1(140.68, 140.56, 140.44, 138.67, 138.55, 138.43), $C_{16,19}$(133.36), C_6(131.02, m), C_7(130.09, 130.06), C_8(127.92, 127.90), C_9(126.04， 125.94), C_{10}(125.42, 125.34), C_{11}(119.33, 119.13), C_{15}(117.21), $C_{17,18}$(115.45), $C_{4,5}$(113.10, m), C_{21}(104.37, 104.25, 103.93, 103.80), C_{14}(90.88), C_{13}(87.20, 87.18).



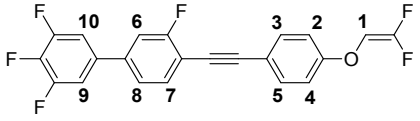
^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): $H_{7,8}$7.55 – 7.47 (2 H, m), $H_{3,5,6}$7.39 – 7.28 (3 H, m), $H_{9,10}$7.24 – 7.15 (2 H, m), $H_{2,4}$ 7.04 – 6.98 (2 H, m),H_1 6.10 (1 H, dd, *J*=14.9, 3.5).

EI-MS m/z (rel. int. %): 404.0(M^+, 100), 374.9(36), 324.0(30), 304.0(10), 202.0(8).

Compound **B3:** The yield was 82% of white crystals with GC purity of 99.7%.



^{13}C NMR (126 MHz, $CDCl_3$)δ (ppm): C_{11}(163.81, 161.80), C_{22}(159.07, 156.85, 156.75, 154.53), C_{20}(157.39), C_2(152.62, 152.59, 150.26, 150.22), C_3(152.54, 152.51, 150.18, 150.14), C_1(139.76), C_6(135.33), C_9(133.88, 133.86), $C_{16,19}$(133.40), C_7(139.80, 139.74), C_8(122.31, 122.29), C_{15}(117.34), $C_{17,18}$(115.40), C_{12}(113.97, 113.79), C_{10}(112.12, 111.99), $C_{4,5}$(111.15, 111.11, 111.02, 110.97), C_{21}(104.37, 104.25, 103.93, 103.80), C_{13}(95.20, 95.17), C_{14}(81.74).



^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): $H_{6,7,8}$ 7.59 – 7.51 (m, 3H), $H_{9,10}$ 7.30 – 7.22 (m, 2H), $H_{3,5}$ 7.18 (m, 2H), $H_{2,4}$ 7.04 – 6.98 (2 H, m), H_1 6.10 (1 H, dd, *J*=14.9, 3.5).

EI-MS m/z (rel. int.%): 404.0(M^+, 100), 374.9(35), 324.0(30), 304.0(10), 202.0(8).

