Electronic Supplementary Material (ESI) for CrystEngComm.

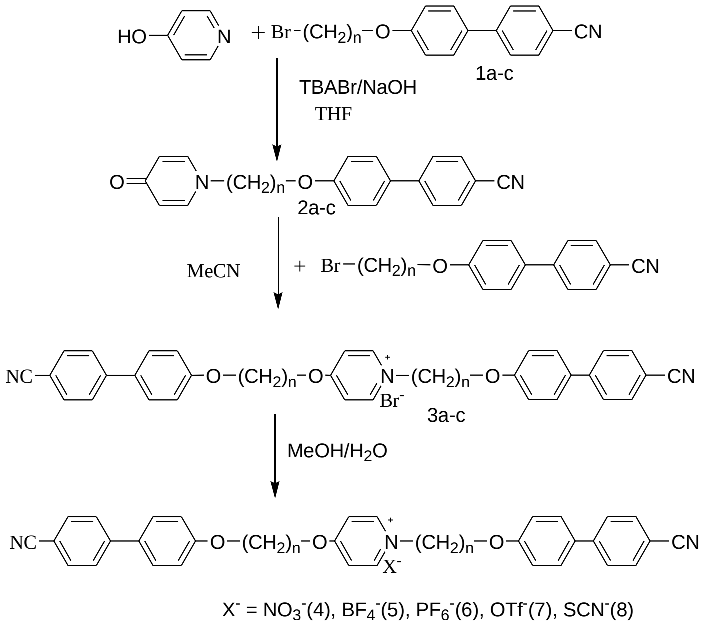
Nematic ionic liquid crystals based on pyridinium salts derived from 4-hydroxypyridine

Amalia Pana[a], Iuliana Pasuk, Marin Micutz[b], Viorel Cîrcu[a]

[a]*Dept. of Inorganic Chemistry, University of Bucharest, 23 Dumbrava Rosie st, sector 2, Bucharest 020464, Romania, e-mail: viorel_carcu@yahoo.com, viorel.circu@chimie.unibuc.ro*
[b]*National Institute of Materials Physics, P.O. Box MG-7, Magurele, 077125, Romania*
[c]*Dept. of Physical Chemistry, University of Bucharest, 4-12 Regina Elisabeta Blvd, sector 3, Bucharest 030018, Romania*

Content

Characterisation methods. All the chemicals were used as supplied. C, H, N analyses were carried out with an EuroEA 3300 instrument. IR spectra were recorded on a Bruker spectrophotometer using KBr discs. UV-VIS absorption spectra were recorded by using a Jasco V-660 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker spectrometer operating at 500 MHz, using $CDCl_3$ as solvent. ^{1}H chemical shifts were referenced to the solvent peak position, δ 7.26 ppm. The phase assignments and corresponding transition temperatures for 4-pyridones compounds **2a-c** and of the final pyridinium salts **3-8a-c**, were evaluated by polarizing optical light microscopy (POM), placed on untreated glass slides, using a Nikon 50iPol microscope equipped with a Linkam THMS600 hot stage and TMS94 control processor. Temperatures and enthalpies of transitions were collected from their corresponding thermograms recorded by using differential scanning calorimetry (DSC) technique employing a Diamond DSC Perkin Elmer instrument. The materials were studied at 10^{o}/min scanning rate after being encapsulated in aluminium pans. Three heating/cooling cycles were performed on each sample. Mesophases were assigned by their optical texture and powder X-ray diffraction data. The powder X-ray diffraction measurements were made on a D8 Advance diffractometer (Bruker AXS GmbH, Germany), in parallel beam setting, with monochromatized Cu–$K_{\alpha1}$ radiation (λ=1.5406 Å), scintillation detector, and horizontal sample stage. The measurements were performed in symmetric (θ-θ) geometry in the 2θ range from 1.5^{o} to 30^{o} in steps of 0.02^{o}, with measuring times per step in the 5-40 s range. The temperature control of the samples during measurements was achieved by adapting a home-made heating stage to the sample stage of the diffractometer. Fluorescence spectra in dichloromethane solution and solid state were recorded on a Jasco FP-6300 spectrofluorometer (operating parameters: band width – 5 nm; data pitch – 0.5 nm; scanning speed – 100 nm/min; spectrum accumulation – 3; path length – 10 mm by using Quartz SUPRASIL cells or solid-state accessory). The quantum yield measurements were performed by using the single-point (comparative) method, with aqueous solution of quinine sulphate in 0.1M sulfuric acid as reference flourophore of known quantum yield (0.58 at 22^{o}C). All these measurements were done in triplicate and the experimental errors, expressed as relative standard deviations, were less than 10%. Thermogravimetric analysis was performed on a TA Q50 TGA instrument using alumina crucibles and nitrogen as purging gas. The heating rate employed was 10°C min^{-1} from room temperature (approx. 25°C) to 550^{o}C.



Scheme 1. Preparation of pyridinium ionic liquid crystals

The synthesis of the pyridones 2a-c

To a mixture of 4-hydroxypyridine (4.34g, 10.8mmol) and tetrabutylammonium bromide (0.43g, 1.35mmol) in tetrahydrofuran, an aqueous 2N NaOH solution (NaOH equivalent to 4-hydroxypyridine) was added. After the solution became clear, 4'-(n-bromoalkyloxy)-biphenyl-4-carbonitrile was added (10.8mmol) and the mixture was heated under reflux for 2 days. After cooling, the solvent was removed by rotary evaporation and the crude product was extracted by dichloromethane:water (1:1). The organic layers were collected and dried on anhydrous Na_2SO_4. The dichloromethane phase was reduced and the residue was purified on a silica gel chromatography column using as an eluent a mixture of dichloromethane:methanol (95:5).

2a. Yield: 46 %. ^{1}H-RMN ($CDCl_3$, 500MHz): 7.64 (q, 4H), 7.51 (d, 2H, J=6.7Hz), 7.28 (d, 2H, J=1Hz), 6.96 (d, 2H, J=1Hz), 6.38 (d, 2H, J=1Hz), 3.99 (t, 2H, J=6.7Hz), 3.79 (t, 2H, J=6.7Hz), 1.86-1.76 (m, 4H), 1.58-1.36 (m, 4H). ^{13}C-RMN ($CDCl_3$, 125MHz): 178.7, 159.5, 145.1, 139.7, 132.5, 131.4, 128.3, 127, 119, 118.7, 115, 110, 67.5, 56.9, 30.8, 28.9, 25.9, 25.6. IR (cm^{-1}): 2938, 2866 (νCH_2), 2224 (νCN), 1639 (νC=O), 1117 (νC-O), 821, 795 (νCH_{arom}), 740 (νCH_{alkyl}).

2b. ^{1}H-RMN ($CDCl_3$, 500MHz): 7.64 (q, 4H), 7.51 (d, 2H, J=1Hz), 7.27 (d, 2H, J=6.7Hz), 6.97 (d, 2H, J=1Hz), 6.38 (d, 2H, J=6.7Hz), 3.98 (t, 2H, J=6.7Hz), 3.75 (t, 2H, J=6.7Hz), 1.81-1.74 (m, 4H), 1.48-1.32 (m, 10H). ^{13}C-RMN ($CDCl_3$, 125MHz): 178.7, 159.7, 145.2, 139.6, 132.5, 131.2, 128.3, 127, 119.1, 118.6, 115, 110, 68, 57, 30.8, 29.6-28.9, 26.1, 25.9. IR (KBr, cm^{-1}): 2928, 2855 (νCH_2), 2222 (νCN), 1638 (νC=O), 1140 (νC-O), 827, 809, 770 (νCH_{arom}), 725 (νCH_{alkyl}).

