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Pyrrolidinium Ionic Liquid Crystals with Pendant Mesogenic Groups

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Pyrrolidinium Ionic Liquid Crystals with Pendant Mesogenic Groups

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Supporting Information

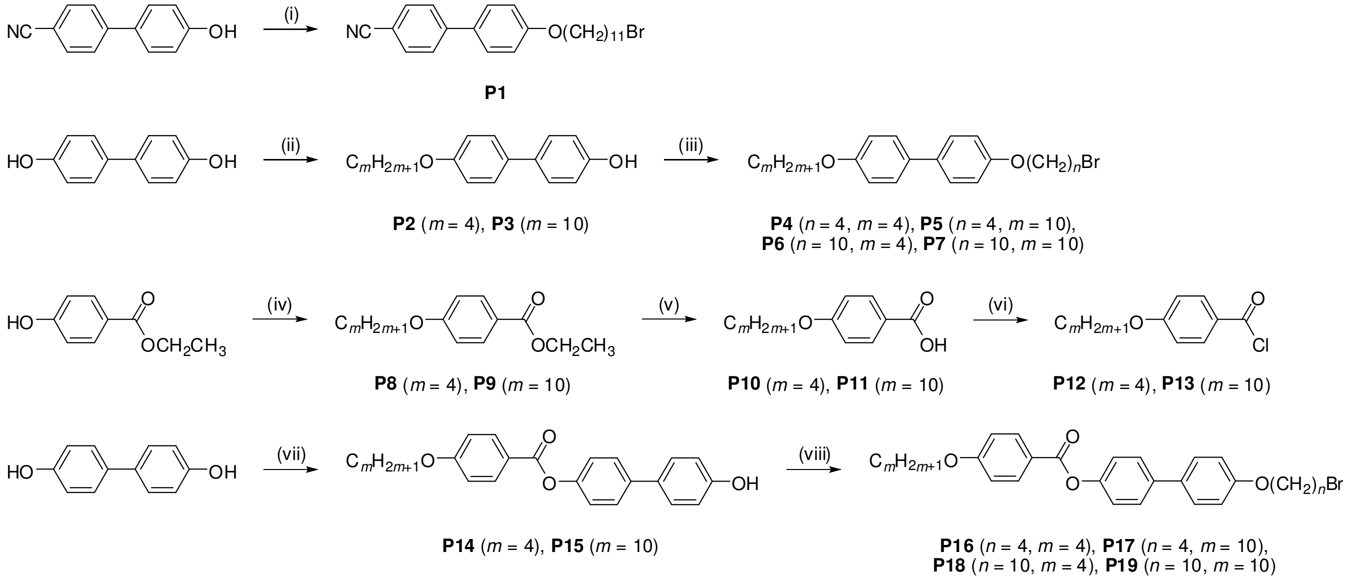
Experimental Section: General

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 300 spectrometer (operating at 300 MHz for ^{1}H). Elemental analyses were obtained on a CE Instruments EA-1110 elemental analyzer. Electrospray ionization (ESI) mass spectra were recorded on a Thermo Finnigan LCQ Advantage mass spectrometer.

Experimental Section: Synthetic Procedures

The synthesis of the precursors is outlined in Scheme S1. 4'-Hydroxy-4-biphenylcarbonitrile and 11-bromo-1-undecanol were coupled *via* the hydroxyl group by a Mitsunobu reaction to give the precursor **P1** (diisopropyl azodicarboxylate (DIAD) was used instead of diethyl azodicarboxylate (DEAD)).[1] Precursors **P4**, **P5**, **P6** and **P7** were prepared in a two-step procedure: 4,4'-biphenol was first monoalkylated with the appropriate 1-bromoalkane to give the intermediates **P2** and **P3**, which were then alkylated with the appropriate dibromoalkane. Precursors **P16**, **P17**, **P18** and **P19** were synthesized by monoesterification of 4,4'-biphenol with acyl chlorides **P12** or **P13**, and subsequent alkylation of intermediates **P14** or **P15** with the appropriate dibromoalkane.

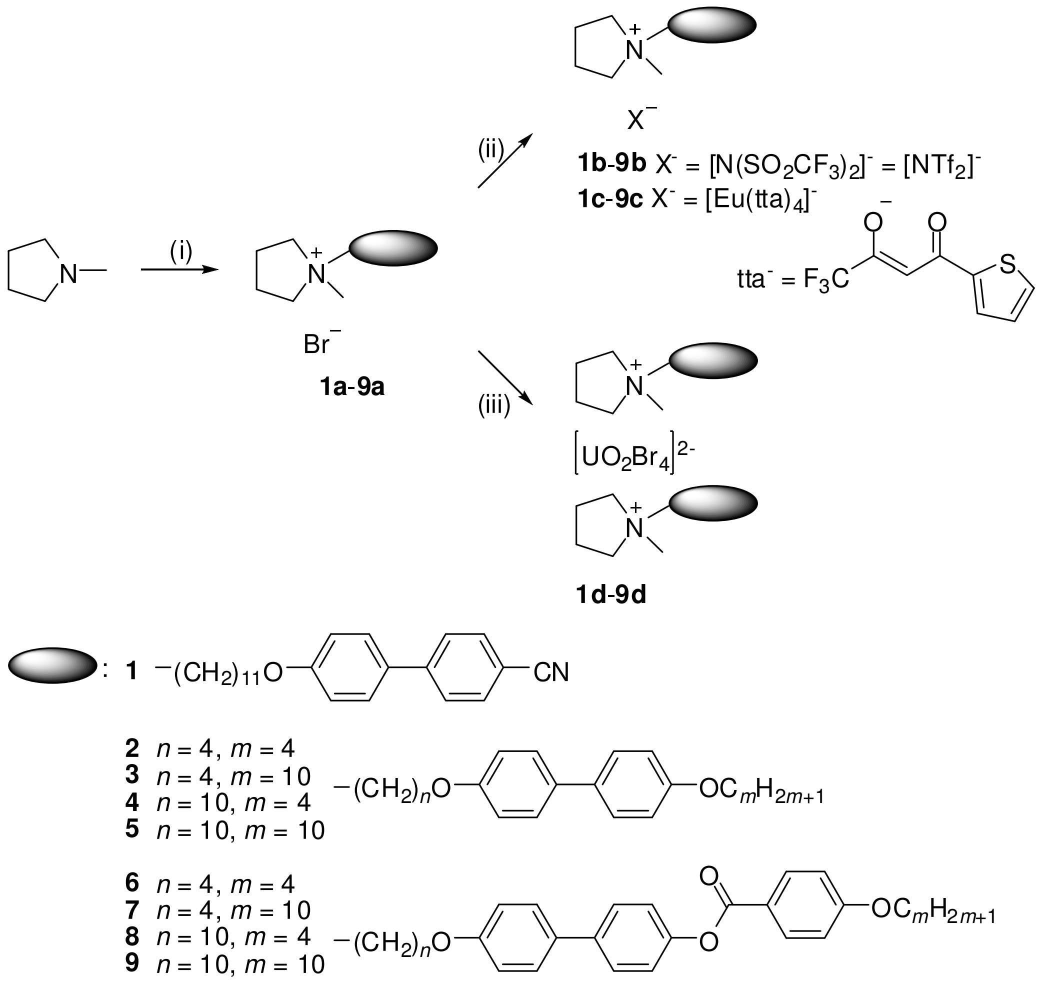
Scheme S1. Synthesis of the precursors.[a]



[a] (i) 11-bromo-1-undecanol, PPh_3, DIAD, Ar, dry THF, rt; (ii) C_4H_9Br, K_2CO_3, KI, Ar, 2-butanone, reflux, or $C_{10}H_{21}Br$, KOH, Ar, DMSO, 80 °C; (iii) $Br(CH_2)_nBr$ ($n = 4$, 10), K_2CO_3, KI, Ar, 2-butanone, reflux; (iv) $C_mH_{2m+1}Br$ ($m = 4$, 10), K_2CO_3, KI, Ar, 2-butanone, reflux; (v) 1. KOH, EtOH/H_2O (5:1), reflux; 2. conc. HCl; (vi) $SOCl_2$, some drops of DMF, Ar, 60 °C; (vii) **P12** or **P13**, dry THF, dry pyridine, Ar, reflux; (viii) $Br(CH_2)_nBr$ ($n = 4$, 10), K_2CO_3, KI, Ar, 2-butanone, reflux.

