

# ELECTRONIC SUPPLEMENTARY INFORMATION

## Ionic liquid crystals based on viologen dimers: not just a tale of tails

Girolamo Casella, Valerio Causin, Federico Rastrelli, and Giacomo Saielli\*

### I) SYNTHESSES

Synthesis of **12.I**

Synthesis of **14.Br**

Synthesis of **16.Br**

Synthesis of **14.2(Tf<sub>2</sub>N)<sub>2</sub>**

Synthesis of **14.14(Tf<sub>2</sub>N)<sub>2</sub>**

Synthesis of **12.4.12(Tf<sub>2</sub>N)<sub>4</sub>**

Synthesis of **14.4.14(Tf<sub>2</sub>N)<sub>4</sub>**

Synthesis of **16.4.16(Tf<sub>2</sub>N)<sub>4</sub>**

### II) SPECTROSCOPIC METHODS

POM

DSC

X-Ray diffraction

NMR

### III) NMR SPECTRA

Fig. S1 <sup>1</sup>H spectrum (500 MHz, MeOD) of **14.2(Tf<sub>2</sub>N)<sub>2</sub>**.

Fig. S2 <sup>13</sup>C spectrum (126 MHz, MeOD) of **14.2(Tf<sub>2</sub>N)<sub>2</sub>**.

Fig. S3 <sup>1</sup>H spectrum (500 MHz, MeOD) of **14.14(Tf<sub>2</sub>N)<sub>2</sub>**.

Fig. S4 <sup>13</sup>C spectrum (126 MHz, MeOD) of **14.14(Tf<sub>2</sub>N)<sub>2</sub>**.

Fig. S5 SS-MAS <sup>13</sup>C spectra (101 MHz) of **14.14(Tf<sub>2</sub>N)<sub>2</sub>** at different temperatures.

Fig. S6 SS-MAS <sup>19</sup>F spectra (376 MHz) of **14.14(Tf<sub>2</sub>N)<sub>2</sub>** at different temperatures.

Fig. S7 <sup>1</sup>H spectrum (500 MHz, MeOD) of **12.4.12(Tf<sub>2</sub>N)<sub>4</sub>**.

Fig. S8 <sup>13</sup>C spectrum (126 MHz, MeOD) of **12.4.12(Tf<sub>2</sub>N)<sub>4</sub>**.

Fig. S9 <sup>1</sup>H spectrum (500 MHz, MeOD) of **14.4.14(Tf<sub>2</sub>N)<sub>4</sub>**.

Fig. S10 <sup>13</sup>C spectrum (126 MHz, MeOD) of **14.4.14(Tf<sub>2</sub>N)<sub>4</sub>**.

Fig. S11 <sup>1</sup>H-<sup>1</sup>H COSY spectrum (400 MHz, MeOD) of **14.4.14(Tf<sub>2</sub>N)<sub>4</sub>**.

Fig. S12 <sup>1</sup>H-<sup>13</sup>C HMQC spectrum (400 MHz, MeOD) of **14.4.14(Tf<sub>2</sub>N)<sub>4</sub>**.

Fig. S13 <sup>1</sup>H-<sup>13</sup>C HMBC spectrum (400 MHz, MeOD) of **14.4.14(Tf<sub>2</sub>N)<sub>4</sub>**.

Fig. S14 <sup>1</sup>H spectrum (500 MHz, MeOD) of **16.4.16(Tf<sub>2</sub>N)<sub>4</sub>**.

Fig. S15 <sup>13</sup>C spectrum (126 MHz, MeOD) of **16.4.16(Tf<sub>2</sub>N)<sub>4</sub>**.

Fig. S16. DSC traces of **12.4.12(Tf<sub>2</sub>N)<sub>4</sub>**.

Fig. S17. DSC traces of **14.4.14(Tf<sub>2</sub>N)<sub>4</sub>**.

Fig. S18. DSC traces of **16.4.16(Tf<sub>2</sub>N)<sub>4</sub>**.

Fig. S19. DSC traces of **14.14**(Tf<sub>2</sub>N)<sub>2</sub>.

Fig. S20. DSC traces of **14.2**(Tf<sub>2</sub>N)<sub>2</sub>.

Fig. S21 Low angle region of the XRD traces of **14.4.14**(Tf<sub>2</sub>N)<sub>4</sub> in the crystal phase (25 °C), SmX phase (125 °C) and SmA phase (200 °C).

Fig. S22 XRD traces of **14.14**(Tf<sub>2</sub>N)<sub>2</sub> in the crystal (25 °C) and SmX (60 °C) phase.

Fig. S23 XRD traces of **12.4.12**(Tf<sub>2</sub>N)<sub>4</sub> in the crystal (25 °C and 75 °C), SmX (125 °C), SmA (165 °C) and isotropic phases (200 °C).

Fig. S24 POM images of **14.14**(Tf<sub>2</sub>N)<sub>2</sub>

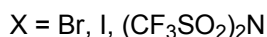
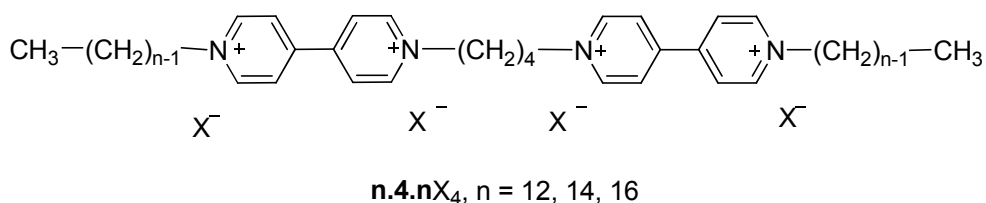
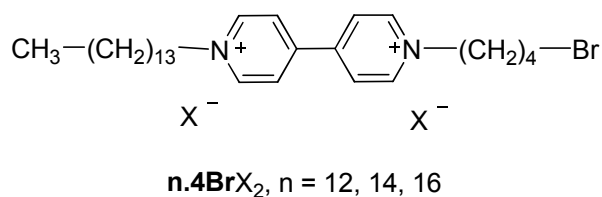
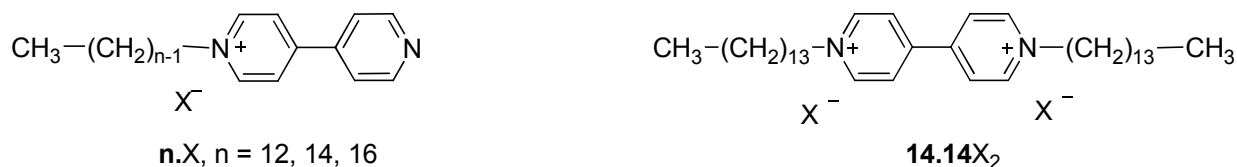
Fig. S25 POM images of **12.4.12**(Tf<sub>2</sub>N)<sub>4</sub>.

Fig. S26 POM images of **16.4.16**(Tf<sub>2</sub>N)<sub>4</sub>.

Fig. S27 POM image of **14.2**(Tf<sub>2</sub>N)<sub>2</sub>.

## SYNTHESES

The synthetic protocol has been reported already in our previous work (M. Bonchio, M. Carraro, G. Casella, V. Causin, F. Rastrelli and G. Saielli *Phys. Chem. Chem. Phys.*, **2012**, *14*, 2710–2717) and closely follows the work of M. F. Pepitone, G. G. Jernigan, J. S. Melinger, O. - Kim *Org. Lett.*, **2007**, *9*, 801–804.



Scheme 1. Structural formulae of the synthesized halide salts.

**I)** Synthesis of the intermediate monoalkylated salts 1-alkyl-4-pyridylpyridinium halides (**n.X**,  $n = 12, 14, 16$ ;  $X = \text{Br, I}$ ) and 1,1'-ditetradecylbipyridinium bromide (**14.14Br<sub>2</sub>**)

### a) 12.I

38.0 mmol (6.00 g) of bipyridine were refluxed with 12.7 mmol (3.13 mL) of 1-iodododecane in 50 mL of acetonitrile for 48 hrs. The solution was cooled to 4 °C and the dark red precipitate filtered and washed with toluene to remove the excess of bipyridine. The precipitate was dissolved in 20 mL of methanol leaving on the filter a small amount of insoluble residue. The methanol solution was concentrated to about 5 mL and stored at 4 °C. After 30 minutes a precipitate was formed, which was filtered and washed with cold acetone. The precipitate resulted fairly soluble in acetone. The volume of the filtrate was reduced again to 5 mL and stored at 4 °C. After 20 min a precipitate is formed which was filtered and added to the previous precipitate in the gooch filter and washed with cold (0 °C) Et<sub>2</sub>O. <sup>1</sup>H NMR (MeOD, 200 MHz):  $\delta = 9.14$  (d,  $J = 7.0$  Hz, 2H); 8.84 (m, 2H); 8.53 (d,  $J = 7.0$  Hz, 2H); 8.00 (m, 2H); 4.70 (t,  $J = 7.9$  Hz, 2H); 2.09 (m, 2H); 1.20–1.50 (m, 18H); 0.90 (t, 3H) ppm. Yield: 47%, 6 mmol (2.7 g).

### b) 14.Br and 14.14Br<sub>2</sub>

107 mmol (16.70 g) of bipyridine were refluxed with 107 mmol (31.8 mL) of 1-bromotetradecane in 150 mL of acetonitrile for 24 hrs. The yellow precipitate (**14.14Br<sub>2</sub>** + **14.Br**) was filtered, treated with warm DMF to separate the viologen (not soluble in DMF) from the monoalkylated (soluble in DMF). The viologen **14.14Br<sub>2</sub>** was then recrystallized from water/acetone 15:85 v/v. Yield 45%, 48.2 mmol (34.3 g). From the filtrate a pale-yellow precipitate was formed, after adding Et<sub>2</sub>O, containing a mixture of **14.Br** and bipyridine, as found from <sup>1</sup>H NMR analysis. The precipitate was filtered and washed with cold (0 °C) Et<sub>2</sub>O to remove the bipyridine. <sup>1</sup>H NMR (MeOD, 200 MHz): δ = 9.11 (d, *J* = 7.0 Hz, 2H); 8.83 (m, 2H); 8.51 (d, *J* = 7.0 Hz, 2H); 7.98 (m, 2H); 4.68 (t, *J* = 7.9 Hz, 2H); 2.07 (m, 2H); 1.20-1.50 (m, 22H); 0.89 (t, 3H) ppm. Yield 35%: 37 mmol (16 g) of **14.Br**.

### c) **16.Br**

64 mmol (10.00 g) of bipyridine were refluxed with 64 mmol (19.57 mL) of 1-bromohexadecane in 250 mL of acetonitrile for 24 hrs. The suspension was stored at 4 °C and after 1 hr was filtered. The precipitate was added to DMF (35 °C). A suspension was formed which was filtered. Et<sub>2</sub>O was added to the filtrate and the flask stored in fridge. After 2 hrs a white precipitate was formed, which was filtered and washed with cold Et<sub>2</sub>O. <sup>1</sup>H NMR (MeOD/D<sub>2</sub>O, 200 MHz): δ = 9.00 (d, *J* = 7.0 Hz, 2H); 8.91 (m, 2H); 8.59 (d, *J* = 7.0 Hz, 2H); 8.08 (m, 2H); 2.16 (m, 2H); 1.20-1.50 (m, 26H); 0.96 (t, 3H) ppm. Yield 17%: 11 mmol (5 g) of **16.Br**.

**II**) Synthesis of the viologens 1,1'-ditetradecylbipyridinium (**14.14**) and the viologen dimers (**m.4.m**) bis(trifluoromethanesulfonyl)amide salts.

