Electronic Supplementary Information (ESI)

Switching of ionic conductivities in columnar liquid-crystalline anilinium salts: effects of alkyl chains, ammonium cations and counter anions on thermal properties and the switching temperatures

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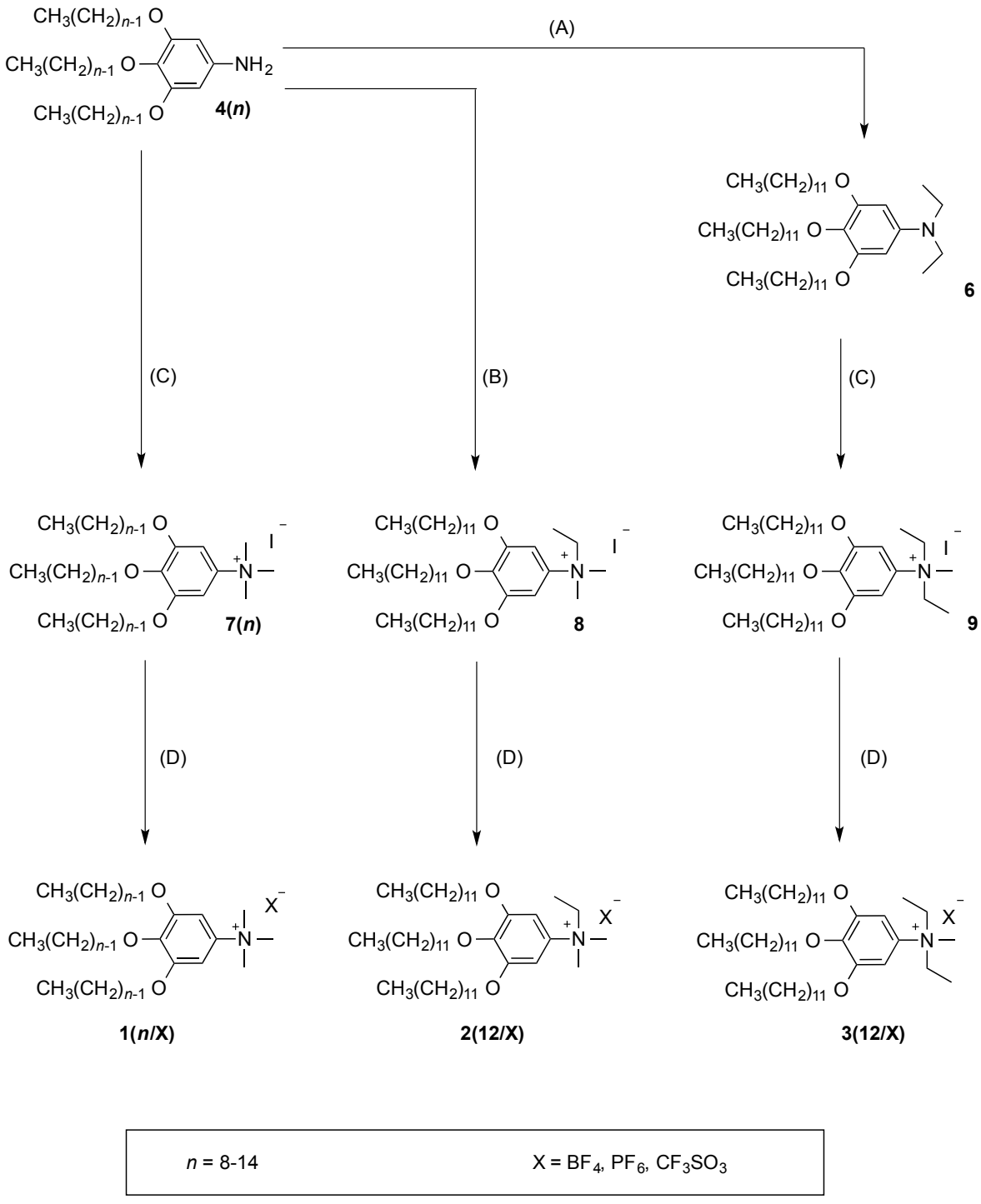
1. Materials and methods

Liquid-crystalline phase transition behaviour was examined with an Olympus BH-51 optical polarizing microscope equipped with a Mettler FP82HT hot-stage. Differential scanning calorimetry (DSC) measurements were conducted with a NETZCH DSC 204 Phoenix system at a cooling rate of 10 °C/min. NMR spectra were recorded using a JEOL JNM-LA400 at 400 MHz for ^{1}H NMR and at 100 MHz for ^{13}C NMR in $CDCl_3$. Chemical shifts of ^{1}H and ^{13}C NMR signals were quoted to internal standard Me_4Si (δ = 0.00) and $CDCl_3$ (δ = 77.00) respectively, and expressed by chemical shifts in ppm (δ), multiplicity, coupling constant (Hz), and relative intensity. Elemental analyses were carried out on a Exeter Analytical Inc. CE-440 Elemental Analyzer. X-ray diffraction (XRD) patterns were obtained by a Rigaku RINT-2500 diffractometer with a heating stage using a Ni-filtered CuK_α radiation, and the samples were placed in a heating stage. Matrix-associated laser desorption ionization time-of-flight mass spectra (MALDI-TOF MS) were recorded on a Bruker Daltonics Autoflex Speed using dithranol as the matrix. All reagents of the highest quality were purchased from Aldrich, Kanto, TCI, or Wako, and were used as received. Unless otherwise noted, all of the reactions were carried out under an argon atmosphere in a dry solvent purchased from Kanto.

2. Synthetic procedures and characterization



Scheme S1 Synthesis of compounds **1**-**3**. (A) EtI, K_2CO_3, CH_3CN, reflux 24h; (B) acetaldehyde, $NaBH(OAc)_3$, THF, r.t., 24h followed by MeI, K_2CO_3, CH_3CN, reflux, 24h; (C) MeI, K_2CO_3, CH_3CN, reflux, 24h; (D) AgX (X=BF_4, PF_6, CF_3SO_3)**,** MeOH, r.t., 3h.

The 3,4,5-Tris(alkyloxy)anilines **4(8)**, **4(10)**, **4(12-14)** were prepared according to the previously described procedures, [S1] from the corresponding 3,4,5-Tris(alkyloxy)nitrobenzene derivatives.

Compound **4(9)**

3,4,5-Tris(nonyloxy)nitrobenzene (1.32 g, 2.41 mmol) was mixed with Pd-C (5 mol%) in THF and stirred under hydrogen gas for 24h. The compound was filtered with celite using ethyl acetate followed by rotavapor. The crude was recrystallized in isopropanol to obtain white solid compound **4(9)** (1.00 g, 1.92 mmol, 80%)

^{1}H NMR (400 MHz, $CDCl_3$): δ= 5.90 (s, 2H; ArH), 3.90 (t, *J*= 6.4 Hz, 4H; CH_2), 3.83 (t, *J*=6.6 Hz, 2H; CH_2), 3.45 (s, 2H; NH_2), 1.80-1.67 (m, 6H; CH_2), 1.46-1.40 (m, 6H; CH_2), 1.27 (m, 30 H; CH_2), 0.87 (t, *J*= 6.4 Hz, 9H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 153.72, 142.28, 131.11, 94.49, 73.58, 68.99, 31.95, 31.90, 30.31, 29.71, 29.66, 29.61, 29.42, 29.30, 26.19, 26.10, 22.68, 14.11; MS (MALDI-TOF): $[M+H]^+$ calcd. for $C_{33}H_{62}NO_3$, 520.473; found, 520.255. Elemental analysis calcd. for $C_{33}H_{61}NO_3$: C 76.24, H 11.83, N 2.69; found: C 76.47, H 12.09, N 2.99.

Compound **4(11)**

3,4,5-Tris(undecyloxy)nitrobenzene (1.86 g, 2.94 mmol) was mixed with Pd-C (5 mol%) in THF and stirred under hydrogen gas for 24h. The compound was filtered with celite using ethyl acetate followed by rotavapor. The crude was recrystallized in isopropanol to obtain white solid compound **4(11)** (0.86 g, 1.42 mmol, 48 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ= 5.91 (s, 2H; ArH), 3.91 (t, *J*= 6.4 Hz, 4H; CH_2), 3.84 (t, *J*=6.8 Hz, 2H; CH_2), 3.46 (s, 2H; NH_2), 1.80-1.67 (m, 6H; CH_2), 1.45-1.41 (m, 6H; CH_2), 1.30-1.26 (m, 42 H; CH_2), 0.88 (t, *J*= 6.8 Hz, 9H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 153.72, 142.28, 131.14, 94.49, 73.57, 68.98, 31.94, 31.92, 30.30, 29.73, 29.70, 29.65, 29.41, 29.39, 29.36, 26.19, 26.09, 22.69, 14.11; MS (MALDI-TOF): $[M+H]^+$ calcd. for $C_{39}H_{74}NO_3$, 604.567; found, 604.357. Elemental analysis calcd. for $C_{39}H_{73}NO_3$: C 77.55, H 12.18, N 2.32; found: C 77.51, H 12.15, N 2.60.

Compound **5**

To a stirred solution of **4(12)** (0.61 g, 0.94 mmol) in acetonitrile were added iodoethane (1.17 g, 7.55 mmol) and potassium carbonate (3.23 g, 23.4 mmol). The suspension was stirred under reflux for 24h. The reaction mixture was concentrated under vacuo. The crude product was purified by silica gel chromatography (elution with hexane/EtOAc) to yield compound **5** (0.5 g, 0.71 mmol, 46 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ= 5.95 (s, 2H; ArH), 3.97 (t, *J*= 6.4 Hz, 4H; CH_2), 3.85 (t, *J*=6.8, 2H; CH_2), 3.27 (q, *J*= 6.8, 4H; CH_2), 1.80-1.70 (m, 6H; CH_2), 1.68-1.18 (m, 54 H; CH_2), 1.32 (t, *J*= 6.8, 6H; CH_3), 0.89 (t, *J*= 6.8 Hz, 9H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 153.69, 144.64, 129.98, 93.16, 73.68, 69.38, 63.11, 44.77, 31.92, 30.34, 29.75, 29.74, 29.70, 29.66, 29.58, 29.47, 29.39, 29.36, 26.21, 26.14, 22.68, 14.10, 12.70; MS (MALDI-TOF):

[M] calcd. for $C_{46}H_{87}NO_3$, 701.669; found, 701.228. Elemental analysis calcd. for $C_{46}H_{87}NO_3$: C 78.68, H 12.49, N 1.99; found: C 78.54, H 12.23, N 2.17.