The synthesis of the pyrrolidinium salts is outlined in Scheme S2. Compounds **1a**-**9a** were prepared by quaternization (Menschutkin reaction) of *N*-methylpyrrolidine with the appropriate precursor.[2] Compounds **1b**-**9b** were synthesized by a metathesis reaction between the bromide salts **1a**-**9a** and lithium bis(trifluoromethylsulfonyl)imide ($LiNTf_2$, Tf = SO_2CF_3). Compounds **1c**-**7c** were prepared by a reaction between the bromide salts **1a**-**7a**, 2-thenoyltrifluoroacetone (Htta), sodium hydroxide, and europium(III) chloride hexahydrate. Compounds **1d**-**9d** were synthesized by a reaction between the bromide salts **1a**-**9a** and uranyl bromide hydrate ($UO_2Br_2{\cdot}xH_2O$) in ethanol. Due to its hygroscopic character, it is difficult to determine the exact number of water molecules, x, in the uranyl bromide salt precursor. The uranyl bromide salt was carefully dried, and when weighing, x was assumed to be zero in order to prevent that compounds **1d-9d** would be contaminated with an excess of uranyl bromide. The uranyl complexes were obtained as anhydrous yellow solids (as confirmed by CHN elemental analysis and thermogravimetry), although no special care was taken to prevent hydration of the salts.

Scheme S2. Synthesis of the pyrrolidinium compounds.[a]

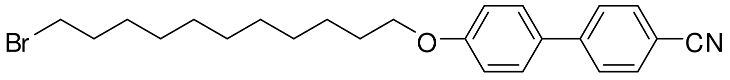


[a] (i) appropriate precursor (**P1**, **P4**, **P5**, **P6**, **P7**, **P16**, **P17**, **P18** or **P19**), Ar, dry toluene, 80 °C; (ii-**1b-9b**) $LiNTf_2$, H_2O/MeOH, 60-65 °C; (ii-**1c-7c**) Htta, NaOH,

$EuCl_3·6H_2O$, H_2O/EtOH, 60-65 °C; (iii) $UO_2Br_2·xH_2O$, EtOH or EtOH/1-BuOH (2:1), 70 °C.

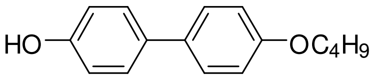
Synthesis of the precursors

Synthesis of ***P1***



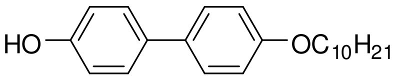
Compound **P1** was prepared by adding diisopropyl azodicarboxylate (DIAD) (25.60 mmol, 5.177 g) dropwise to an ice-cooled stirred solution of 4'-hydroxy-4-biphenylcarbonitrile (25.60 mmol, 4.998 g), 11-bromo-1-undecanol (25.60 mmol, 6.431 g) and triphenylphosphine (25.60 mmol, 6.715 g) in dry THF (50 mL) under an argon atmosphere. The solution (with exclusion of light) was allowed to warm up to room temperature and was stirred for 24 h. The solvent was removed under reduced pressure and the crude product was purified on a silica column with chloroform/*n*-hexane (50:50) as the eluent. The product was recrystallized from *n*-hexane to obtain white needle-like crystals. The pure compound was dried *in vacuo* at 50 °C. Yield: 72% (7.90 g). δ_H (300 MHz, $CDCl_3$): 1.26-1.51 (m, 14H, CH_2), 1.75-1.90 (m, 4H, $\mathbf{CH_2}$-CH_2-Br and $\mathbf{CH_2}$-CH_2-O), 3.40 (t, 2H, CH_2-Br), 4.00 (t, 2H, CH_2-O), 6.98 (d, 2H, H-aryl, J = 8.4 Hz), 7.52 (d, 2H, H-aryl, J = 8.4 Hz), 7.59-7.72 (m, 4H, H-aryl). Calcd. for $C_{24}H_{30}BrNO$ (428.41): C 67.29, H 7.06, N 3.27. Found: C 67.17, H 7.25, N 3.24. Transition temperatures (°C): Cr · (N · 66 ·) 77 · I (lit. Cr · (N · 66 ·) 77 · I[3]).

Synthesis of ***P2***



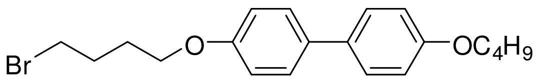
1-Bromobutane (124.00 mmol, 16.990 g) was added dropwise to a stirred solution of 4,4'-dihydroxybiphenyl (136.40 mmol, 25.399 g) in 2-butanone (150 mL). Potassium carbonate (124.00 mmol, 17.138 g) and a catalytic amount of potassium iodide were added and the mixture was refluxed for 24 h under an argon atmosphere. After cooling to room temperature, the reaction mixture was poured into 600 mL of cold water. The solution was neutralized with concentrated HCl (37 wt.%). 2-Butanone was removed under reduced pressure. The remaining aqueous suspension was extracted with diethyl ether (3 × 400 mL). The organic extract was dried over anhydrous $MgSO_4$, and diethyl ether was partly removed under reduced pressure. Silica was added, and the crude product was adsorbed to the silica under removal of the solvent under reduced pressure. The crude product was then purified on a *dry-packed* silica column with toluene as the eluent. The pure product was obtained as a white powder and was dried *in vacuo* at 50 °C. Yield: 24% (7.25 g). δ_H (300 MHz, $CDCl_3$): 0.97 (t, 3H, CH_3, J = 7.4 Hz), 1.50 (sextet, 2H, $\mathbf{CH_2}$-CH_3, J = 7.4 Hz), 1.76 (quintet, 2H, O-CH_2-$\mathbf{CH_2}$, J = 7.0 Hz), 4.01 (t, 2H, O-CH_2, J = 6.4 Hz), 6.90 (d, 2H, H-aryl, J = 8.3 Hz), 6.96 (d, 2H, H-aryl, J = 8.6 Hz), 7.44 (d, 2H, H-aryl, J = 8.3 Hz), 7.49 (d, 2H, H-aryl, J = 8.6 Hz), 8.35 (s, 1H, OH). Calcd. for $C_{16}H_{18}O_2$ (242.31): C 79.31, H 7.49. Found: C 79.04, H 7.67. Transition temperatures (°C): Cr · 170 · I (lit. Cr · 172 · I [4]).