2c. Yield:65% ^{1}H-RMN ($CDCl_3$, 500MHz): 7.74 (q, 4H), 7.52 (d, 2H, J=1Hz), 7.33 (d, 2H, J=6.7Hz), 6.98 (d, 2H, J=1Hz), 6.39 (d, 2H, J=6.7Hz), 4.02 (t, 2H, J=6.7Hz), 3.75 (t, 2H, J=6.7Hz), 1.85-1.67 (m, 4H), 1.40-1.23 (m, 12H). ^{13}C-RMN ($CDCl_3$, 125MHz): ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.68 – 7.61 (m, 4H), 7.51 (d, 2H, J=6.7Hz), 6.97 (d, 2H, J=8.7Hz), 6.43 (d, 2H, J=8.7 Hz), 3.99 (t, 2H, J=6.5 Hz), 3.79 (t, 2H, J=7.1Hz), 1.79 – 1.75 (m, 4H), 1.46 – 1.35 (m, 12H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 179.0, 159.8, 145.3, 139.8, 132.6, 131.3, 128.4, 127.1, 119.2, 118.7, 115.4, 110.0, 68.2, 57.2, 31.0, 30.9, 29.4, 29.3, 29.2, 29.1, 29.0, 26.2, 26.1. IR (KBr, cm^{-1}): 2923, 2855 (νCH_2), 2224 (νCN), 1638 ($\nu C{=}O$), 1114 ($\nu C{-}O$), 824, 797 (νCH_{arom}), 735 (νCH_{alkyl}).

Synthesis of pyridinium bromide salts

The corresponding pyridone compound **2a-c** (5.4 mmol) was dissolved in acetonitrile. 4'-(n-bromoalkyloxy)-biphenyl-4-carbonitrile (8.07mmol) was added and the mixture was heated under reflux (85˚C) under nitrogen overnight. The formation of the final product was observed by TLC (R_f=0.27, CH_2Cl_2). In the next step, the solvent was reduced by rotary evaporation. The solid was purified by repeated crystallization from dichloromethane:ethyl ether to give the bromide salts as white solids.

3a. Yield: 84 %. Anal. Calcd. for $C_{43}H_{44}BrN_3O_3{\cdot}H_2O$: C%68.98, H%6.19, N%5.61 Found: C%69.11, H%6.56, N%5.36. ^{1}H-RMN ($CDCl_3$, 300MHz): 9.15 (d, 2H, J=6.15Hz), 7.67-7.63 (m, 8H), 7.54-7.50 (m, 4H), 7.42 (d, 2H, J=6.5Hz), 6.99-6.95 (m, 4H), 4.75 (t, 2H, J=7.06Hz), 4.30 (t, 2H, J=6.43Hz), 4.04-3.97 (m, 4H), 1.82-1.75 (m, 8H), 1.56-1.54 (m, 8H). ^{13}C-RMN ($CDCl_3$, 75MHz): 170.2, 159.5, 146.2, 145.1, 132.5, 131.3, 128.3, 127, 119, 115, 113.9, 110, 71.4, 67.6, 60, 31.4, 29, 28.8, 28.3, 25.7, 25.5, 25.4. IR (cm^{-1}): 2943, 2856 (νCH_2), 2223 (νCN), 1522 ($\nu C{=}N$), 1119 ($\nu C{-}O$), 829, 751 (νCH_{arom}), 733 (νCH_{alkyl}).

3b. Yield: 87 %. Anal. Calcd. for $C_{49}H_{56}BrN_3O_3{\cdot}H_2O$: C%70.66, H%7.02, N%5.05 Found: C%70.47, H%7.31, N%4.84. ^{1}H-RMN ($CDCl_3$, 300MHz): 9.13 (d, 2H, J=6.7Hz), 7.67 (m, 8H), 7.50 (d, 4H), 7.43 (d, 2H), 6.97 (d, 4H), 4.71 (t, 2H, J=1Hz), 4.28 (t, 2H, J=6.7Hz), 4.01-3.95 (m, 4H), 1.90-1.73 (m, 8H), 1.46-1.24 (m, 20H). ^{13}C-RMN ($CDCl_3$, 75MHz): 170.3, 159.7, 146.2, 145.2, 132.6, 131.2, 128.3, 127, 119.1, 115.1, 113.9, 110, 71.6, 68.1, 60.2, 31.6, 29.7-29.0, 28.4, 26.1, 25.6. IR (cm^{-1}): 2935, 2854 (νCH_2), 2225 (νCN), 1523 ($\nu C{=}N$), 1116 ($\nu C{-}O$), 855, 821 (νCH_{arom}), 725 (νCH_{alkyl}).

3c. Yield: 76%. Anal. Calcd. for $C_{51}H_{60}BrN_3O_3{\cdot}H_2O$: C%71.15, H%7.26, N%4.88 Found: C%70.89, H%7.45, N%4.75. ^{1}H-RMN ($CDCl_3$, 300MHz): 9.01 (d, 2H, J=6.7Hz), 7.66 (m, 8H), 7.53 (d, 4H), 7.43 (d, 2H), 6.98 (d, 4H), 4.67 (t, 2H, J=1Hz), 4.31 (t, 2H, J=6.7Hz), 4.03-3.98 (m, 4H), 1.98-1.77 (m, 8H), 1.46-1.25 (m, 24H). ^{13}C-RMN ($CDCl_3$, 75MHz): 159.8, 146, 145.2, 132.6, 131.3, 128.3, 127.1, 119.1, 115.1, 114.1, 68, 31.5, 29.4-29.0, 28.4, 26.1, 25.6. IR (cm^{-1}): 2926, 2853 (νCH_2), 2223 (νCN), 1522 ($\nu C{=}N$), 1117 ($\nu C{-}O$), 852, 826 (νCH_{arom}), 727 (νCH_{alkyl}), 534.

The exchange reactions with different counterions

*The synthesis of NO_3^- salts **4a-c**.* To a solution of the bromide salt **3a-c** (0.12 mmol) in methanol, an equivalent amount of $AgNO_3$ (0.02g, 0.12mmol) dissolved in water was added. The mixture was stirred at room temperature for 1h and the resulting precipitate was filtered off, washed with cold methanol and recrystallized from a mixture of dichloromethane:ethyl ether.

4a. Yield:78 %. Anal. Calcd. for $C_{43}H_{44}N_4O_6$: C%72.45, H%6.22, N%7.86 Found: C%71.86, H%6.73, N%7.55. ^{1}H-RMN ($CDCl_3$, 500MHz): 8.85 (d, 2H, J=7.4Hz), 7.66 (m, 8H), 7.51 (m, 4H), 7.39 (d, 2H, J=7.1Hz), 6.97 (m, 4H), 4.56 (t, 2H, J=7.3Hz), 4.29 (t, 2H, J=6.4Hz), 4.00 (m, 4H), 1.8-1.22 (m, 16H). ^{13}C-RMN ($CDCl_3$, 125MHz): 170.4, 159.6, 146, 145.1, 132.6, 131.4, 128.4, 127.1, 127, 119.1, 115.1, 115, 114, 110.1, 77.4, 77, 76.6, 71.4, 67.8, 67.6, 65.8, 60.2, 31.3, 29.0, 28.8, 28.4, 25.7, 25.4. IR (cm^{-1}): 2945, 2859 (νCH_2), 2224 (νCN), 1601 (νCH_{arom}), 1523 ($\nu C{=}N$), 1384 (νNO_3^-), 1254 ($\nu C{-}O$), 828 (νCH_{arom}), 735 (νCH_{alkyl}).