### **14.2(Tf<sub>2</sub>N)<sub>2</sub>**

1.15 mmol (500 mg) of 14BPBr were refluxed with 24.12 mmol (1.8 mL) of bromoethane in 25 mL of acetonitrile at 80 °C. After 3 hr a precipitate was formed. The reaction was left to react for 72 hrs. The suspension was then cooled to room temperature and the precipitate was filtered and washed with cold (0 °C) acetone. Yield: 79% (540 mg) of **14.2Br<sub>2</sub>**. 0.55 mmol (300 mg) of **14.2Br<sub>2</sub>** were dissolved in 10 mL of methanol and added with 10 mL of methanol solution containing 1.41 mmol (405 mg) of LiTf<sub>2</sub>N and the solution stirred for 4 hrs. The solvent was evaporated under *vacuum* and a white precipitate was formed after adding water to the flask. The white precipitate was then filtered and washed with water until the removal of the halide ions (essay with acidic solution of silver nitrate) and dried under vacuum in presence of CaCl<sub>2</sub> for two weeks. <sup>1</sup>H NMR (MeOD, 500 MHz): δ = 9.25 (d, *J* = 7.0 Hz, 2H); 9.23 (d, *J* = 7.0 Hz, 2H); 8.62 (d, *J* = 7.0 Hz, 4H); 4.90 (q, *J* = 7.3, 2H); 4.73 (t, *J* = 7.6 Hz, 4H); 2.09 (broad, 2H); 1.73 (t, *J* = 7.3 Hz, 3H); 1.43 (broad, 4H); 1.32-1.29 (broad, 18H); 0.91 (t, *J* = 6.8 Hz, 3H) ppm. <sup>13</sup>C NMR (MeOD, 126 MHz): δ = 151.42, 147.02, 146.82, 128.32, 128.29, 121.2 (q, <sup>1</sup>*J*(<sup>13</sup>C, <sup>19</sup>F) = 321 Hz), 63.38, 58.79, 33.06, 32.55, 30.78, 30.74, 30.71, 30.62, 30.46, 30.12, 27.20, 23.72, 16.66, 14.42 ppm. **Elemental analysis** C<sub>30</sub>H<sub>42</sub>N<sub>4</sub>S<sub>4</sub>O<sub>8</sub>F<sub>12</sub>: Found C 38.57%, H 4.55%, N 5.82%, S 13.97%; Calcd C 38.21%, H 4.49%, N 5.94%, S 13.60%. **ESI-MS**: *m/z* = 662 [**14.2Tf<sub>2</sub>N**]<sup>+</sup>, 191 [**14.2**]<sup>2+</sup>.

### **14.14(Tf<sub>2</sub>N)<sub>2</sub>**

300 mg of **14.14Br<sub>2</sub>** obtained as a by-product from the synthesis of **14.Br**, were dissolved in 10 mL of methanol and added with 10 mL of methanol solution containing 365 mg of LiTf<sub>2</sub>N for 4 hrs. The solvent was evaporated under *vacuum* and a white precipitate was formed after adding water to the flask. The white precipitate was then filtered and washed with water until the removal of the halide ions (essay with acidic solution of silver nitrate) and dried under vacuum in presence of CaCl<sub>2</sub>. Yield: 85%. <sup>1</sup>H NMR (MeOD, 500 MHz) δ = 9.24 (d, *J* = 6.7 Hz, 4H); 8.63 (d, *J* = 6.7

Hz, 4H); 4.73 (q,  $J = 7.6$ , 4H); 2.09 (broad, 4H); 1.43 (broad, 4H); 1.32-1.29 (broad, 40H); 0.90 (t,  $J = 6.7$  Hz, 6H) ppm.  $^{13}\text{C}$  NMR (MeOD, 126 MHz)  $\delta = 151.41, 147.03, 128.30, 121.2$  (q,  $^1J(^{13}\text{C}, ^{19}\text{F}) = 321$  Hz), 63.37, 33.06, 32.57, 30.78, 30.74, 30.71, 30.63, 30.47, 30.13, 27.21, 23.72, 14.42 ppm. **Elemental analysis:**  $\text{C}_{42}\text{H}_{66}\text{N}_4\text{S}_4\text{O}_8\text{F}_{12}$  : Found C 45.48 %, H 5.97 %, N 5.00 %, S 11.65 % ; Calcd C 45.40 %, H 5.99 %, N 5.04 %, S 11.54 %. **ESI-MS:**  $m/z = 830$  [ $\mathbf{14.14}\text{Tf}_2\text{N}$ ] $^+$ , 275 [ $\mathbf{14.14}$ ] $^{2+}$ .

#### 12.4.12(Tf<sub>2</sub>N)<sub>4</sub>

0.88 mmol (400 mg) of **12.I** were refluxed with 17.6 mmol (2.1 mL) of 1,4-dibromobutane in 25 mL of acetonitrile at 80 °C for 72 hrs. The suspension was then cooled to room temperature and the precipitate was filtered and washed with cold (0 °C) acetone obtaining 380 mg of **12.4Br(I,Br)**. Yield 63%.

0.54 mmol (360 mg) of **12.4Br(I,Br)** were then refluxed with 2.7 mmol (1.22 g) of **12.I** in 30 mL of acetonitrile. As the temperature reached 80 °C a suspension was still observed; thus methanol was added dropwise until a clear solution was obtained. The solution was refluxed for 72 hrs. The suspension was then cooled at room temperature and stored at 4 °C for 2 hrs. The precipitate was filtered and washed with cold acetone and then recrystallized with 20 mL of an acetonitrile/methanol mixture, 19:1 v/v. The precipitate was washed with cold acetone and dried under vacuum in presence of  $\text{CaCl}_2$  for two weeks. Yield 70% (350 mg) of **12.4.12I<sub>2</sub>Br<sub>2</sub>**.

0.31 mmol (350 mg) of **12.4.12I<sub>2</sub>Br<sub>2</sub>** were dissolved in 320 mL of methanol; 10 mL of methanol solution containing 1.64 mmol (470 mg) of  $\text{LiTf}_2\text{N}$  were added and left to react under stirring at room temperature for 2 hrs. The volume of the solution was then reduced to about 10 mL and water was added until a white precipitate was formed. The suspension was left to react for 2 hrs and stored at 4 °C. The white precipitate was then filtered and washed with water until the removal of the halide ions (essay with acidic solution of silver nitrate) and dried in vacuum in presence of  $\text{CaCl}_2$  for two weeks. Yield 88%.  $^1\text{H}$  NMR (MeOD, 500 MHz):  $\delta = 9.23$  (d,  $J = 6.7$  Hz, 4H); 9.18 (d,  $J = 6.7$  Hz, 4H); 8.62 (d,  $J = 6.7$  Hz, 4H); 8.60 (d,  $J = 6.7$  Hz, 4H); 4.83 (t broad, 4H); 4.74 (t,  $J = 7.5$  Hz, 4H); 2.24 (broad, 4H); 2.08 (broad, 4H); 1.41 (broad, 8H); 1.31-1.29 (broad, 28H); 0.90 (t,  $J = 6.7$  Hz, 6H) ppm.  $^{13}\text{C}$  NMR (MeOD, 126 MHz)  $\delta$  151.72, 151.32, 147.06, 128.57, 128.32, 121.11 (q,  $^1J(^{13}\text{C}, ^{19}\text{F}) = 321$  Hz); 63.38, 62.34, 33.05, 32.54, 30.71, 30.62, 30.46, 30.12, 28.84, 27.17, 14.42 ppm. **Elemental analysis:**  $\text{C}_{56}\text{H}_{74}\text{N}_8\text{S}_8\text{O}_{16}\text{F}_{24}$  : Found C 36.79 %, H 4.20 %, N 6.18 %, S 14.42 % ; Calcd C 36.80 %, H 4.08 %, N 6.13 %, S 14.04 %. **ESI-MS:**  $m/z = 1546$  [ $\mathbf{12.4.12}(\text{Tf}_2\text{N})_3$ ] $^+$ , 634 [ $\mathbf{12.4.12}(\text{Tf}_2\text{N})_2$ ] $^{2+}$ , 329 [ $\mathbf{12.4.12}(\text{Tf}_2\text{N})$ ] $^{3+}$ .

#### 14.4.14(Tf<sub>2</sub>N)<sub>4</sub>

2.30 mmol (1000 mg) of **14.Br** were refluxed with 45.97 mmol (5.49 mL) of 1,4-dibromobutane in 70 mL of Acetonitrile at 80 °C for 48 hrs. The suspension was then cooled to room temperature and the precipitate was filtered and washed with cold (0 °C) acetone obtaining 1317 mg of **14.4Br(Br)<sub>2</sub>**. Yield: 88%.

2.03 mmol (1317 mg) of **14.4Br(Br)<sub>2</sub>** were refluxed with 10.0 mmol (4.4 g) of **14.Br** in 50 mL of acetonitrile. As the temperature reached 80 °C a suspension was still observed; thus methanol was added dropwise until a clear solution was obtained. The solution was refluxed for 72 hrs. The suspension was then cooled at room temperature and stored at 4 °C for 2 hrs. The precipitate was filtered and washed with cold acetone and then recrystallized with 20 mL of acetonitrile/methanol mixture 19:1 v/v. The precipitate was washed with cold acetone and dried under vacuum in presence of  $\text{CaCl}_2$  for two weeks. Yield 80% (1000 mg) of **14.4.14Br<sub>4</sub>**.

0.92 mmol (1000 mg) of **14.4.14Br<sub>4</sub>** were dissolved in 150 mL of methanol and 10 mL of methanol solution containing 4.63 mmol (1330 mg) of  $\text{LiTf}_2\text{N}$  were added. The solution was stirred at room temperature for 2 hrs. The volume of the solution was then reduced to about 10 mL and water was added until a white precipitate was formed. The suspension

was left to react for further 2 hrs and stored in fridge. The white precipitate was then filtered, washed with water until the removal of the halide ions (essay with acidic solution of silver nitrate) and dried under vacuum in presence of  $\text{CaCl}_2$  for two weeks. Yield 87%.  $^1\text{H NMR}$  (MeOD, 500 MHz)  $\delta$  = 9.24 (d,  $J$  = 6.8 Hz, 4H); 9.19 (d,  $J$  = 6.8 Hz, 4H); 8.63 (d,  $J$  = 6.8 Hz, 4H); 8.60 (d,  $J$  = 6.8 Hz, 4H); 4.83 (broad, 4H); 4.72 (t,  $J$  = 6.9 Hz, 4H); 2.24 (broad, 4H); 2.08 (m, 4H); 1.41 (broad, 8H); 1.29 (broad, 36 H); 0.90 (t,  $J$  = 6.7 Hz, 6H) ppm.  $^{13}\text{C NMR}$  (126 MHz, MeOD)  $\delta$  = 151.72, 151.32, 147.07, 128.57, 128.31, 121.12 (q,  $^1J(^{13}\text{C}, ^{19}\text{F})$  = 321 Hz), 63.38, 62.34, 33.07, 32.55, 30.78, 30.74, 30.72, 30.63, 30.47, 30.13, 28.84, 27.18, 23.73, 14.43 ppm. **Elemental analysis:**  $\text{C}_{60}\text{H}_{82}\text{N}_8\text{S}_8\text{O}_{16}\text{F}_{24}$ : Found C 38.43%, H 4.69 %, N 5.90 %, S 13.67 %; Calcd C 38.25%, H 4.39 %, N 5.95 %, S 13.62 %. **ESI-MS:**  $m/z$  = 1603 [ $\mathbf{14.4.14}(\text{Tf}_2\text{N})_3$ ] $^+$ , 662 [ $\mathbf{14.4.14}(\text{Tf}_2\text{N})_2$ ] $^{2+}$ .

#### **16.4.16(Tf<sub>2</sub>N)<sub>4</sub>**

1.52 mmol (700 mg) of **16.Br** were refluxed with 30.31 mmol (3.62 mL) of 1,4-dibromoethane in 15 mL of Acetonitrile at 80 °C for 24 hrs. The suspension was then cooled to room temperature and the precipitate was filtered and washed with cold (0 °C) acetone. Yield 83% (848 mg) of **16.4Br(Br)<sub>2</sub>**.