Synthesis of ***P3***



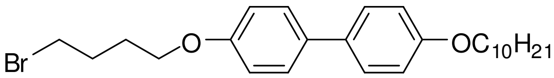
4,4'-Dihydroxybiphenyl (150.00 mmol, 27.932 g) was dissolved in DMSO (150 mL), and KOH (450.00 mmol, 25.250 g) was added. Then 1-bromodecane (150.00 mmol, 33.177 g) was added dropwise. The reaction mixture was stirred for 3 h at 80 °C under an argon atmosphere. After cooling to room temperature, 200 mL of cold water was added. The solution was neutralized with concentrated HCl (37 wt.%). The precipitate was filtered off and was recrystallized from chloroform and from methanol to obtain the pure compound as a white powder, which was dried *in vacuo* at 50 °C. Yield: 25% (12.01 g). δ_H (300 MHz, $CDCl_3$): 0.88-0.90 (m, 3H, CH_3), 1.30-1.48 (m, 14H, CH_2), 1.79-1.84 (m, 2H, O-CH_2-C**H_2**), 4.00 (t, 2H, O-CH_2, $J = 6.3$ Hz), 6.88-6.96 (m, 4H, H-aryl), 7.43-7.48 (m, 4H, H-aryl), 8.25 (s, 1H, OH). Calcd. for $C_{22}H_{30}O_2 \cdot 0.25H_2O$ (330.98): C 79.84, H 9.29. Found: C 79.47, H 9.50. Transition temperatures (°C): $Cr_1 \cdot 107 \cdot Cr_2 \cdot 120 \cdot Cr_3 \cdot 148 \cdot I$ (lit. $T_m = 151$ °C [5]).

*Synthesis of **P4***



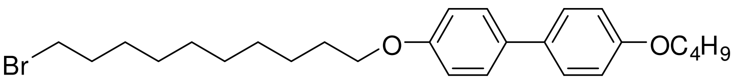
1,4-Dibromobutane (56.76 mmol, 12.255 g) was added dropwise to a stirred solution of compound **P2** (5.16 mmol, 1.250 g) in 2-butanone (80 mL). Potassium carbonate (5.68 mmol, 0.784 g) and a catalytic amount of potassium iodide were added and the mixture was refluxed for 48 h under an argon atmosphere. After cooling to room temperature, 300 mL of dichloromethane was added. The white precipitate (inorganic salts) was filtered off and washed with dichloromethane. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was recrystrallized from *n*-hexane to obtain the pure compound as a white powder, which was dried *in vacuo* at 50 °C. Yield: 71% (1.39 g). δ_H (300 MHz, $CDCl_3$): 0.98 (t, 3H, CH_3, J = 7.4 Hz), 1.51 (sextet, 2H, $C\mathbf{H}_2$-CH_3, J = 7.4 Hz), 1.79 (quintet, 2H, $C\mathbf{H}_2$-CH_2-CH_3, J = 6.9 Hz), 1.96 (quintet, 2H, O-CH_2-$C\mathbf{H}_2$-CH_2-CH_2-Br, J = 6.5 Hz), 2.09 (quintet, 2H, O-CH_2-CH_2-$C\mathbf{H}_2$-CH_2-Br, J = 6.5 Hz), 3.50 (t, 2H, CH_2-Br, J = 6.5 Hz), 3.99 (t, 2H, O-CH_2, J = 6.5 Hz), 4.02 (t, 2H, O-CH_2, J = 6.1 Hz), 6.90-6.98 (m, 4H, H-aryl), 7.46 (d, 4H, H-aryl, J = 8.3 Hz). Calcd. for $C_{20}H_{25}BrO_2$ (377.32): C 63.66, H 6.68. Found: C 63.42, H 6.71. Transition temperatures (°C): Cr · 135 · I.

*Synthesis of **P5***



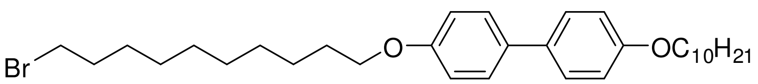
1,4-Dibromobutane (168.47 mmol, 36.374 g) was added dropwise to a stirred solution of compound **P3** (15.32 mmol, 5.000 g) in 2-butanone (150 mL). Potassium carbonate (16.85 mmol, 2.328 g) and a catalytic amount of potassium iodide were added and the mixture was refluxed for 48 h under an argon atmosphere. After cooling to room temperature, 400 mL of dichloromethane was added. The white precipitate (inorganic salts) was filtered off and washed with dichloromethane. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was recrystrallized from *n*-hexane to obtain the pure compound as a white powder, which was dried *in vacuo* at 50 °C. Yield: 88% (6.20 g). δ_H (300 MHz, $CDCl_3$): 0.89 (t, 3H, CH_3, *J* = 7.0 Hz), 1.23-1.54 (m, 14H, CH_2), 1.80 (quintet, 2H, O-CH_2-C**H**$_2$, *J* = 7.0 Hz), 1.96 (quintet, 2H, O-CH_2-C**H**$_2$, *J* = 6.3 Hz), 2.08 (quintet, 2H, C**H**$_2$-CH_2-Br, *J* = 6.6 Hz), 3.50 (t, 2H, CH_2-Br, *J* = 6.6 Hz), 3.98 (t, 2H, O-CH_2, *J* = 7.0 Hz), 4.03 (t, 2H, O-CH_2, *J* = 6.3 Hz), 6.90-6.97 (m, 4H, H-aryl), 7.43-7.49 (m, 4H, H-aryl). Calcd. for $C_{26}H_{37}BrO_2$ (461.47): C 67.67, H 8.08. Found: C 67.55, H 8.18. Transition temperatures (°C): Cr · 108 · SmA · 114 · I.

Synthesis of ***P6***



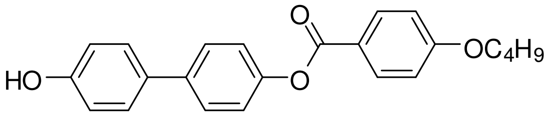
A solution of 1,10-dibromodecane (56.76 mmol, 17.032 g) in 2-butanone (20 mL) was added dropwise to a stirred solution of compound **P2** (5.16 mmol, 1.250 g) in 2-butanone (80 mL). Potassium carbonate (5.68 mmol, 0.784 g) and a catalytic amount of potassium iodide were added and the mixture was refluxed for 48 h under an argon atmosphere. After cooling to room temperature, 300 mL of dichloromethane was added. The white precipitate (inorganic salts) was filtered off and washed with dichloromethane. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was recrystrallized from *n*-hexane to obtain the pure compound as a white powder, which was dried *in vacuo* at 50 °C. Yield: 69% (1.65 g). δ_H (300 MHz, $CDCl_3$): 0.99 (t, 3H, CH_3, J = 7.4 Hz), 1.28-1.60 (m, 14H, CH_2), 1.73-1.93 (m, 6H, CH_2), 3.41 (t, 2H, CH_2-Br, J = 6.8 Hz), 3.99 (m, 4H, O-CH_2), 6.91-7.03 (m, 4H, H-aryl), 7.43-7.55 (m, 4H, H-aryl). Calcd. for $C_{26}H_{37}BrO_2$ (461.47): C 67.67, H 8.08. Found: C 67.80, H 8.01. Transition temperatures (°C): Cr · 111 · I.