4b. Yield: 53%. Anal. Calcd. for $C_{49}H_{56}N_4O_6$: C%73.84, H%7.08, N%7.03 Found: C%73.36, H%7.57, N%6.85. ^{1}H-RMN ($CDCl_3$, 500MHz): 8.85 (d, 2H, J=7.4Hz), 7.65 (m, 8H), 7.50 (m, 4H), 7.40 (d, 2H, J=7.4Hz), 6.97 (m, 4H), 4.52 (t, 2H, J=7.5Hz), 4.27 (t, 2H, J=6.5Hz), 4.00 (m, 4H), 1.94-1.76 (m, 8H), 1.45-1.25 (m, 20H). ^{13}C-RMN ($CDCl_3$, 125MHz): 170.4, 159.7, 146, 145.2, 132.5, 131.2, 128.3, 127, 119.1, 115.1, 113.9, 110, 77.2, 71.5, 68.1, 60.3, 31.4, 29.3-28.9, 26, 25.9, 25.6. IR (cm^{-1}): 2935, 2854 (νCH_2), 2225 (νCN), 1603 (νCH_{arom}), 1523 (νC=N), 1385 (νNO_3^-), 1251 (νC-O), 824 (νCH_{arom}), 727 (νCH_{alkyl}).

4c. Yield: 66%. Anal. Calcd. for $C_{51}H_{60}N_4O_6$: C%74.24, H%7.33, N%6.79 Found: C%73.77, H%7.81, N%6.48. ^{1}H-RMN ($CDCl_3$, 500MHz): 8.88 (d, 2H, J=7.4Hz), 7.64 (m, 8H), 7.51 (m, 4H), 7.40 (d, 2H, J=7.4Hz), 6.98 (m, 4H), 4.53 (t, 2H, J=7.5Hz), 4.27 (t, 2H, J=6.5Hz), 4.01-3.95 (m, 4H), 1.93-1.75 (m, 8H), 1.46-1.28 (m, 24H). ^{13}C-RMN ($CDCl_3$, 125MHz): 170.4, 159.7, 146, 145.2, 132.5, 131.2, 128.3, 127, 119.1, 115, 113.9, 109.9, 71.5, 68.1, 60.3, 31.4, 29.4-28.4, 26.1, 26, 25.9, 25.6. IR (cm^{-1}): 2926, 2853 (νCH_2), 2223 (νCN), 1603 (νCH_{arom}), 1523 (νC=N), 1384 (νNO_3^-), 1117 (νC-O), 853, 826 (νCH_{arom}), 727 (νCH_{alkyl}).

*The synthesis of BF_4^- salts **5a-c**.* To a solution of the bromide salts **3a-c** (0.12mmol) in methanol, an equivalent amount of NH_4BF_4 (0.013g, 0.12mmol) dissolved in water was added. The mixture was stirred at room temperature for 1h and the resulted precipitate was filtered, washed with cold methanol and recrystallized from dichloromethane:ethyl ether.

5a. Yield: 75 %. Anal. Calcd. for $C_{43}H_{44}BF_4N_3O_3$: C%70.02, H%6.01, N%5.70 Found: C%69.81, H%6.43, N%5.45. ^{1}H-RMN ($CDCl_3$, 500MHz): 8.60 (d, 2H, J=7.4Hz), 7.63 (m, 8H), 7.51 (m, 4H), 7.35 (d, 2H, J=7.4Hz), 6.96 (m, 4H), 4.46 (t, 2H, J=7.4Hz), 4.26 (t, 2H, J=6.4Hz), 3.98 (m, 4H), 1.84-1.25 (m, 16H). ^{13}C-RMN ($CDCl_3$, 125MHz): 170.4, 159.6, 145.6, 145.1, 132.5, 131.3, 128.3, 127, 119.1, 115, 114, 110, 77.4, 77, 76.6, 71.3, 67.7, 67.6, 60.2, 31.1, 29.7, 29, 28.8, 28.3, 25.6, 25.4. IR (cm^{-1}): 2943, 2864 (νCH_2), 2224 (νCN), 1601 (νCH_{arom}), 1524 (νC=N), 1253 (νC-O), 1059 (νBF_4^-), 823 (νCH_{arom}), 733 (νCH_{alkyl}).

5b. Yield: 76 %. Anal. Calcd. for $C_{49}H_{56}BF_4N_3O_3$: C%71.61, H%6.87, N%5.11 Found: C%71.45, H%6.96, N%4.88. ^{1}H-RMN ($CDCl_3$, 500MHz): 8.74 (d, 2H, J=7.4Hz), 7.65 (m, 8H), 7.53 (m, 4H), 7.36 (d, 2H, J=7.4Hz), 6.97 (m, 4H), 4.53 (t, 2H, J=7.4Hz), 4.27 (t, 2H, J=6.7Hz), 3.93 (m, 4H), 1.89-1.76 (m, 8H), 1.47-1.25 (m, 20H). ^{13}C-RMN ($CDCl_3$, 125MHz): 170.3, 159.7, 145.8, 145.2, 132.5, 131.2, 128.3, 127, 119.1, 115, 113.9, 110, 77.4, 77.2, 77, 76.6, 71.5, 68, 60.3, 31.3, 29.3-29.04, 28.9, 28.4, 26, 25.9, 25.6. IR (cm^{-1}): 2934, 2853 (νCH_2), 2225 (νCN), 1603 (νCH_{arom}), 1523 (νC=N), 1252 (νC-O), 1068 (νBF_4^-), 823 (νCH_{arom}), 725 (νCH_{alkyl}).

5c. Yield: 83%. Anal. Calcd. for $C_{51}H_{60}BF_4N_3O_3$: C%72.08, H%7.12, N%4.94 Found: C%71.79, H%7.53, N%4.56. ^{1}H-RMN ($CDCl_3$, 300MHz): 8.66 (d, 2H, J=7.3Hz), 7.69 (m, 8H), 7.53 (m, 4H), 7.37 (d, 2H, J=7.3Hz), 6.98 (m, 4H), 4.50 (t, 2H, J=7.4Hz), 4.28 (t, 2H, J=6.3Hz), 4.05-3.97 (m, 4H), 1.95-1.74 (m, 8H), 1.48-1.25 (m, 24H). ^{13}C-RMN ($CDCl_3$, 125MHz): 170.5, 159.8, 145.6, 145.3, 132.6, 131.3, 128.3, 127.1, 119.1, 115.1, 114, 110, 71.6, 68.1, 60.5, 31.3, 29.4-29.1, 28.9, 28.4, 26, 25.6. IR (cm^{-1}): 2934, 2853 (νCH_2), 2225 (νCN), 1602 (νCH_{arom}), 1523 (νC=N), 1252 (νC-O), 1061 (νBF_4^-), 823 (νCH_{arom}), 725 (νCH_{alkyl}).

*The synthesis of PF_6^- salts **6a-c**.* To a solution of bromide salts **3a-c** (0.12mmol) in methanol, an equivalent amount of NH_4PF_6 (0.02g, 0.12mmol) dissolved in water was added. The mixture was stirred at room temperature for 1h and the resulted precipitate was filtered, washed with methanol and recrystallized from dichloromethane:ethyl ether.

6a. Yield: 51 %. Anal. Calcd. for $C_{43}H_{44}F_6N_3O_3P$: C%64.90, H%5.57, N%5.28 Found: C%64.46, H%5.93, N%5.02. ^{1}H-RMN ($CDCl_3$, 500MHz): 8.43 (d, 2H, J=7.3Hz), 7.63 (m, 8H), 7.50 (m, 4H), 7.30 (d, 2H, J=7.3Hz), 6.95 (m, 4H), 4.38 (t, 2H, J=7.4Hz), 4.24 (t, 2H, J=6.3Hz), 3.97 (m, 4H), 1.92-1.23 (m, 16H). ^{13}C-RMN ($CDCl_3$, 125MHz): 170.5, 159.6, 145.2, 145.1, 132.5, 131.2, 128.3, 127, 119.1, 115, 114, 109.9, 77.4, 77, 76.6, 71.3, 67.7, 67.6, 60.3, 30.9, 29.7, 29, 28.3, 25.6, 25.5, 25.3. IR (cm^{-1}): 2944, 2865 (νCH_2), 2221 (νCN), 1602 (νCH_{arom}), 1523 (νC=N), 1250 (νC-O), 838 (νPF_6^-), 739 (νCH_{alkyl}).