2. Fig. S1, Table S1 and Table S2

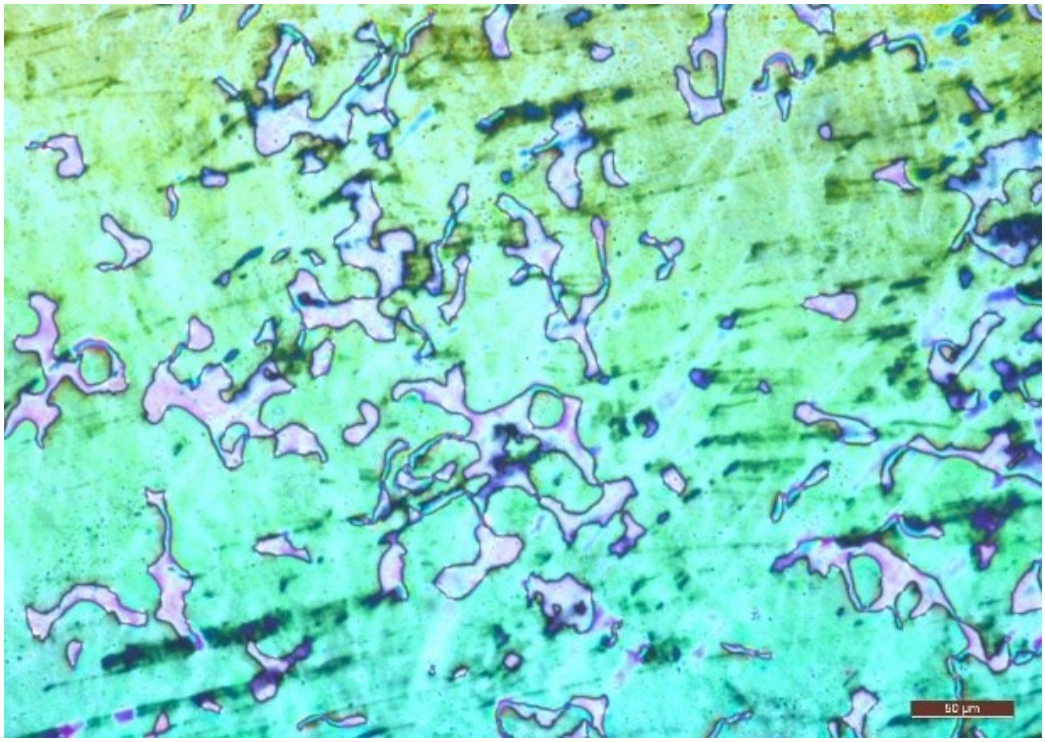
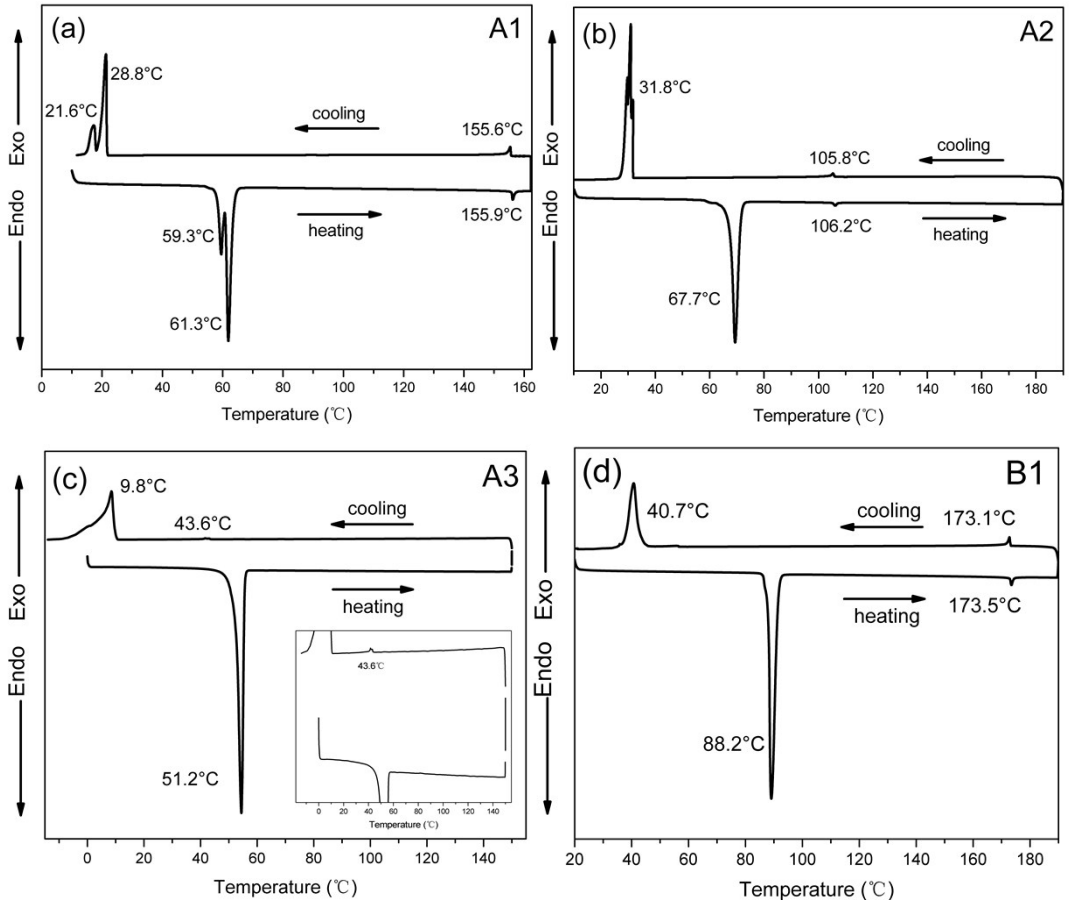