Synthesis of ***P7***



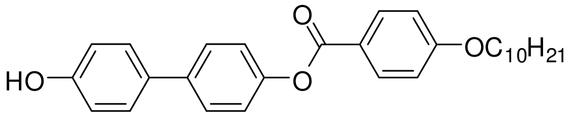
A solution of 1,10-dibromodecane (350.00 mmol, 105.025 g) in acetone (70 mL) was added dropwise to a stirred solution of compound **P3** (30.00 mmol, 9.794 g) in acetone (150 mL). Potassium carbonate (33.00 mmol, 4.561 g) and a catalytic amount of potassium iodide were added and the mixture was refluxed for 15 h under an argon atmosphere. After cooling to room temperature, 400 mL of dichloromethane was added. The white precipitate (inorganic salts) was filtered off and washed with dichloromethane. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was recrystrallized from *n*-hexane to obtain the pure compound as a white powder, which was dried *in vacuo* at 50 °C. Yield: 63% (10.43 g). δ_H (300 MHz, $CDCl_3$): 0.88-0.91 (m, 3H, CH_3), 1.30-1.46 (m, 26H, CH_2), 1.79-1.90 (m, 6H, O-CH_2-$\mathbf{CH_2}$ and Br-$\mathbf{CH_2}$-CH_2), 3.43 (t, 2H, CH_2-Br, J = 6.6 Hz), 4.00 (t, 4H, O-CH_2, J = 6.3 Hz), 6.96 (d, 4H, H-aryl, J = 8.4 Hz), 7.48 (d, 4H, H-aryl, J = 8.4 Hz). Calcd. for $C_{32}H_{49}BrO_2 \cdot 0.5H_2O$ (554.64): C 69.30, H 9.09. Found: C 69.22, H 9.58. Transition temperatures (°C): Cr · 99 · I.

Synthesis of ***P14***



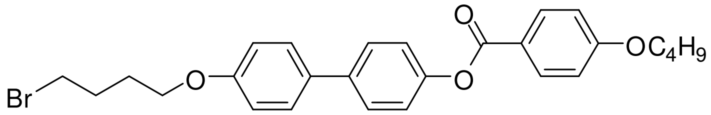
4-(Butyloxy)benzoic acid (152.65 mmol, 29.650 g) was dissolved in 60 mL of thionyl chloride. A few drops of DMF were added. The reaction mixture was stirred for 6 h at 60 °C under an argon atmosphere. The excess of thionyl chloride was removed under reduced pressure. The remaining acyl chloride was immediately dissolved in dry THF (30 mL). This solution was added dropwise to a stirred solution of 4,4’-dihydroxybiphenyl (324.90 mmol, 60.500 g) in dry THF (300 mL) and dry pyridine (40 mL). The reaction mixture was refluxed for 15 h under an argon atmosphere. After the reaction mixture was cooled to room temperature it was filtered. The solvent was removed under reduced pressure until about 100 mL remained. Then 300 mL of cold water was added. The formed precipitate was filtered off and washed with water, ethanol and *n*-hexane. The crude product could not be purified completely (after column chromatography (silica, *n*-hexane/ethyl acetate (70:30)) and an attempt to recrystallize the crude product from acetone, disubstituted byproduct still remained), and was used in the next synthesis step without further purification. Yield: could not be calculated (impure product) (26.201 g).

Synthesis of ***P15***



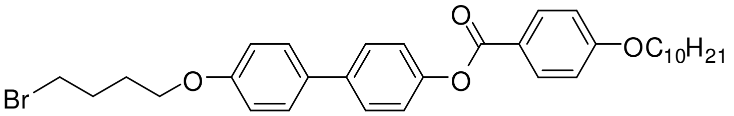
4-(Decyloxy)benzoic acid (100.33 mmol, 27.930 g) was dissolved in 60 mL of thionyl chloride. A few drops of DMF were added. The reaction mixture was stirred for 6 h at 60 °C under an argon atmosphere. The excess of thionyl chloride was removed under reduced pressure. The remaining acyl chloride was immediately dissolved in dry THF (30 mL). This solution was added dropwise to a stirred solution of 4,4'-dihydroxybiphenyl (252.46 mmol, 47.010 g) in dry THF (300 mL) and dry pyridine (40 mL). The reaction mixture was refluxed for 15 h under an argon atmosphere. After the reaction mixture was cooled to room temperature it was filtered. The solvent was removed under reduced pressure until about 100 mL remained. Then 300 mL of cold water was added. The formed precipitate was filtered off and washed with water, ethanol and *n*-hexane. The crude product was purified on a silica column with chloroform as the eluent. The product was recrystallized from acetone to obtain the pure compound as a white powder, which was dried *in vacuo* at 50 °C. Yield: 34% (15.16 g). δ_H (300 MHz, $CDCl_3$): 0.87-0.89 (m, 3H, CH_3), 1.29-1.48 (m, 14H, CH_2), 1.81-1.85 (m, 2H, O-CH_2-C**H**$_2$), 4.05 (t, 2H, O-CH_2, *J* = 6.5 Hz), 4.95 (s, 1H, OH), 6.87 (d, 2H, H-aryl, *J* = 8.5 Hz), 6.98 (d, 2H, H-aryl, *J* = 8.4 Hz), 7.24 (d, 2H, H-aryl, *J* = 8.5 Hz), 7.44 (d, 2H, H-aryl, *J* = 8.4 Hz), 7.55 (d, 2H, H-aryl, *J* = 8.5 Hz), 8.16 (d, 2H, H-aryl, *J* = 8.5 Hz). Calcd. for $C_{29}H_{34}O_4{\cdot}2H_2O$ (482.61): C 72.17, H 7.94. Found: C 71.97, H 7.78. Transition temperatures (°C): Cr · (SmC · 174 ·) 175 · N · 207 · I (lit. Cr · (SmC · 171.9 ·) 175.5 · N · 205.5 · I [6]).

*Synthesis of **P16***



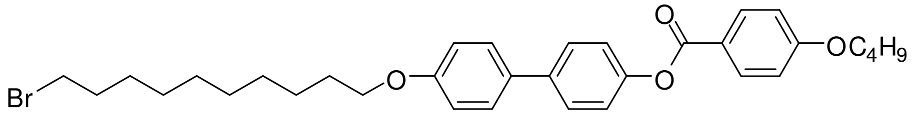
1,4-Dibromobutane (327.60 mmol, 70.732 g) was added dropwise to a stirred solution of compound **P14** (36.45 mmol, 13.210 g) in 2-butanone (150 mL). Potassium carbonate (38.22 mmol, 5.282 g) and a catalytic amount of potassium iodide were added and the mixture was refluxed for 15 h under an argon atmosphere. After cooling to room temperature, 300 mL of dichloromethane was added. The white precipitate (inorganic salts) was filtered off and washed with dichloromethane. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was recrystrallized from *n*-hexane, and was further purified on a silica column with chloroform/*n*-hexane (5:1) as the eluent. The pure product was obtained as a white powder and was dried *in vacuo* at 50 °C. Yield: could not be calculated (impure starting product) (10.808 g). δ_H (300 MHz, $CDCl_3$): 1.00 (t, 3H, CH_3, *J* = 7.3 Hz), 1.49-1.56 (m, 2H, CH_2), 1.77-2.13 (m, 6H, O-CH_2-$\mathbf{CH_2}$ and Br-CH_2-$\mathbf{CH_2}$), 3.51 (t, 2H, CH_2-Br, *J* = 6.4 Hz), 4.01-4.08 (m, 4H, O-CH_2), 6.95-6.99 (m, 4H, H-aryl), 7.23 (d, 2H, H-aryl, *J* = 8.6 Hz), 7.51 (d, 2H, H-aryl, *J* = 8.4 Hz), 7.58 (d, 2H, H-aryl, *J* = 8.6 Hz), 8.16 (d, 2H, H-aryl, *J* = 8.8 Hz). Calcd. for $C_{27}H_{29}BrO_4{\cdot}0.5H_2O$ (506.43): C 64.03, H 5.97. Found: C 64.30, H 5.54. Transition temperatures (°C): Cr · 157 · N · 229 · I.