6b. Yield: 89%. Anal. Calcd. for $C_{49}H_{56}F_6N_3O_3P$: C%66.88, H%6.41, N%4.78 Found: C%66.56, H%6.73, N%4.63. ^{1}H-RMN ($CDCl_3$, 500MHz): 8.41 (d, 2H, J=7.4Hz), 7.65 (m, 8H), 7.52 (m, 4H), 7.30 (d, 2H, J=7.4Hz), 6.98 (m, 4H), 4.37 (t, 2H, J=7.3Hz), 4.25(t, 2H, J=6.7Hz), 3.98 (m, 4H), 1.90-1.76 (m, 8H), 1.45-1.21 (m, 20H). ^{13}C-RMN ($CDCl_3$, 125MHz): 170.5, 159.7, 145.2, 132.5, 131.2, 128.3, 127, 119.1, 115.1, 114, 109.9, 77.4, 77.2, 77, 76.6, 71.5, 68, 65.8, 60.5, 31.1, 29.3-29.02, 28.7, 28.3, 25.9, 25.5. IR (cm^{-1}): 2936, 2865 (νCH_2), 2221 (νCN), 1603 (νCH_{arom}), 1525 (νC=N), 1248 (νC-O), 834 (νPF_6^-), 738 (νCH_{alkyl}).

6c. Yield: 75%. Anal. Calcd. for $C_{51}H_{60}F_6N_3O_3P$: C%67.46, H%6.67, N%4.63 Found: C%67.14, H%6.95, N%4.42. ^{1}H-RMN ($CDCl_3$, 300MHz): 8.45 (d, 2H, J=7.4Hz), 7.68 (m, 8H), 7.52 (m, 4H), 7.33 (d, 2H, J=7.4Hz), 6.98 (m, 4H), 4.39 (t, 2H, J=7.3Hz), 4.26 (t, 2H, J=6.7Hz), 4.01-3.96 (m, 4H), 1.90-1.76 (m, 8H), 1.45-1.25 (m, 24H). ^{13}C-RMN ($CDCl_3$, 75MHz): 170.6, 159.8, 145.3, 145.2, 132.5, 131.2, 128.3, 127, 119.1, 115, 114, 110, 71.6, 68.1, 60.5, 31.1, 29.4-28.8, 28.4, 25.9, 25.6. IR (cm^{-1}): 2931, 2856 (νCH_2), 2225 (νCN), 1603 (νCH_{arom}), 1524 (νC=N), 1180 (νC-O), 834 (νPF_6^-), 740 (νCH_{alkyl}).

The synthesis of OTf $^-$ salts ***7a-c***. To a solution of the corresponding bromide salts **3a-c** (0.07mmol) in methanol, an equivalent amount of $AgCF_3SO_3$ (19mg, 0.07mmol) dissolved in water was added. The mixture was stirred at room temperature for 1h avoiding light. The suspension was filtered through Celite, washed with warm methanol and kept in the freezer. The resulted precipitate was filtered and recrystallized one more time from a mixture of dichloromethane:ethyl ether.

7a. Yield: 43%. Anal. Calcd. for $C_{44}H_{44}F_3N_3O_6S$: C%66.07, H%5.54, N%5.25 Found: C%65.84, H%5.75, N%5.02. ^{1}H-RMN ($CDCl_3$, 500MHz): 8.65 (d, 2H, J=7.3Hz), 7.68-7.59 (m, 8H), 7.53-7.48 (m, 4H), 7.36 (d, 2H, J=7.3Hz), 6.98-6.93 (m, 4H), 4.49 (t, 2H, J=7.3Hz), 4.28 (t, 2H, J=6.7Hz), 4.02-3.94 (m, 4H), 1.82-1.78 (m, 8H), 1.54-1.41 (m, 8H). ^{13}C-RMN ($CDCl_3$, 125MHz): 170.4, 159.6, 145.7, 145.1, 132.5, 131.3, 128.3, 127, 119.1, 115, 114, 110, 71.4, 67.7, 60.2, 31.1, 29.0-28.3, 25.6, 25.4. IR (cm^{-1}): 2942, 2865 (νCH_2), 2225 (νCN), 1603 (νCH_{arom}), 1524 (νC=N), 1270, 1223, 659 (νOTf^-), 1181 (νC-O), 826 (νCH_{arom}), 754 (νCH_{alkyl}).

7b. Yield: 55%. Anal. Calcd. for $C_{50}H_{56}F_3N_3O_6S$: C%67.93, H%6.38, N%4.75 Found: C%67.61, H%6.75, N%4.47. ^{1}H-RMN ($CDCl_3$, 500MHz): 8.65 (d, 2H, J=7.4Hz), 7.68 (m, 8H), 7.52 (m, 4H), 7.37 (d, 2H, J=7.4Hz), 6.97 (m, 4H), 4.46 (t, 2H, J=7.3Hz), 4.27 (t, 2H, J=6.7Hz), 4.00 (m, 4H), 1.86-1.78 (m, 8H), 1.45-1.32 (m, 20H). ^{13}C-RMN ($CDCl_3$, 125MHz): 170.5, 159.7, 145.7, 145.2, 132.5, 131.2, 128.3, 127, 119.1, 115, 114, 110, 68, 60.4, 31.2, 29.3-28.3, 26, 25.9, 25.6. IR (cm^{-1}): 2925, 2857 (νCH_2), 2228 (νCN), 1603 (νCH_{arom}), 1522 (νC=N), 1266, 1216, 660 (νOTf^-), 1180 (νC-O), 858, 828 (νCH_{arom}), 754, 727 (νCH_{alkyl}).

7c. Yield: 56%. Anal. Calcd. for $C_{52}H_{60}F_3N_3O_6S$: C%68.47, H%6.63, N%4.61 Found: C%68.02, H%6.96, N%4.38. ^{1}H-RMN ($CDCl_3$, 500MHz): 8.58 (d, 2H, J=7.4Hz), 7.69 (m, 8H), 7.53 (m, 4H), 7.36 (d, 2H, J=7.4Hz), 6.99 (m, 4H), 4.45 (t, 2H, J=7.3Hz), 4.28 (t, 2H, J=6.7Hz), 4.02-3.97 (m, 4H), 1.89-1.77 (m, 8H), 1.46-1.31 (m, 24H). ^{13}C-RMN ($CDCl_3$, 125MHz): 170.5, 159.8, 145.6, 145.2, 132.6, 131.2, 128.3, 127.1, 119.1, 115.1, 114, 110, 71.6, 68.1, 60.5, 31.3, 29.4-28.9, 28.4, 26, 25.6. IR (cm^{-1}): 2926, 2853 (νCH$_2$), 2284 (νCN), 1603 (νCH$_{arom}$), 1524 (νC=N), 1256, 1213, 660 (νOTf$^-$), 1181 (νC-O), 853, 822 (νCH$_{arom}$), 724 (νCH$_{alkyl}$).

*The synthesis of SCN$^-$ salts **8a-c***. To a solution of the corresponding bromide salt **3a-c** (0.07mmol) in methanol, an equivalent amount of NH_4SCN (5mg, 0.07mmol) dissolved in minimum amount of water was added. The mixture was stirred at room temperature for 1h and the resulted precipitate was filtered, washed with methanol and recrystallized from a mixture of dichloromethane:ethyl ether.