Fig. S1 POM image of **A1**: thread-like texture of the nematic mesophase at 92.6°C in the heating process



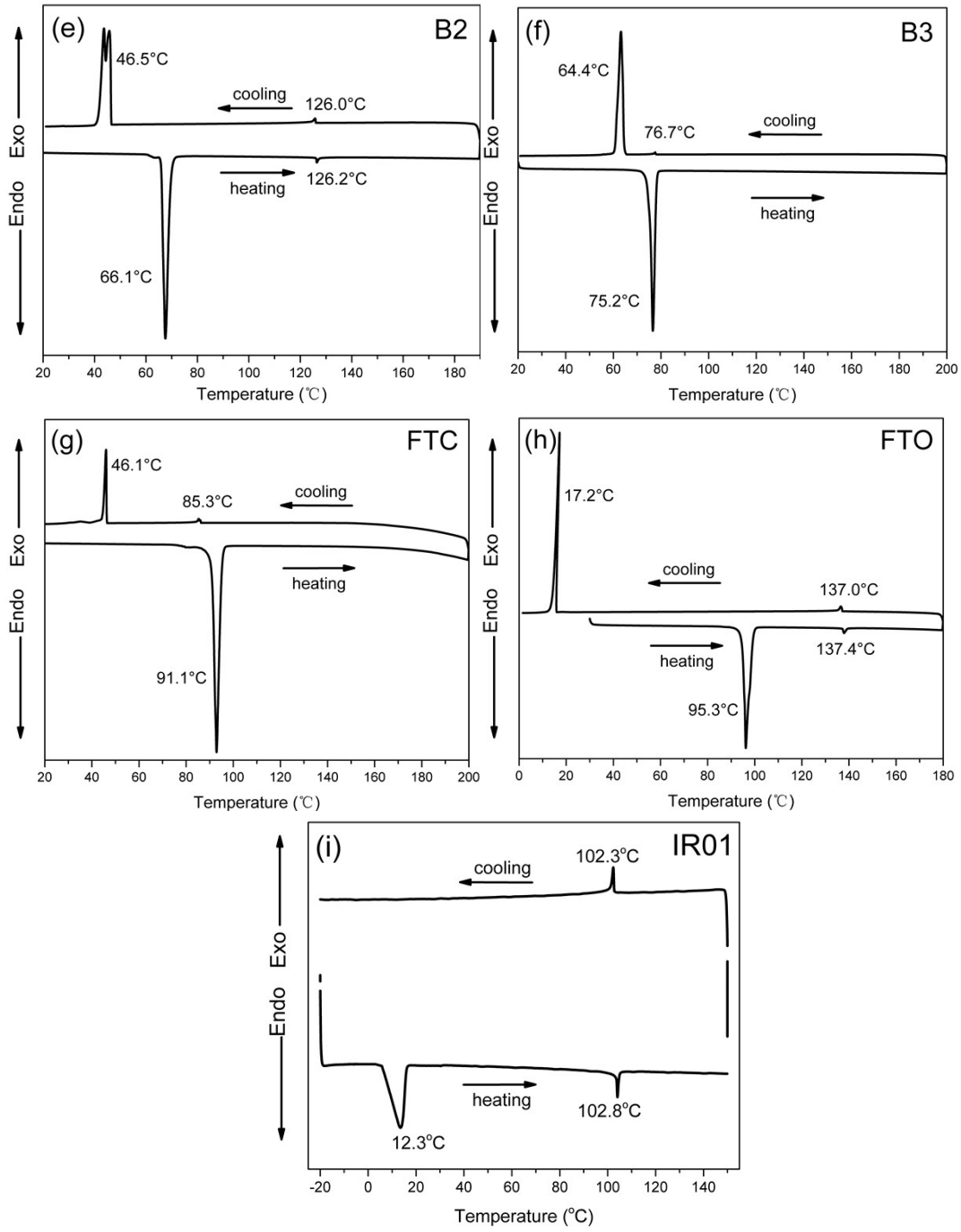


Fig. S2 DSC curves of (a) A1, (b) A2, (c) A3, (d) B1, (e) B2, (f) B3, (g) FTC, (h) FTO, and (i) IR01.

Table S1. Chemical structures, compositions and properties of mixture **CJOE-001**

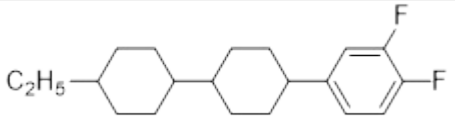
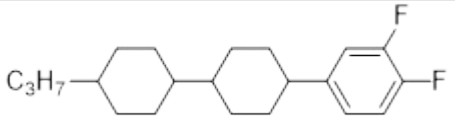
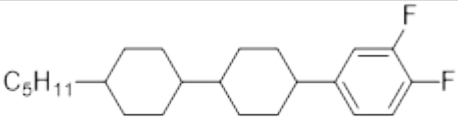
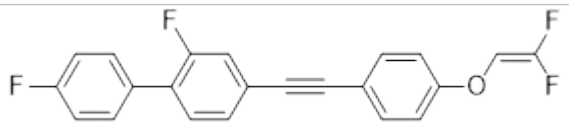