Synthesis of ***P17***



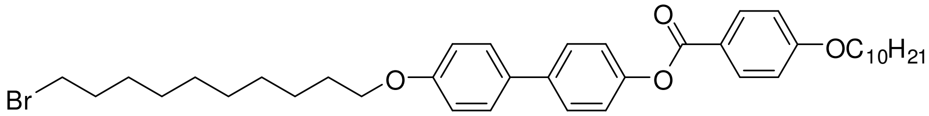
1,4-Dibromobutane (164.70 mmol, 35.560 g) was added dropwise to a stirred solution of compound **P15** (18.29 mmol, 8.170 g) in acetone (100 mL). Potassium carbonate (19.22 mmol, 2.656 g) and a catalytic amount of potassium iodide were added and the mixture was refluxed for 15 h under an argon atmosphere. After cooling to room temperature, 200 mL of dichloromethane was added. The white precipitate (inorganic salts) was filtered off and washed with dichloromethane. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was recrystallized from *n*-hexane to obtain the pure compound as a white powder, which was dried *in vacuo* at 50 °C. Yield: 57% (6.06 g). δ_H (300 MHz, $CDCl_3$): 0.89-0.91 (m, 3H, CH_3), 1.31-1.57 (m, 14H, CH_2), 1.80-2.14 (m, 6H, O-CH_2-C$\mathbf{H}_2$ and Br-C$\mathbf{H}_2$-CH_2), 3.51-3.55 (m, 2H, CH_2-Br), 4.07 (t, 4H, O-CH_2, J = 5.9 Hz), 6.98-7.01 (m, 4H, H-aryl), 7.25-7.28 (m, 2H, H-aryl), 7.53 (d, 2H, H-aryl, J = 8.2 Hz), 7.60 (d, 2H, H-aryl, J = 8.2 Hz), 8.18 (d, 2H, H-aryl, J = 8.3 Hz). Calcd. for $C_{33}H_{41}BrO_4 \cdot 0.5H_2O$ (590.59): C 67.11, H 7.17. Found: C 67.11, H 7.08. Transition temperatures (°C): Cr · (SmX_1 · 99 ·) 122 · SmX_2 · 123 · SmC · 156 · SmA · 184 · N · 201 · I.

Synthesis of ***P18***



A solution of 1,10-dibromodecane (322.20 mmol, 96.683 g) in 2-butanone (70 mL) was added dropwise to a stirred solution of compound **P14** (35.84 mmol, 12.990 g) in 2-butanone (150 mL). Potassium carbonate (37.59 mmol, 5.195 g) and a catalytic amount of potassium iodide were added and the mixture was refluxed for 15 h under an argon atmosphere. After cooling to room temperature, 400 mL of dichloromethane was added. The white precipitate (inorganic salts) was filtered off and washed with dichloromethane. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was recrystrallized from *n*-hexane, and was further purified on a silica column with chloroform/*n*-hexane (5:1) as the eluent. The pure product was obtained as a white powder and was dried *in vacuo* at 50 °C. Yield: could not be calculated (impure starting product) (12.403 g). δ_H (300 MHz, $CDCl_3$): 1.00 (t, 3H, CH_3, *J* = 7.3 Hz), 1.32-1.56 (m, 14H, CH_2), 1.79-1.88 (m, 6H, O-CH_2-**C**$\mathbf{H}_2$ and **C**$\mathbf{H}_2$-CH_2-Br), 3.41 (t, 2H, CH_2-Br, *J* = 6.5 Hz), 3.98-4.08 (m, 4H, O-CH_2), 6.96-6.99 (m, 4H, H-aryl), 7.24 (d, 2H, H-aryl, *J* = 8.8 Hz), 7.51 (d, 2H, H-aryl, *J* = 8.4 Hz), 7.58 (d, 2H, H-aryl, *J* = 8.8 Hz), 8.16 (d, 2H, H-aryl, *J* = 9.0 Hz). Calcd. for $C_{33}H_{41}BrO_4{\cdot}0.5H_2O$ (590.59): C 67.11, H 7.17. Found: C 67.33, H 7.41. Transition temperatures (°C): Cr · (SmX · 107 · SmC · 116 ·) 123 · N · 186 · I.

Synthesis of ***P19***



A solution of 1,10-dibromodecane (134.10 mmol, 40.239 g) in acetone (35 mL) was added dropwise to a stirred solution of compound **P15** (14.87 mmol, 6.640 g) in acetone (80 mL). Potassium carbonate (15.64 mmol, 2.162 g) and a catalytic amount of potassium iodide were added and the mixture was refluxed for 15 h under an argon atmosphere. After cooling to room temperature, 200 mL of dichloromethane was added. The white precipitate (inorganic salts) was filtered off and washed with dichloromethane. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and washed with water. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was recrystallized from *n*-hexane to obtain the pure compound as a white powder, which was dried *in vacuo* at 50 °C. Yield: 72% (7.13 g). δ_H (300 MHz, $CDCl_3$): 0.89-0.91 (m, 3H, CH_3), 1.30-1.54 (m, 26H, CH_2), 1.83-1.85 (m, 6H, O-CH_2-**C**$\mathbf{H}_2$ and Br-CH_2-**C**$\mathbf{H}_2$), 3.41-3.46 (m, 2H, CH_2-Br), 4.00-4.07 (m, 4H, O-CH_2), 6.99 (m, 4H, H-aryl), 7.23-7.27 (m, 2H, H-aryl), 7.53 (d, 2H, H-aryl, *J* = 8.3 Hz), 7.60 (d, 2H, H-aryl, *J* = 8.1 Hz), 8.18 (d, 2H, H-aryl, *J* = 8.6 Hz). Calcd. for $C_{39}H_{53}BrO_4{\cdot}0.5H_2O$ (674.75): C 69.42, H 8.07. Found: C 69.77, H 8.34. Transition temperatures (°C): Cr · 98 · SmX · 119 · SmC · 152 · SmA · 161 · N · 173 · I.

Synthesis of $UO_2Br_2 \cdot xH_2O$

Uranium(VI) oxide dihydrate (10.00 mmol, 3.221 g) was boiled thoroughly in water (100 mL) for 1 h. The suspension was allowed to cool to room temperature. Then concentrated HBr (48 wt.% aqueous solution) (20.00 mmol, 3.372 g) was added dropwise to the reaction mixture under constant stirring in a fumehood. The mixture was slowly heated to 60 °C, and hydrogen peroxide (30 wt.% aqueous solution) was added dropwise over a total period of at least 30 minutes until all solid reagents had been dissolved. At this point, the solution should be very dark brown to brown-red. The solution was stirred further, and was concentrated at 60 °C under reduced pressure to a total volume of approximately 30 mL. The solution was set aside for crystallization over P_2O_5 in a desiccator until no liquid was visible anymore. The dark brown, hygroscopic crystals were further dried over silica in a desiccator for two to three weeks. The final recipient should be closed very tightly and be kept in a desiccator.