1.18 mmol (800 mg) of **16.4Br(Br)<sub>2</sub>** were then refluxed with 8.26 mmol (3810 mg) of **16.Br** in 30 mL of acetonitrile. Once the solution reached 80 °C a suspension remained; thus methanol was added dropwise until a clear solution was obtained. After 96 hrs the reaction was stopped and cooled at room temperature and stored at 4 °C for 2 hrs. The precipitate was filtered and washed with cold acetone and then recrystallized with 10 mL of an acetone/water solution 9:1 v/v. The precipitate was washed with cold acetone and dried in vacuum in presence of  $\text{CaCl}_2$  for two weeks. Yield 42% (570 mg) of **16.4.16Br<sub>4</sub>**.

0.44 mmol (500 mg) **16.4.16Br<sub>4</sub>** were dissolved in 150 mL of methanol. Some impurities suspended were filtered with a Watmann 40 Paper filter before adding 10 mL of a methanol solution containing 2.29 mmol (658 mg) of  $\text{LiTf}_2\text{N}$ ; this was left to react under stirring to room temperature for 2 hrs. The volume of the solution was then reduced to about 50 mL and water was added until a white precipitate was formed. The suspension was left to react for further 2 hrs and stored at 4 °C. The white precipitate was then filtered, washed with water until the removal of the halide ions (essay with acidic solution of silver nitrate) and dried under vacuum in presence of  $\text{CaCl}_2$  for two weeks.  $^1\text{H NMR}$  (MeOD, 500 MHz)  $\delta$  = 9.24 (d,  $J$  = 6.8 Hz, 4H); 9.19 (d,  $J$  = 6.8 Hz, 4H); 8.63 (d,  $J$  = 6.8 Hz, 4H); 8.60 (d,  $J$  = 6.8 Hz, 4H); 4.83 (t broad, 4H); 4.72 (t,  $J$  = 7.5 Hz, 4H); 2.24 (broad, 4H); 2.07 (q,  $J$  = 7.0 Hz, 4H); 1.42-1.41 (broad, 8H); 1.29 (broad, 44H); 0.90 (t,  $J$  = 6.7 Hz, 6H).  $^{13}\text{C NMR}$  (MeOD, 126 MHz)  $\delta$  = 151.72, 151.31, 147.07, 128.57, 128.31, 121.12 (q,  $^1J(^{13}\text{C}, ^{19}\text{F})$  = 321 Hz), 63.38, 62.34, 33.07, 32.55, 30.78, 30.75, 30.72, 30.64, 30.47, 30.14, 28.84, 27.19, 23.73, 14.43 ppm. **Elemental analysis:**  $\text{C}_{64}\text{H}_{90}\text{N}_8\text{S}_8\text{O}_{16}\text{F}_{24}$ : Found C 39.18%, H 4.71 %, N 5.48 %, S 13.14 %; Calcd C 39.62%, H 4.68 %, N 5.78 %, S 13.22 %. **ESI-MS:**  $m/z$  = 1658 [ $\mathbf{16.4.16}(\text{Tf}_2\text{N})_3$ ] $^+$ , 689 [ $\mathbf{16.4.16}(\text{Tf}_2\text{N})_2$ ] $^{2+}$ . We also observed two intense peaks in the ESI-MS spectrum at  $m/z$  = 1630 and 675, corresponding to a monocationic and dicationic species, respectively (as inferred from the spacing of the isotope peaks), that could not be assigned.

## **EXPERIMENTAL TECHNIQUES**

### **POM (Polarized Optical Microscopy)**

The textures of the samples were studied with a Leica DM4000M Polarized light microscope. The samples were placed between a glass slide and a cover slip. A Mettler FP82HT hot stage was used to control the temperature. The samples were heated at 10 °C min<sup>-1</sup> beyond the melting temperature determined by DSC experiments, and subsequently cooled at 10 °C min<sup>-1</sup> to room temperature. The photomicrographs were taken between cross-polarizers with a Leica DFC280

digital camera.

### **DSC**

All the measurements of Differential Scanning Calorimetry (DSC) were carried out with a TA Instruments mod. 2920 calorimeter operating under an N<sub>2</sub> atmosphere. Samples weighing about 5 mg closed in aluminum pans were used throughout the experiments. Indium of high purity was used for calibrating the DSC temperature and enthalpy scales. Four ramps were included in the temperature program: one heating ramp at 10 °C/min from -20 °C to 300 °C min<sup>-1</sup>, followed by a cooling step to -20 °C at 10 °C min<sup>-1</sup> and by another analogous heating/cooling cycle. The repetition of two similar heating/cooling ramps was done to assess the repeatability of the phase transitions.

### **X-Ray diffraction**

The XRD (X-ray Diffraction) patterns were recorded by a Philips X'Pert PRO diffractometer, working in the reflection geometry and equipped with a graphite monochromator on the diffracted beam (CuKα radiation). Temperature dependent XRD spectra were gathered with an Anton Paar TTK450 temperature control cell, in the diffraction angular range 1.5–30° 2θ.

### **NMR**

Solution (CD<sub>3</sub>OD) NMR spectra were acquired at 300 K with Bruker Avance (400 MHz) and Avance III (500 MHz) spectrometers operating at <sup>1</sup>H and <sup>13</sup>C frequencies of 400.13 and 100.62 MHz (Bruker Avance) and 500.13 and 125.77 MHz (Avance III), respectively. <sup>1</sup>H and <sup>13</sup>C signals of the solvent has been taken as internal references (δ<sup>1</sup>H = 3.31 ppm ; δ<sup>13</sup>C = 49.0 ppm with respect to TMS).

Solid State NMR spectra (SSNMR) were collected on a Varian 400 equipped with a narrow bore, triple resonance T3 MAS probe spinning 4 mm rotors and operating at <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F frequencies of 400.36, 100.68 and 376.85 MHz, respectively. The <sup>13</sup>C CPMAS spectra were acquired at 5 kHz MAS with 1200 scans and a repetition delay of 3 s, while the <sup>19</sup>F spectra were acquired at 10 kHz MAS. For <sup>13</sup>C spectra the contact time for CP was 1 ms, and an acquisition time of 50 ms was used. The chemical shifts were referenced against the CH<sub>2</sub> resonance observed for adamantane at 38.48 ppm with respect to the signal for neat TMS.

## NMR

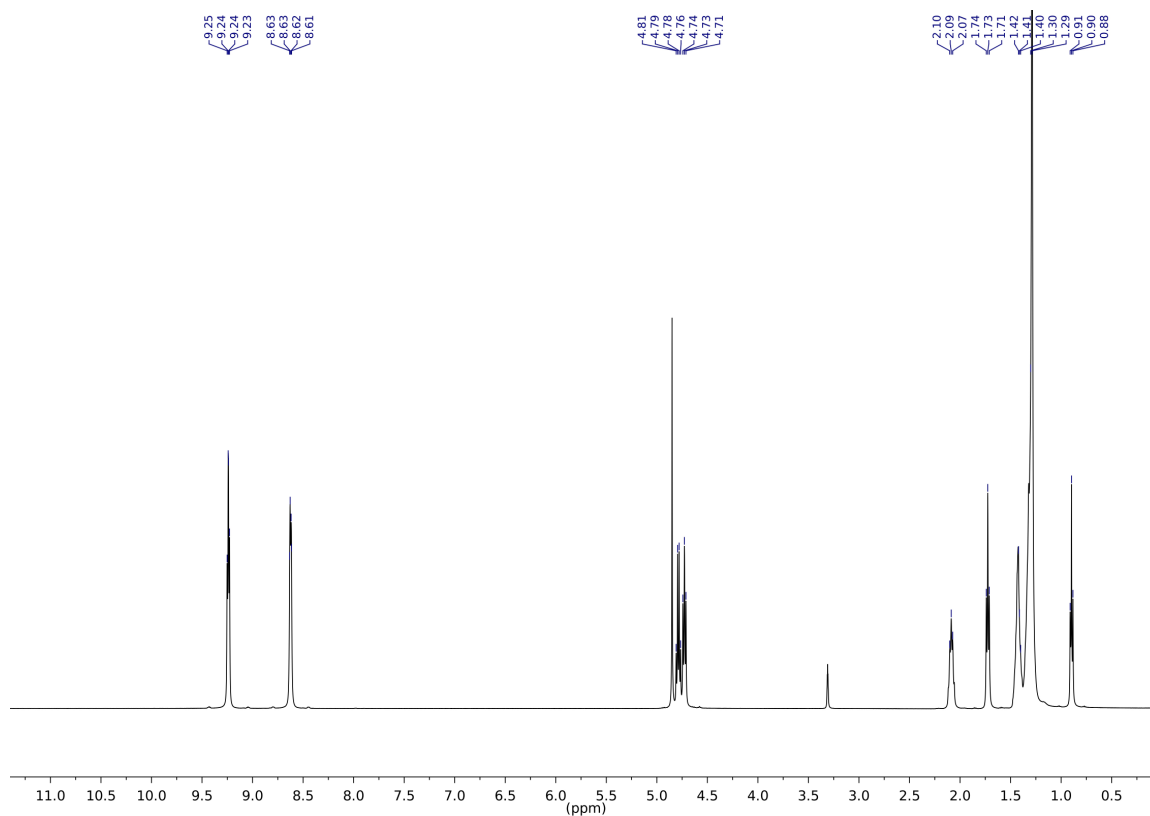


Fig. S1  $^1\text{H}$  spectrum (500 MHz, MeOD) of  $14.2(\text{Tf}_2\text{N})_2$ .

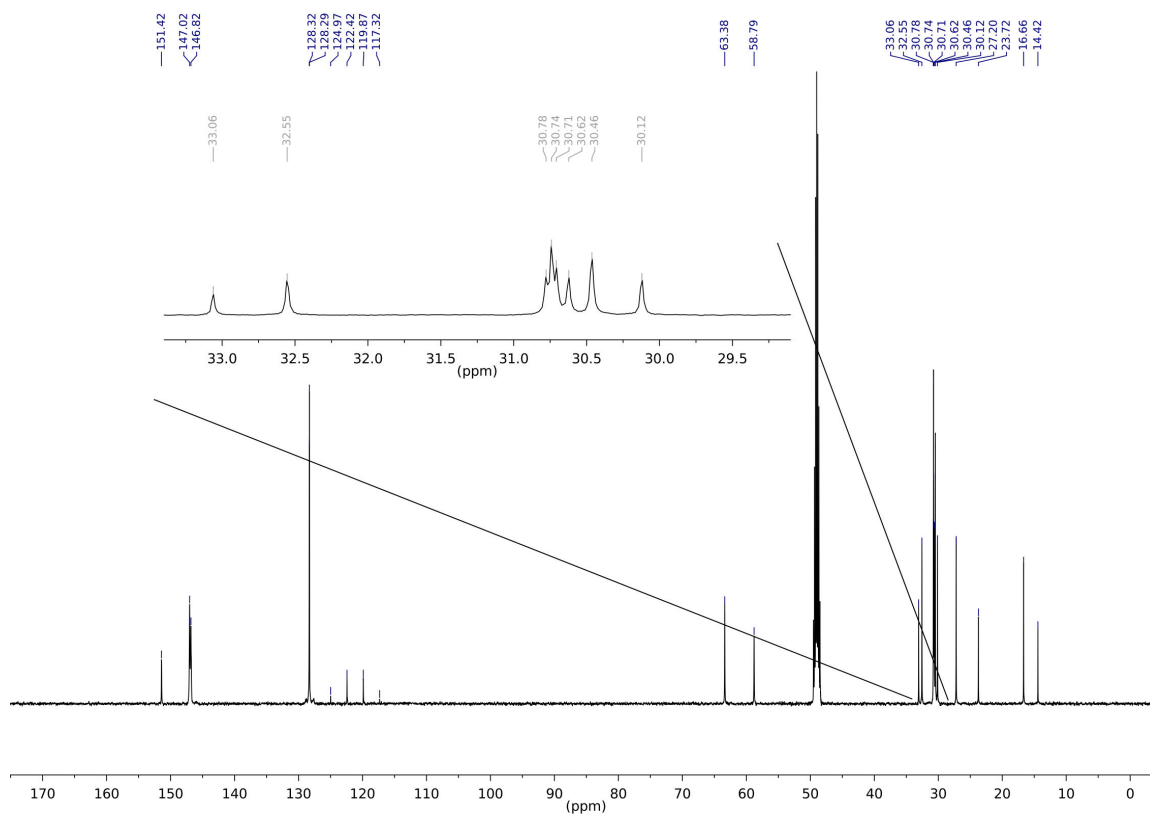


Fig. S2  $^{13}\text{C}$  spectrum (126 MHz, MeOD) of  $14.2(\text{Tf}_2\text{N})_2$ .