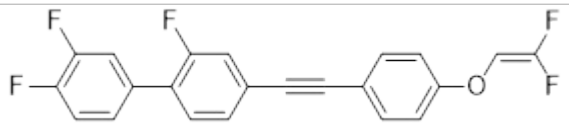
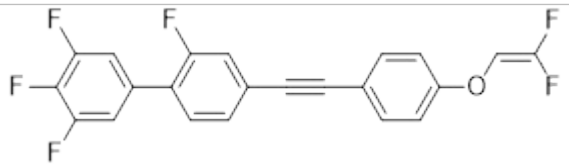
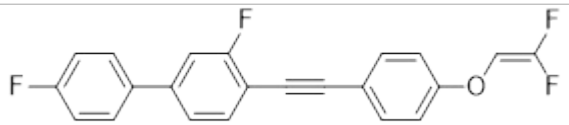
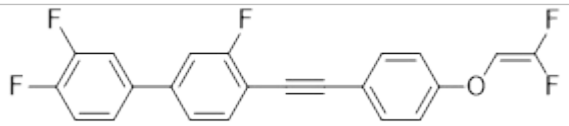
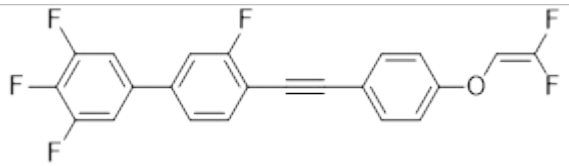
Structures	wt%
	33.3%
	33.3%
	33.3%
Properties: Δn(589nm, 25°C)=0.0795, $\Delta\varepsilon$(1 KHz, 25°C)=6.13, γ_1(1 KHz, 25°C)= 158.1 mPa s Clearing point: 113.7°C.	

Table S2. Compositions of mixture **IR01**

Abbr.	Structures	wt%
A1		19.3
A2		16.4
A3		27.3
B1		4.2
B2		18.9
B3		13.9