Synthesis of the pyrrolidinium compounds

*Synthesis of compounds **1a**-**9a***

A solution of 1-methylpyrrolidine (1 eq.) in dry toluene (5 mL) was added dropwise to a stirred solution of the appropriate precursor (1.05 eq.) in dry toluene (50 mL) at 60 °C. The mixture was stirred for 48 h at 80 °C under an argon atmosphere. A precipitate was formed, filtered off and washed carefully with (warm) toluene, (warm) ethyl acetate and diethyl ether. The crude product was purified on a silica column with chloroform/methanol (90:10) as the eluent (not necessary for compound **1a**). The purified product was dissolved in chloroform and filtered through a Grace cellulose filter (0.45 μm) mounted on a syringe to remove traces of silica. After recrystallization from methanol/diethyl ether, the pure product was obtained as a white powder, which was dried *in vacuo* at 50 °C. **1a**: Yield: 39% (2.30 g). δ_H (300 MHz, $CDCl_3$): 1.31-1.37 (m, 14H, CH_2), 1.75-1.81 (m, 4H, N-CH_2-C**H**$_2$ and O-CH_2-C**H**$_2$), 2.31 (s, 4H, pyrr. H-3 and H-4), 3.32 (s, 3H, N-CH_3), 3.65-3.70 (m, 2H, N-CH_2), 3.85-3.87 (m, 4H, pyrr. H-2 and H-5), 4.01 (t, 2H, O-CH_2, *J* = 6.2 Hz), 7.00 (d, 2H, H-aryl, *J* = 8.4 Hz), 7.54 (d, 2H, H-aryl, *J* = 8.2 Hz), 7.64-7.71 (m, 4H, H-aryl). δ_C (75 MHz, $CDCl_3$): 24.52, 26.39, 26.81, 29.59, 29.64, 29.75, 29.86, 49.02, 64.56, 64.82, 68.54, 74.38, 110.33, 115.48, 119.54, 127.45, 128.70, 131.57, 132.94, 145.67. Calcd. for $C_{29}H_{41}BrN_2O$ (513.55): C 67.82, H 8.05, N 5.45. Found: C 67.48, H 8.37, N 5.11. ESI-MS (methanol, m/z): 433.6, $[M - Br^-]^+$; 947.2, $[M + M - Br^-]^+$. **2a**: Yield: 63% (2.05 g). δ_H (300 MHz, $CDCl_3$): 0.99 (t, 3H, CH_3, *J* = 7.4 Hz), 1.51 (sextet, 2H, CH_2, *J* = 7.4 Hz), 1.79 (quintet, 2H, CH_2, *J* = 7.1 Hz), 1.88-2.10 (m, 4H, CH_2), 2.24-2.34 (m, 4H, pyrr.H-3 and H-4), 3.30 (s, 3H, N-CH_3), 3.79-3.89 (m, 6H, N-CH_2 and pyrr. H-2 and H-5), 3.99 (t, 2H, O-CH$_2$, *J* = 6.6 Hz), 4.06 (t, 2H, O-CH$_2$, *J* = 5.3 Hz), 6.94 (d, 4H, H-aryl, *J* = 8.2 Hz), 7.42-7.49 (m, 4H, H-aryl). δ_C (75 MHz, CDCl$_3$): 13.99, 19.38, 21.29, 21.81, 26.23, 31.47, 48.79, 63.85, 64.64, 66.93, 67.90, 114.85, 114.90, 127.73, 127.88, 133.09, 133.94, 157.73, 158.46. Calcd. for $C_{25}H_{36}BrNO_2{\cdot}0.5H_2O$ (471.47): C 63.69, H 7.91, N 2.97. Found: C 63.52, H 8.07, N 2.93. ESI-MS (methanol, m/z): 382.5, $[M - Br^-]^+$; 843.4, $[M + M - Br^-]^+$. **3a**: Yield: 62% (1.80 g). δ_H (300 MHz, CDCl$_3$): 0.88 (t, 3H, CH$_3$, *J* = 7.0 Hz), 1.23-1.53 (m, 14H, CH$_2$), 1.73-2.09 (m, 6H, CH$_2$), 2.23-2.34 (m, 4H, pyrr.H-3 and H-4), 3.31 (s, 3H, N-CH$_3$), 3.80-3.89 (m, 6H, N-CH$_2$ and pyrr. H-2 and H-5), 3.97 (t, 2H, O-CH$_2$, *J* = 6.5 Hz), 4.06 (t, 2H, O-CH$_2$, *J* = 5.3 Hz), 6.93 (d, 4H, H-aryl, *J* = 8.2 Hz), 7.42-7.48 (m, 4H, H-aryl). δ_C (75 MHz, CDCl$_3$): 14.26, 21.29, 21.80, 22.82, 26.21, 29.45, 29.55, 29.71, 32.02, 48.76, 63.82, 64.63, 66.91, 68.23, 114.84, 114.90, 127.88, 133.06, 133.97, 157.70, 158.46. Calcd. for $C_{31}H_{48}BrNO_2$ (546.62): C 68.11, H 8.85, N 2.56. Found: C 67.81, H 9.11, N 2.49. ESI-MS (methanol, m/z): 466.8, $[M - Br^-]^+$; 1011.7, $[M + M - Br^-]^+$. **4a**: Yield: 58% (1.68 g). δ_H (300 MHz, CDCl$_3$): 0.98 (t, 3H, CH$_3$, *J* = 7.4 Hz), 1.26-1.58 (m, 14H, CH$_2$), 1.68-1.84 (m, 6H, CH$_2$), 2.23-2.34 (m, 4H, pyrr.H-3 and H-4), 3.28 (s, 3H, N-CH$_3$), 3.59-3.67 (m, 2H, N-CH$_2$), 3.73-3.89 (m, 4H, pyrr. H-2 and H-5), 3.98 (t, 4H, O-CH$_2$, *J* = 6.2 Hz), 6.94 (d, 4H, H-aryl, *J* = 8.4 Hz), 7.46 (d, 4H, H-aryl, *J* = 8.6 Hz). δ_C (75 MHz, CDCl$_3$): 14.01, 19.39, 21.78, 24.22, 26.11, 26.51, 29.37, 29.46, 31.49, 48.74, 64.31, 64.56, 67.90, 68.14, 114.87, 127.75, 133.36, 133.42, 158.31, 158.37. Calcd. for $C_{31}H_{48}BrNO_2{\cdot}0.5H_2O$ (555.63): C 67.01, H 8.89, N 2.52. Found: C 66.60, H 9.01, N 2.56. ESI-MS (methanol, m/z): 466.9, $[M - Br^-]^+$; 1013.5, $[M + M - Br^-]^+$. **5a**: Yield: 44% (0.86 g). δ_H (300 MHz, CDCl$_3$): 0.88 (t, 3H, CH$_3$, *J* = 7.4 Hz), 1.28-1.46 (m, 26H, CH$_2$), 1.77-1.79 (m, 6H, O-CH$_2$-C**H**$_2$ and N-CH$_2$-C**H**$_2$), 2.30 (m, 4H, pyrr. H-3 and H-4), 3.29 (s, 3H, N-CH$_3$), 3.63-3.67 (m, 2H, N-CH_2), 3.83-3.85 (m, 4H, pyrr. H-2 and H-5), 3.96-4.00 (m, 4H, O-CH_2), 6.94 (d, 4H, H-aryl, *J* = 8.4 Hz), 7.46 (d, 4H, H-aryl, *J* = 8.4 Hz). δ_C (75 MHz, $CDCl_3$): 14.51, 22.05, 23.06, 24.49, 26.38, 26.45, 26.78, 29.65, 29.71, 29.79, 29.97, 32.29, 49.02, 64.58, 64.82, 68.41, 68.50, 74.39, 115.15; 128.00, 133.61, 133.70, 158.59. Calcd. for $C_{37}H_{60}BrNO_2\cdot H_2O$ (648.80): C 68.50, H 9.63, N 2.16. Found: C 68.30, H 10.09, N 2.22. ESI-MS (methanol, m/z): 550.7, [M - Br$^-$]$^+$; 1181.5, [M + M - Br$^-$]$^+$. **6a**: Yield: 43% (2.73 g). δ_H (300 MHz, $CDCl_3$): 1.00 (t, 3H, $CH_{3,}$ *J* = 7.4 Hz), 1.48-1.56 (m, 2H, CH_3-C**H**$_2$), 1.77-1.84 (m, 2H, CH_2), 1.94-2.05 (m, 4H, pyrr. H-3 and H-4), 2.29-2.31 (m, 4H, O-CH_2-C**H**$_2$), 3.31 (s, 3H, N-CH_3), 3.84-3.89 (m, 6H, N-CH_2, pyrr. H-2 and H-5), 4.03-4.10 (m, 4H, O-CH_2), 6.95-6.99 (m, 4H, H-aryl), 7.24 (d, 2H, H-aryl, *J* = 8.4 Hz), 7.51 (d, 2H, H-aryl, *J* = 8.7 Hz), 7.57 (d, 2H, H-aryl, *J* = 8.4 Hz), 8.15 (d, 2H, H-aryl, *J* = 8.9 Hz). δ_C (75 MHz, $CDCl_3$): 14.23, 19.59, 21.32, 21.91, 26.18, 31.53, 48.76, 64.67, 64.97, 67.08, 68.42, 114.72, 115.24, 118.13, 121.76, 122.39, 122.57, 128.00, 132.69, 133.46, 138.66, 150.51, 158.62, 164.04, 164.44. Calcd. for $C_{32}H_{40}BrNO_4\cdot H_2O$ (600.58): C 63.99, H 7.05, N 2.33. Found: C 63.69, H 6.68, N 2.32. ESI-MS (methanol, m/z): 502.5, [M - Br$^-$]$^+$; 1083.5, [M + M - Br$^-$]$^+$. **7a**: Yield: 47% (1.37 g). δ_H (300 MHz, $CDCl_3$): 0.89 (t, 3H, CH_3, *J* = 7.4 Hz), 1.28-1.33 (m, 14H, CH_2), 1.83 (m, 2H, N-CH_2-**CH**$_2$,), 1.96-1.99 (m, 4H, O-CH_2-**CH**$_2$), 2.30-2.31 (m, 4H, pyrr. H-3 and H-4), 3.33 (s, 3H, N-CH_3), 3.85-3.90 (m, 6H, N-CH_2, pyrr. H-2 and H-5), 4.02-4.09 (m, 4H, O-CH_2), 6.95-6.99 (m, 4H, H-aryl), 7.24 (d, 2H, H-aryl, *J* = 8.3 Hz), 7.52 (d, 2H, H-aryl, *J* = 8.4 Hz), 7.57 (d, 2H, H-aryl, *J* = 8.3 Hz), 8.15 (d, 2H, H-aryl, *J* = 8.8 Hz). δ_C (75 MHz, $CDCl_3$): 14.53, 21.54, 22.07, 23.07, 26.38, 26.48, 29.49, 29.70, 29.76, 29.95, 32.29, 49.02, 64.12, 64.90, 67.24, 68.74, 114.72, 115.24, 121.81, 122.52, 128.03, 128.58, 132.68, 133.58, 138.63, 150.48, 158.56, 163.98, 165.50. Calcd. for $C_{38}H_{52}BrNO_4\cdot H_2O$ (684.74): C 66.65, H