Compound **6**

To a mixture of compound **4(12)** (1.0 g, 1.55 mmol) and sodium triacetoxyborohydride (0.43 g, 2.0 mmol) in THF, a solution of acetaldehyde (0.082 g, 1.86 mmol) in THF was added. The reaction mixture was then allowed to stir at room temperature for 24h. It was then quenched with water followed by extraction with CH_2Cl_2. The organic layer was washed with sodium bicarbonate solution, dried over $MgSO_4$ and solvent was evaporated under vacuo. The crude product was purified by silica-gel chromatography to give 3,4,5-tris(dodecyloxy)-*N*-ethylaniline (an unstable compound), this compound was immediately allowed to react with iodomethane (1.68 g, 11.8mmol) and potassium carbonate (0.164 g, 1.1mmol) in acetonitrile. The suspension was stirred under reflux for 24h. The reaction mixture was concentrated under vacuo. The crude product was purified by silica-gel chromatography (elution with $CHCl_3$/MeOH; 5-10% MeOH) to yield compound **6** (0.76 g, 0.91 mmol, 59%)

^{1}H NMR (400 MHz, $CDCl_3$): δ= 6.85 (s, 2H; ArH), 4.45 (q, *J*= 6.8 Hz, 2H; CH_2), 4.11 (t, *J*=6.4 Hz, 4H; CH_2), 3.97 (t, *J*= 6 Hz, 2H; CH_2), 3.86 (s, 6H, CH_2), 1.85-1.69 (m, 6H; CH_2), 1.51-1.46 (m, 6 H; CH_2), 1.34-1.25 (m, 48 H; CH_2), 1.25 (t, *J*= 7 Hz, 3H; CH_3), 0.87 (t, *J*= 6.6 Hz, 9H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 154.21, 139.71, 138.98, 99.98, 73.77, 71.02, 65.09, 55.00, 32.02, 29.81, 29.73, 29.57, 29.46, 29.40, 26.18, 22.78, 14.21, 9.26; MS (MALDI-TOF): $[M-I]^+$ calcd. for $C_{46}H_{88}NO_3$, 702.68; found, 702.51. Elemental analysis calcd. for $C_{46}H_{88}INO_3$: C 66.56, H 10.69, N 1.69; found: C 66.53, H 10.73, N 1.68.

General procedure (C) for the preparation of 3,4,5-Tris(alkyloxy)-N,N,N-trialkylbenzenammonium iodides (**7(*n*)** and **8**).

To a stirred solution of the corresponding aniline [**4(*n*)**, **5**] in acetonitrile were added with iodomethane in excess and potassium carbonate. The suspension was stirred under reflux for 24 h. The reaction mixture was concentrated under vacuo. The crude product was purified by silica gel chromatography (elution with $CHCl_3$/MeOH) to yield the corresponding anilinium iodides (**7(*n*)** and **8**).

Compound **7(8)**

Prepared according to the general procedure (C): Compound **4(8)** (3.28 g, 6.87 mmol), iodomethane (14.53 g, 103 mmol), potassium carbonate (3.37 g, 24 mmol) to yield compound **7(8)** (1.66 g, 2.57 mmol, 37 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.00 (s, 2H; ArH), 4.13 (t, *J*= 6.4 Hz, 4H; CH_2), 4.05-3.94 (m, 11 H; CH_2; CH_3), 1.85 (m, 4H; CH_2), 1.75-1.68 (m, 2H; CH_2), 1.52-1.45 (m, 6 H; CH_2), 1.36-1.27 (m, 24 H; CH_2), 0.87 (t, *J*= 6.6 Hz, 9 H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 153.92, 142.54, 139.53, 98.96, 73.62, 70.89, 57.87, 31.85, 31.79, 30.23, 29.45, 29.37, 29.31, 29.26, 29.23, 26.05, 25.98, 22.64, 14.07; MS (MALDI-TOF): $[M-I]^+$ calcd. for $C_{33}H_{62}NO_3$, 520.472; found, 520.132. Elemental analysis calcd. for $C_{33}H_{62}INO_3$: C 61.19, H 9.65, N 2.16; found: C 61.30, H 9.66, N 2.29.

Compound **7(9)**

Prepared according to the general procedure (C): Compound **4(9)** (0.9 g, 1.73 mmol), iodomethane (1.47 g, 10.4 mmol), potassium carbonate (0.84 g, 6.1 mmol) to yield compound **7(9)** (0.95 g, 1.37 mmol, 79 %)
^{1}H NMR (400 MHz, $CDCl_3$): δ= 6.99 (s, 2H; ArH), 4.14 (t, *J*= 6.2 Hz, 4H; CH_2), 4.05-3.95 (m, 11 H; CH_2; CH_3), 1.86-1.79 (m, 4H; CH_2), 1.76-1.70 (m, 2H; CH_2), 1.53-1.46 (m, 6H, CH_2), 1.38-1.28 (m, 30 H; CH_2), 0.88 (t, *J*= 6.4 Hz, 9 H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 154.22, 142.78 139.89, 99.14, 73.81, 71.06, 58.03, 32.01, 31.99, 29.74, 29.66, 29.63, 29.54, 29.44, 29.38, 26.17, 26.11, 22.76, 14.17; MS (MALDI-TOF): $[M-I]^+$calcd. for $C_{36}H_{68}NO_3$, 562.519; found, 562.240. Elemental analysis calcd. for $C_{36}H_{68}INO_3$: C 62.68, H 9.94, N 2.03; found: C 62.74, H 9.79, N 2.20.

Compound **7(10)**
Prepared according to the general procedure (C): Compound **4(10)** (0.70g, 1.25 mmol), iodomethane (2.66 g, 18.7mmol), potassium carbonate (0.64 g, 4.63 mmol) to yield compound **7(10)** (0.585 g, 0.80 mmol, 64 %)
^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.00 (s, 2H; ArH), 4.13 (t, *J*= 6.2 Hz, 4H; CH_2), 4.01-3.95 (m, 11 H; CH_2; CH_3), 1.85-1.79 (m, 4H; CH_2), 1.77-1.69 (m, 2H; CH_2), 1.53-1.43 (m, 6H, CH_2), 1.37-1.27 (m, 36 H; CH_2), 0.88 (t, *J*= 6.8 Hz, 9 H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 153.87, 142.55, 139.42, 98.95, 73.57, 70.88, 57.85, 31.85, 30.21, 29.59, 29.41, 29.30, 26.03, 22.62, 14.04; MS (MALDI-TOF): $[M-I]^+$ calcd. for $C_{39}H_{74}NO_3$, 604.566; found, 604.319. Elemental analysis calcd. for $C_{39}H_{74}INO_3$: C 64.00, H 10.19, N 1.91; found: C 64.06, H 10.09, N 1.99.

Compound **7(11)**
Prepared according to the general procedure (C): Compound **4(11)** (0.86 g, 1.42 mmol), iodomethane (1.19 g, 8.5 mmol), potassium carbonate (0.69 g, 4.99 mmol) to yield compound **7(11)** (0.95 g, 1.20 mmol, 85 %)
^{1}H NMR (400 MHz, $CDCl_3$): δ= 6.98 (s, 2H; ArH), 4.12 (t, *J*= 6.4 Hz, 4H; CH_2), 4.02-3.94 (m, 11 H; CH_2; CH_3), 1.85-1.80 (m, 4H; CH_2), 1.75-1.68 (m, 2H; CH_2), 1.52-1.42 (m, 6H, CH_2), 1.36-1.23 (m, 42 H; CH_2), 0.87 (t, *J*= 6.8 Hz, 9 H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 154.27, 142.89, 139.82, 99.24, 73.88, 71.15, 58.12, 30.44, 29.89, 29.86, 29.83, 29.73, 29.64, 29.54, 29.48, 26.27, 26.21, 22.85, 14.26; MS (MALDI-TOF): $[M-I]^+$ calcd. for $C_{42}H_{80}NO_3$, 646.613; found, 646.407. Elemental analysis calcd. for $C_{42}H_{80}INO_3$: C 65.18, H 10.42, N 1.81; found: C 65.33, H 10.50, N 1.92.

Compound **7(12)**
Prepared according to the reference S2

Compound **7(13)**
Prepared according to the general procedure (C): Compound **4(13)** (1.06 g, 1.54 mmol), iodomethane (2.74 g, 19.3 mmol), potassium carbonate (0.75 g, 5.46 mmol) to yield compound **7(13)** (0.54 g, 0.63 mmol, 41 %)
^{1}H NMR (400 MHz, $CDCl_3$): δ= 6.97 (s, 2H; ArH), 4.12 (t, *J*= 6.6 Hz, 4H; CH_2), 3.98-3.94 (m, 11 H; CH_2; CH_3), 1.85-1.78 (m, 4H; CH_2), 1.75-1.68 (m, 2H; CH_2), 1.52-1.41 (m, 6H, CH_2), 1.32-1.25 (m, 54 H; CH_2), 0.87 (t, *J*= 7 Hz, 9 H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 154.07, 142.59, 139.70, 98.99, 73.76, 71.00, 57.97, 32.03, 30.36, 29.82, 29.77, 29.65, 29.57, 29.47, 29.29, 26.18, 26.14, 22.79, 14.22; MS (MALDI-TOF): $[M-I]^+$calcd. for $C_{48}H_{92}NO_3$,

730.707; found, 730.549. Elemental analysis calcd. for $C_{48}H_{92}INO_3$: C 67.18, H 10.81, N 1.63; found: C 67.30, H 10.68, N 1.81.

Compound **7(14)**
Prepared according to the general procedure (C): Compound **4(14)** (0.15 g, 0.21 mmol), Iodomethane (0.63 g, 4.44 mmol), potassium carbonate (0.17 g, 1.23 mmol) to yield compound **7(14)** (0.03 g, 0.34 mmol, 16 %)
^{1}H NMR (400 MHz, $CDCl_3$): δ= 6.99 (s, 2H; ArH), 4.13 (t, *J*= 6.4 Hz, 4H; CH_2), 3.96-3.93 (m, 11 H; CH_2; CH_3), 1.85-1.78 (m, 4H; CH_2), 1.75-1.68 (m, 2H; CH_2), 1.52-1.43 (m, 6H, CH_2), 1.36-1.26 (m, 60 H; CH_2), 0.87= (t, *J*= 7 Hz, 9 H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 153.96, 142.53, 139.60, 98.95, 73.66, 70.93, 57.88, 31.92, 30.26, 29.72, 29.66, 29.55, 29.46, 29.36, 29.30, 26.09, 26.03, 22.68, 14.10; MS (MALDI-TOF): $[M-I]^+$calcd. for $C_{51}H_{98}NO_3$, 772.754; found, 772.660. Elemental analysis calcd. for $C_{51}H_{98}INO_3$: C 68.04, H 10.97, N 1.56; found: C 68.23, H 11.35, N 1.72.

Compound **8**
Prepared according to the general procedure (C): Compound **(5)** (0.83 g, 1.19 mmol), iodomethane (9.0 g, 64 mmol) to yield compound **(8)** (0.87 g, 1.0 mmol, 86 %)
^{1}H NMR (400 MHz, $CDCl_3$): δ= 6.76 (s, 2H; ArH), 4.41 (m, 4H; CH_2), 4.10 (t, *J*= 6.4 Hz, 4 H; CH_2), 3.99 (t, *J*= 6.4, 2H; CH_2), 3.62 (s, 3H; CH_3), 1.86-1.7 (m, 6 H; CH_2), 1.5 (m, 6H; CH_2), 1.26 (m, 48H; CH_2), 1.14 (t, *J*= 7.2, 6H; CH_3), 0.89 (t, *J*=6.8, 9H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 154.20, 139.42, 135.70, 100.89, 73.67, 70.98, 64.88, 46.19, 31.91, 30.27, 29.70, 29.65, 29.62, 29.53, 29.47, 29.36, 29.32, 26.10, 26.03, 22.68, 14.09, 8.79; MS (MALDI-TOF): [M−I]+ calcd. for $C_{47}H_{90}NO_3$, 716.692; found, 716.665. Elemental analysis calcd. for $C_{47}H_{90}INO_3$: C 66.87, H 10.75, N 1.66; found: C 66.88, H 10.44, N 1.81.

