

## Supporting Information

# Synthesis and study of hybrid hydrogen-bonded bent-core liquid crystal complexes containing C<sub>60</sub>- and Si-based proton donors

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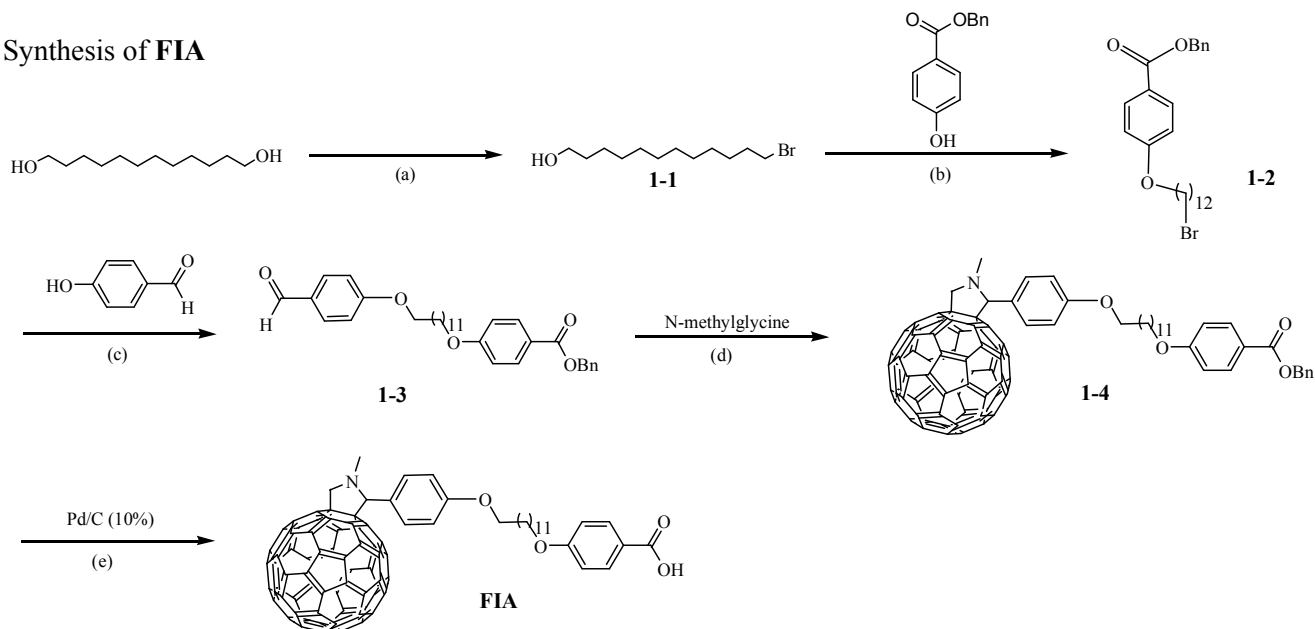
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## Contents

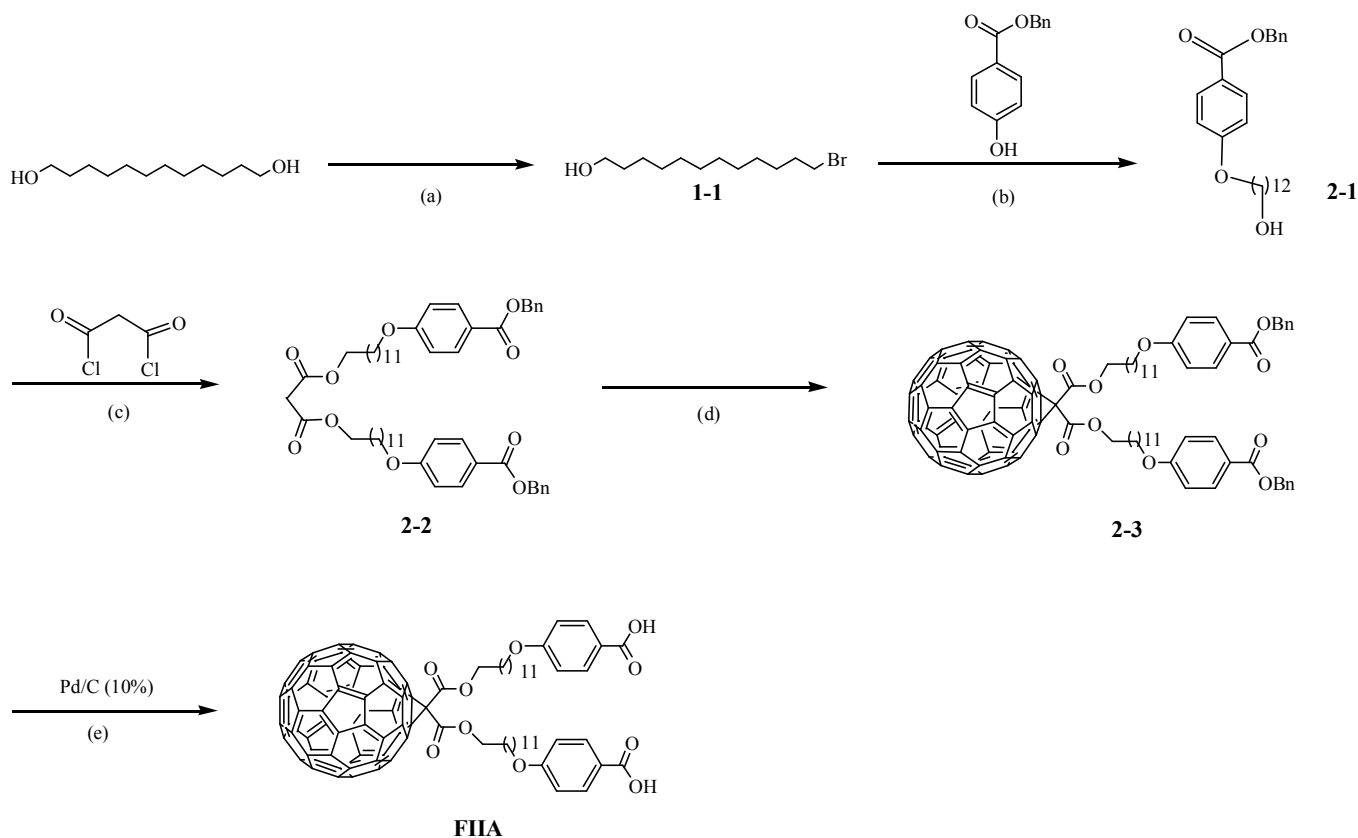
1. Synthesis Section	page S2
2. Fig. S1	page S10
3. Fig. S2	page S11
4. Fig. S3	page S12
5. Fig. S4	page S13
6. Fig. S5	page S14
7. Fig. S6	page S14
8. Fig. S7	page S15
9. Fig. S8	page S16
10. Fig. S9	page S18
11. Fig. S10	page S19
12. Fig. S11	page S23
13. Fig. S12	page S24
14. Fig. S13	page S15
15. Table S1	page S25
16. Table S2	page S26
17. References	page S27

## A. Synthesis of FIA



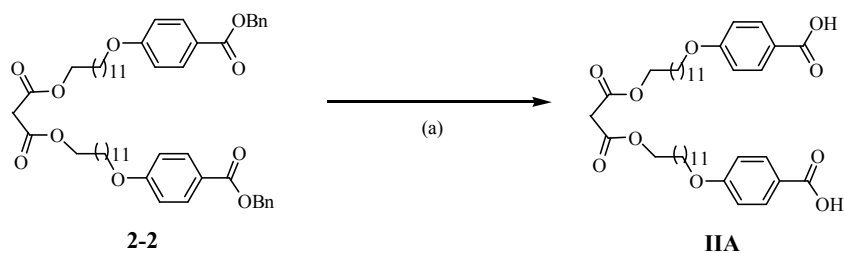
Reagents and conditions: (a) HBr, toluene, reflux, 24 h; (b) DIAD, PPh<sub>3</sub>, THF, 0°C, 1 h, then r.t., 24 h; (c) (1) K<sub>2</sub>CO<sub>3</sub>, acetonitrile, reflux, 8 h (2) HCl; (d) C<sub>60</sub>, chlorobenzene, reflux 24 h; (e) HCOONH<sub>4</sub>, MeOH-THF

## B. Synthesis of FIIA



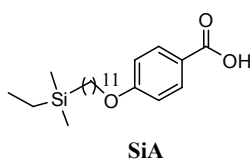
Reagents and conditions: (a) HBr, toluene, reflux, 24 h; (b) K<sub>2</sub>CO<sub>3</sub>, acetone, reflux, 24 h; (c) DMAP, CH<sub>2</sub>Cl<sub>2</sub>, r.t., 2 h; (d) C<sub>60</sub>, DBU, I<sub>2</sub>, toluene, r.t., 10 mins; (e) HCOONH<sub>4</sub>, MeOH-THF

### C. Synthesis of **IIA**

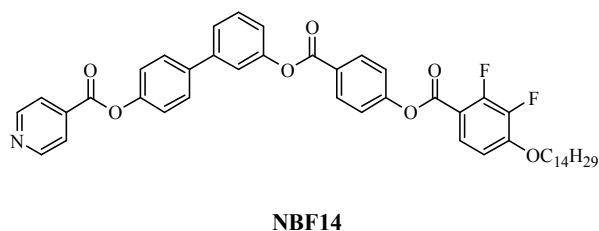


Reagents and conditions: (a) Pd/C (10%) H<sub>2</sub>

### D. Structure of **SiA**



### E. Structure of **NBF14**



**Scheme S1.** Synthesis of **FIA**, **FIIA** and **IIA** as well as the structures of **SiA** and **NBF14**.

#### A. Synthesis of **FIA**

**Synthesis of 12-Bromododecan-1-ol, (1-1).** Into a 250 mL double necked flask, 1,12-Dodecanediol (7.5 g, 37.06 mmol) was dissolved in dry toluene (150 mL). The system was added with 48% HBr (5.07 mL HBr, 44.48 mmol) at 115°C and refluxed overnight. After completing the reaction checked with TLC plates, water was used to the extraction of organic part. After removing water by using MgSO<sub>4</sub>, solvent was removed by evaporation under reduced pressure. The residue was purified by silica gel column chromatography (n-hexane/EtOAc) to afford **1-1** as a light yellow liquid. Yield: 80%. <sup>1</sup>H NMR (300 MHz,

CDCl<sub>3</sub>)  $\delta$  (ppm): 3.67 (t,  $J$  = 6.5 Hz, 2H), 3.42 (t,  $J$  = 7.0 Hz, 2H), 1.81–1.91 (m, 2H), 1.53–1.61 (m, 2H), 1.25–1.48 (m, 16H)

**Synthesis of Benzyl 4-((12-bromododecyl)oxy)benzoate, (1-2).** Into a 250 mL double necked flask, **1-1** (5.578 g, 21.03 mmol), benzyl 4-hydroxybenzoate (4 g, 17.52 mmol) and triphenyl phosphine (6.908 g, 26.29 mmol) were pre-vacuumed for about an hour then pumped at least three times in gaseous nitrogen. Dry THF (100 mL) and DIAD (5.315 g, 26.29 mmol, at ice bath condition) were injected into the flask and stirred for 24 h at room temperature. After completing the reaction checked with TLC plates, the residue was washed with CH<sub>2</sub>Cl<sub>2</sub>, and water was used to the extraction of organic part. After removing water by using MgSO<sub>4</sub>, solvent was removed by evaporation under reduced pressure. The residue was purified by silica gel column chromatography (n-hexane/CH<sub>2</sub>Cl<sub>2</sub>) to afford **1-2** as a white liquid. Yield: 78%. <sup>1</sup>H NMR (300 MHz, DMSO)  $\delta$  (ppm): 7.90 (d,  $J$  = 7.2 Hz, 2H), 7.40–7.30 (m, 5H), 7.01 (d,  $J$  = 7.2 Hz, 2H), 5.29 (s, 2H), 4.01 (t,  $J$  = 6.3 Hz, 2H), 3.24 (t,  $J$  = 6.9 Hz, 2H), 1.73–1.67 (m, 4H), 1.38–1.23 (m, 16H)