8a. Yield: 83%. Anal. Calcd. for $C_{44}H_{44}N_4O_3S$: C%74.55, H%6.26, N%7.90 Found: C%74.22, H%6.54, N%7.65. ^{1}H-RMN (CDCl$_3$, 500MHz): 8.91 (d, 2H, J=7.2Hz), 7.68-7.59 (m, 8H), 7.52-7.44 (m, 6H), 6.98-6.94 (m, 4H), 4.66 (t, 2H, J=7.3Hz), 4.33 (t, 2H, J=6.7Hz), 4.01 (m, 4H), 1.90-1.77 (m, 8H), 1.55-1.46 (m, 8H). ^{13}C-RMN (CDCl$_3$, 125MHz): 170.4, 159.6, 145.8, 145.1, 132.5, 131.3, 128.3, 127, 119.1, 115, 114.1, 110, 71.5, 67.7, 60.2, 31.3, 29.0-28.3, 25.7, 25.4. IR (cm^{-1}): 2939, 2859 (νCH$_2$), 2222 (νCN), 2049 (νSCN$^-$), 1603 (νCH$_{arom}$), 1522 (νC=N), 1183 (νC-O), 827 (νCH$_{arom}$), 731 (νCH$_{alkyl}$).

8b. Yield: 66%. Anal. Calcd. for $C_{50}H_{56}N_4O_3S$: C%75.72, H%7.12, N%7.06 Found: C%75.49, H%7.37, N%6.87. ^{1}H-RMN (CDCl$_3$, 500MHz): 8.88 (d, 2H, J=7.2Hz), 7.65 (m, 8H), 7.51 (m, 4H), 7.45 (d, 2H, J=7.2Hz), 6.97 (m, 4H), 4.62 (t, 2H, J=7.3Hz), 4.32 (t, 2H, J=6.7Hz), 4.01-3.96 (m, 4H), 1.88-1.73 (m, 8H), 1.46-1.24 (m, 20H). ^{13}C-RMN (CDCl$_3$, 125MHz): 170.4, 159.7, 145.7, 145.2, 132.5, 131.2, 128.3, 127, 119.1, 115, 114.1, 110, 71.7, 68.1, 60.4, 31.4, 29.3-28.9, 28.4, 26.1, 25.9, 25.6. IR (cm^{-1}): 2935, 2853 (νCH$_2$), 2225 (νCN), 2056 (νSCN$^-$), 1603 (νCH$_{arom}$), 1523 (νC=N), 1180 (νC-O), 820 (νCH$_{arom}$), 728 (νCH$_{alkyl}$).

8c. Yield: 77%. Anal. Calcd. for $C_{52}H_{60}N_4O_3S$: C%76.06, H%7.37, N%6.82 Found: C%76.32, H%7.42, N%6.59. ^{1}H-RMN (CDCl$_3$, 300MHz): 8.81 (d, 2H, J=7.2Hz), 7.65 (m, 8H), 7.52 (m, 4H), 7.45 (d, 2H, J=7.1Hz), 6.98 (m, 4H), 4.58 (t, 2H, J=7.3Hz), 4.31 (t, 2H, J=6.7Hz), 4.01-3.96 (m, 4H), 1.88-1.73 (m, 8H), 1.44-1.24 (m, 24H). ^{13}C-RMN (CDCl$_3$, 75MHz): 170.4, 159.7, 145.7, 145.2, 132.5, 131.2, 128.3, 127, 119.1, 115, 114.1, 109.9, 71.6, 68.1, 60.5, 31.4, 29.4-28.4, 26.1, 25.6. IR (cm^{-1}): 2926, 2852 (νCH$_2$), 2222 (νCN), 2050 (νSCN$^-$), 1603 (νCH$_{arom}$), 1523 (νC=N), 1180 (νC-O), 821 (νCH$_{arom}$), 728 (νCH$_{alkyl}$).

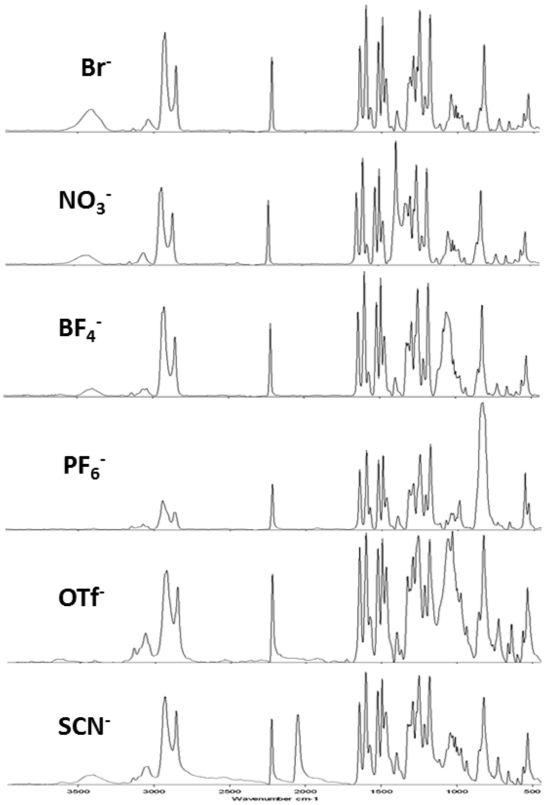


Fig. S1. The IR spectra of the **3-8c** series.

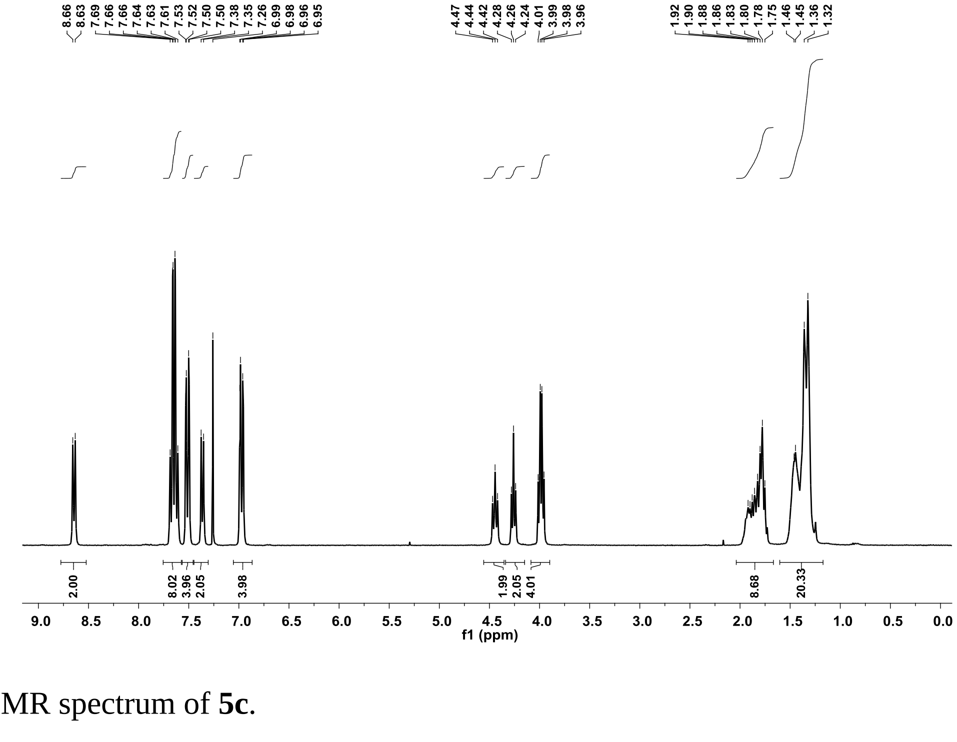


Fig. S2. The ^{1}H-NMR spectrum of **5c**.