General procedure (D) for the synthesis of compounds (**1(*n*/X)**, **2(*n*/X)** and **3(*n*/X)**)

A solution of $AgBF_4$ or $AgPF_6$ or $AgCF_3SO_3$ in MeOH (20-30 mL) was added dropwise to a stirred solution of the *N,N,N*-trialkyl-3,4,5-trialkyloxyanilinium iodide [**7(*n*)**, **6** or **8**] in MeOH (5-10 mL) at room temperature. The reaction mixture was stirred for 3h, protected from light. The resulting precipitate of silver iodide was removed by filtration and the solvent was removed *in vacuo*. The residue was purified by silica gel chromatography (eluent: $CHCl_3$:MeOH = 95:5) and recrystallized twice from the mixed solvent of EtOAc and MeOH to give the desired product.

Compound **1(8/BF_4)**
Prepared according to the general procedure (D): Compound **7(8)** (0.46 g, 0.71 mmol), $AgBF_4$ (0.23 g, 1.07 mmol) to yield compound **1(8/BF_4)** (0.235 g, 0.39 mmol, 54 %)
^{1}H NMR (400 MHz, $CDCl_3$): δ= 6.83 (s, 2H; ArH), 4.04 (t, *J*= 6.4 Hz, 4H; CH_2), 3.96 (t, *J*=6.6, 2H; CH_2), 3.66 (s, 9H; CH_3), 1.85-1.78 (m, 4H; CH_2), 1.76-1.69 (m, 2 H; CH_2), 1.51-1.42 (m, 6H; CH_2), 1.29 (m, 24 H; CH_2), 0.88 (t, *J*= 7 Hz, 9H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 153.96, 141.98, 139.53, 98.37, 73.68, 70.06, 57.36, 31.89, 31.82, 30.26, 29.49, 29.36, 29.28, 26.04, 22.68, 14.11; MS (MALDI-TOF): $[M-BF_4]^+$ calcd. for $C_{33}H_{62}NO_3$, 520.472; found, 520.393. Elemental analysis calcd. for $C_{33}H_{62}BF_4NO_3$: C 65.23, H 10.28, N 2.31; found: C 65.41, H 10.34, N 2.37.

Compound **1(9/BF_4)**
Prepared according to the general procedure (D): Compound **7(9)** (0.53 g, 0.77 mmol), $AgBF_4$ (0.229 g, 1.18 mmol) to yield compound **1(9/BF_4)** (0.30 g, 0.45 mmol, 59 %)
^{1}H NMR (400 MHz, $CDCl_3$): δ= 6.84 (s, 2H; ArH), 4.04 (t, *J*= 6.4 Hz, 4H; CH_2), 3.96 (t, *J*=6.6, 2H; CH_2), 3.65 (s, 9H; CH_3), 1.84-1.77 (m, 4H; CH_2), 1.76-1.69 (m, 2 H; CH_2), 1.53-1.42 (m, 6H; CH_2), 1.26 (m, 30H; CH_2), 0.87 (t, *J*= 6.6 Hz, 9H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 153.96, 142.07, 139.50, 98.42, 73.67, 70.05, 57.33, 31.94, 31.92, 30.29, 29.68, 29.60, 29.57, 29.44, 29.38, 29.31, 26.07, 26.05, 22.69, 14.11; MS (MALDI-TOF): $[M\text{-}BF_4]^+$ calcd. for $C_{36}H_{68}NO_3$, 562.519; found, 562.332. Elemental analysis calcd. for $C_{36}H_{68}BF_4NO_3$: C 66.55, H 10.55, N 2.16; found: C 66.78, H 10.60, N 2.21.

Compound **1(10/BF_4)**
Prepared according to the general procedure (D): Compound **7(10)** (0.21 g, 0.28 mmol), $AgBF_4$ (0.087 g, 0.44 mmol) to yield compound **1(10/BF_4)** (0.097 g, 0.14 mmol, 50 %)
^{1}H NMR (400 MHz, $CDCl_3$): δ= 6.84 (s, 2H; ArH), 4.04 (t, *J*= 6.4 Hz, 4H; CH_2), 3.96 (t, *J*= 6.6 Hz, 2H; CH_2), 3.65 (s, 9H; CH_3), 1.84-1.77 (m, 4H; CH_2), 1.76-1.69 (m, 2 H; CH_2), 1.51-1.42 (m, 6H; CH_2), 1.34-1.26 (m, 36H; CH_2), 0.87 (t, *J*=6.8, 9H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 154.06, 142.04, 139.69, 98.47, 73.77, 70.19, 57.47, 32.01, 30.36, 29.81, 29.76, 29.72, 29.68, 29.51, 29.45, 29.38, 26.14, 22.78, 14.21; MS (MALDI-TOF): $[M\text{-}BF_4]^+$calcd. for $C_{39}H_{74}NO_3$, 604.566; found 604.427; Elemental analysis calcd. for $C_{39}H_{74}BF_4NO_3$: C 67.71, H 10.78, N 2.02; found: C 67.98, H 10.92, N 2.03.

Compound **1(11/BF_4)**
Prepared according to the general procedure (D): Compound **7(11)** (0.60 g, 0.90 mmol), $AgBF_4$ (0.27 g, 1.36 mmol) to yield compound **1(11/BF_4)** (0.29 g, 0.39 mmol, 44 %)
^{1}H NMR (400 MHz, $CDCl_3$): δ= 6.83 (s, 2H; ArH), 4.04 (t, *J*= 6.4 Hz, 4H; CH_2), 3.96 (t, *J*=6.6, 2H; CH_2), 3.66 (s, 9H; CH_3), 1.85-1.78 (m, 4H; CH_2), 1.76-1.69 (m, 2H; CH_2), 1.51-1.44 (m, 6H; CH_2), 1.26 (m, 42H; CH_2), 0.87 (t, *J*=6.8, 9H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 153.96, 142.00, 139.57, 98.37, 73.66, 70.07, 57.36, 31.92, 30.26, 29.72, 29.68, 29.66, 29.63, 29.55, 29.42, 29.36, 29.29, 26.04, 22.68, 14.11; MS (MALDI-TOF): $[M\text{-}BF_4]^+$calcd. for $C_{42}H_{80}NO_3$, 646.613; found, 646.588. Elemental analysis calcd. for $C_{42}H_{80}BF_4NO_3$: C 68.74, H 10.99, N 1.91; found: C 68.51, H 11.20, N 1.99.

Compound **1(12/BF_4)**
Prepared according to the reference S2

Compound **1(12/PF_6)**
Prepared according to the reference S2

Compound **1(12/CF_3SO_3)**
Prepared according to the general procedure (D): Compound **7(12)** (0.61 g, 0.94 mmol), $AgCF_3SO_3$ (0.23 g, 0.91 mmol) to yield compound **1(12/CF_3SO_3)** (0.24 g, 0.29 mmol, 95 %).
^{1}H NMR (400 MHz, $CDCl_3$): δ= 6.88 (s, 2H; ArH), 4.05 (t, *J*= 6.4 Hz, 4H; CH_2) , 3.96 (t, *J*=

6.4 Hz, 2 H; CH_2), 3.70 (s, 9H; CH_3), 1.81 (m, 4H; CH_2), 1.72 (m, 2H; CH_2) , 1.45 (m, 6H; CH_2), 1.26 (m, 48H; CH_2), 0.87 (t, *J*=6.4, 9H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): *δ*= 154.04, 142.11, 139.66, 98.59, 73.66, 70.11, 57.46, 31.86, 30.20, 29.64, 29.59, 29.56, 29.48, 29.34, 29.30, 29.21, 25.96, 22.61, 14.01; MS (MALDI-TOF): $[M- CF_3SO_3]^+$ calcd. for $C_{45}H_{86}NO_3$, 688.661; found, 687.717; Elemental analysis calcd. for $C_{46}H_{86}F_3NO_6S$: C 65.91, H 10.34, N 1.67; found: C 65.82, H 10.12, N 1.77.

Compound **1(13/BF_4)**
Prepared according to the general procedure (D): Compound **7(13)** (0.5 g, 0.58 mmol), $AgBF_4$ (0.19 g, 0.96 mmol) to yield **6** compound **1(13/BF_4)** (0.29 g, 0.36 mmol, 62 %)
^{1}H NMR (400 MHz, $CDCl_3$): *δ*= 6.83 (s, 2H; ArH), 4.04 (t, *J*= 6.4 Hz, 4H; CH_2), 3.96 (t, *J*=6.8, 2H; CH_2), 3.65 (s, 9H; CH_3), 1.85-1.78 (m, 4H; CH_2), 1.76-1.69 (m, 2H, CH_2), 1.51-1.42 (m, 6H; CH_2), 1.34-1.25 (m, 54H; CH_2), 0.87 (t, *J*= 6.8 Hz, 9H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): *δ*= 153.94, 141.99, 139.50, 98.36, 73.65, 70.04, 57.32, 31.92, 30.27, 29.72, 29.67, 29.65, 29.56, 29.43, 29.37, 29.28, 26.05, 22.68, 14.11; MS (MALDI-TOF): $[M-BF_4]^+$calcd. for $C_{48}H_{92}NO_3$, 730.707; found, 730.893. Elemental analysis calcd. for $C_{48}H_{92}BF_4NO_3$: C 70.47, H 11.34, N 1.71; found: C 70.66, H 11.79, N 1.88.

Compound **1(14/BF_4)**
Prepared according to the general procedure (D): Compound **7(14)** (0.41 g, 0.48 mmol), $AgBF_4$ (0.16 g, 0.80 mmol) to yield compound **1(14/BF_4)** (0.31 g, 0.38 mmol, 80 %)
^{1}H NMR (400 MHz, $CDCl_3$): *δ*= 6.84 (s, 2H; ArH), 4.04 (t, *J*= 6.4 Hz, 4H; CH_2), 3.96 (t, *J*= 6.6 Hz, 2H; CH_2), 3.65 (s, 9H; CH_3), 1.84-1.77 (m, 4H; CH_2), 1.76-1.69 (m, 2 H; CH_2), 1.51-1.44 (m, 6H; CH_2), 1.25 (m, 60H; CH_2), 0.87 (t, *J*=6.8, 9H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): *δ*= 153.97, 141.96, 139.60, 98.38, 73.67, 70.10, 57.37, 31.92, 30.27, 29.72, 29.67, 29.65, 29.56, 29.43, 29.37, 29.29, 26.05, 22.68, 14.11; MS (MALDI-TOF): $[M-BF_4]^+$ calcd. for $C_{51}H_{98}NO_3$, 772.754; found, 773.006. Elemental analysis calcd. for $C_{51}H_{98}BF_4NO_3$: C 71.22, H 11.48, N 1.63; found: C 71.42, H 11.72, N 1.73.