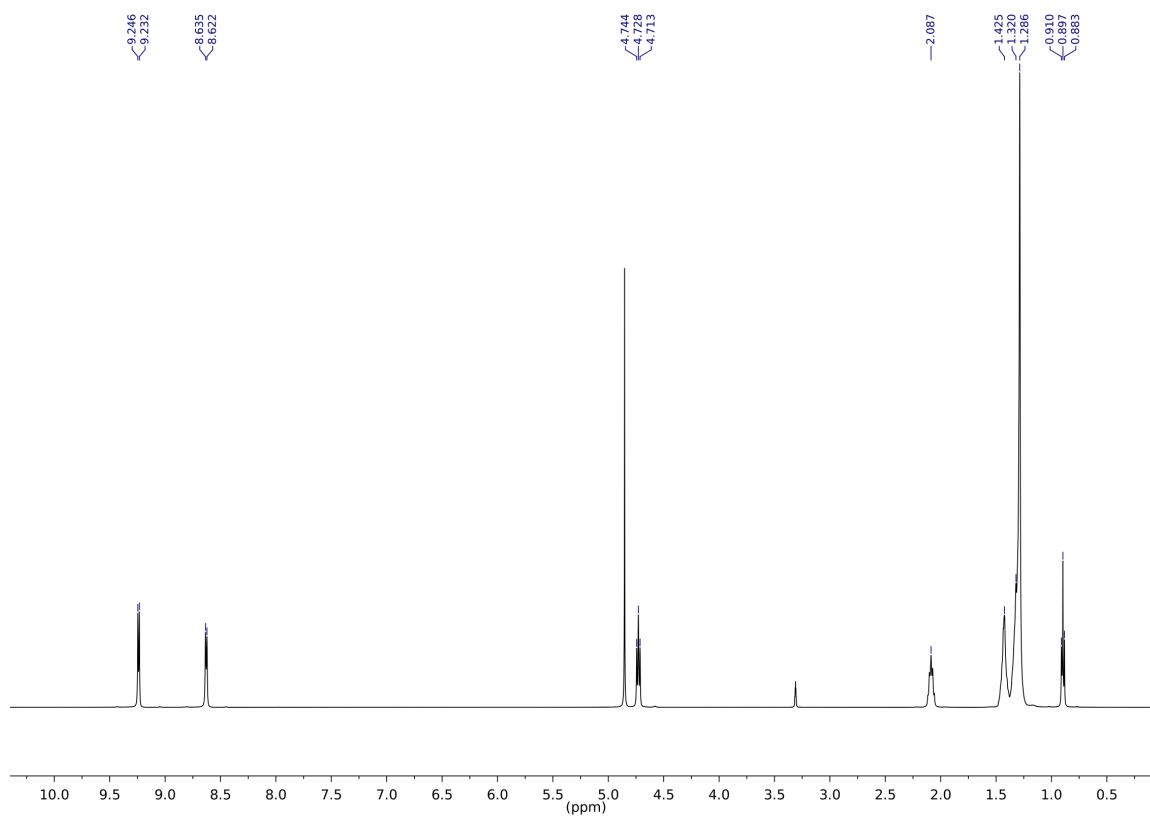


Fig. S3  $^1\text{H}$  spectrum (500 MHz, MeOD) of  $14.14(\text{Tf}_2\text{N})_2$ .

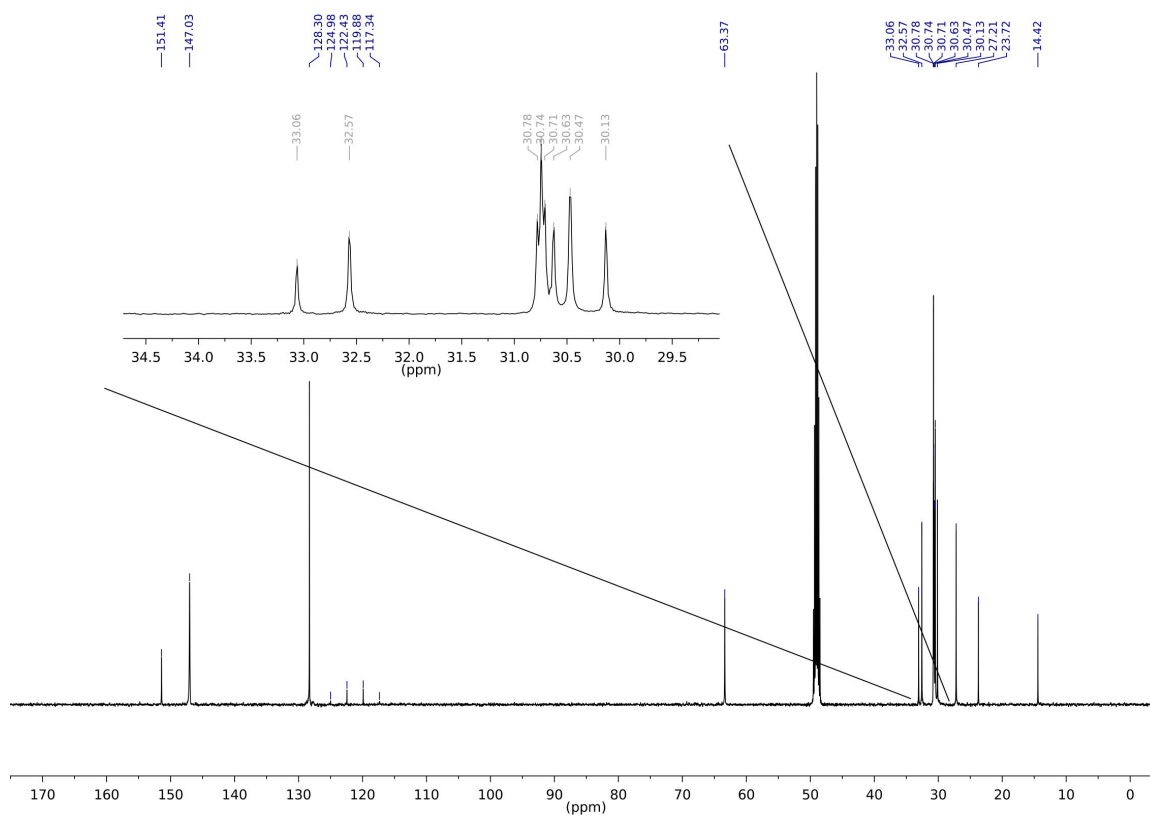
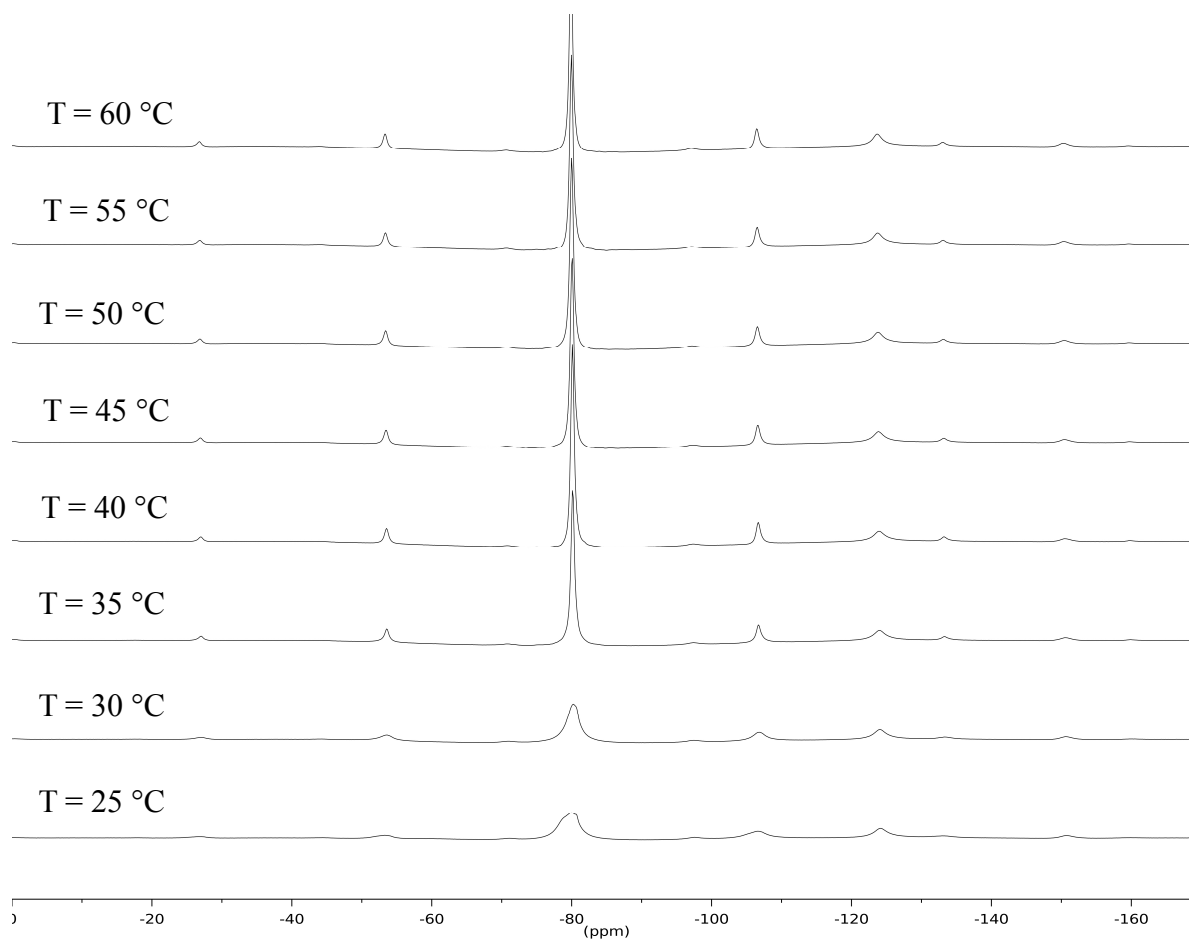