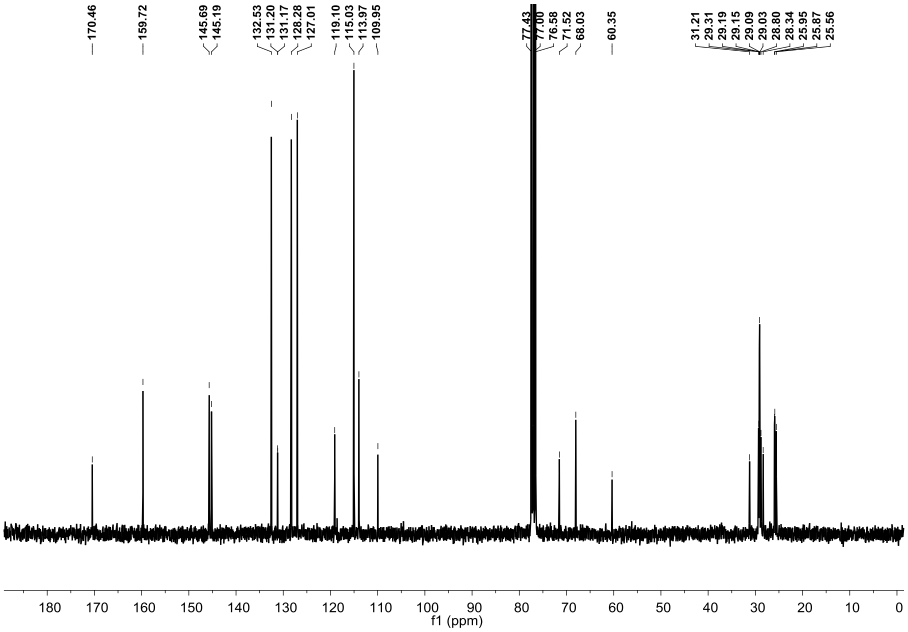


Fig. S3. The ^{13}C-NMR spectrum of **5c**.

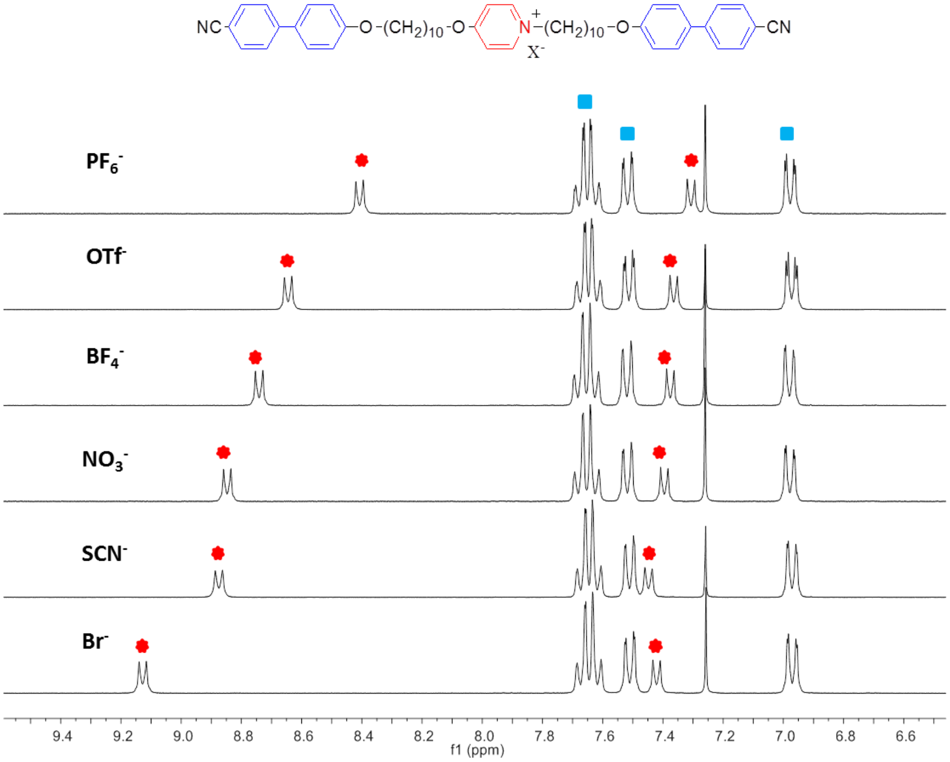


Fig. S4. The influence of the counterion on the pyridinium doublet in the ^{1}H-NMR spectra of **3-8c** series.

Table S1. Decomposition temperatures (T_{onset} values) for selected pyridinium ionic liquid crystals

Compound	X^-	$T_{onset}/^oC$
3a	Br^-	269

3b	Br^-	257
4a	NO_3^-	239
4b	NO_3^-	207
5b	BF_4^-	261
6b	PF_6^-	301
7b	OTf^-	286
8c	SCN^-	302

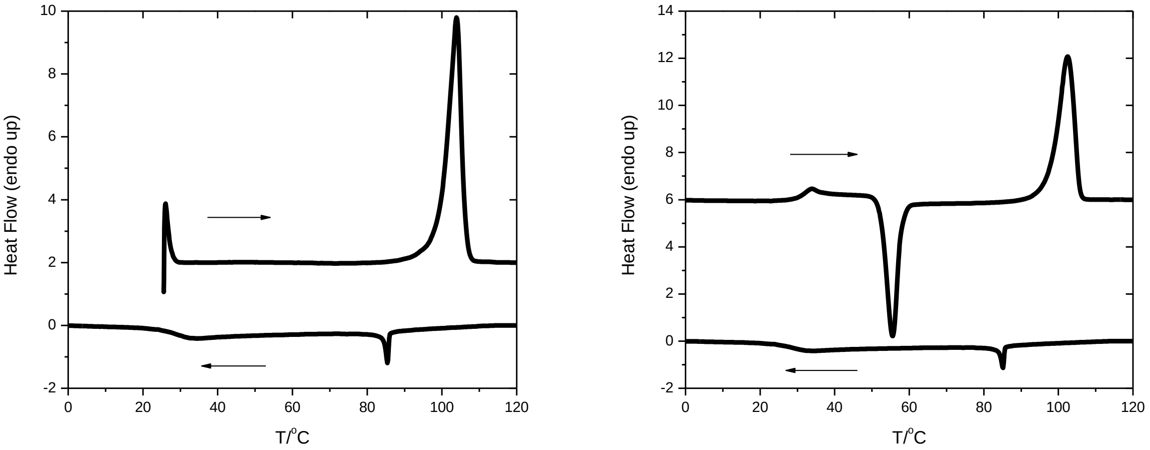


Fig. S5. The DSC traces for **4c** corresponding to the first(left) and second(right) heating-cooling cycles.

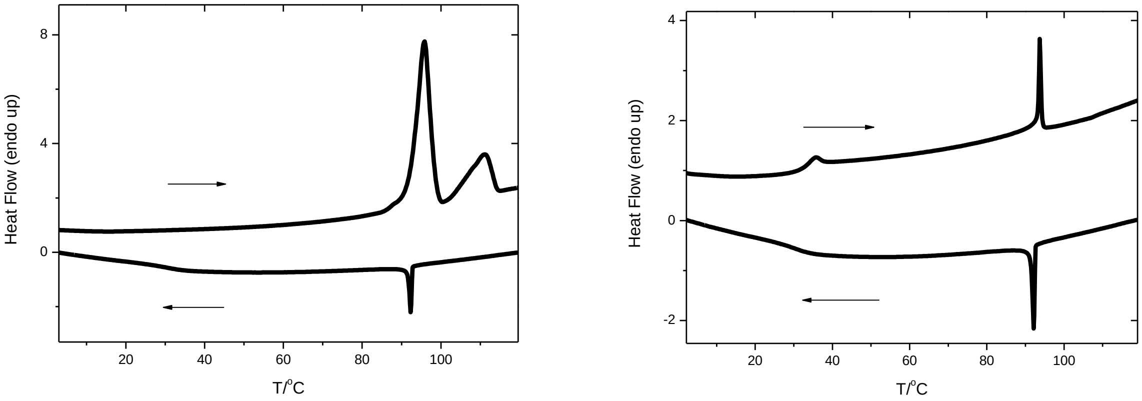


Fig. S6. The DSC traces for **4b** corresponding to the first (left) and second (right) heating-cooling cycles.