Compound **2(12/BF_4)**
Prepared according to the general procedure (D): Compound **8** (0.20 g, 0.24 mmol), $AgBF_4$ (0.061 g, 0.31 mmol) to yield compound **2(12/BF_4)** (0.075 g, 0.095 mmol, 39.4 %)
^{1}H NMR (400 MHz, $CDCl_3$): *δ*= 6.74 (s, 2H; ArH), 4.05-3.97 (m, 6H; CH_2), 3.57 (s, 6H; CH_2), 3.49 (d, 2H; CH_2), 1.84-1.77 (m, 4H; CH_2), 1.76-1.69 (m, 2H; CH_2) 1.51-1.44 (m, 6H, CH_2), 1.34-1.25 (m, 48 H; CH_2), 1.20 (t, *J*= 7.2 Hz, 3H; CH_3), 0.87 (t, *J*= 6.8 Hz, 9H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): *δ*= 154.08, 139.51, 138.50, 99.42, 73.66, 70.14, 64.80, 54.24, 31.93, 30.28, 29.72, 29.69, 29.67, 29.64, 29.55, 29.45, 29.37, 29.31, 26.06, 22.69, 14.11, 9.00; MS (MALDI-TOF): $[M-BF_4]^+$ calcd. for $C_{46}H_{88}NO_3$, 702.676; found, 702.637. Elemental analysis calcd. for $C_{46}H_{88}BF_4NO_3$: C 69.94, H 11.23, N 1.77; found: C 70.02, H 11.57, N 1.99.

Compound **2(12/PF_6)**
Prepared according to the general procedure (D): Compound **8** (0.17 g, 0.207 mmol), $AgPF_6$ (0.073 g, 0.29 mmol) to yield compound **2(12/PF_6)** (0.020 g, 0.024 mmol, 11 %)
^{1}H NMR (400 MHz, $CDCl_3$): *δ*= 6.69 (s, 2H; ArH), 4.05-3.91 (m, 6H; CH_2), 3.53 (s, 6H; CH_2), 1.86-1.79 (m, 4H; CH_2), 1.76-1.70 (m, 2H; CH_2), 1.55-1.45 (m, 8H, CH_2), 1.35-1.26 (m, 48 H; CH_2), 1.13 (t, *J*= 7 Hz, 3H; CH_3), 0.87 (t, *J*= 6.8 Hz, 9H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$):

δ= 154.15, 139.62, 138.32, 99.24, 73.71, 70.14, 65.06, 54.30, 31.94, 30.29, 29.73, 29.68, 29.65, 29.56, 29.44, 29.38, 29.30, 26.02, 22.70, 14.12, 8.98; MS (MALDI-TOF): $[M\text{-}PF_6]^+$ calcd. for $C_{46}H_{88}NO_3$, 702.676; found, 702.699. Elemental analysis calcd. for $C_{46}H_{88}PF_6NO_3$: C 65.14, H 10.46, N 1.65; found: C 65.20, H 10.45, N 1.81.

Compound **2(12/CF_3SO_3)**
Prepared according to the general procedure (D): Compound **8** (0.15 g, 0.181 mmol), $AgCF_3SO_3$ (0.060 g, 0.23 mmol) to yield compound **2(12/CF_3SO_3)** (0.046 g, 0.054 mmol, 30 %)
^{1}H NMR (400 MHz, $CDCl_3$): δ= 6.82 (s, 2H; ArH), 4.11-3.96 (m, 6H; CH_2), 3.62 (s, 6H; CH_2), 1.85-1.78 (m, 4H; CH_2), 1.76-1.70 (m, 2H; CH_2), 1.56-1.43 (m, 8H, CH_2), 1.37-1.30 (m, 48 H; CH_2), 1.14 (t, *J*= 7.2 Hz, 3H; CH_3), 0.88 (t, *J*= 6.8 Hz, 9H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 154.34, 139.82, 138.80, 122.50, 119.31, 99.74, 73.83, 70.35, 65.09, 54.48, 32.02, 29.84, 29.81, 29.76, 29.72, 29.64, 29.51, 29.46, 29.38, 26.13, 22.78, 14.19, 9.09; MS (MALDI-TOF): $[M\text{-}CF_3SO_3]^+$ calcd. for $C_{46}H_{88}NO_3$, 702.676; found, 702.621. Elemental analysis calcd. for $C_{47}H_{88}F_3NO_6S$: C 66.24, H 10.41, N 1.64; found: C 66.28, H 10.55, N 1.82.

Compound **3(12/BF_4)**
Prepared according to the general procedure (D): Compound **9** (0.24 g, 0.28 mmol), $AgBF_4$ (0.16 g, 0.85 mmol) to yield compound **3 (12/BF_4)** (0.22 g, 0.27 mmol, 98 %).
^{1}H NMR (400 MHz, $CDCl_3$): δ= 6.67 (s, 2H; ArH), 4.02 (m, 10H; CH_2), 3.40 (s, 3 H; CH_3), 1.80 (m, 6H; CH_2), 1.46 (m, 6H; CH_2), 1.26 (m, 48H; CH_2), 1.13 (t, *J*= 6.8 Hz, 6H; CH_3), 0.88 (t, *J*= 6.8 Hz, 9H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 154.16, 139.39, 135.38, 100.44, 73.65, 70.17, 64,65, 45.49, 31.92, 30.29, 29.71, 29.66, 29.63, 29.55, 29.46, 29.37, 29.33, 26.07, 26.04, 22.68, 14.10, 8.62; MS (MALDI-TOF): $[M- BF_4]+$ calcd. for $C_{47}H_{90}NO_3$, 716.692; found, 716.342; Elemental analysis calcd. for $C_{47}H_{90}BF_4NO_3$: C 70.21, H 11.28, N 1.74; found: C 70.13, H 11.25, N 1.99.

Compound **3(12/PF_6)**
Prepared according to the general procedure (D): Compound **9** (0.26 g, 0.30 mmol), $AgPF_6$ (0.25 g, 0.98 mmol) to yield compound **3(12/PF_6)** (0.20 g, 0.23 mmol, 75 %).
^{1}H NMR (400 MHz, $CDCl_3$): δ= 6.61 (s, 2H; ArH), 4.00 (m, 8H; CH_2), 3.83 (t, *J*= 6.4 Hz, 2H; CH_2), 3.38 (s, 3 H; CH_3), 1.81 (m, 4H; CH_2), 1.75 (m, 2H; CH_2), 1.48 (m, 6H; CH_2), 1.26 (m, 48H; CH_2), 1.14 (t, *J*= 7.2 Hz, 6H; CH_3), 0.88 (t, *J*= 6.4 Hz, 9H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 154.21, 139.41, 135.27, 100.21, 73.67, 70.12, 64.79, 45.52, 31.92, 30.29, 29.71, 29.69, 29.66, 29.63, 29.55, 29.45, 29.37, 29.31, 26.02, 22.68, 14.10, 13.72, 8.55; MS (MALDI-TOF): $[M- PF_6]+$ calcd. for $C_{47}H_{90}NO_3$, 716.692; found, 716.416; Elemental analysis calcd. for $C_{47}H_{90}F_6NO_3P$: C 65.47, H 10.52, N 1.62; found: C 65.50, H 10.54, N 1.78.

Compound **3(12/CF_3SO_3)**
Prepared according to the general procedure (D): Compound **9** (0.25 g, 0.29 mmol), $AgCF_3SO_3$ (0.22 g, 0.88 mmol) to yield compound **3(12/CF_3SO_3)** (0.21 g, 0.24 mmol, 81 %).
^{1}H NMR (400 MHz, $CDCl_3$): δ= 6.70 (s, 2H; ArH), 4.14-4.97 (m, 10H; CH_2) , 3.44 (s, 3H; CH_3), 1.80 (m, 4H; CH_2), 1.75 (m, 2H; CH_2) , 1.48 (m, 6H; CH_2), 1.26 (m, 48H; CH_2), 1.13 (t,

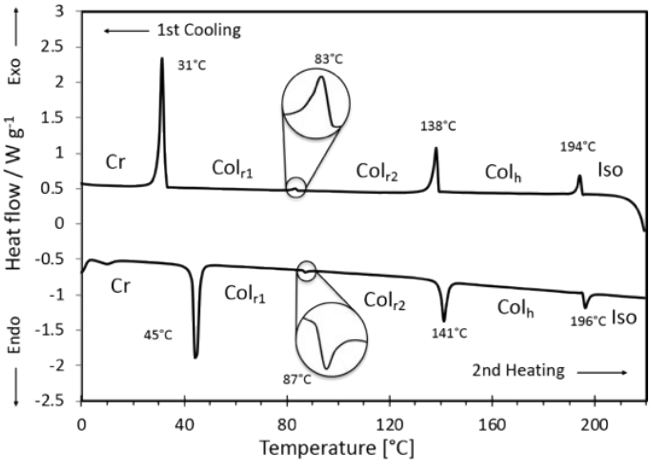
J= 6.8 Hz, 6H; CH_3), 0.87 (t, *J*=6.4, 9H; CH_3 ^{13}C NMR (100 MHz, $CDCl_3$): *δ*= 154.19, 139.50, 135.49, 100.60, 73.67, 70.25, 64.72, 31.93, 30.31, 29.76, 29.72, 29.67, 29.63, 29.56, 29.46, 29.39, 29.38, 29.32, 26.07, 22.70, 14.11, 8.65; MS (MALDI-TOF): [M− CF_3SO_3]+ calcd. for $C_{47}H_{90}NO_3$, 716.692; found, 716.738; Elemental analysis calcd. for $C_{48}H_{90}F_3NO_6S$: C 66.55, H 10.47, N 1.62; found: C 66.42, H 10.21, N 1.71.

The synthesis of *N*,*N*,*N*-triethylanilinium derivatives was unsuccessful upon treatment of the wedge-shaped anilines and excess iodoethane. The preparation of this derivative was abandoned because we expected undesirable LC behaviour as it can be deduced from the bulkier derivatives **3(12/X)**.

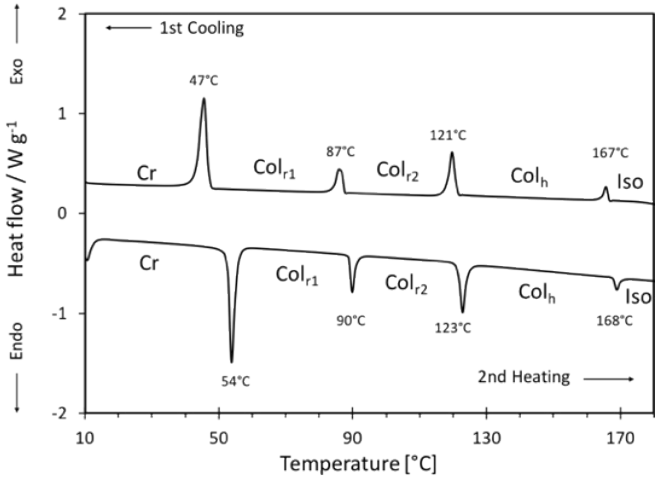
3. Thermal properties

3.1 Differential scanning calorimetry measurements

a)



b)



c)

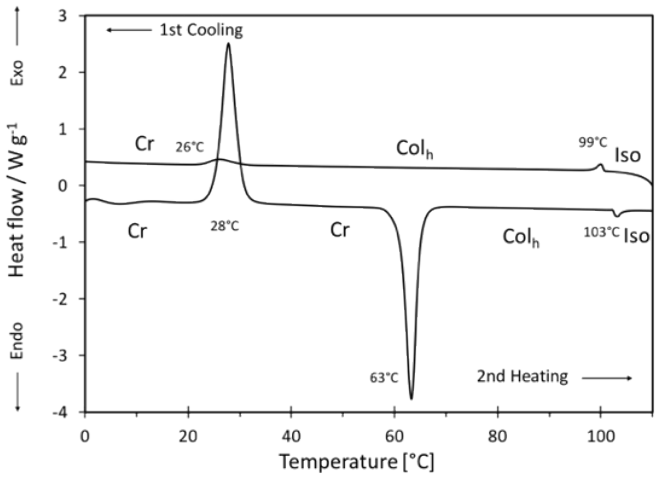


Fig. S1 DSC thermograms for the series of compounds **1(12/X)** at the scan rate of 10 k min^{-1}: a) **1(12/BF_4)**; b) **1(12/PF_6)**; c) **1(12/CF_3SO_3)**. Cr: crystalline phase; Col_r: rectangular columnar phase; Col_h: hexagonal columnar phase; Iso: isotropic phase.