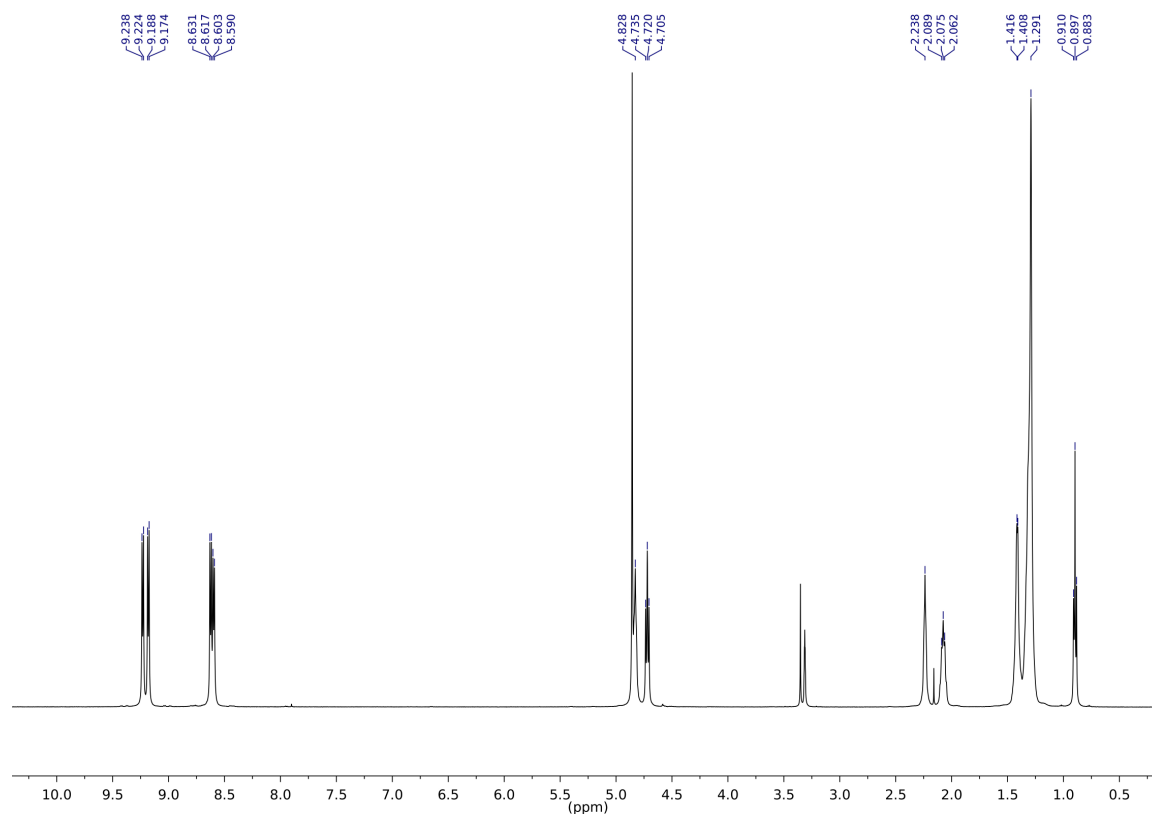
Fig. S4  $^{13}\text{C}$  spectrum (126 MHz, MeOD) of  $14.14(\text{Tf}_2\text{N})_2$ .



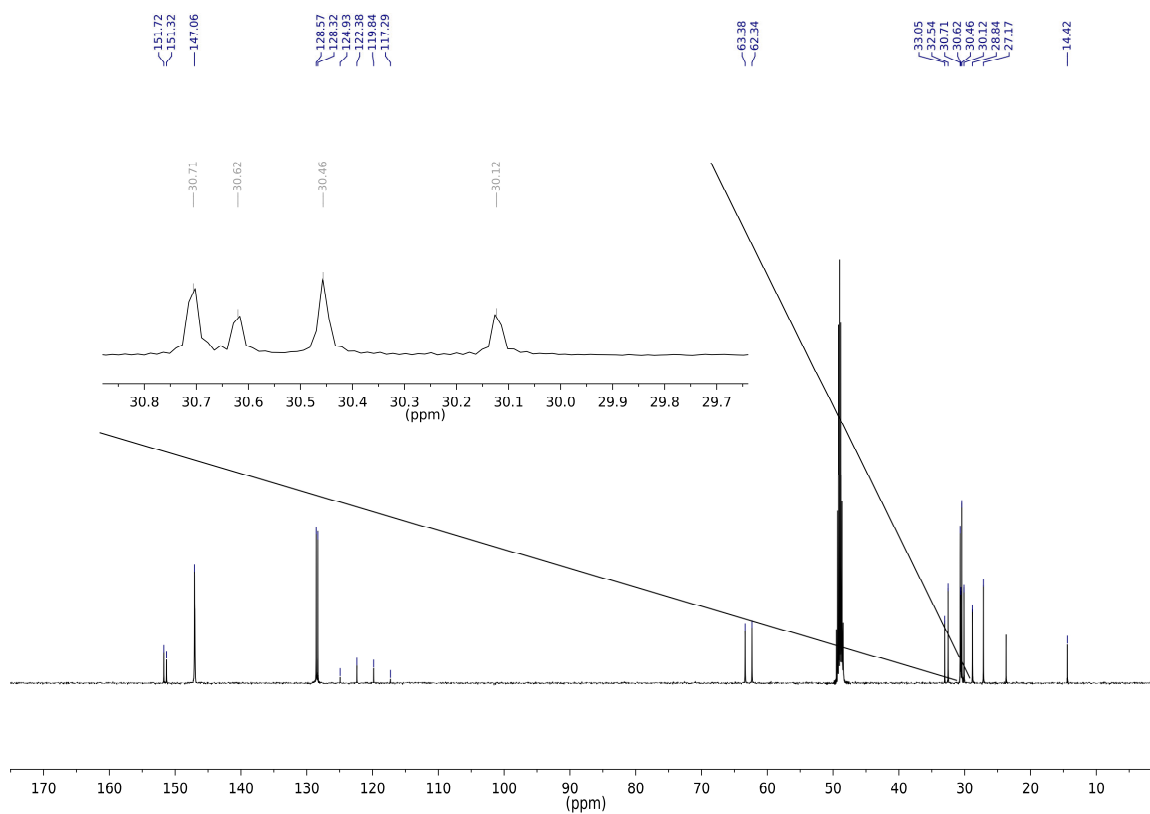
**Fig. S5** SS-MAS  $^{13}\text{C}$  spectrum (101 MHz) of  $14.14(\text{Tf}_2\text{N})_2$ . Spinning side bands are marked with an asterisk.



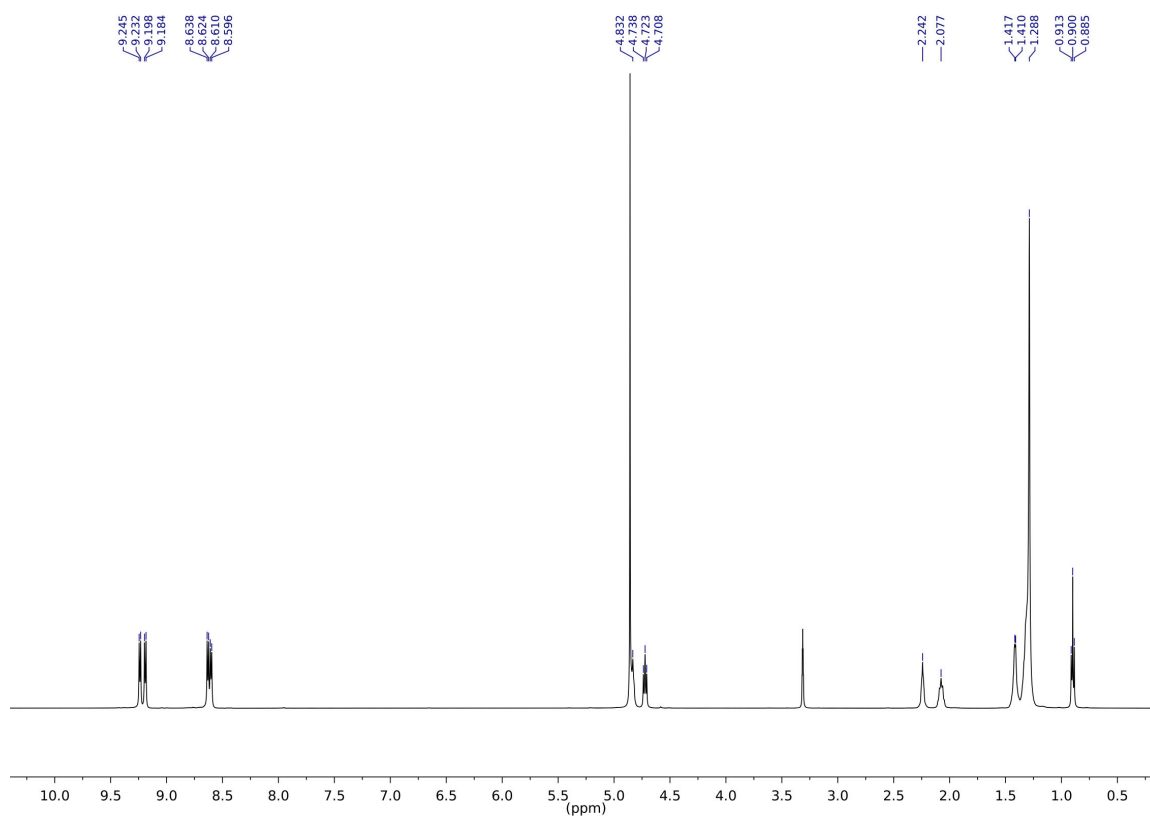
**Fig. S6** SS-MAS  $^{19}\text{F}$  spectra (376 MHz) of **14.14**( $\text{Tf}_2\text{N}$ ) $_2$  acquired at different temperatures. Spinning side bands (SSB) are marked with an asterisk. The resonance at -125 ppm, with its own SSB, is due to Teflon.



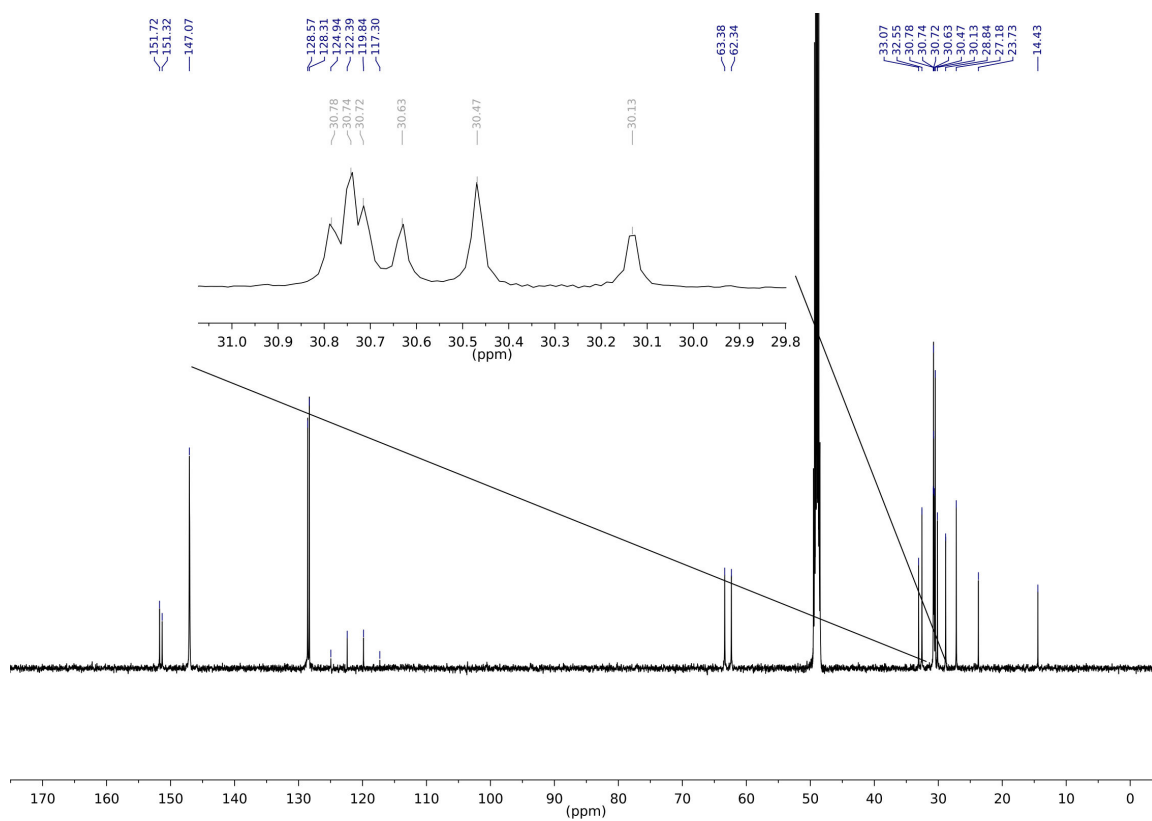
**Fig. S7**  $^1\text{H}$  spectrum (500 MHz, MeOD) of **12.4.12**( $\text{Tf}_2\text{N}$ ) $_4$ .