7.95, N 2.05. Found: C 66.31, H 8.36, N 2.16. ESI-MS (methanol, m/z): 586.6, [M - Br$^-$]$^+$; 1253.4, [M + M - Br$^-$]$^+$. **8a**: Yield: 42% (2.87 g). δ_H (300 MHz, $CDCl_3$): 1.00 (t, 3H, CH_3, *J* = 7.4 Hz), 1.32-1.53 (m, 14H, CH_2), 1.77-1.84 (m, 6H, N-CH_2-C**H**$_2$, pyrr. H-3 and H-4), 2.29 (m, 4H, O-CH_2-C**H**$_2$), 3.28 (s, 3H, N-CH_3), 3.62-3.68 (m, 2H, N-CH_2), 3.82-3.84 (m, 4H, pyrr. H-2 and H-5), 3.98-4.08 (m, 4H, O-CH_2), 6.96-6.99 (m, 4H, H-aryl), 7.24 (d, 2H, H-aryl, *J* = 8.6 Hz), 7.51 (d, 2H, H-aryl, *J* = 8.8 Hz), 7.58 (d, 2H, H-aryl, *J* = 8.6 Hz), 8.15 (d, 2H, H-aryl, *J* = 8.9 Hz). δ_C (75 MHz, $CDCl_3$): 14.23, 19.59, 22.03, 24.50, 26.35, 26.80, 29.61, 29.73, 31.52, 48.98, 64.55, 64.80, 68.42, 114.69, 115.24, 121.85, 122.43, 128.01, 128.46, 132.67, 133.09, 138.85, 150.39, 159.13, 163.98. Calcd. for $C_{38}H_{52}BrNO_4 \cdot H_2O$ (684.74): C 66.65, H 7.95, N 2.05. Found: C 66.36, H 7.94, N 1.96. ESI-MS (methanol, m/z): 586.6, [M - Br$^-$]$^+$; 1251.7, [M + M - Br$^-$]$^+$. **9a**: Yield: 49% (1.79 g). δ_H (300 MHz, $CDCl_3$): 0.89 (t, 3H, CH_3, *J* = 7.4 Hz), 1.29-1.47 (m, 26H, CH_2), 1.80-1.85 (m, 6H, O-CH_2-C**H**$_2$ en N-CH_2-C**H**$_2$), 2.29 (m, 4H, pyrr. H-3 and H-4), 3.28 (s, 3H, N-CH_3), 3.62-3.68 (m, 2H, N-CH_2), 3.63-3.87 (m, 4H, pyrr. H-2 and H-5), 4.00-4.07 (m, 4H, O-CH_2), 6.96-6.99 (m, 4H, H-aryl), 7.23-7.27 (m, 2H, H-aryl), 7.51 (d, 2H, H-aryl, *J* = 8.3 Hz), 7.58 (d, 2H, H-aryl, *J* = 8.3 Hz), 8.15 (d, 2H, H-aryl, *J* = 8.3 Hz). δ_C (75 MHz, $CDCl_3$): 14.53, 22.03, 23.07, 24.49, 26.37, 26.80, 29.49, 29.62, 29.71, 29.95, 32.29, 48.98, 64.57, 64.82, 68.42, 68.73, 114.69, 115.24, 121.85, 122.43, 128.02, 128.46, 132.67, 133.09, 138.85, 150.39, 152.62, 159.13, 163.98, 165.50. Calcd. for $C_{44}H_{64}BrNO_4 \cdot 2H_2O$ (786.92): C 67.16, H 8.71, N 1.78. Found: C 66.99, H 8.60, N 1.86. ESI-MS (methanol, m/z): 670.8, [M - Br$^-$]$^+$.