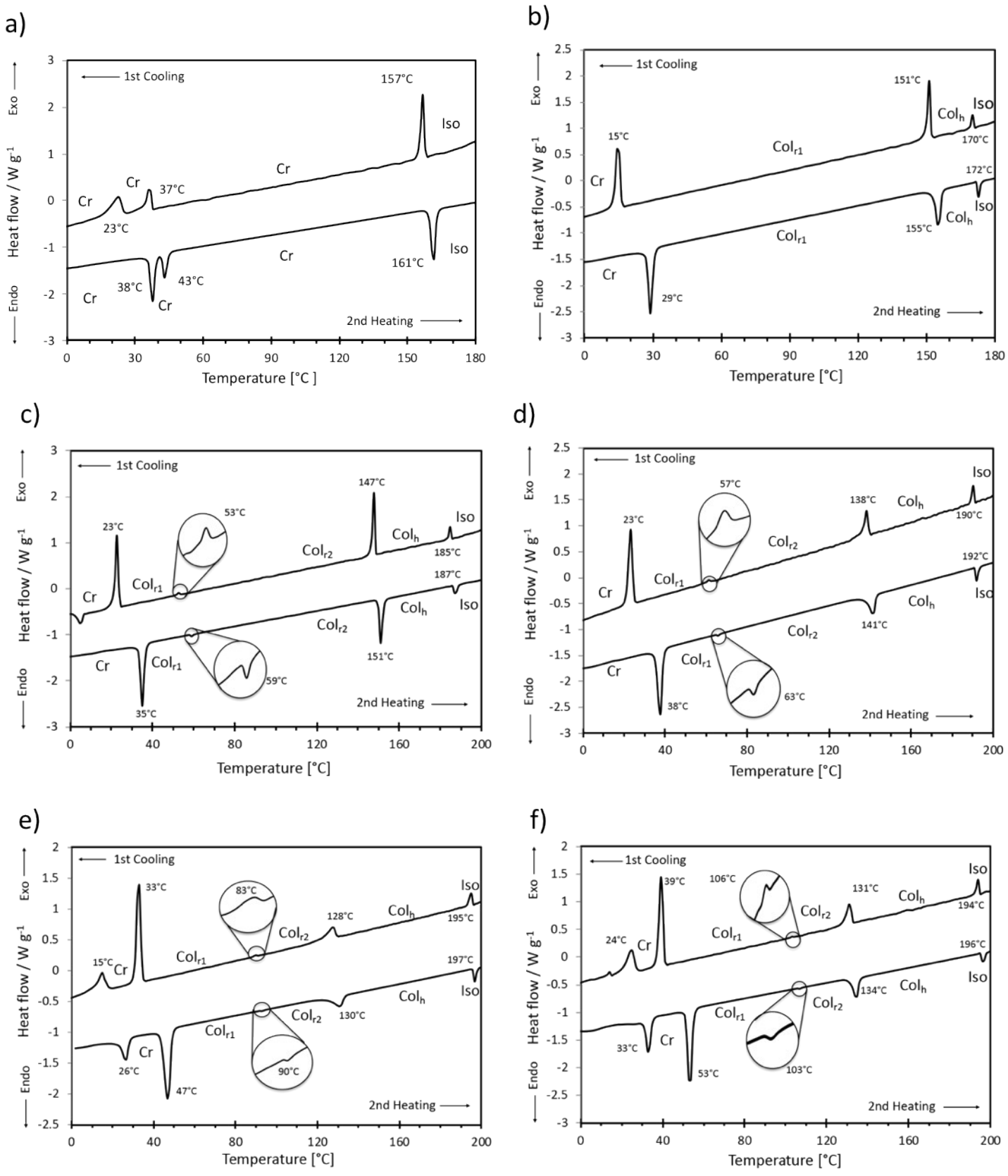


Fig. S2 DSC thermograms for the series of compounds **1(*n*/BF_4)** at the scan rate of 10 k min^{-1}: a) **1(8/BF_4)**; b) **1(9/BF_4)**; c) **1(10/BF_4)**; d) **1(11/BF_4)**; e) **1(13/BF_4)**; f) **1(14/BF_4)**. Cr: crystalline phase; Col_r: rectangular columnar phase; Col_h: hexagonal columnar phase; Iso: isotropic phase.

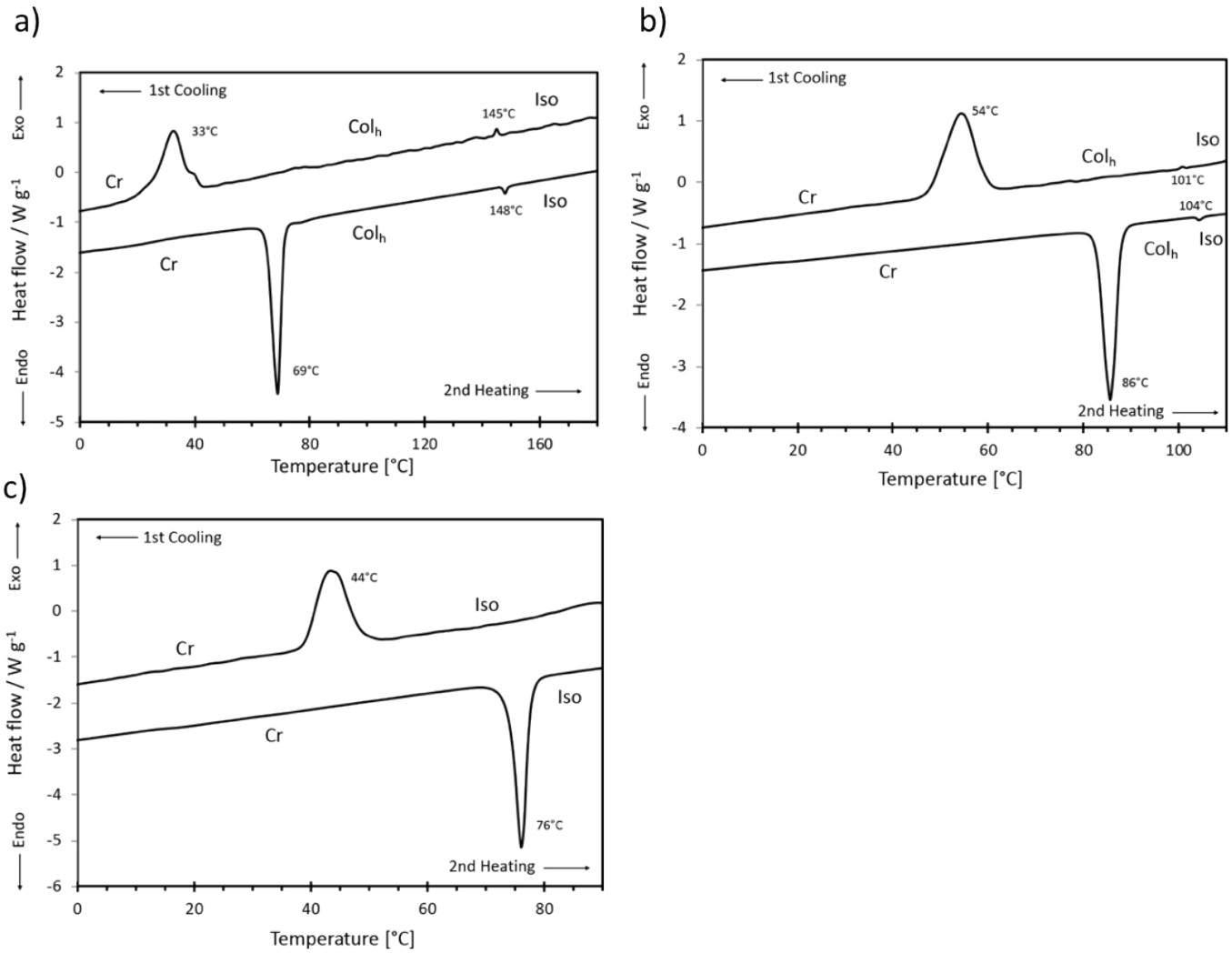


Fig. S3 DSC thermograms for the series of compounds **2** at scan rate of 10 k min^{-1}: a) **2(12/BF_4)**; b) **2(12/PF_6)**; c) **2(12/CF_3SO_3)**. Cr: crystalline phase; Col_h: hexagonal columnar phase; Iso: isotropic phase.