**Synthesis of Benzyl 4-((12-(4-formylphenoxy)dodecyl)oxy)benzoate, (1-3).** Into a double neck bottle (500 mL), 4-hydroxybenzaldehyde (0.81 g, 6.64 mmol) was stirred and dissolved in acetonitrile (200 mL). K<sub>2</sub>CO<sub>3</sub> (2.5 g, 18.1 mmol) and KI of minute quantity were added in the solution and refluxed at 90°C. Solution of **1-2** (10.70 g, 22.5 mmol) into acetonitrile (100 mL) was dropped into the double neck flask slowly and reacted for at least eight hours. Furthermore, TLC plates were used to determine the reaction was complete. After cooling to room temperature, the mixture was added with HCl (aqueous) until pH value about 2 ~ 3. After removal of the solvent by evaporation under reduced pressure, the residue was extracted with water and EtOAc. Then, the organic layer was dried over anhydrous MgSO<sub>4</sub> After removal of

the solvent by evaporation under reduced pressure, the residue was purified by silica gel column chromatography (*n*-hexane/EtOAc) to afford **1-3** as a white solid. Yield: 82%. <sup>1</sup>H NMR (300 MHz, DMSO) δ (ppm): 9.83 (s, 1H), 7.91 (d, *J* = 8.7 Hz, 2H), 7.83 (d, *J* = 8.7 Hz, 2H), 7.40–7.30 (m, 5H), 7.09 (d, *J* = 8.7 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 5.29 (s, 2H), 4.08–3.99 (m, 4H), 1.73–1.67 (m, 4H), 1.38–1.23 (m, 16H)

**Synthesis of Benzyl4-((12-(4-(1-methylfulleropyrrolidin-2-yl)phenoxy)dodecyl)oxy)benzoate, (1-4).** Into a 500 mL round bottom flask, C<sub>60</sub> (0.32 g, 0.445 mmol) stirred and dissolved in chlorobenzene (300 mL). **1-3** (0.15 g, 0.295 mmol) and N-methylglycine (0.04 g, 0.445 mmol) were added into the flask. After refluxing at 135°C for 12 hours, TLC plates were used to make sure the reaction was complete. After cooling to room temperature, solvent was removed by evaporation under reduced pressure. Then the residue was purified by silica gel column chromatography (*n*-hexane/toluene) to afford **1-4** as a brown solid. Yield: 40%.

**Synthesis of 4-((12-(4-(1-methylfulleropyrrolidin-2-yl)phenoxy)dodecyl)oxy)benzoic acid, (FIA).** Into a double neck bottle (500 mL), **1-4** (0.1 g, 7.9 × 10<sup>-2</sup> mmol) was pre-vacuumed for about an hour then pumped at least three times in nitrogen. THF (100 mL), 10% Pd-C (10 mg, work as catalyst), toluene (dried, 20 mL) and HCOONH<sub>4</sub> (0.015 g, 0.24 mmol) were added in the flask. The mixture was stirred at 60°C for 2 hours. Then the TLC plates were used to make sure the reaction was complete. THF was used to wash the residue. After being concentrated and dried, the mixture was recrystallized by THF/*n*-hexane to afford **FIA** as a brown solid. Yield: 65%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 8.00 (d, *J* = 9.0 Hz, 2H), 7.40 (m, 4H), 6.88 (d, 2H), 4.96 (d, *J* = 9.0 Hz, 1H), 4.87 (s, 1H), 4.22 (d, *J* = 9.0 Hz, 1H), 4.01-3.92 (m, 4H), 2.78 (s, 3H), 1.75 (m, 4H), 1.36-1.23 (m, 16H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ (ppm) = 26.26, 29.38, 29.84, 30.60, 34.49, 40.29, 66.61, 68.23, 68.48, 70.22, 114.37, 114.81, 122.50, 124.73, 128.35, 128.95, 136.08, 139.83, 140.16, 140.41,

141.79, 141.94, 142.08, 142.25, 143.4, 144.65, 144.87, 144.97, 145.39, 145.52, 145.59, 145.76, 146.03, 146.38, 146.46, 146.55, 147.07, 147.33, 147.55, 159.44, 163.32, 166.49. Anal. Calcd for C<sub>88</sub>H<sub>39</sub>NO<sub>4</sub>: C, 90.01; H, 3.35; N, 1.19. Found: C, 90.58; H, 2.86; N, 0.99 (similar to the previous report,<sup>1</sup> the elemental analysis deviates by more than 0.5 % may resulted from difficult purification due to the high polarity of C<sub>60</sub>-based molecules). MS (FAB-) *m/z*: 1173.3 (M); found, 1174.6

## B. Synthesis of FIIA

**Synthesis of Benzyl 4-((12-hydroxydodecyl)oxy)benzoate, (2-1).** Into a double neck bottle (500 mL), benzyl 4-hydroxybenzoate (6.00 g, 26.3 mmol) was stirred and dissolved in acetone (200 mL). K<sub>2</sub>CO<sub>3</sub> (9 g, 65.7 mmol) and KI of minute quantity were added in the solution and refluxed at 70°C. Solution of **1-1** (8.364 g, 31.5 mmol) into acetone (100 mL) was dropped into the double neck flask slowly and reacted for at least 12 hours. TLC plates were used to make sure the reaction was complete. After cooling to room temperature, the solvent was removed by evaporation under reduced pressure, and the residue was extracted with water and EtOAc, then, the organic layer was dried over anhydrous MgSO<sub>4</sub>. After being concentrated and dried, the mixture was purified by silica gel column chromatography (*n*-hexane/EtOAc) to afford **2-1** as a white solid. Yield: 92%. <sup>1</sup>H NMR (300 MHz, DMSO) δ (ppm): 7.91 (d, *J* = 8.7 Hz, 2H), 7.40–7.30 (m, 5H), 7.01 (d, *J* = 8.7 Hz, 2H), 5.29 (s, 2H), 4.01 (t, *J* = 6.6 Hz, 2H), 3.30 (m, 2H), 1.73–1.61 (m, 4H), 1.38–1.13 (m, 16H)

**Synthesis of Bis(12-(4-((benzyloxy)carbonyl)phenoxy)dodecyl) malonate, (2-2).** Into a round bottle (500 mL), **2-1** (0.52 g, 1.25 mmol), DMAP (0.15 g, 1.25 mmol, catalyst) and CH<sub>2</sub>Cl<sub>2</sub> (dried, 100 mL) were stirred

and dissolved well; and malonyl dichloride (0.061 mL, 0.62 mmol) was dropped slowly into the flask. The mixture was reacted for two hours at room temperature. The solvent was removed by evaporation under reduced pressure, and the mixture was purified by silica gel column chromatography (*n*-hexane/CH<sub>2</sub>Cl<sub>2</sub>) to afford **2-2** as a white solid. Yield: 78%. <sup>1</sup>H NMR (300 MHz, DMSO) δ (ppm): 7.90 (d, *J* = 9.0 Hz, 4H), 7.50–7.30 (m, 10H), 7.01 (d, *J* = 9.0 Hz, 4H), 5.29 (s, 4H), 4.04–3.96 (m, 8H), 3.45 (s, 2H), 1.75–1.58 (m, 4H), 1.56–1.44 (m, 4H), 1.42–1.10 (m, 32H)

**Synthesis of Bis(12-(4-((benzyloxy)carbonyl)phenoxy)dodecyl)(1,2-methanofullerene C<sub>60</sub>)-61,61-malonate, (2-3).** Into a 500 mL round bottom flask, C<sub>60</sub> (0.57 g, 79 mmol) was pre-vacuumed for about an hour then pumped at least three times in nitrogen. **2-2** (0.47 g, 0.53 mmol), I<sub>2</sub> (0.13 g, 0.53 mmol) and toluene (dried, 300 mL) were added and stirred to dissolve into the flask. After stirring for 10 minutes, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, catalyst, 0.8 mL, 5.3 mmol) was injected into the flask in nitrogen. After stirring for 10 minutes, the residue was washed by water for three times, and the organic layer was dried over anhydrous MgSO<sub>4</sub>. After being concentrated and dried, the mixture was purified by silica gel column chromatography (toluene/EtOAc) to afford **2-3** as a black brown gel. Yield: 35%.

**Synthesis of 4,4'-(((malonylbis(oxy))bis(dodecane-12,1-diyl))bis(oxy))(1,2-methanofullerene C<sub>60</sub>)-61,61-dibenzoic acid, (FIIA).** Into a double neck bottle (500 mL), **2-3** (0.5 g, 0.31 mmol) was pre-vacuumed for about an hour then pumped at least three times in nitrogen. THF (100 mL), 10% Pd-C (catalyst, 50 mg), toluene (dried, 20 mL) and HCOONH<sub>4</sub> (0.03 g, 0.48 mmol) were added in the flask. The mixture was stirred at 60°C for 2 hours. Then the TLC plates were used to make sure the reaction was complete. THF was used to wash the residue. After being concentrated and dried, the mixture was recrystallized by THF/*n*-hexane

to afford **IIA** as a brown solid. Yield: 50%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.96 (d,  $J = 9.0$  Hz, 4H), 6.90 (d,  $J = 8.8$  Hz, 4H), 4.47 (m,  $J = 6.6$  Hz, 4H), 4.01 (t,  $J = 6.6$  Hz, 4H), 1.89 (m, 8H), 1.43–1.29 (m, 32H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 26.01, 28.52, 29.13, 29.21, 29.40, 29.58, 67.31, 68.18, 114.05, 122.30, 131.55, 138.50, 138.59, 138.67, 139.12, 139.13, 139.18, 140.13, 140.34, 141.02, 141.20, 141.54, 141.84, 142.05, 142.32, 142.51, 142.85, 143.02, 143.36, 143.57, 144.01, 144.34, 144.58, 145.09, 145.11, 145.28, 145.37, 145.54, 146.02, 146.15, 146.45, 146.93, 147.21, 147.68, 162.93, 166.89. Anal. Calcd for  $\text{C}_{101}\text{H}_{58}\text{O}_{10}$ : C, 84.74; H, 4.08. Found: C, 85.33; H, 4.55 (similar to the previous report,<sup>1</sup> the elemental analysis deviates by more than 0.5 % may resulted from difficult purification due to the high polarity of  $\text{C}_{60}$ -based molecules). MS (FAB+)  $m/z$ : 1430.4 (M); found, 1431.1.

### C. Synthesis of **IIA**

**Synthesis of 4,4'-(((malonylbis(oxy))bis(dodecane-12,1-diyl))bis(oxy))dibenzoic acid, (IIA).** Into a double neck bottle (500 mL), **2-2** (5.00 g, 7.01 mmol), THF (200 mL), 10% Pd-C (catalyst, 2.5 g) were mixed and stirred overnight. TLC plates were used to make sure the reaction was finished. The residue was washed with  $\text{CH}_2\text{Cl}_2$ . After being concentrated and dried, the mixture was recrystallized by  $\text{CH}_2\text{Cl}_2/n$ -hexane to afford **IIA** as a white solid. Yield: 95%.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm) = 7.85 (d,  $J = 9.0$  Hz, 4H), 6.97 (d,  $J = 8.7$  Hz, 4H), 4.05–3.97 (m, 8H), 3.46 (s, 2H), 2.11–2.00 (m, 8H). 1.80–1.50 (m, 8H), 1.45–1.30 (m, 24H). Anal. Calcd for  $\text{C}_{41}\text{H}_{60}\text{O}_{10}$ : C, 69.07; H, 8.48. Found: C, 68.77; H, 8.41.

### D. Structure of **4-(Dimethylethylsiloxyl) undecyloxybenzoic acid, (SiA)**



The H-donor **SiA** was synthesized and reported in the reference,<sup>2</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 8.05 (d, *J* = 9.0 Hz, 2H), 6.95 (d, *J* = 9.0 Hz, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 1.81 (m, 2H), 1.52–1.32 (m, 16H), 0.92 (t, *J* = 8.1 Hz, 3H), 0.48 (t, *J* = 7.8 Hz, 4H), 0.01 (s, 6H). Anal. Calcd for C<sub>22</sub>H<sub>38</sub>O<sub>3</sub>Si : C, 69.79; H, 10.12. Found: C, 69.62; H, 10.05.