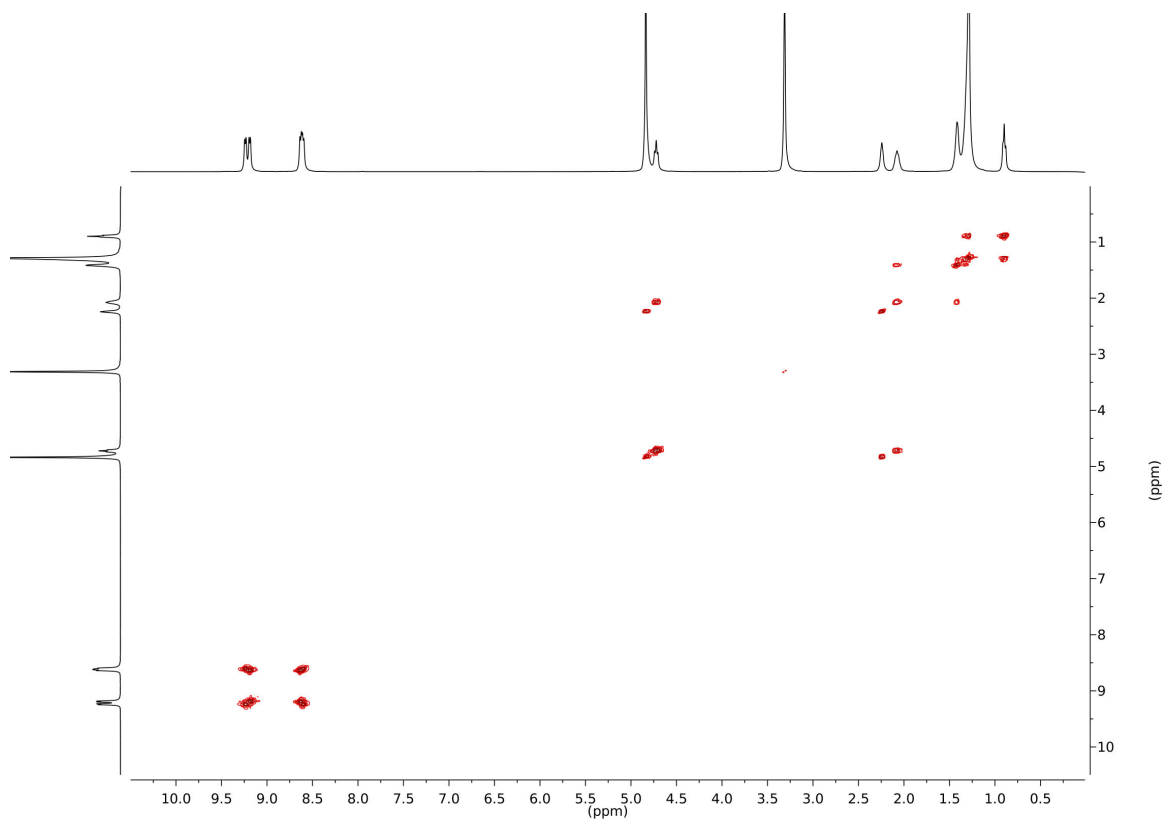
**Fig. S8**  $^{13}\text{C}$  spectrum (126 MHz, MeOD) of **12.4.12**( $\text{Tf}_2\text{N}$ )<sub>4</sub>.



**Fig. S9**  $^1\text{H}$  spectrum (500 MHz, MeOD) of **14.4.14**( $\text{Tf}_2\text{N}$ )<sub>4</sub>.



**Fig. S10** <sup>13</sup>C spectrum (126 MHz, MeOD) of **14.4.14**(Tf<sub>2</sub>N)<sub>4</sub>.



**Fig. S11** <sup>1</sup>H-<sup>1</sup>H COSY spectrum (400 MHz, MeOD) of **14.4.14**(Tf<sub>2</sub>N)<sub>4</sub>.

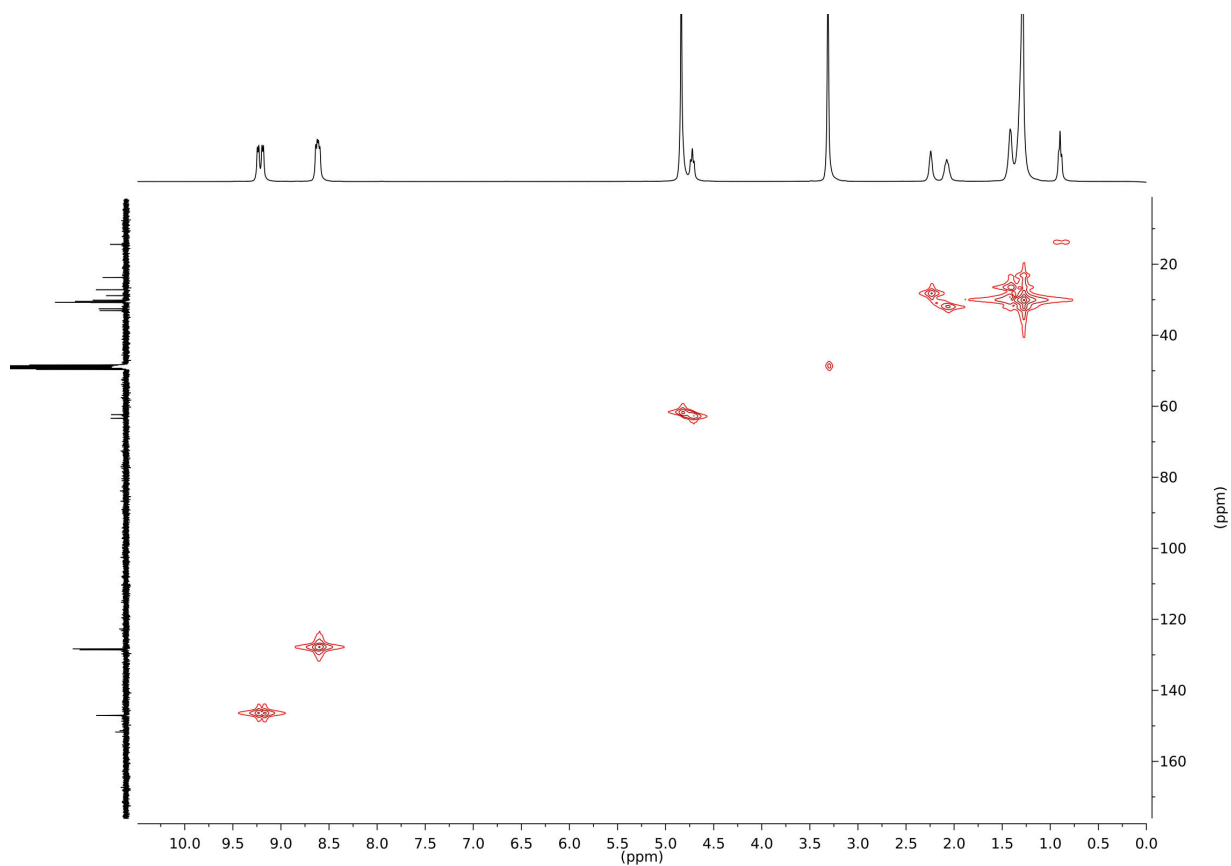


Fig. S12  $^1\text{H}$ - $^{13}\text{C}$  HMQC spectrum (400 MHz, MeOD) of **14.4.14**( $\text{Tf}_2\text{N}$ )<sub>4</sub>.

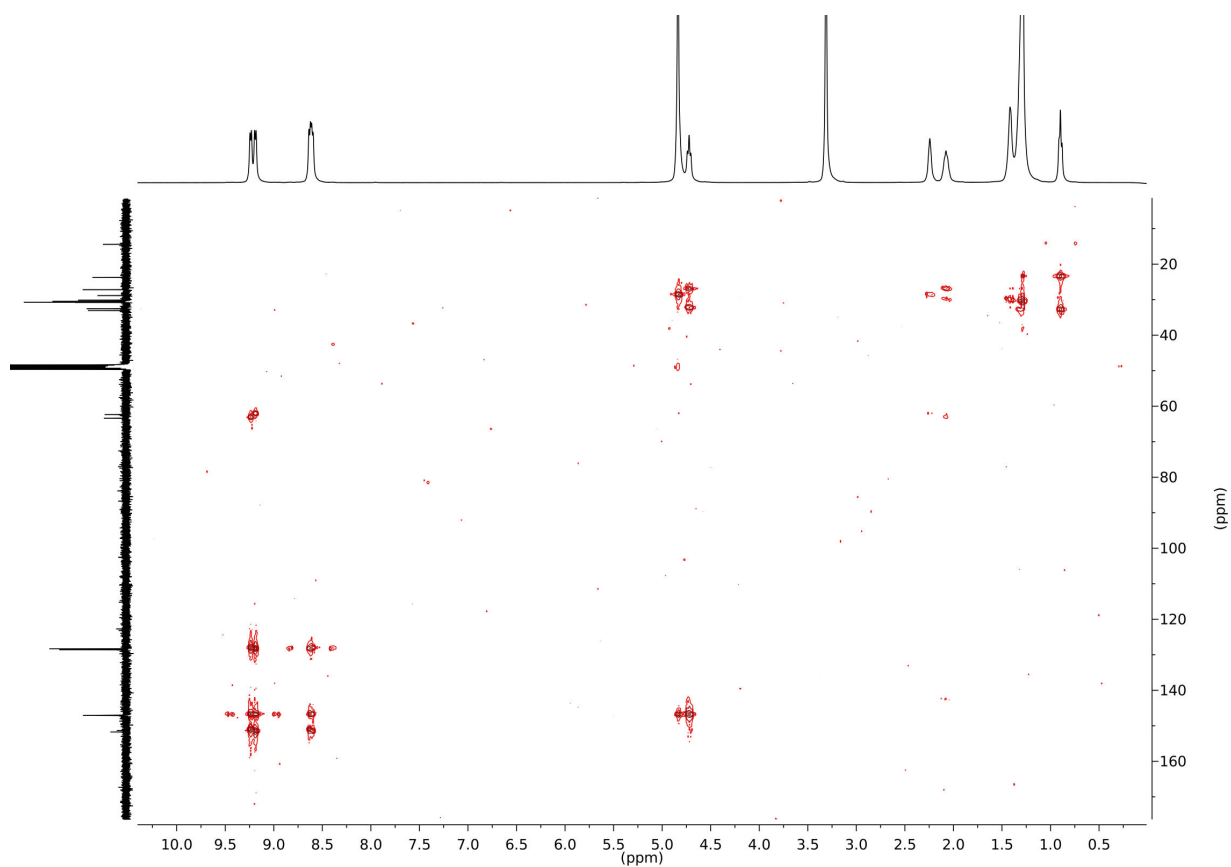


Fig. S13  $^1\text{H}$ - $^{13}\text{C}$  HMBC spectrum (400 MHz, MeOD) of **14.4.14**( $\text{Tf}_2\text{N}$ )<sub>4</sub>.