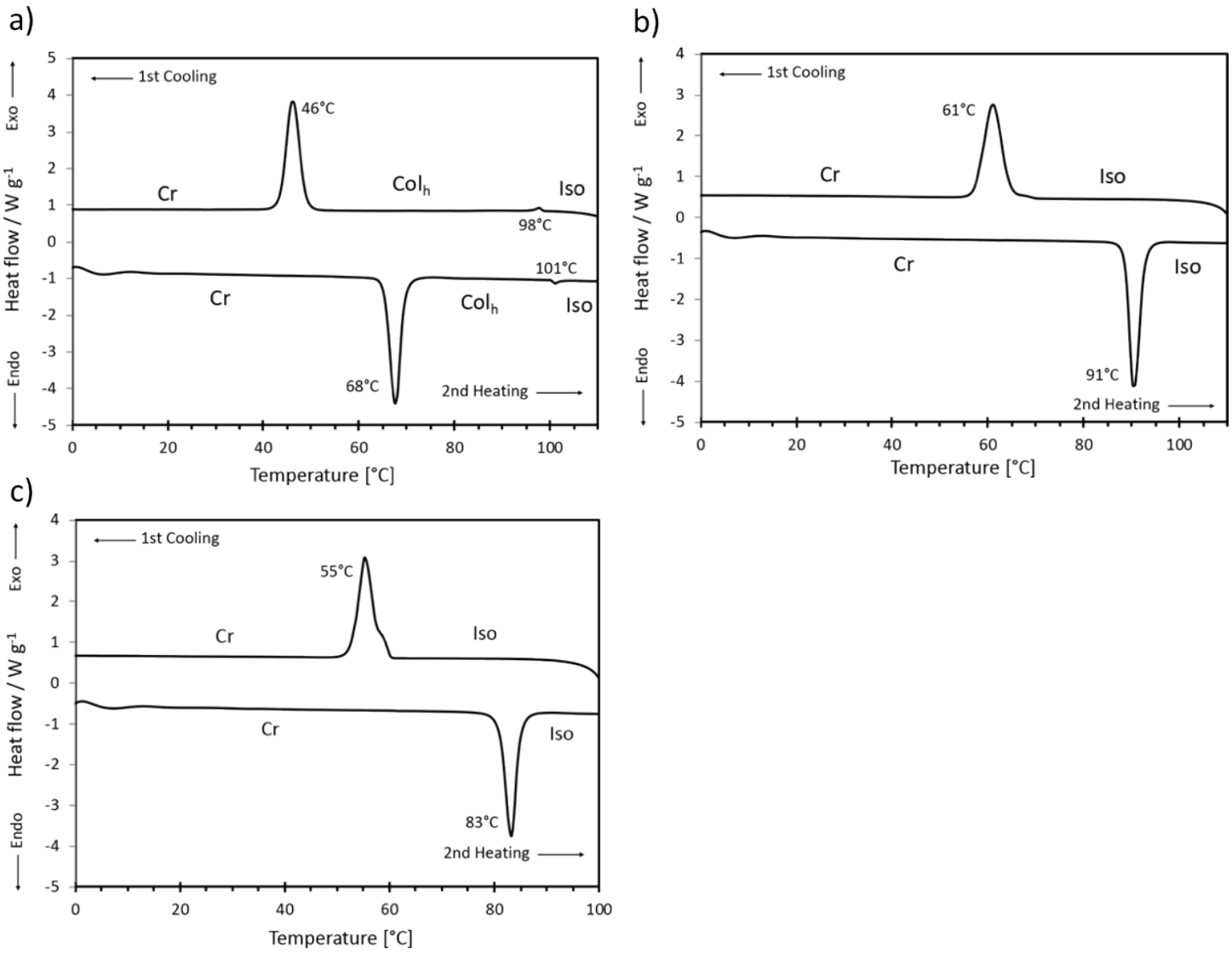


Fig. S4 DSC thermograms for the series of compounds **3** at scan rate of 10 k min^{-1}: a) **3(12/BF$_4$)**; b) **3(12/PF$_6$)**; c) **3(12/CF$_3$SO$_3$)**. Cr: crystalline phase; Col$_h$: hexagonal columnar phase; Iso: isotropic phase.

Table S1 Thermal properties of compounds **1-3**

Compound	**Phase Transition Behaviour[a]**								
1(12/BF_4)	Cr	45 (16.0)	Col_{r1}	87 (0.2)	Col_{r2}	141 (7.4)	Col_h	196 (1.7)	Iso
1(12/PF_6)	Cr	53 (10.8)	Col_{r1}	89 (2.7)	Col_{r2}	122 (4.6)	Col_h	168 (1.2)	Iso
1(12/CF_3SO_3)	Cr	61 (45.7)					Col_h	103 (0.6)	Iso
2(12/BF_4)	Cr	65 (60.5)					Col_h	147 (1.0)	Iso
2(12/PF_6)	Cr	83 (47.0)					Col_h	104 (0.42)	Iso
2(12/CF_3SO_3)	Cr	74 (50.3)							Iso
3(12/BF_4)	Cr	65 (46.6)					Col_h	100 (0.48)	Iso
3(12/PF_6)	Cr	89 (50.4)							Iso
3(12/CF_3SO_3)	Cr	81 (41.4)							Iso
1(8/BF_4)	Cr	38 (7.8)	Cr	43 (3.6)	Cr			161(9.9)	Iso
1(9/BF_4)	Cr	29 (11.7)	Col_{r1}			155 (7.9)	Col_h	173 (1.4)	Iso
1(10/BF_4)	Cr	35 (12.1)	Col_{r1}	59 (0.2)	Col_{r2}	151 (7.1)	Col_h	187 (1.6)	Iso
1(11/BF_4)	Cr	38 (15.3)	Col_{r1}	63 (0.07)	Col_{r2}	141 (5.9)	Col_h	191 (1.6)	Iso
1(12/BF_4)	Cr	45 (16.0)	Col_{r1}	87 (0.2)	Col_{r2}	141 (7.4)	Col_h	196 (1.7)	Iso
1(13/BF_4)	Cr	47 (20.1)	Col_{r1}	90 (0.1)	Col_{r2}	130 (4.8)	Col_h	197 (1.7)	Iso
1(14/BF_4)	Cr	53 (19.5)	Col_{r1}	103 (0.1)	Col_{r2}	134 (6.1)	Col_h	196 (1.5)	Iso

[a] Phase transition behaviour was determined by differential scanning calorimetry on the second heating process. The scan rate is 10 °C/min. Phase transition temperatures are given in °C and the enthalpies, in parenthesis, in kJ mol^{-1}. Cr: crystalline phase; Col_{r1}, Col_{r2}: rectangular columnar phase; Col_h: hexagonal columnar phase; Iso: isotropic phase.

3.2 Polarizing optical microscope observation

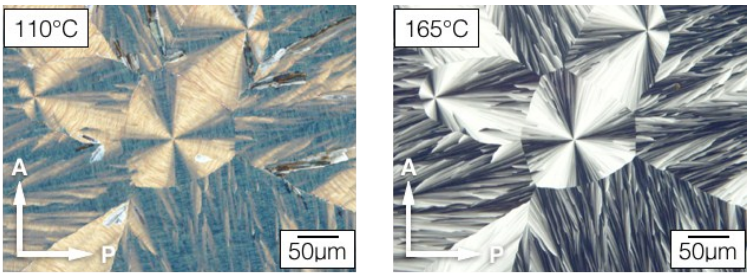


Fig. S5 Polarizing optical micrographs of **1(9/BF_4)** in the Col_{r2} phase at 110 °C, in the Col_h phase at 165 °C.

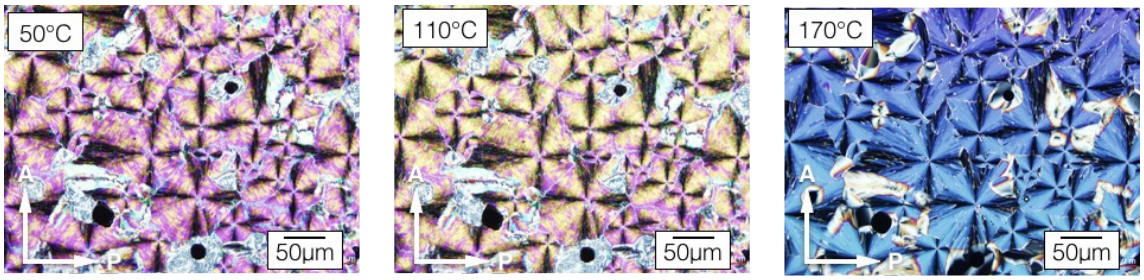


Fig. S6 Polarizing optical micrographs of **1(10/BF_4)** in the Col_{r1} phase at 50 °C, in the Col_{r2} phase at 110 °C and in the Col_h phase at 170 °C.

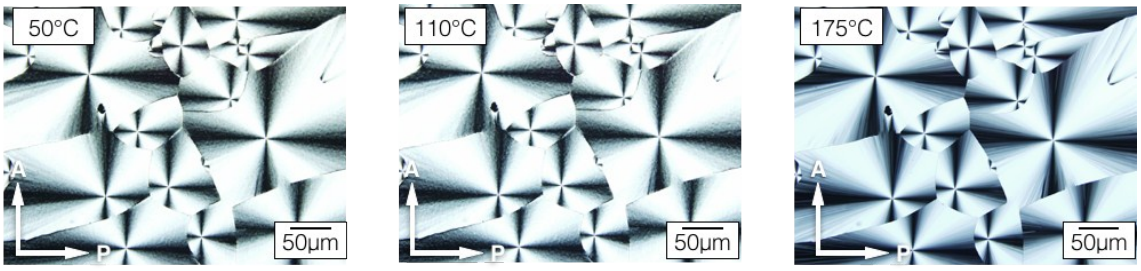


Fig. S7 Polarizing optical micrographs of **1(11/BF_4)** in the Col_{r1} phase at 50 °C, in the Col_{r2} phase at 110 °C and at 175 °C in the Col_h phase.

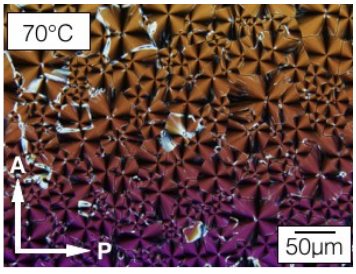


Fig. S8 Polarizing optical micrograph of **1(12/CF_3SO_3)** in the Col_h phase at 70 °C.

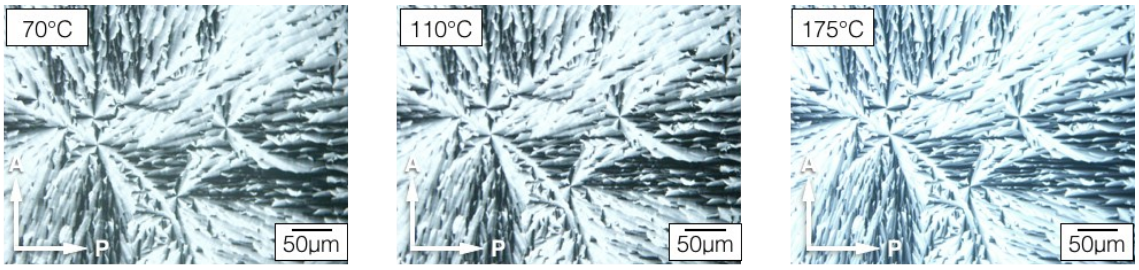


Fig. S9 Polarizing optical micrographs of **1(13/BF_4)** in the Col_{r1} phase at 70 °C, in the Col_{r2} phase at 110 °C and in the Col_h phase at 175 °C.

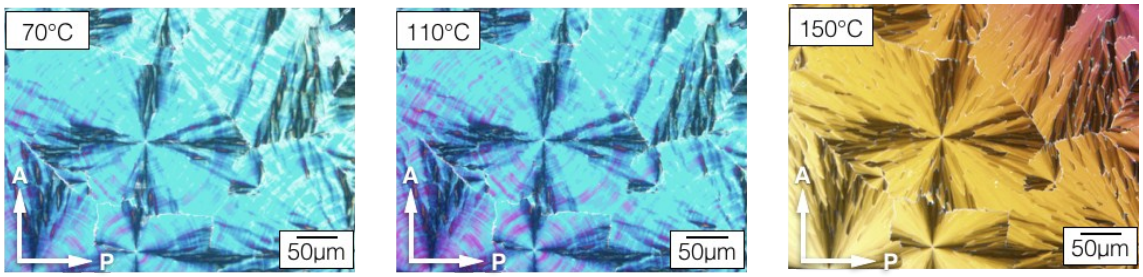


Fig. S10 Polarizing optical micrographs of **1(14/BF_4)** in the Col_{r1} phase at 70 °C, in the Col_{r2} phase at 110 °C and in the Col_h phase at 150 °C.

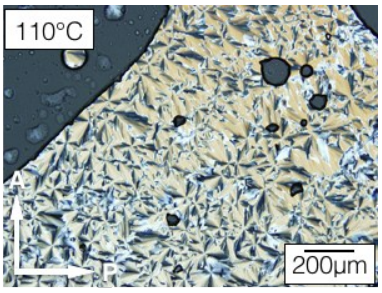


Fig. S11 Polarizing optical micrograph of **2(12/BF_4)** in the Col_h phase at 110 °C.

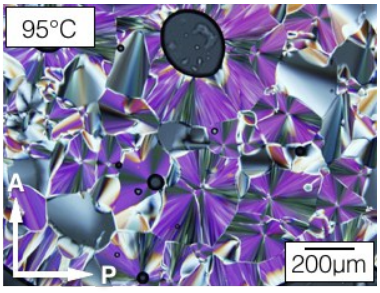


Fig. S12 Polarizing optical micrograph of **2(12/PF_6)** in the Col_h phase at 95 °C.