E. Structure of **3'-(4-(2,3-Difluoro-4-(tetradecyloxy)benzoyloxy)benzoyloxy)biphenyl-4-yl isonicotinate, (NBF14)**.

The steps of H-acceptor **NBF14** was reported in the reference,<sup>3</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 8.87 (d, 2H), 8.29 (d, *J* = 8.3 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.86 (m, 1H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 4.7 Hz, 2H), 7.46 (s, 1H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.23–7.19 (m, 1H), 6.89–6.82 (m, 1H), 4.10 (t, *J* = 6.3 Hz, 2H), 1.80–1.75 (m, 2H), 1.43–1.28 (m, 22H), 0.86 (t, *J* = 6.3 Hz, 3H). Anal. Calcd for C<sub>46</sub>H<sub>47</sub>F<sub>2</sub>NO<sub>7</sub>: C, 72.33; H, 6.20; N, 1.83. Found: C, 72.15; H, 6.42; N, 1.83.

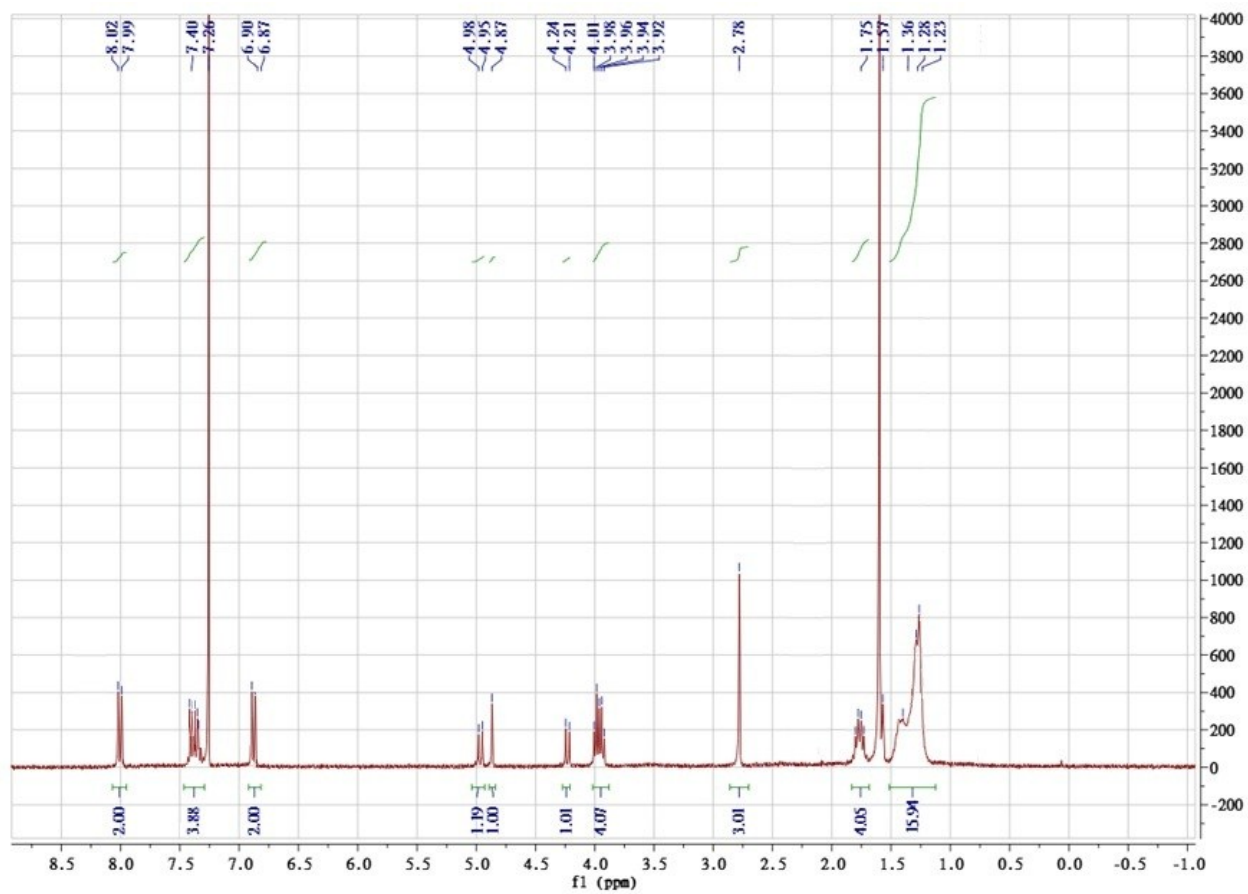
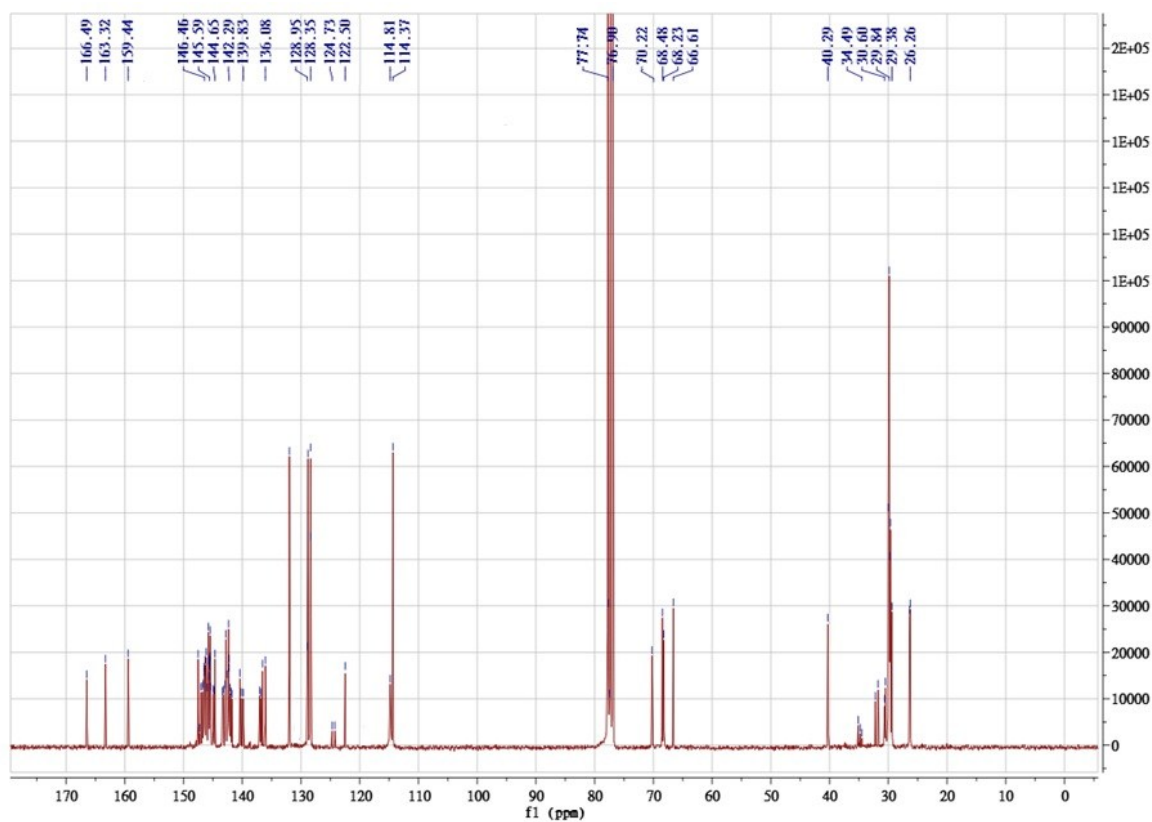


Fig. S1  $^1\text{H}$  NMR spectrum of FIA in  $\text{CDCl}_3$ .

(a)



(b)