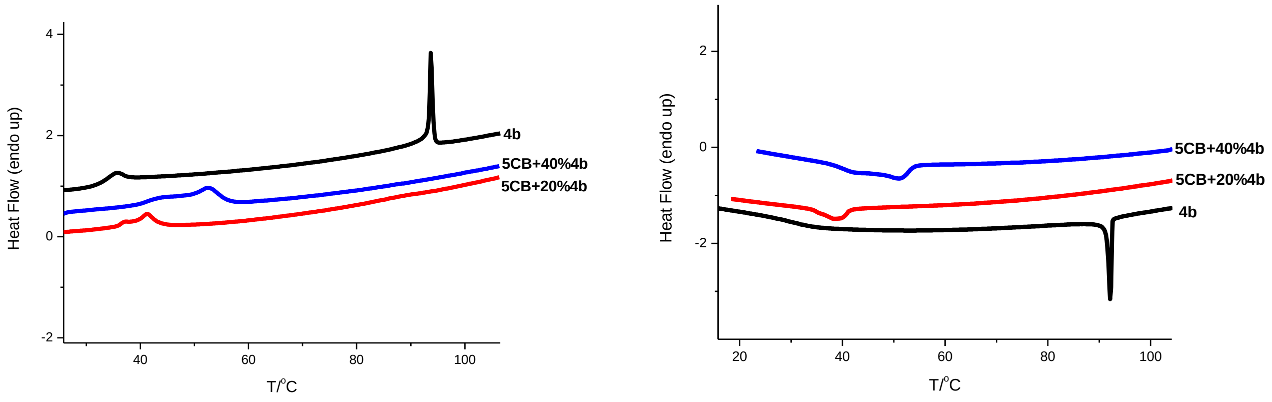


Fig. S7. The DSC traces for **4b** and mixtures of 5CB with **4b** (20 and 40%wt.)

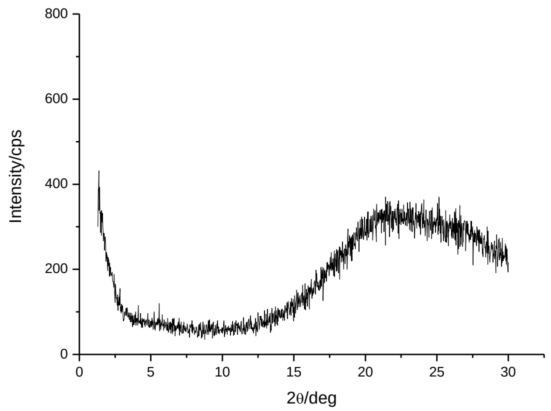


Fig. S8. The XRD pattern for **3b** at 62°C.

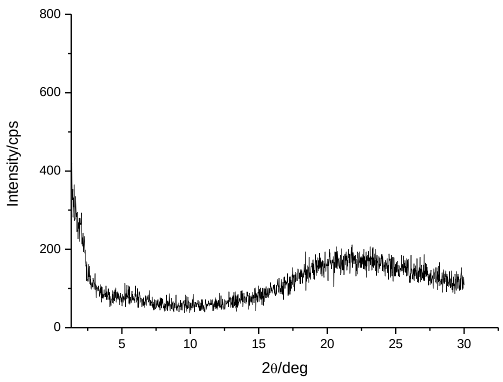


Fig. S9. The XRD pattern for **5b** at 62°C.

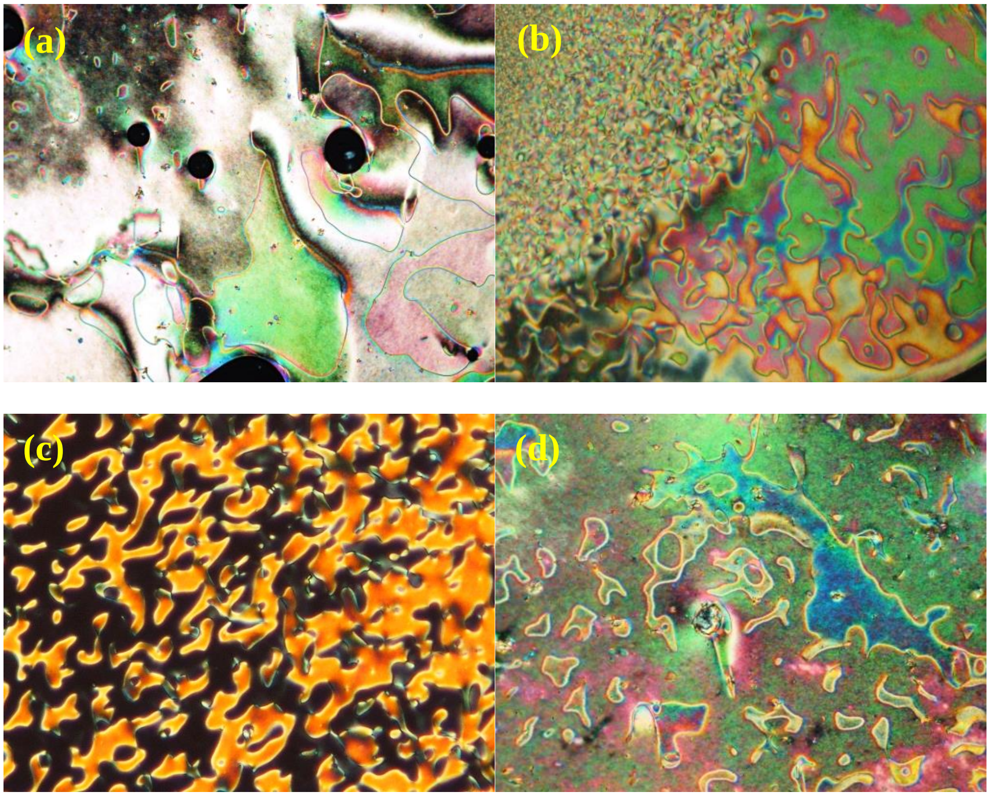


Fig. S10. POM pictures for **3b** taken at 82^{o}C(a); **4a** at 60^{o}C (b); **4c** at 75^{o}C (c) and **8a** at 55^{o}C (d), on cooling from the isotropic phase.

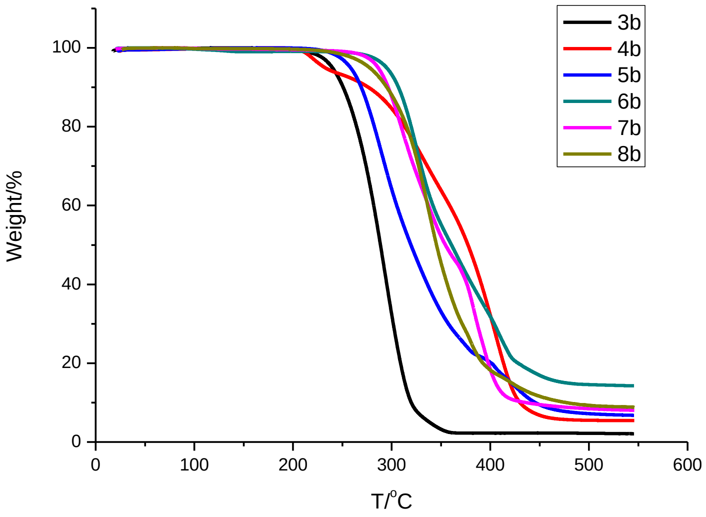


Fig. S11. The TG curves for **3-8b** series, recorded in the 25 – 550^{o}C range.