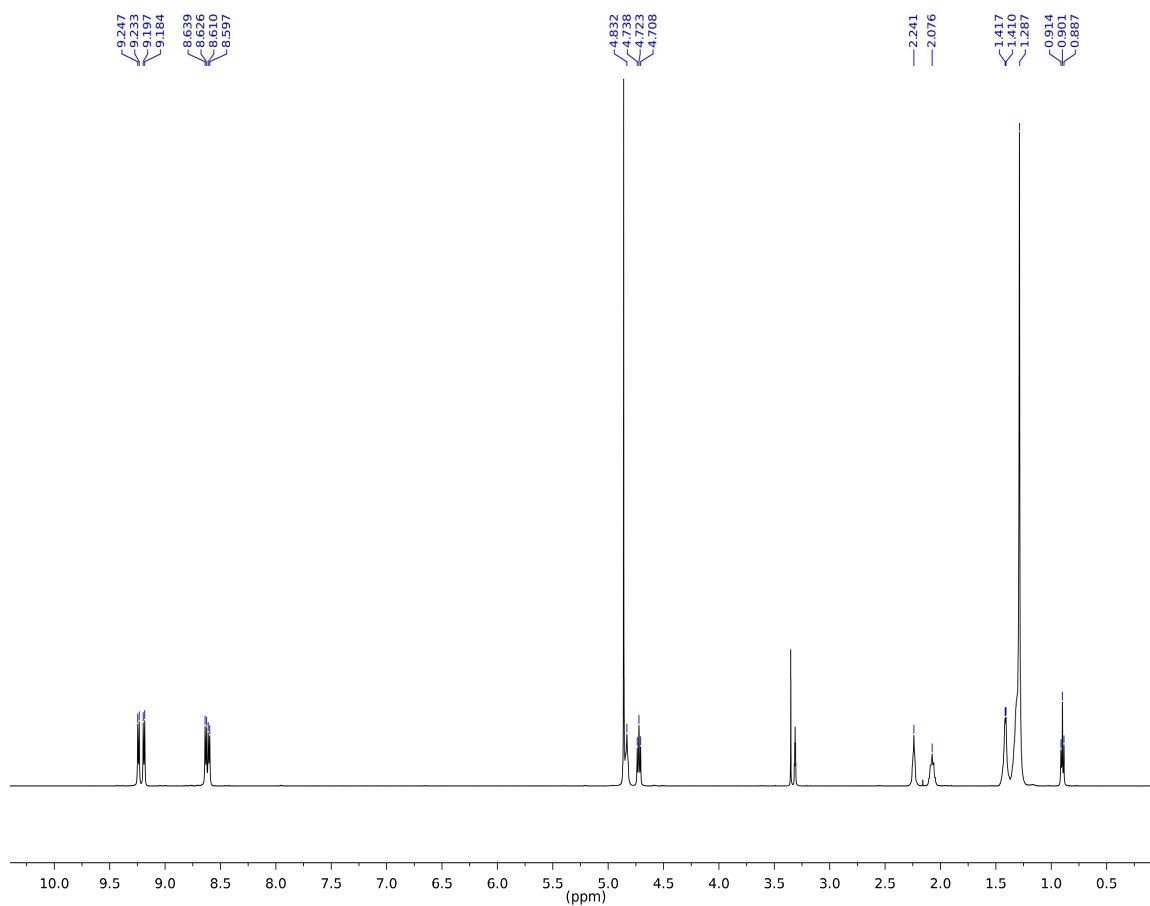


Fig. S14  $^1\text{H}$  spectrum (500 MHz, MeOD) of **16.4.16**( $\text{Tf}_2\text{N}$ )<sub>4</sub>.

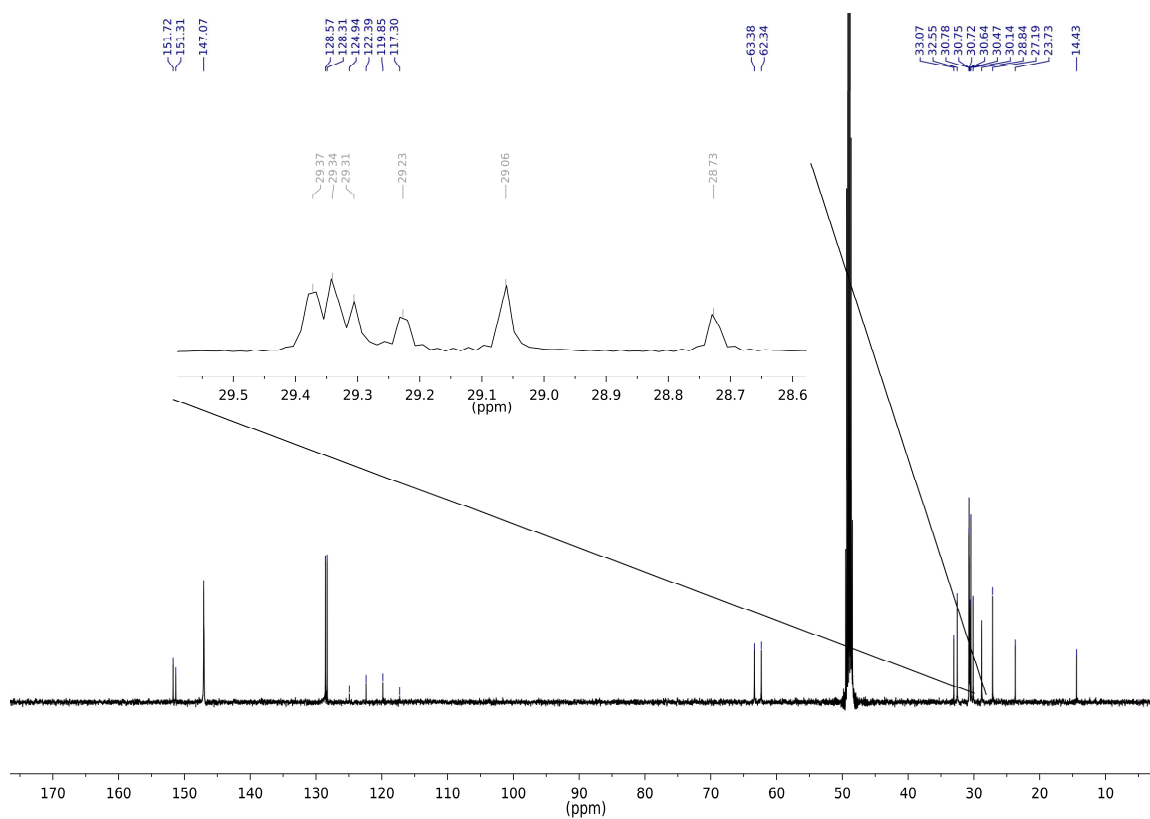
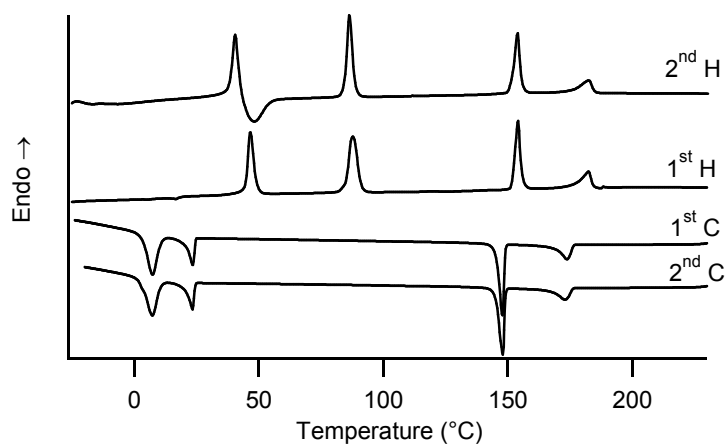
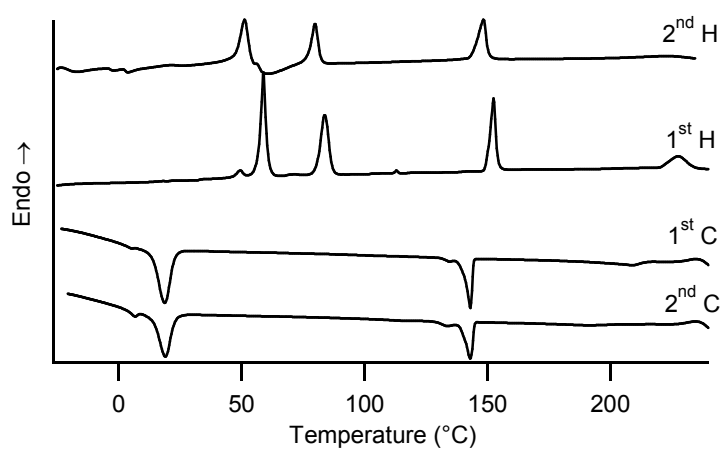


Fig. S15  $^{13}\text{C}$  spectrum (126 MHz, MeOD) of **16.4.16**( $\text{Tf}_2\text{N}$ )<sub>4</sub>.

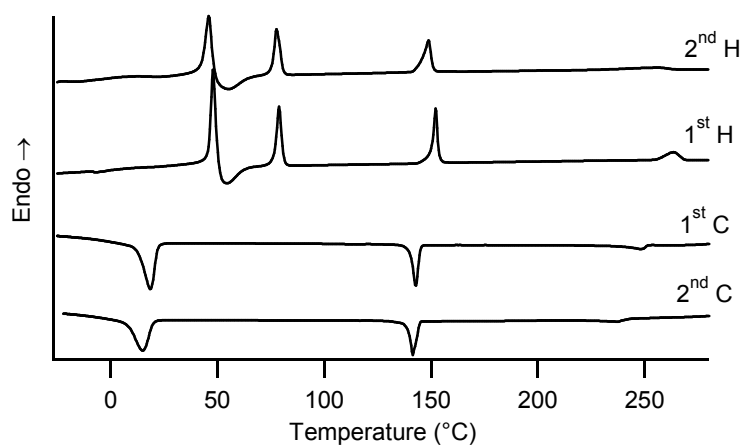
## DSC



**Fig. S16.** DSC traces of 12.4.12(Tf<sub>2</sub>N)<sub>4</sub>.

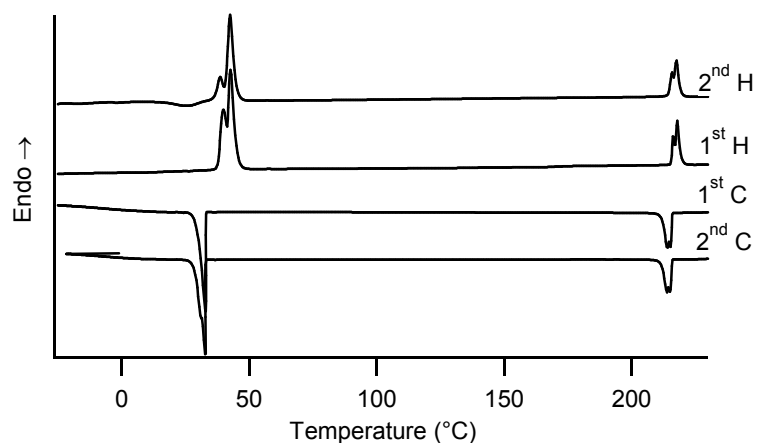


**Fig. S17.** DSC traces of 14.4.14(Tf<sub>2</sub>N)<sub>4</sub>.

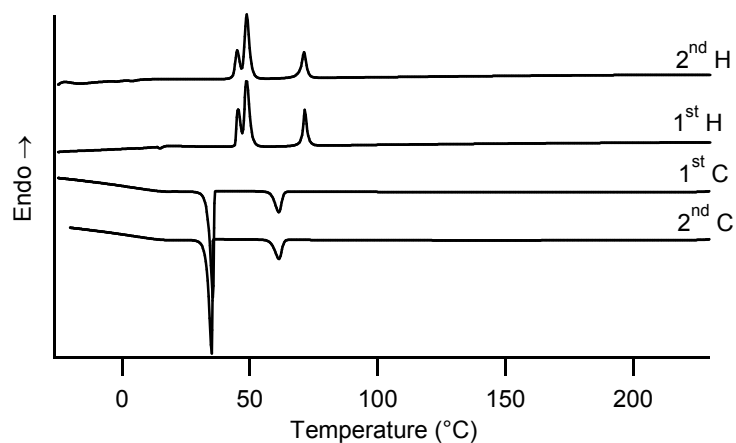


**Fig. S18.** DSC traces of 16.4.16(Tf<sub>2</sub>N)<sub>4</sub>.



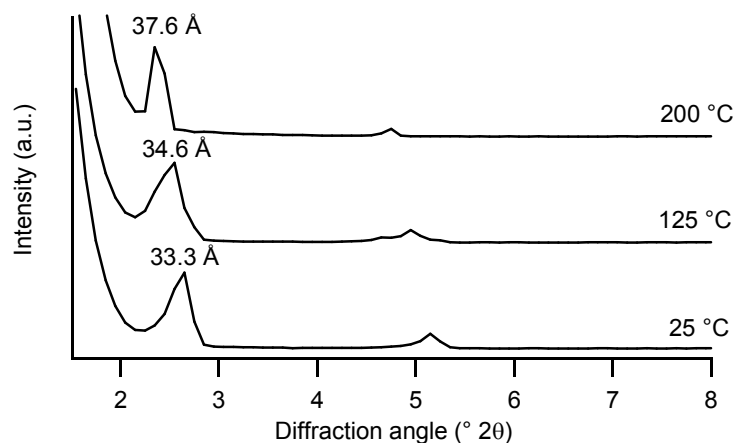


**Fig. S19.** DSC traces of **14.14**(Tf<sub>2</sub>N)<sub>2</sub>. The peak corresponding to the melting appears as two closely spaced peaks differing by less than 1 °C. The structure is highly reproducible and might indicate a very narrow range of SmA phase. This however could not be detected under the microscope. The data reported in Table 1 of the main text are referred to the whole area of the transition.