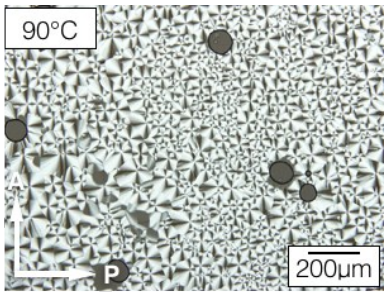


Fig. S13 Polarizing optical micrograph of **3(12/BF_4)** in the Col_h phase at 90 °C.

3.3 X-ray diffraction measurements

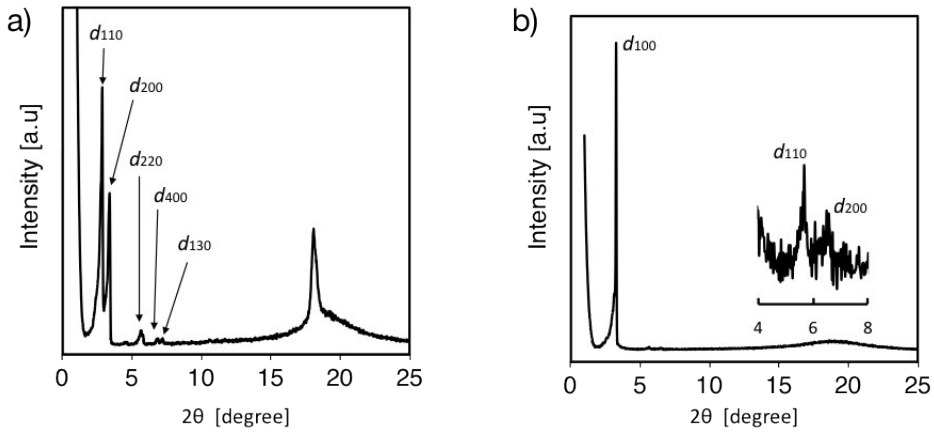


Fig. S14 Wide-angle X-ray diffraction patterns of **1(9/BF_4)**: a) at 110 °C in the Col_{r2} phase and b) at 165 °C in the Col_h phase.

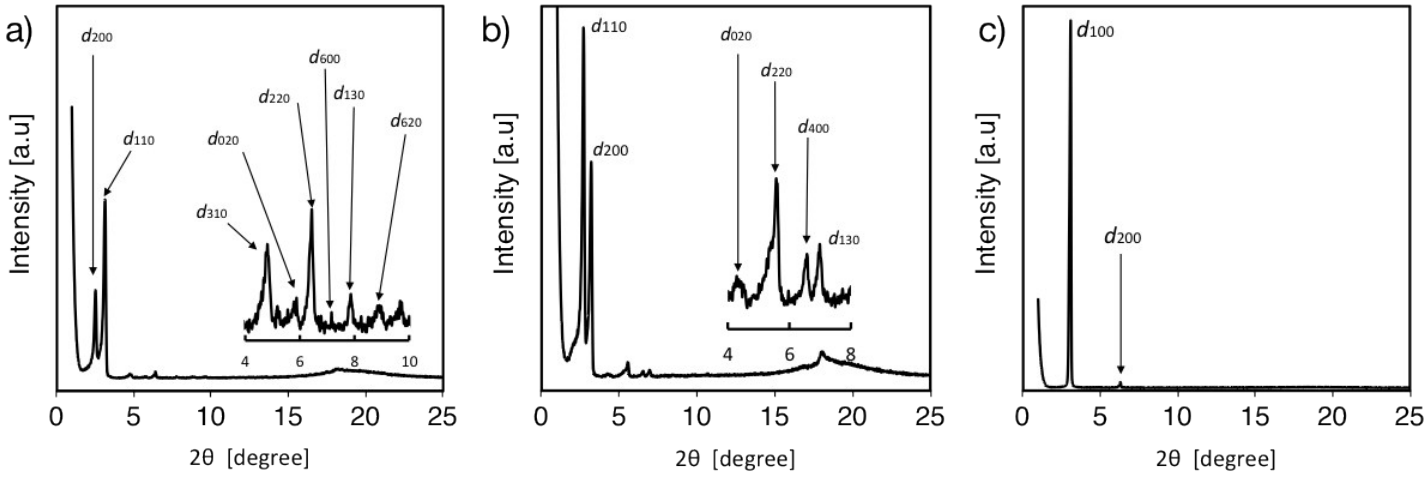


Fig. S15 Wide-angle X-ray diffraction patterns of the **1(10/BF_4)**: a) at 50 °C in the Col_{r1} phase, b) at 110 °C in the Col_{r2} phase and c) at 170 °C in the Col_h phase.

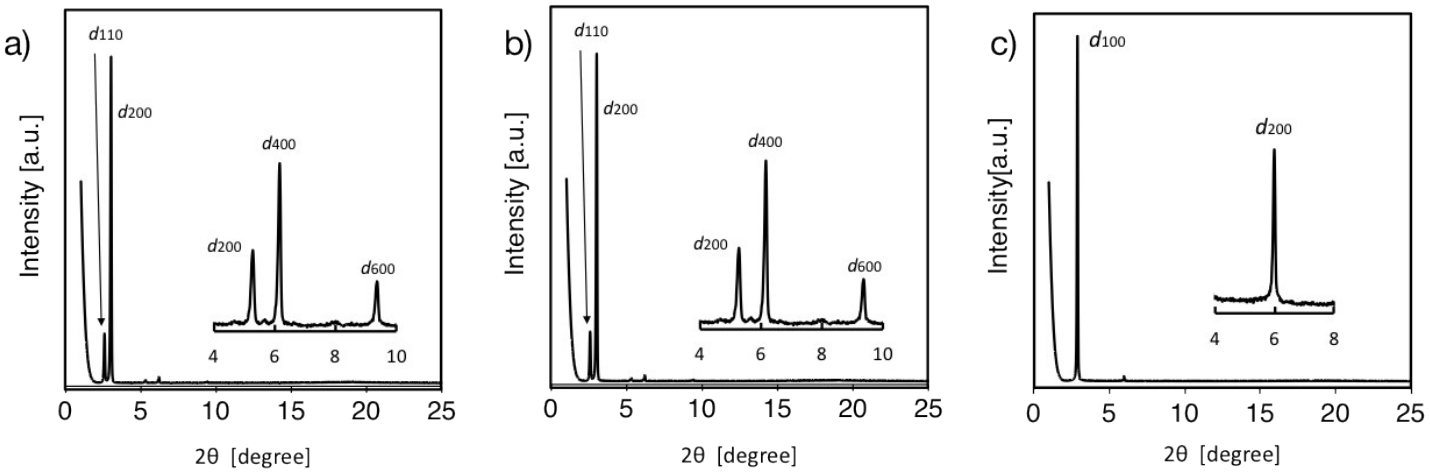


Fig. S16 Wide-angle X-ray diffraction patterns of the **1(11/BF_4)**: a) at 50 °C in the Col_{r1} phase, b) at 110 °C in the Col_{r2} phase and c) at 160 °C in the Col_h phase.

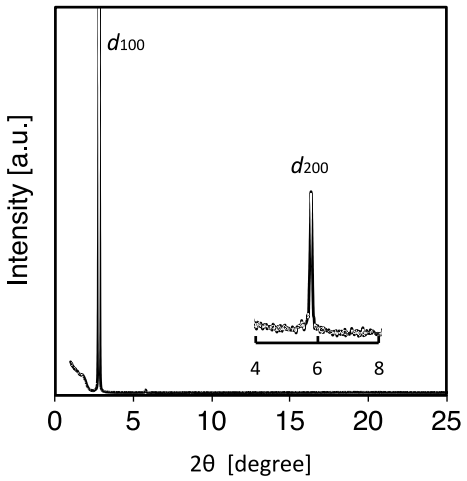


Fig. S17 Wide-angle X-ray diffraction pattern of the **1(12/CF_3SO_3)**: at 80 °C in the Col_h phase.

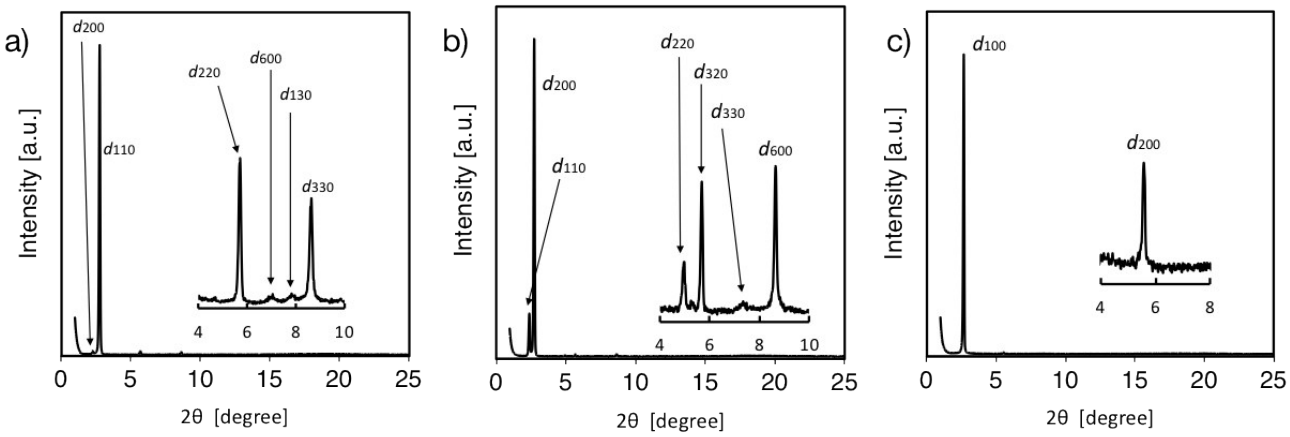


Fig. S18 Wide-angle X-ray diffraction patterns of the **1(13/BF_4)**: a) at 70 °C in the Col_{r1} phase, b) at 110 °C in the Col_{r2} phase and c) at 150 °C in the Col_h phase.

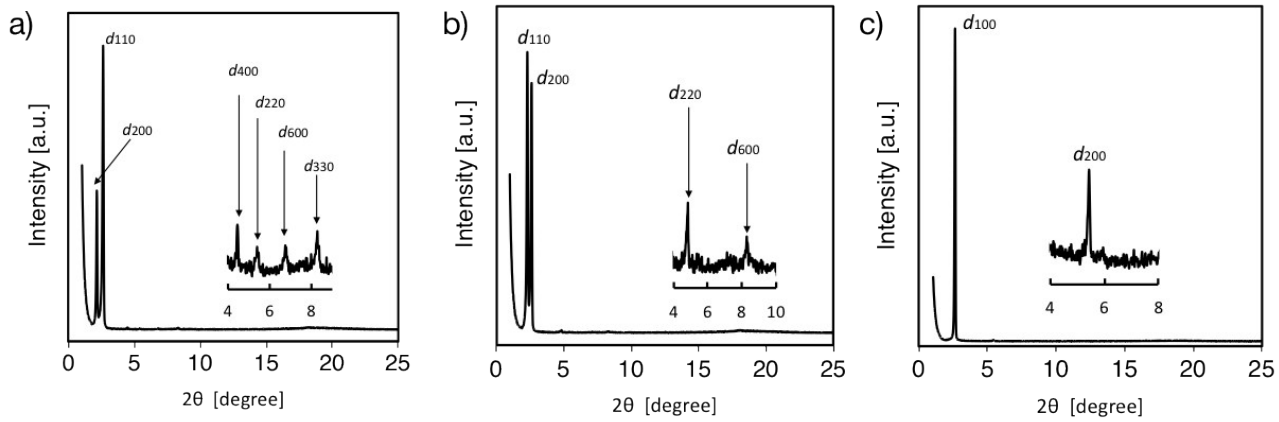


Fig. S19 Wide-angle X-ray diffraction patterns of the **1(14/BF_4)**: a) at 70 °C in the Col_{r1} phase, b) at 110 °C in the Col_{r2} phase and c) at 150 °C in the Col_h phase.