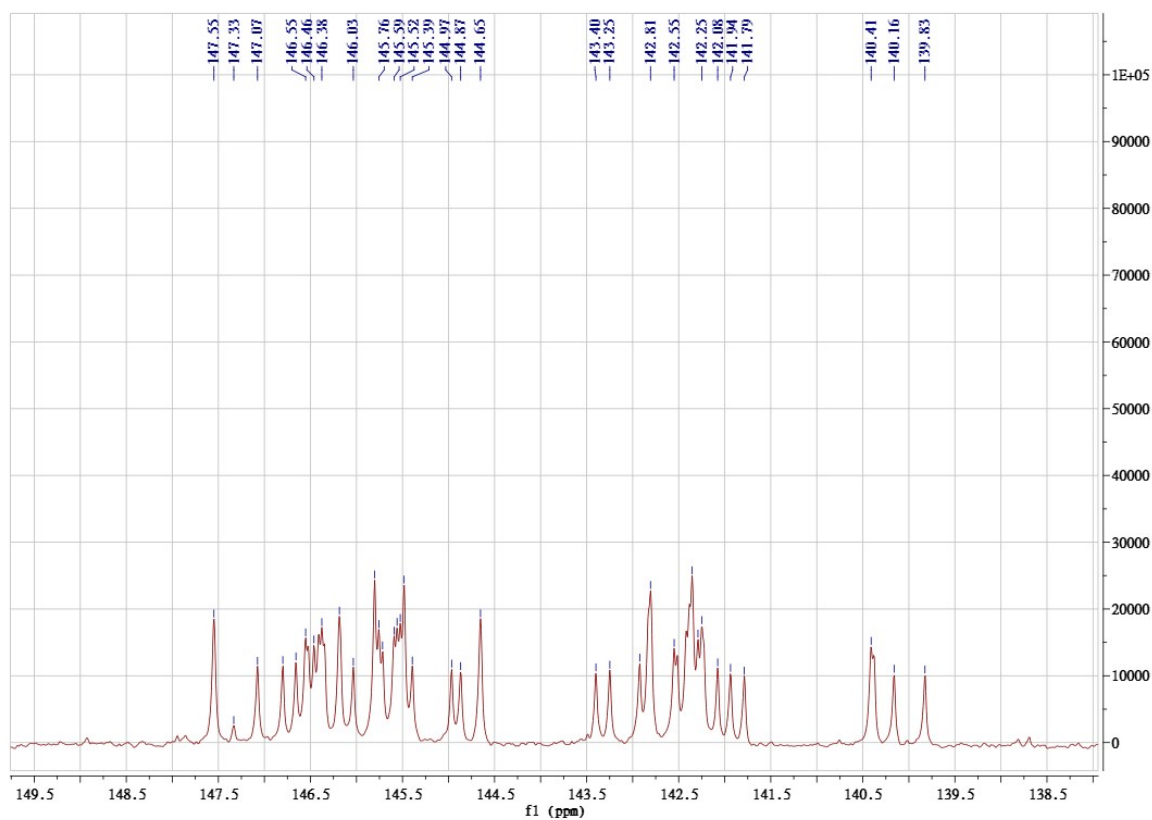
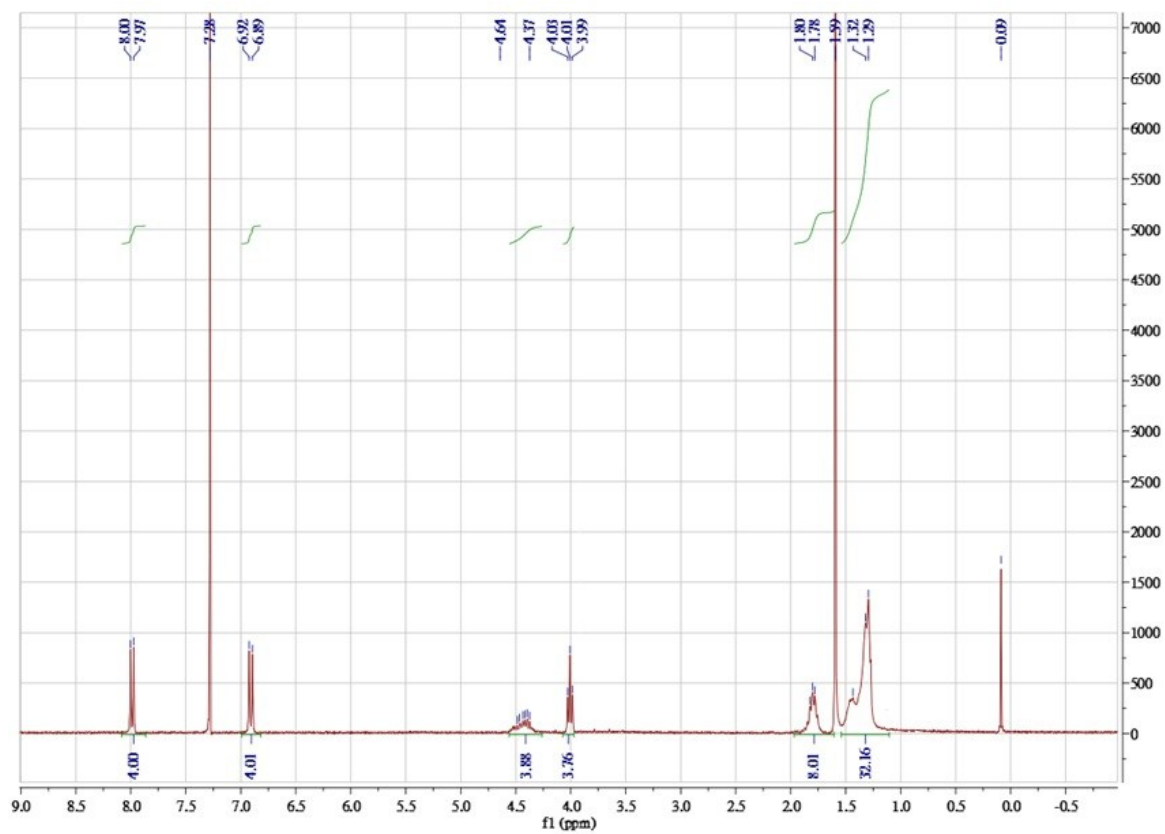
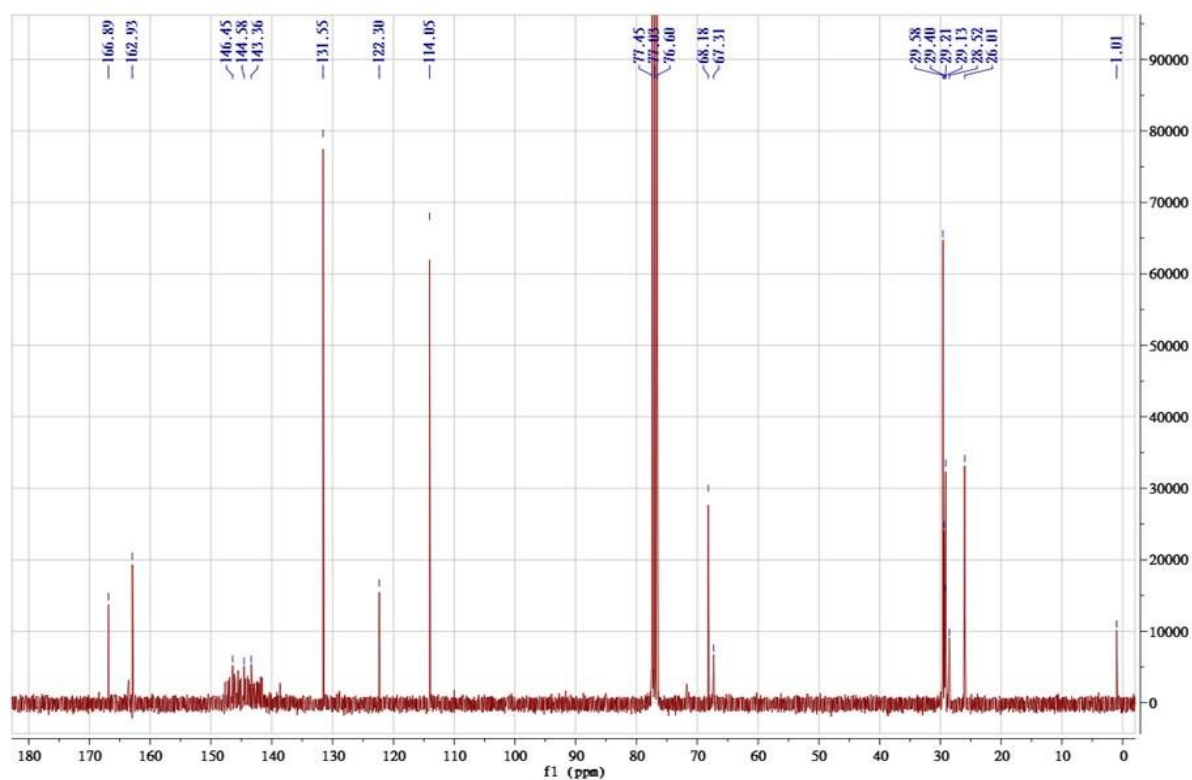


Fig. S2 (a) full and (b) expanded  $^{13}\text{C}$  NMR spectra of FIA in  $\text{CDCl}_3$ .

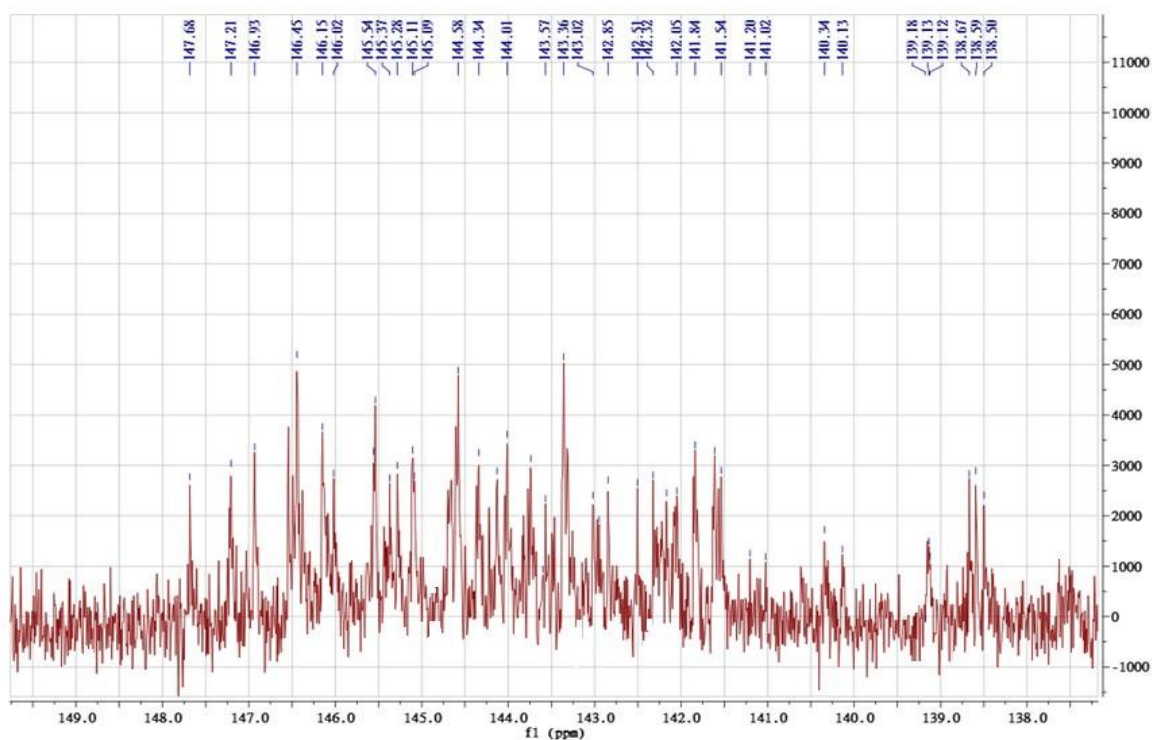


**Fig. S3**  $^1\text{H}$  NMR spectrum of FIIA in  $\text{CDCl}_3$ .

(a)



(b)



**Fig. S4** (a) full and (b) expanded  $^{13}\text{C}$  NMR spectra of **FIIA** in  $\text{CDCl}_3$ .

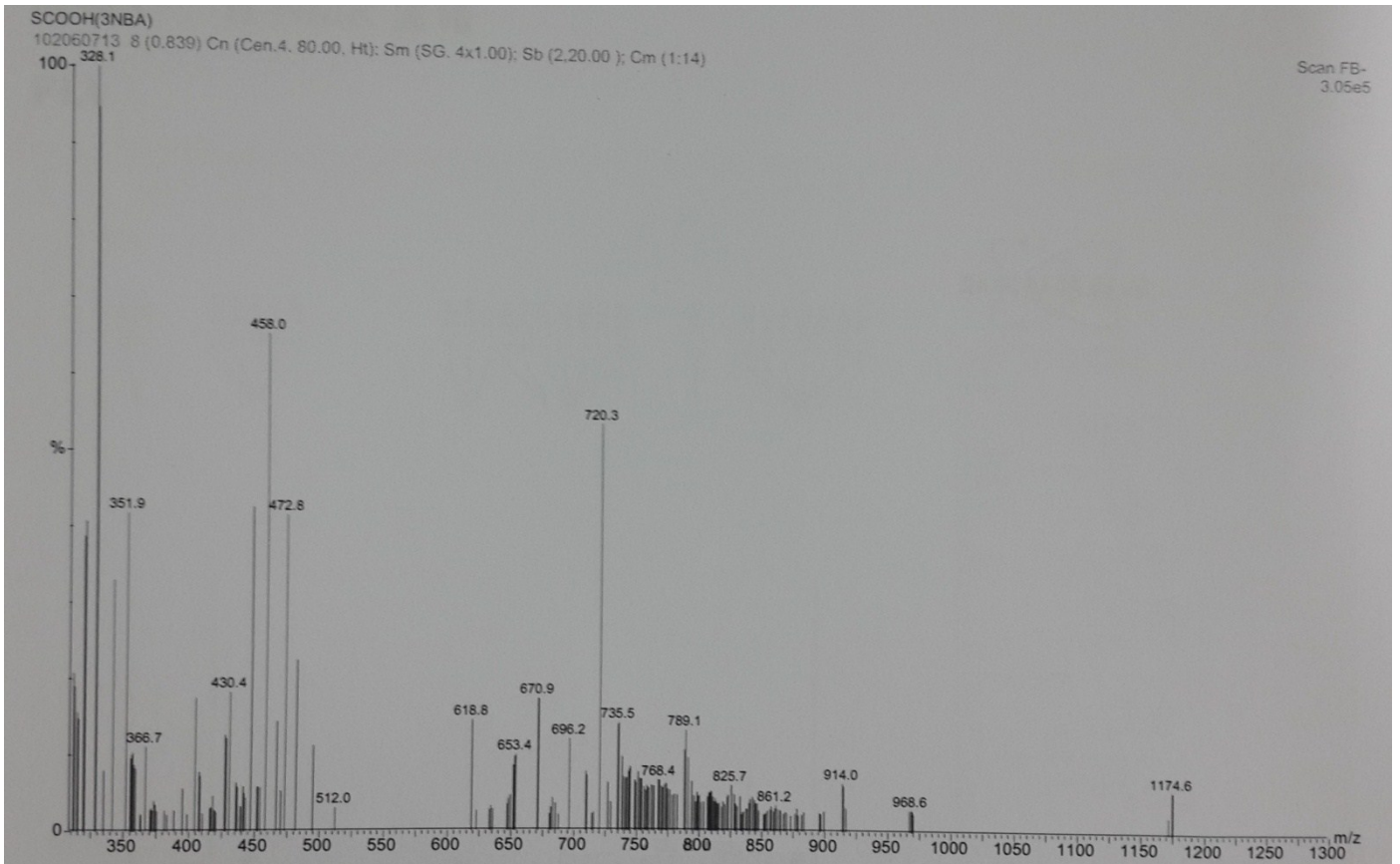


Fig. S5 Mass spectrum of FIA.