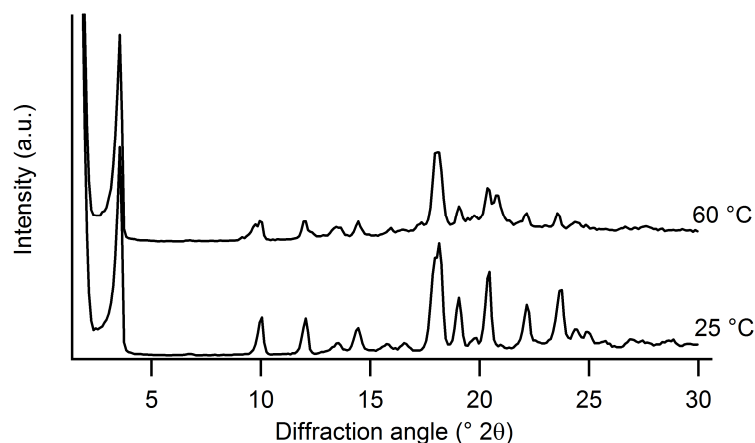


**Fig. S20.** DSC traces of **14.2**(Tf<sub>2</sub>N)<sub>2</sub>.

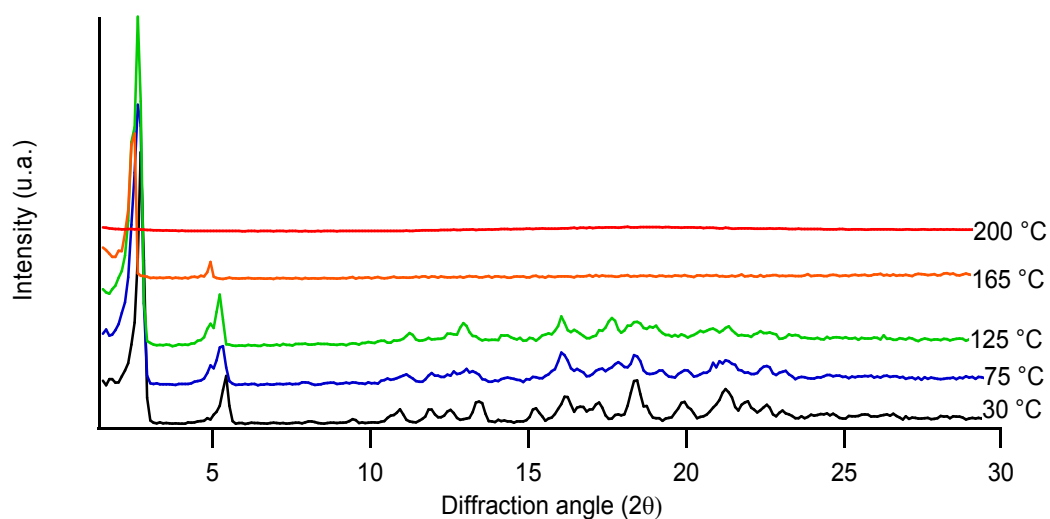
## XRD



**Fig. S21** Low angle region of the XRD traces of **14.4.14**(Tf<sub>2</sub>N)<sub>4</sub> in the crystal phase (25 °C), SmX phase (125 °C) and SmA phase (200 °C).

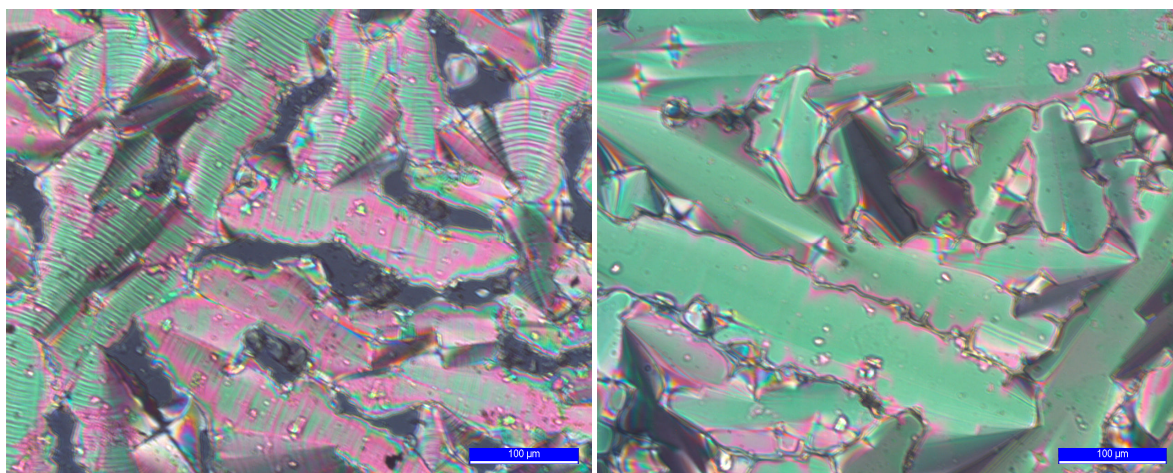


**Fig. S22** XRD traces of **14.14**(Tf<sub>2</sub>N)<sub>2</sub> in the crystal (25 °C) and SmX (60 °C) phase. The first peak corresponds to a layer thickness of 24.9 Å where the C-C distance between the two methyl groups of the cation in the all-trans conformation is 37.3 Å (optimized at the PM3 semiempirical level).

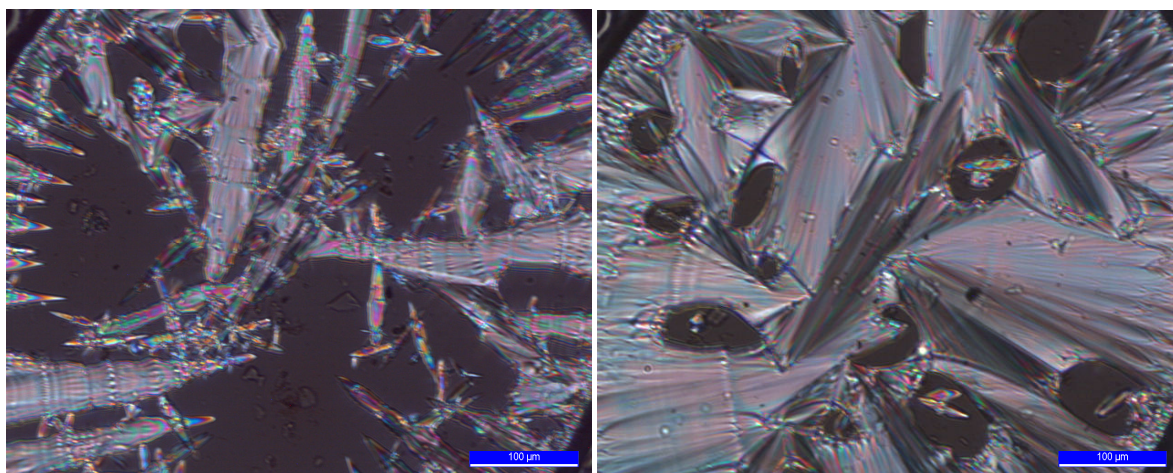


**Fig. S23** XRD traces of **12.4.12**(Tf<sub>2</sub>N)<sub>4</sub> in the crystal (25 °C and 75 °C), SmX (125 °C), SmA (165 °C) and isotropic phases (200 °C). The first peak corresponds to a layer thickness of 32.5 Å at 30 °C and 34.6 Å at 165 °C. C-C distance between the two methyl groups of the cation in the all-trans conformation is 47.1 Å.

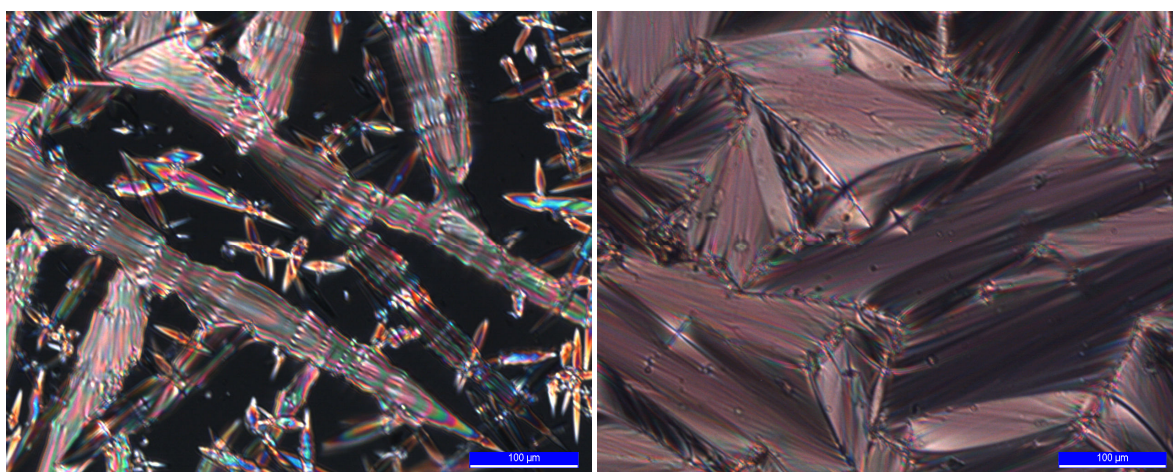
**POM:**



**Fig. S24** POM images of **14.14** on cooling from the melt (SmX phase) showing (left) striated and (right) mosaic textures. The blue bar is 100 μm.

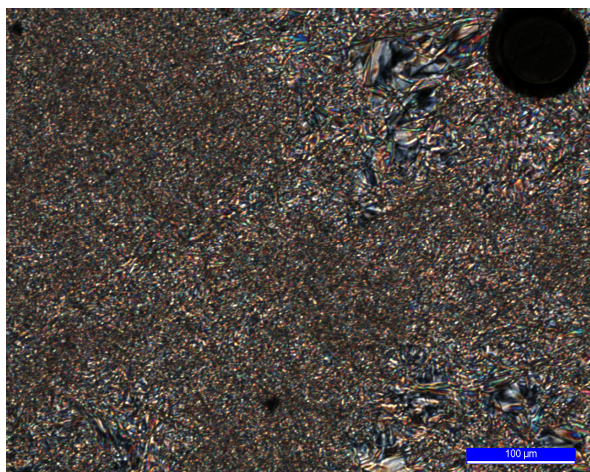


**Fig. S25** POM images of **12.4.12** on cooling from the melt (SmA phase) showing fan-shaped textures. The blue bar is 100 μm.



**Fig. S26** POM images of **16.4.16** on cooling from the melt (SmA phase) showing fan-shaped and focal conic textures. The blue bar is 100 μm.





**Fig. S27** POM image of **14.2** on cooling from the melt (Crystal phase) showing a fine texture. The blue bar is 100 μm.