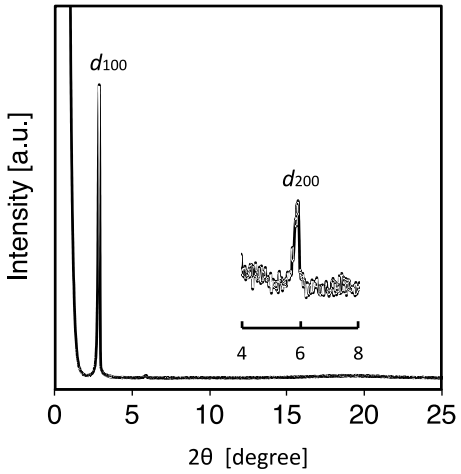


Fig. S20 Wide-angle X-ray diffraction pattern of the **2(12/BF_4)** at 110 °C in the Col_h phase.

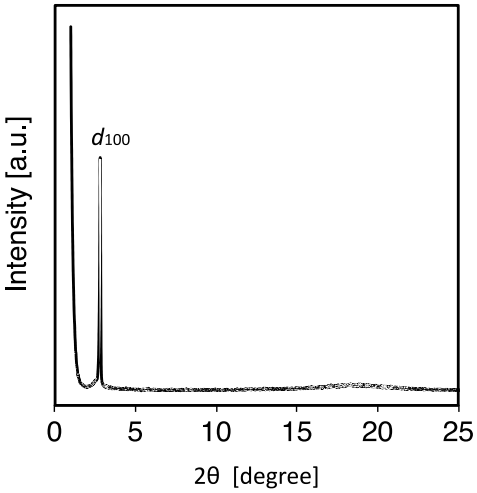


Fig. S21 Wide-angle X-ray diffraction pattern of the **2(12/PF_6)**: at 95 °C in the Col_h phase.

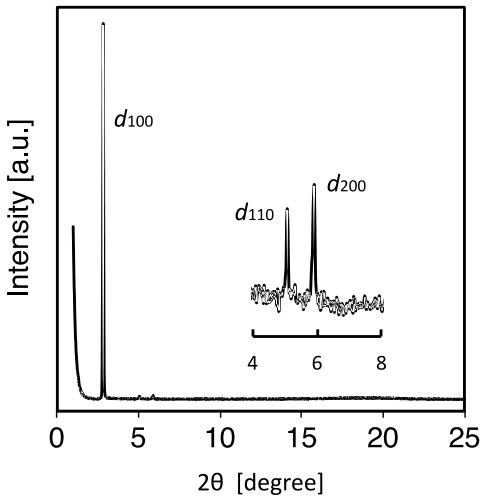


Fig. S22 Wide-angle X-ray diffraction pattern of the **3(12/BF_4)**: at 85 °C in the Col_h phase.

3.4 Thermal stability

Under ambient conditions, the samples show no decomposition for 5 years according to 1H NMR spectrometry. Under high temperatures, we have been working with these compounds at temperatures between 100 and 200 °C for periods of 120 minutes, and no decomposition was observed (monitored by 1H NMR).

The thermal gravimetric analysis (TGA) of the compound **1(14/BF_4)** has been performed. The results indicate that the samples do not decompose at temperatures below 230 °C, while the working temperatures of our switches are below 200 °C. More than 60% of the compound is decomposed by 400 °C and the 90% of the compound is decomposed by 600 °C.

4. Ionic Conductivity Measurements

Dynamic ionic conductivities were measured by using a Schlumberger Solartron 1260 impedance analyzer (frequency range: 10 Hz~10 MHz, applied voltage: 0.3 V) with a custom set-up temperature controller (heating/cooling rate: 2.0 °C/min). Ionic conductivity was calculated to be the product of 1/resistance (Ω-1) and cell constant (cm- 1) measured by KCl aqueous standard solution. The influence of the heating and cooling rate on the switch of ionic conductivities was examined.

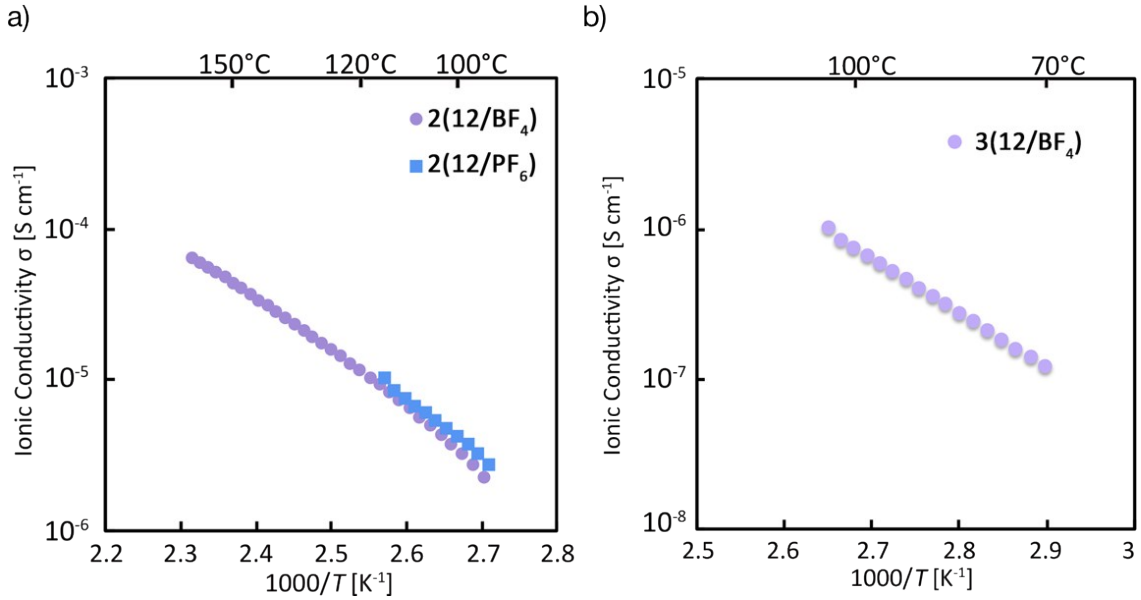


Fig. S23 Ionic conductivity measurement of a) **2(12/BF_4)** and **2(12/PF_6)** b) **3(12/BF_4)**.

Four successive heating-cooling cycles lasting 40 minutes were performed for compound **1(9-14/BF_4)** with continuous ionic conductivity measurement. The thermal switch of ionic conductivities by four orders of magnitude can be achieved at the heating and cooling rate of at least 10 °C min^{-1}. The switch of the conductivity occurs by the Col_r-Col_h phase transition and it is assumed that the switching behaviour is not dependent on the heating and cooling rate.

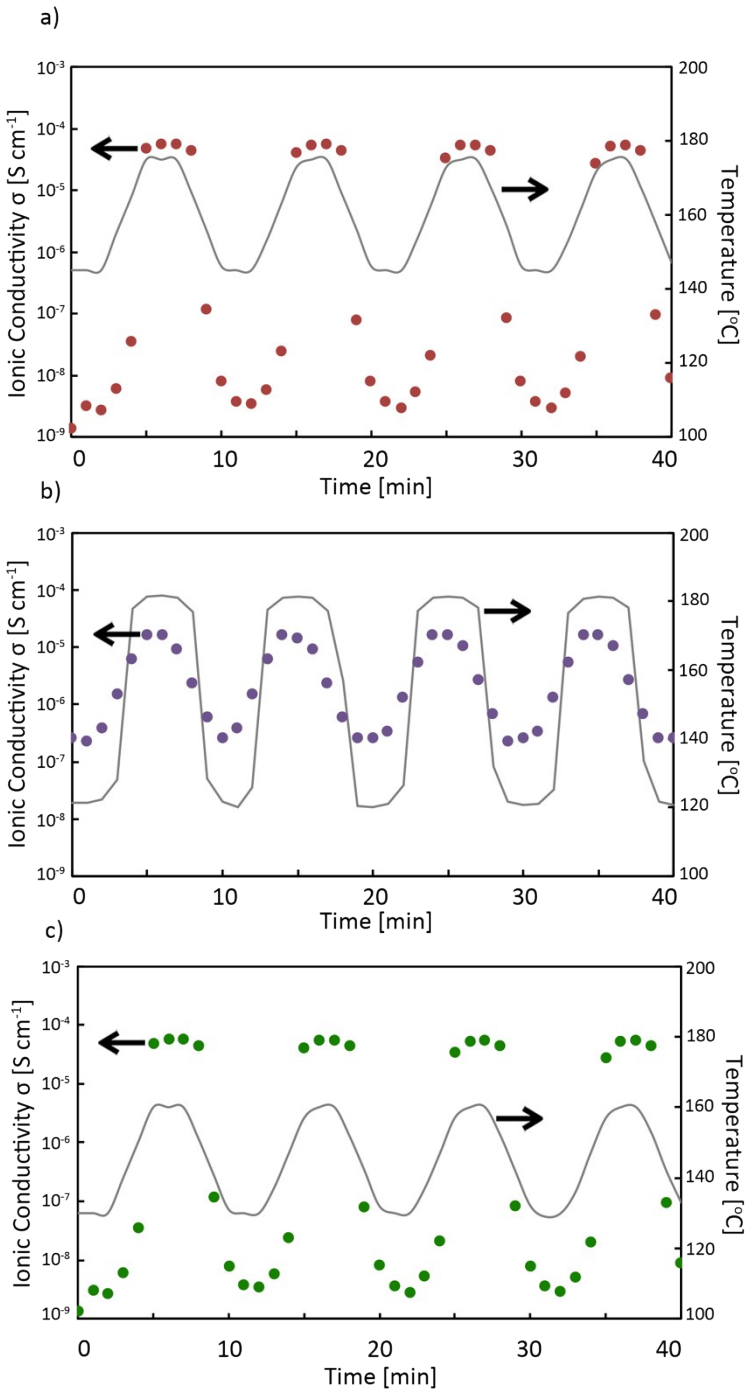


Fig. S24 The ionic conductivity as a function of temperature and time for a) **1(10/BF_4)**, b) **1(12/BF_4)** and c) **1(13/BF_4)** as the function of time. The dots represent ionic conductivity value and the grey line represent the corresponding temperature.

5. References

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S2 B. Soberats, M. Yoshio, T. Ichikawa, X. Zeng, H. Ohno, G. Ungar and T. Kato, *J. Am. Chem. Soc.*, 2015, **137**, 13212-13215.