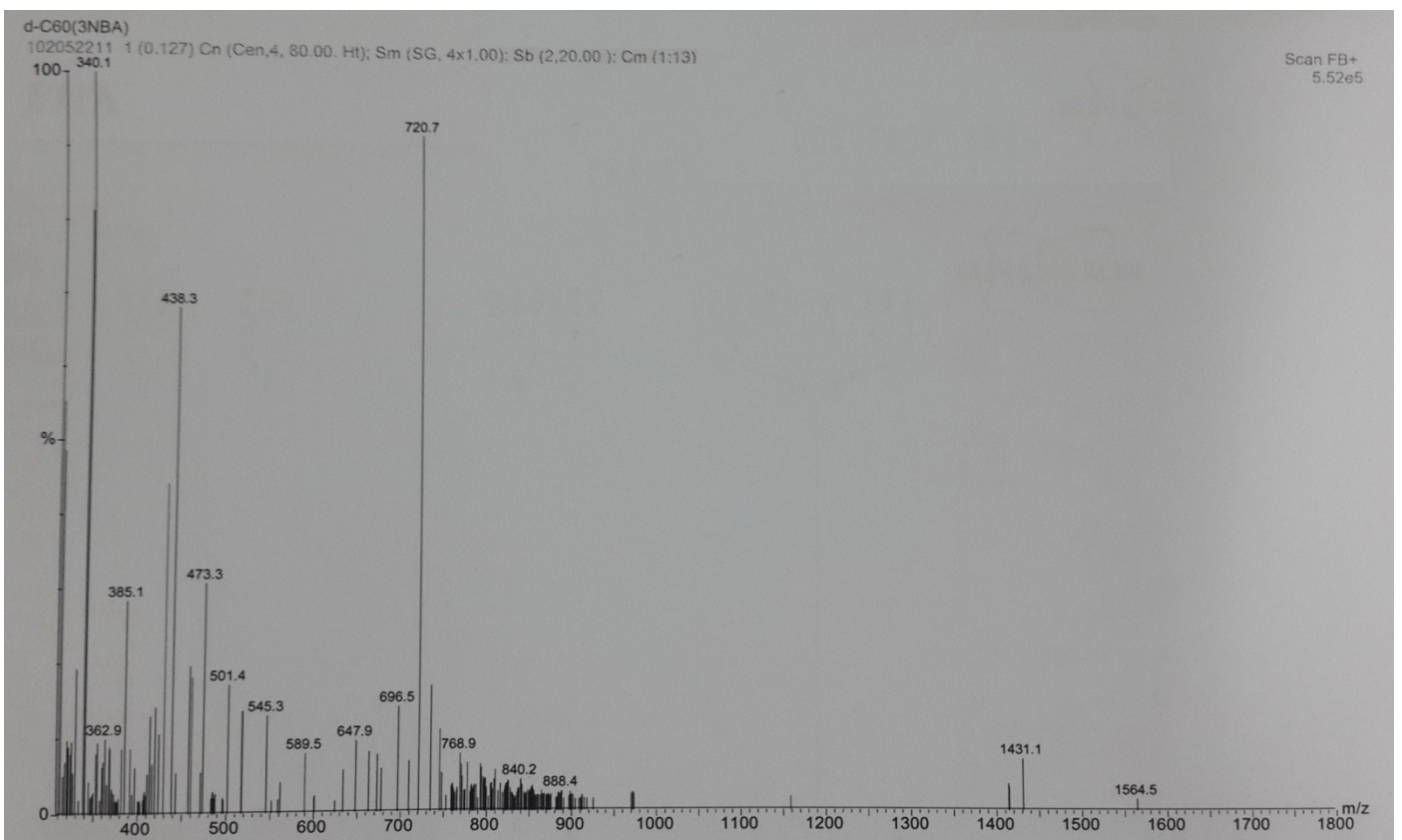
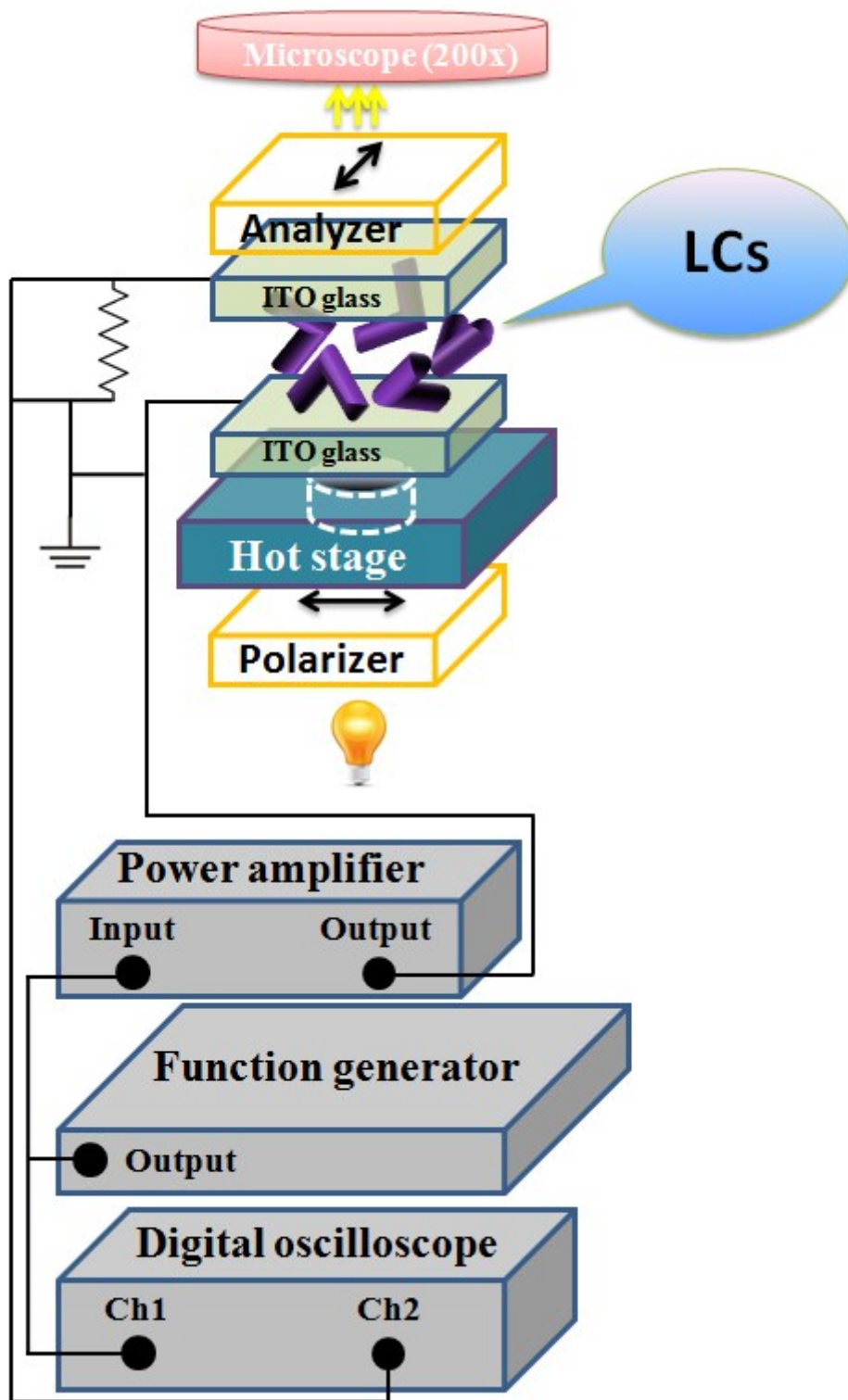
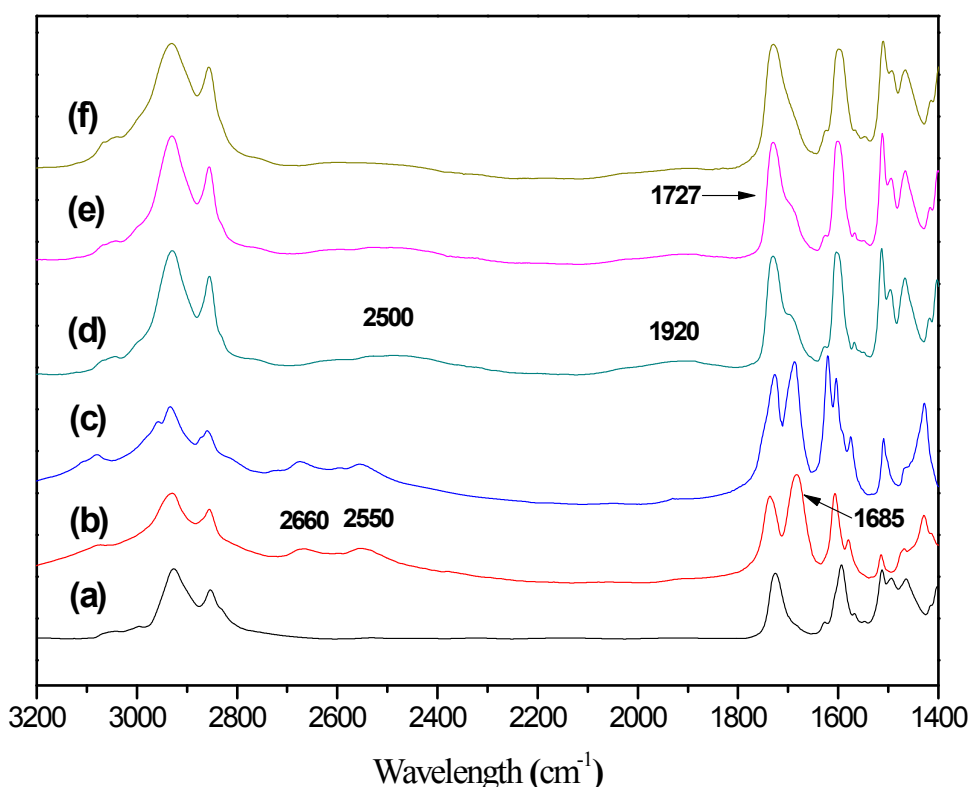


Fig. S6 Mass spectrum of FIIA.