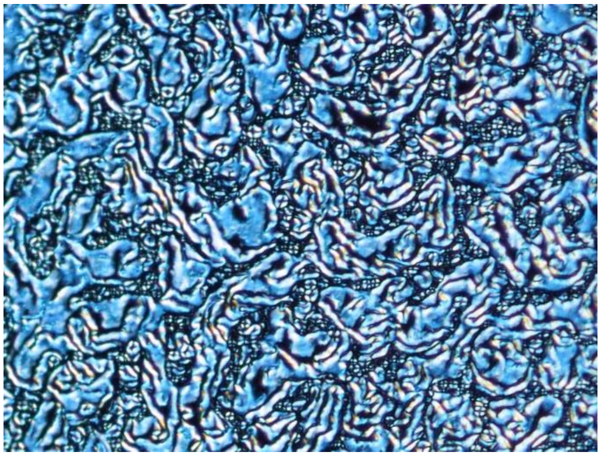


Fig. S12. POM picture of **4b** doped with **9** (~1.5wt%) at 42^{o}C on cooling from the isotropic phase.

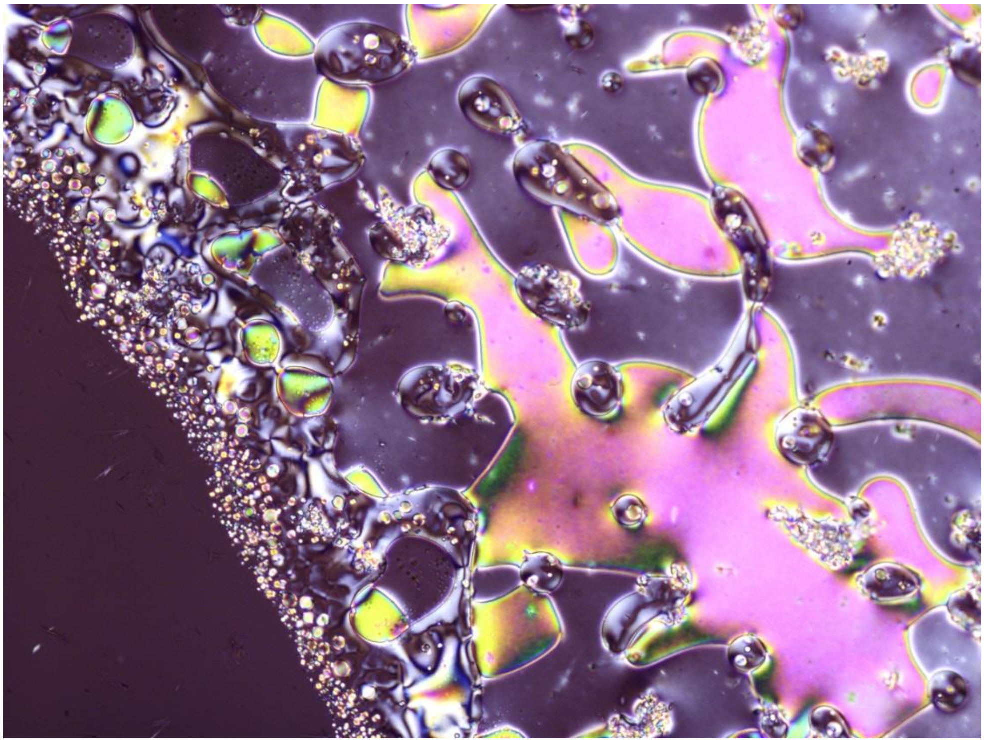


Fig. S13. POM picture of a mixture of 5CB and **4b** (40%wt.) at 53^{o}C, showing the development of a nematic phase from the isotropic melt.

Table S2. UV-VIS and emission properties of the pyridinium ionic liquid crystals

Compound	X^-	Absorption, λ_{max}/nm ($\varepsilon x10^{-4}/M^{-1\cdot}cm^{-1}$)	Emission in CH_2Cl_2 solution: λ_{em}/nm (λ_{exc}/nm; Φ/%)	Emission in solid state (λ_{exc}=280nm)
3a	Br^-	255(3.7), 261(3.8), 295(10.5)	361(295; 47)	372
3b	Br^-	255(1.5), 260(1.5), 296(4.4)	363(296; 65)	367
3c	Br^-	253(2.2), 296 (5.3)	362 (296, 54)	366
4a	NO_3^-	255(1.6), 260(1.7), 295(5.0)	362(295; 52)	376
4b	NO_3^-	255(2.5), 260(2.4), 295(5.3)	363(295; 60)	370
4c	NO_3^-	254 (2.2), 297(5.4)	363(297, 54)	366
5a	BF_4^-	255(5.6), 259(5.7), 295(19.1)	361(295; 52)	376
5b	BF_4^-	255(1.6), 260(1.6), 296(4.3)	363(296; 67)	370
5c	BF_4^-	254 (2.8), 297 (6.5)	363 (297; 57)	370

6a	PF$_6^-$	255(2.4), 259(2.4), 294(5.9)	361(294; 48)	392
6b	PF$_6^-$	255(2.5), 260(2.5), 295(5.2)	362(295; 68)	367
6c	PF$_6^-$	254(4.1), 297 (9.1)	363 (297, 61)	370
7a	OTf$^-$	254 (4.0), 259 (3.9)(sh), 296(9.6)	363(296; 68)	374
7b	OTf$^-$	254 (4.1), 259 (3.9) (sh), 296 (9.2)	363 (296; 74)	374
7c	OTf$^-$	254(2.6), 297 (6.1)	362 (297, 52)	372
8a	SCN$^-$	253 (2.6), 296 (6.3)	361 (296, 32)	382
8b	SCN$^-$	254 (2.3), 297 (5.5)	362 (297, 50)	378
8c	SCN$^-$	254 (2.8), 297 (6.5)	363 (297, 54)	380

Quantum yield of quinine sulfate (reference) is considered as high as 58% in 0.1M H_2SO_4, 22^{0}C*

* J.R. Lakowicz, Principles of Fluorescence Spectroscopy, 2nd Ed., Kluwer Academic Press Publishers, New York, London, Moscow, Dordrecht, 1999

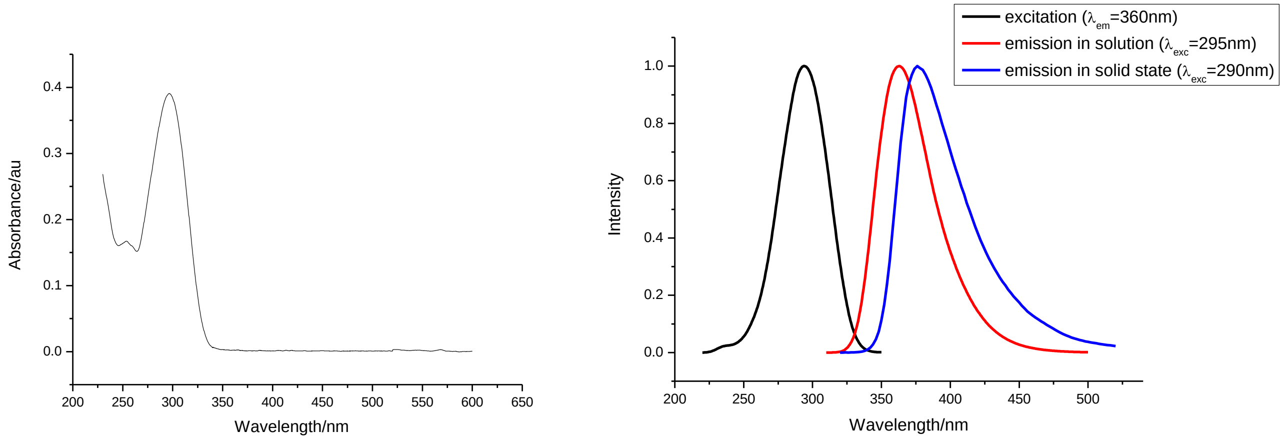


Fig. S14. The UV-VIS (left) and normalised emission and excitation spectra (right) for **8c**.