**Fig. S7** Setup for spontaneous polarization measurement.

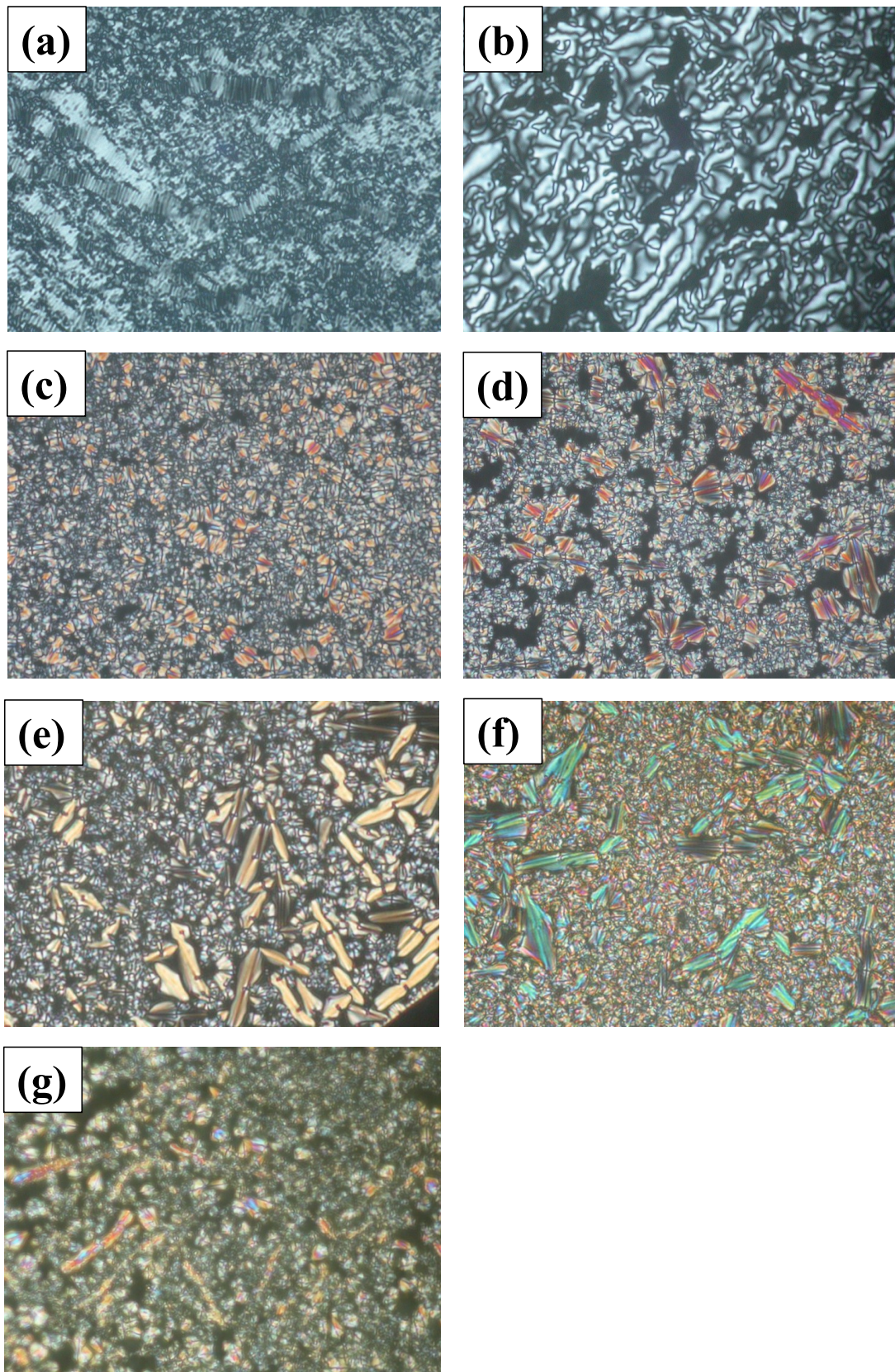


**Fig. S8** FT-IR spectra recorded for (a) pure proton acceptor **NBF14**, (b) pure proton donor **FIIA**, (c) pure proton donor **SiA**, and (d) H-bonded complex **FIIA50** at room temperature, (e) H-bonded complex **FIIA50** in the SmCP phase at 95°C and (f) in the isotropic state at 125 °C. (cooling from the isotropic state).

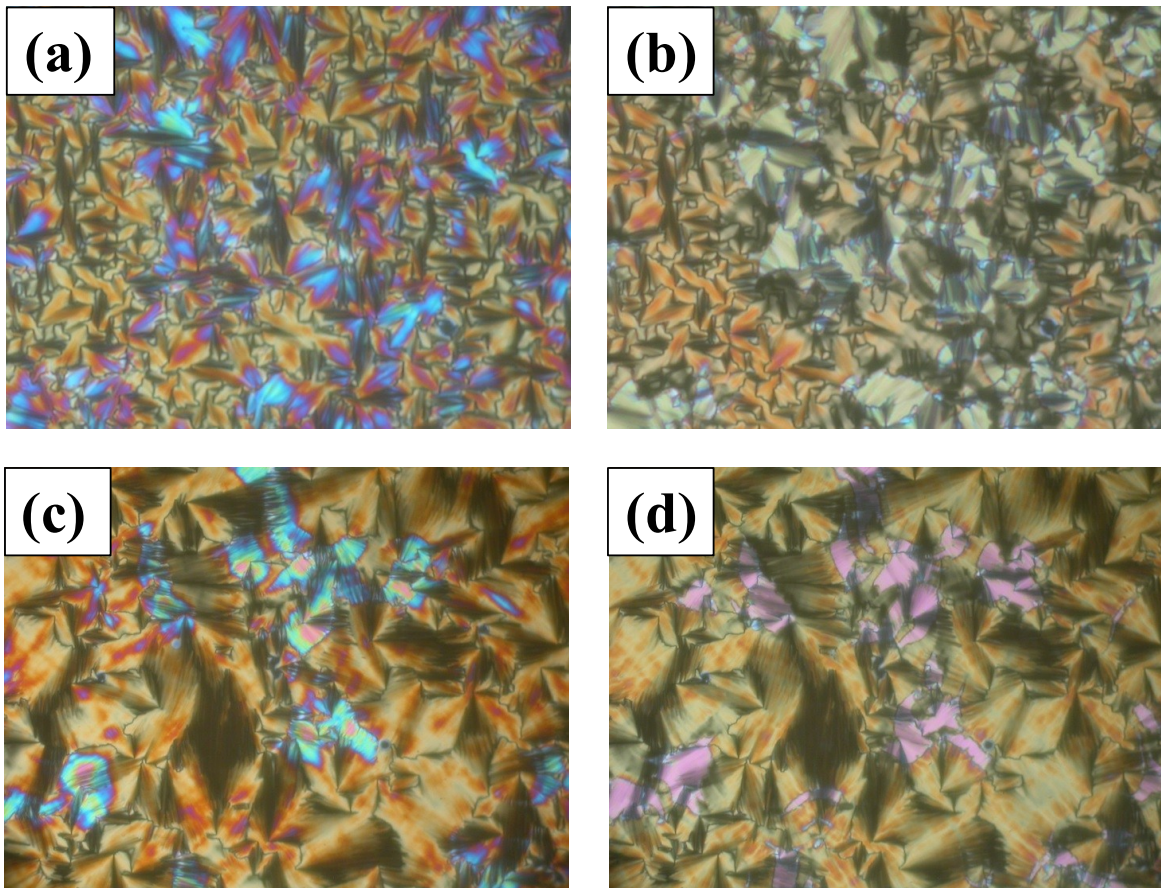
The existence of hydrogen bonds in the mesophases can be confirmed by temperature-various FTIR spectroscopy. Therefore, the IR spectra of proton acceptor **NBF14**, proton donors **FIIA** and **SiA**, and H-bonded complex **FIIA50** at room temperature are shown in Fig. S2, which are compared to analyze the formation of hydrogen bonds. In contrast to the O-H bands of pure proton donor (H-bonded dimer) **SiA** at 2660 and 2550  $\text{cm}^{-1}$  (similar to proton donor **FIIA**), the weaker O-H bands observed at 1925 and 2500  $\text{cm}^{-1}$  in H-bonded complex **FIIA50** are indicative of stronger hydrogen bonding between the pyridyl groups of proton acceptor **NBF14** and the carboxylic acids of proton donors **FIIA** and **SiA** in the H-bonded complex **FIIA50**. On the other hand, a stretching vibration of C=O at 1685  $\text{cm}^{-1}$  in pure proton donor **SiA** is shifted



toward higher wavenumber and overlapped with the band of the ester carbonyl group at  $1727\text{ cm}^{-1}$  in H-bonded complex **FIIA50**, which shows that the carbonyl group was in a less associated state than that in the pure H-bonded dimer state of proton donor **SiA**. These results suggest that hydrogen bonds were formed between proton acceptor **NBF14** and proton donors **FIIA** and **SiA** in the solid state of H-bonded complex **FIIA50**. In addition, when cooling from the isotropic state to the SmCP phase at  $95^{\circ}\text{C}$ , two broad O-H bands centered at  $2660$  and  $2550\text{ cm}^{-1}$  still persist due to the stable H-bands. These consequences show that hydrogen bonds were formed between proton acceptor **NBF14** and proton donors **FIIA** and **SiA** in the SmCP phase. The characteristic bands centered at  $1920\text{ cm}^{-1}$  and  $2500\text{ cm}^{-1}$  were observed to become broader and weaker in the isotropic state.

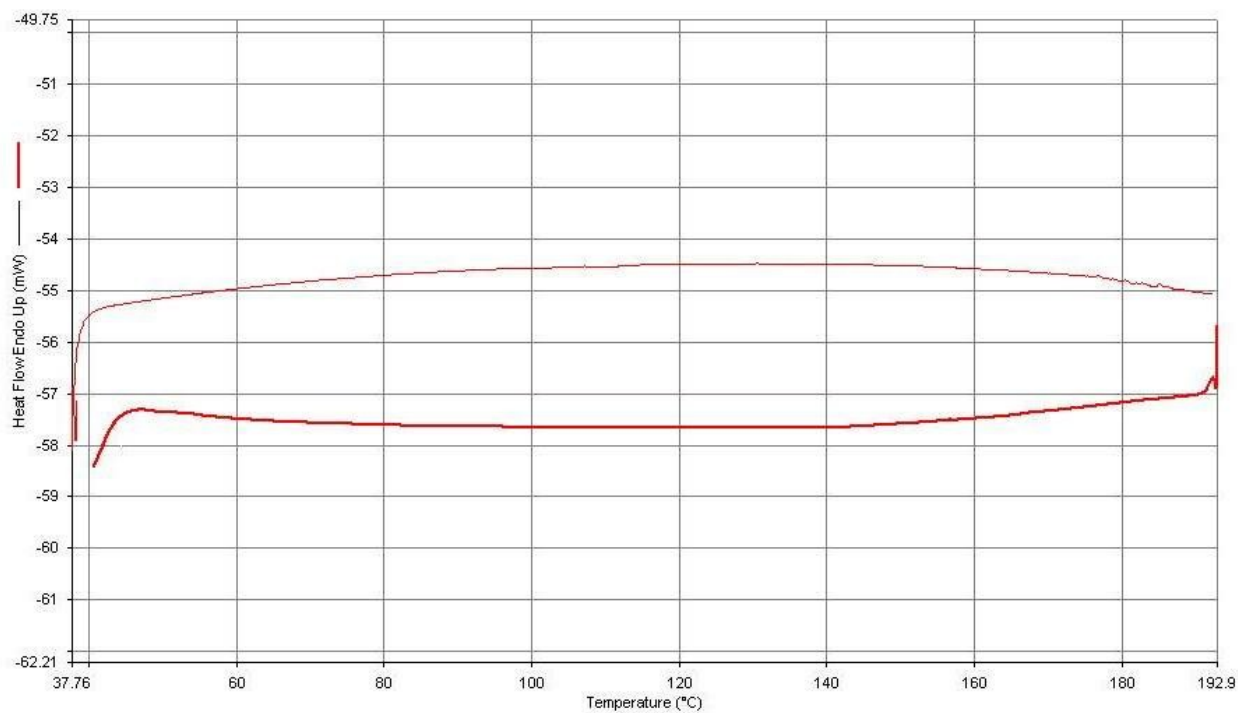


**Fig. S9** POM images obtained upon cooling from the isotropic phase: (a) the schlieren and fan-shaped textures of **SiA100** in the  $\text{SmCP}_A$  phase at  $105^\circ\text{C}$ , (b) the schlieren texture of **IIA100** in the  $\text{SmC}$  phase at  $126.5^\circ\text{C}$  and (c), (d) the fan-shaped and non-specific grainy textures of the  $\text{SmCP}_A$  phase in **FIA4** at  $100^\circ\text{C}$  and **FIIA4** at  $105^\circ\text{C}$ , respectively, (e) **FIA24** at  $103^\circ\text{C}$ , (f) **FIIA24** at  $99^\circ\text{C}$  and (g) **FIA90** obtained in the  $\text{SmCP}_F$  phase at  $75^\circ\text{C}$ .

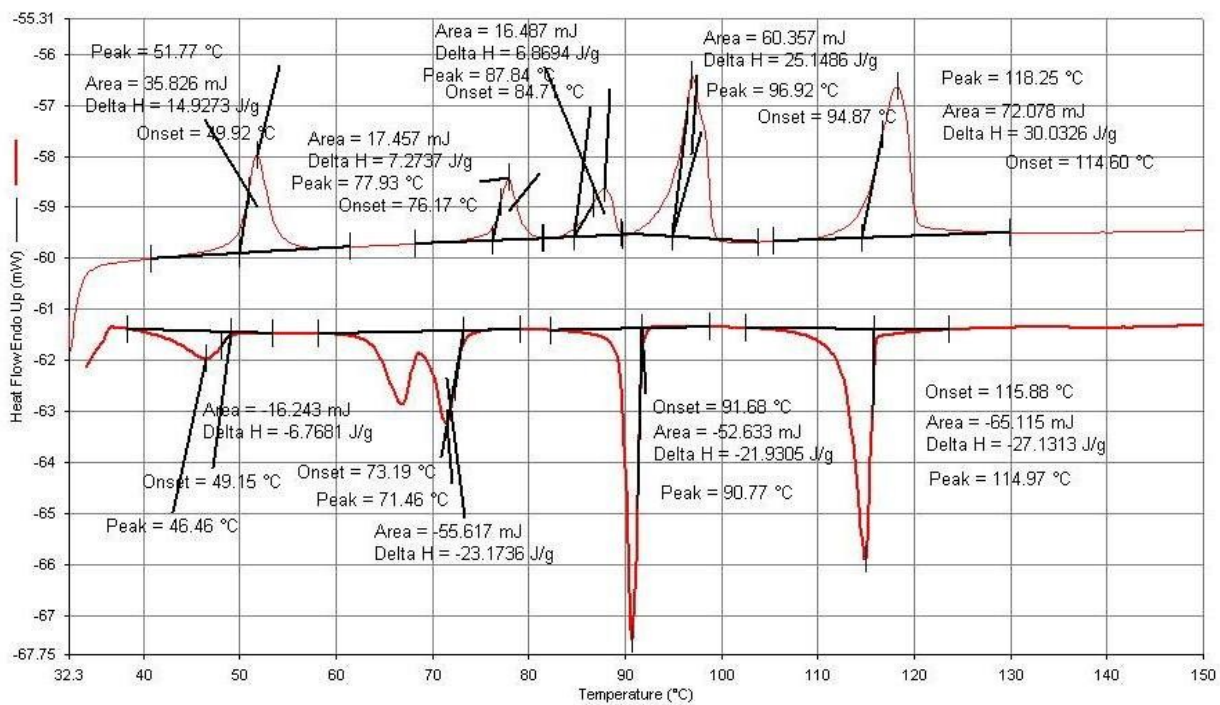


**Fig. S10** POM images of the birefringent fan-shaped texture obtained in the  $\text{SmCP}_A$  and  $\text{SmCP}_F$  phases of **FIA24** and **FIA76**, respectively, under a triangular-wave electric field (frequency of 50 Hz) at 90 °C (cooling). **FIA24**: (a) 11V/ $\mu\text{m}$ , (b) 0 V/ $\mu\text{m}$ , **FIA76**: (c) 23 V/ $\mu\text{m}$ , (d) 0 V/ $\mu\text{m}$ . (non-rubbed LC cells with a 9  $\mu\text{m}$  cell gap).

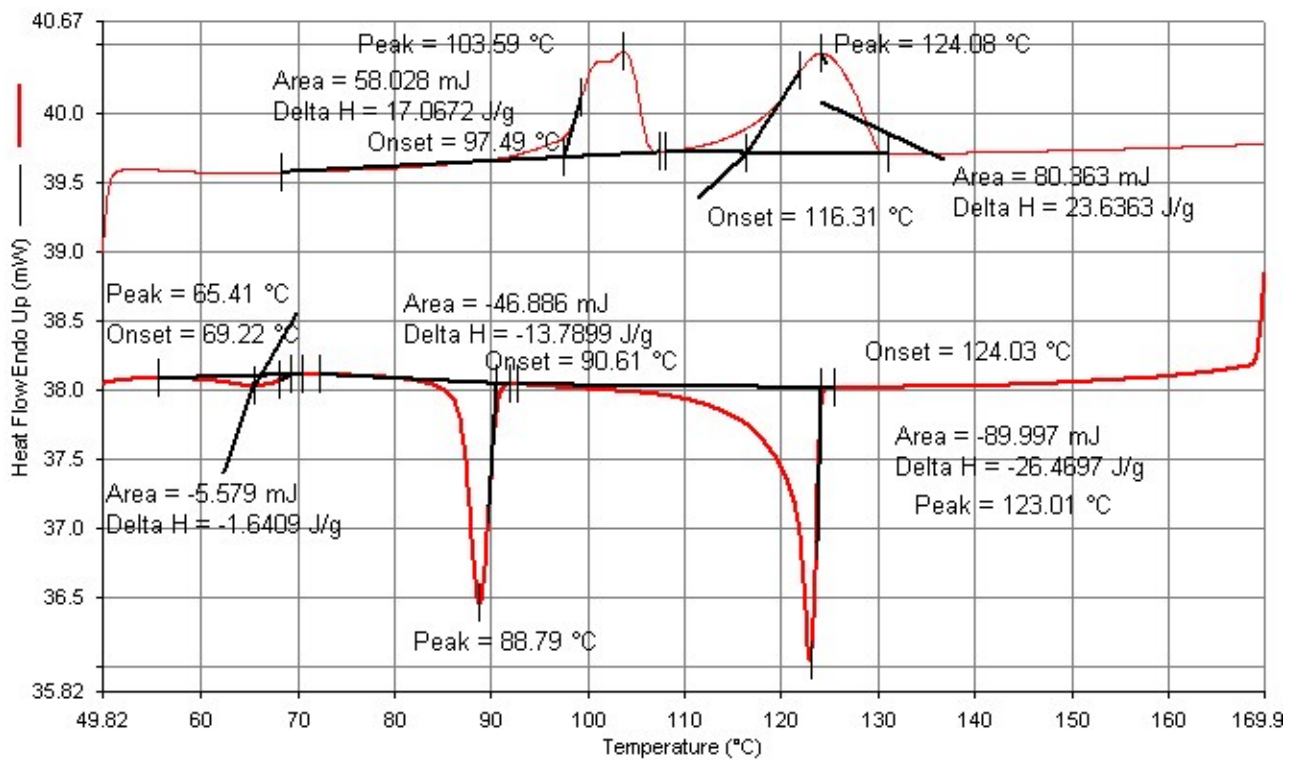
(a)



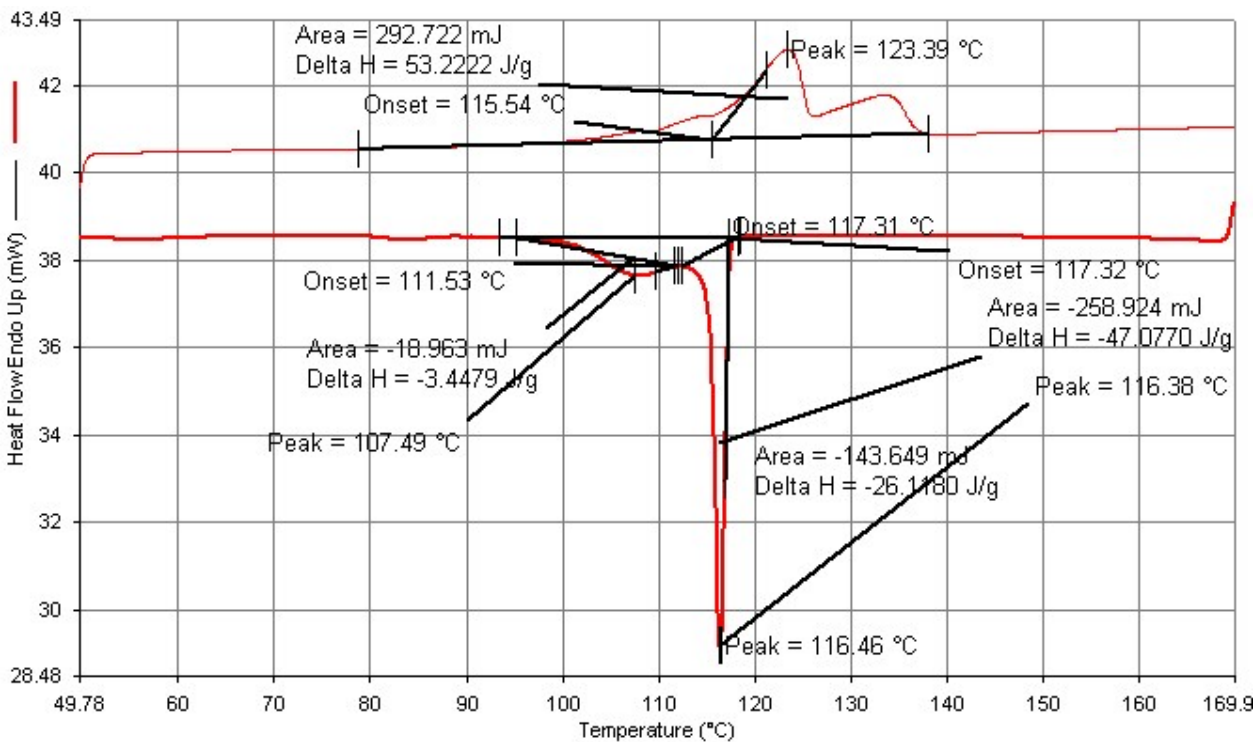
(b)



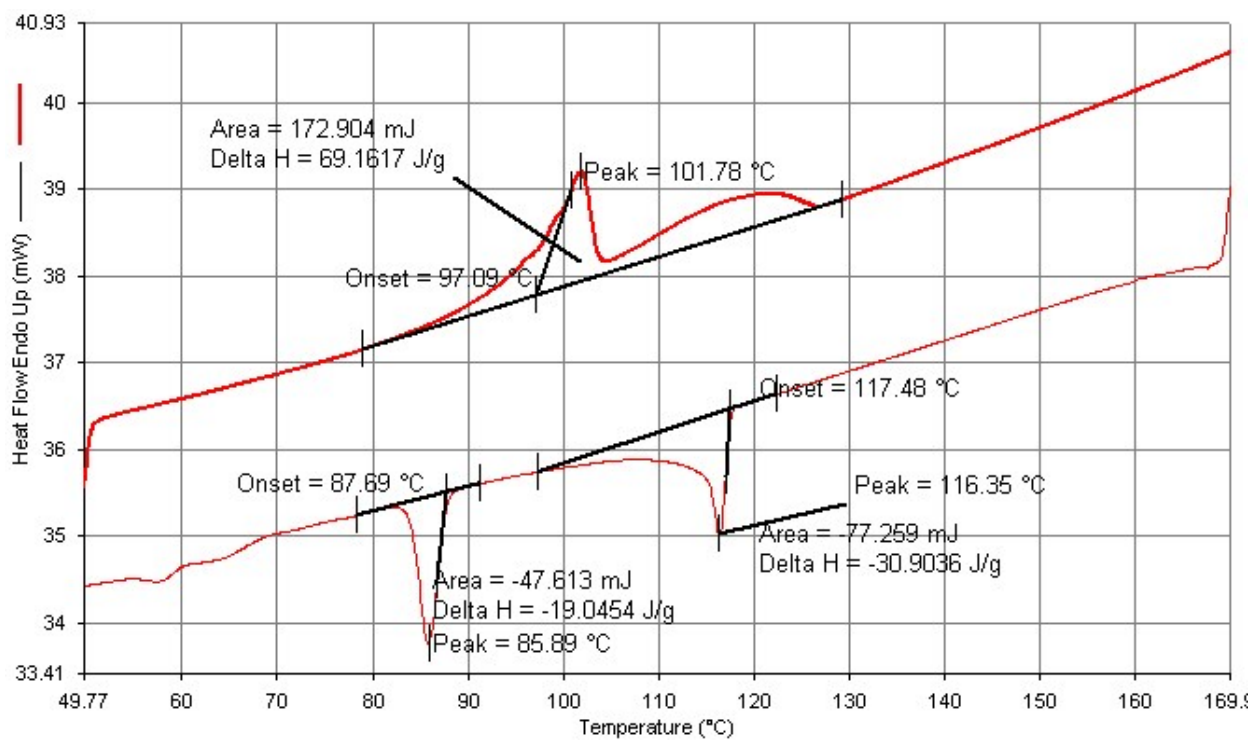
(c)



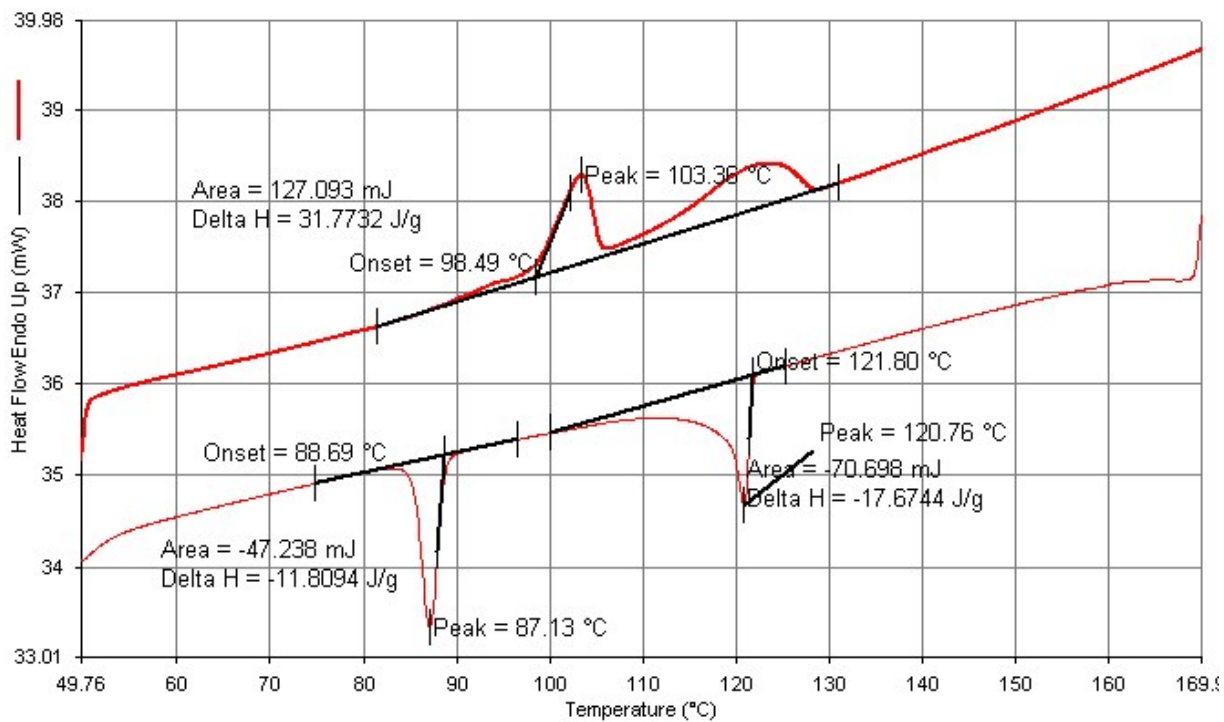
(d)



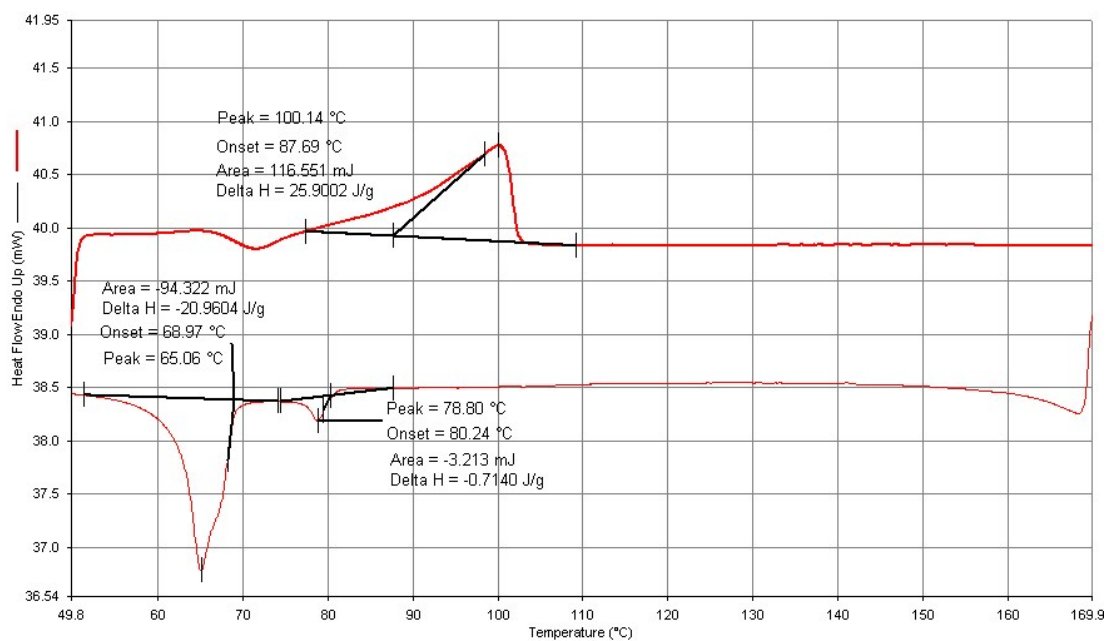
(e)



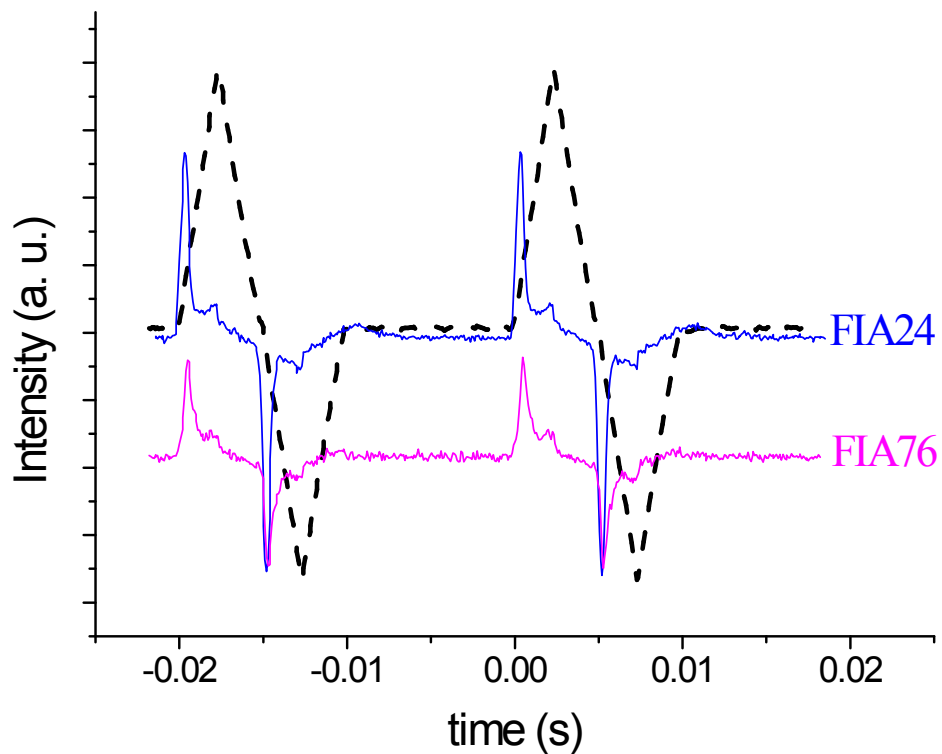
(f)



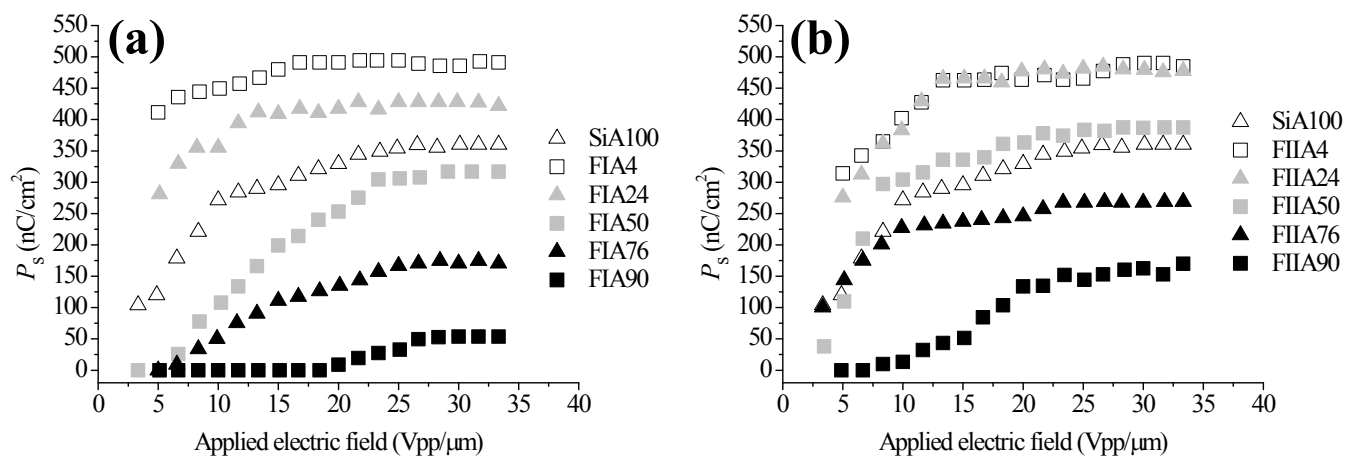
(g)



**Fig. S11** DSC thermograms obtained during the the 2<sup>nd</sup> heating (top) and 1<sup>st</sup> cooling (bottom) scans at a rate of 5°C/min: (a) FIA (b) SiA (c) SiA100, (d) IIA100, (e) FIA4, (f) FIIA4 and (g) FIA90.



**Fig. S12** Detailed switching current responses to the applied triangular waveform in the mesomorphic phases of **FIA24** (SmCP<sub>A</sub>) and **FIA76** (SmCP<sub>F</sub>).



**Fig. S13** Spontaneous polarization values vs. applied electric field of (a) **FIAx** and (b) **FIIAx** series.



**Table S1** Blending ratios of (a) **FIAx** and (b) **FIIAx** series

**(a)**

	<b>FIA</b>	<b>SiA</b>	<b>NBF14</b>	<b>x</b>	<b>wt%</b>
FIA100	100 mol%		100 mol%	100	100
FIA90	90 mol%	10 mol%	100 mol%	90	94
FIA76	76 mol%	24 mol%	100 mol%	76	84
FIA50	50 mol%	50 mol%	100 mol%	50	63
FIA24	24 mol%	76 mol%	100 mol%	24	35
FIA4	4 mol%	96 mol%	100 mol%	4	7

**(b)**

	<b>FIIA</b>	<b>SiA</b>	<b>NBF14</b>	<b>x</b>	<b>wt%</b>
FIIA100	50 mol%		100 mol%	100	100
FIIA90	45 mol%	10 mol%	100 mol%	90	92
FIIA76	38 mol%	24 mol%	100 mol%	76	80
FIIA50	25 mol%	50 mol%	100 mol%	50	56
FIIA24	12 mol%	76 mol%	100 mol%	24	29
FIIA4	2 mol%	96 mol%	100 mol%	4	5

**Table S2** Crystallographic parameters of synthesized compounds and hybrid complexes

Compound	Miller index	Q space/nm <sup>-1</sup>	d-spacing/nm	Theoretical length/nm	Tilt angle/°
<b>FIA100</b>				7.6	
<b>SiA100</b>	(01)	1.263	4.975	6.5	40.1
	(02)	2.541			
	(03)	3.817			
<b>FIIA100</b>				7.4	
<b>IIA100</b>	(01)	1.203	5.223	6.6	37.7
<b>FIA4</b>	(01)	1.257	4.999		
	(02)	2.535			
	(03)	3.798			
<b>FIA24</b>	(01)	1.273	4.936		
	(02)	2.545			
	(03)	3.844			
<b>FIA50</b>	(01)	1.314	4.782		
	(02)	2.633			
	(03)	3.947			
<b>FIA76</b>	(01)	1.317	4.771		
	(02)	2.641			
	(03)	3.978			
<b>FIA90</b>	(01)	1.355	4.637		
	(02)	2.742			
	(03)	4.057			
<b>FIIA4</b>	(01)	1.257	4.999		
	(02)	2.525			
	(03)	3.803			
<b>FIIA24</b>	(01)	1.278	4.916		
	(02)	2.568			
	(03)	3.863			
<b>FIIA50</b>	(01)	1.310	4.796		
	(02)	2.628			
	(03)	3.946			
<b>FIIA76</b>	(01)	1.312	4.789		
	(02)	2.625			
	(03)	3.950			
<b>FIIA90</b>	(01)	1.314	4.782		
	(02)	2.635			
	(03)	3.961			

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