*Synthesis of compounds **1b**-**9b***

*Compound **1b**:* A suspension of bromide salt **1a** (1 eq.) in water (10 mL) was heated to 60 °C, and methanol was added until a clear solution was formed. A concentrated aqueous solution of $LiNTf_2$ (Tf = SO_2CF_3) (1.5 eq.) was added dropwise and the turbid reaction mixture was stirred for 3 h at 60 °C. Then the solvent was removed under reduced pressure. The crude product was dissolved in 20 mL of chloroform, and washed three times with 15 mL of water. After removal of chloroform under reduced pressure, a clear (supercooled) liquid remained. The pure product was dried *in vacuo* at 50 °C. Yield: 91% (0.18 g). δ_H (300 MHz, $CDCl_3$): 1.26-1.52 (m, 14H, CH_2), 1.71-1.85 (m, 4H, N-CH_2-C$\mathbf{H}_2$ and O-CH_2-C$\mathbf{H}_2$), 2.22-2.32 (m, 4H, pyrr. H-3 and H-4), 3.04 (s, 3H, N-CH_3), 3.26-3.34 (m, 2H, N-CH_2), 3.47-3.57 (m, 4H, pyrr. H-2 and H-5), 4.00 (t, 2H, O-CH_2, J = 6.4 Hz), 6.98 (d, 2H, H-aryl, J = 8.5 Hz), 7.52 (d, 2H, H-aryl, J = 8.7 Hz), 7.61-7.71 (m, 4H, H-aryl). δ_C (75 MHz, $CDCl_3$): 21.67, 24.00, 26.11, 26.29, 29.10, 29.43, 29.55, 48.61, 64.72, 64.97, 68.27, 77.36, 110.09, 115.21, 117.83, 119.29, 122.09, 127.18, 128.46, 131.32, 132.69, 145.40, 159.93. Calcd. for $C_{31}H_{41}F_6N_3O_5S_2\cdot0.5H_2O$ (722.80): C 51.51, H 5.86, N 5.81. Found: C 51.39, H 5.39, N 5.58. ESI-MS (methanol, m/z): 433.6, $[M - [NTf_2]^-]^+$; 1146.1, $[M + M - [NTf_2]^-]^+$; 280.1, $[NTf_2]^-$ (observed in negative mode); 992.8, $[M + [NTf_2]^-]^-$ (observed in negative mode).

*Compounds **2b**-**9b**:* A solution of the appropriate bromide salt (compounds **2a**-**9a**) (1 eq.) in methanol (40 mL) was heated to 65 °C. A concentrated aqueous solution of $LiNTf_2$ (2 eq.) was added dropwise and the reaction mixture was stirred for 3 h at 65 °C. Methanol was then removed under reduced pressure. The white precipitate was filtered off, washed with water and dried *in vacuo* at 50 °C. **2b**: Yield: 76% (0.23 g).

δ_H (300 MHz, CD_2Cl_2): 1.01 (t, 3H, CH_3, J = 7.4 Hz), 1.53 (sextet, 2H, CH_2, J = 7.4 Hz), 1.80 (quintet, 2H, CH_2, J = 7.0 Hz), 1.87-1.97 (m, 2H, CH_2), 1.98-2.11 (m, 2H, CH_2), 2.25-2.35 (m, 4H, pyrr.H-3 and H-4), 3.08 (s, 3H, N-CH_3), 3.40-3.48 (m, 2H, N-CH_2), 3.49-3.58 (m, 4H, pyrr. H-2 and H-5), 4.02 (t, 2H, O-CH_2, J = 6.4 Hz), 4.10 (t, 2H, O-CH_2, J = 5.5 Hz), 6.98 (m, 4H, H-aryl), 7.47-7.55 (m, 4H, H-aryl). δ_C (75 MHz, CD_2Cl_2): 13.91, 19.50, 21.38, 21.90, 26.16, 31.62, 48.98, 64.89, 65.15, 66.98, 68.05, 114.93, 114.99, 118.02, 122.27, 127.75, 127.84, 133.04, 133.93, 157.97, 158.70. Calcd. for $C_{27}H_{36}F_6N_2O_6S_2$ (662.70): C 48.93, H 5.48, N 4.23. Found: C 49.01, H 5.17, N 4.19. ESI-MS (methanol, m/z): 382.6, $[M - [NTf_2]^-]^+$; 1044.3, $[M + M - [NTf_2]^-]^+$. **3b**: Yield: 82% (0.19 g). δ_H (300 MHz, $CDCl_3$): 0.88 (t, 3H, CH_3, J = 7.0 Hz), 1.23-1.52 (m, 14H, CH_2), 1.73-2.04 (m, 6H, CH_2), 2.18-2.29 (m, 4H, pyrr.H-3 and H-4), 3.03 (s, 3H, N-CH_3), 3.37-3.45 (m, 2H, N-CH_2), 3.46-3.55 (m, 4H, pyrr. H-2 and H-5), 3.97 (t, 2H, O-CH_2, J = 6.6 Hz), 4.03 (t, 2H, O-CH_2, J = 5.4 Hz), 6.89-6.96 (m, 4H, H-aryl), 7.42-7.49 (m, 4H, H-aryl). δ_C (75 MHz, $CDCl_3$): 14.26, 21.15, 21.70, 22.82, 25.94, 26.20, 29.46, 29.55, 29.72, 32.05, 48.65, 64.78, 66.74, 68.24, 114.81, 114.92, 127.73, 127.87, 133.14, 133.70, 158.49. Calcd. for $C_{33}H_{48}F_6N_2O_6S_2$ (746.86): C 53.07, H 6.48, N 3.75. Found: C 53.38, H 6.63, N 3.62. ESI-MS (methanol, m/z): 466.7, $[M - [NTf_2]^-]^+$; 1212.3, $[M + M - [NTf_2]^-]^+$. **4b**: Yield: 74% (0.20 g). δ_H (300 MHz, CD_2Cl_2): 1.01 (t, 3H, CH_3, J = 7.4 Hz), 1.33-1.58 (m, 14H, CH_2), 1.73-1.87 (m, 6H, CH_2), 2.24-2.32 (m, 4H, pyrr.H-3 and H-4), 3.04 (s, 3H, N-CH_3), 3.23-3.33 (m, 2H, N-CH_2), 3.43-3.56 (m, 4H, pyrr. H-2 and H-5), 4.01 (t, 4H, O-CH_2, J = 6.6 Hz), 6.96 (d, 4H, H-aryl, J = 8.6 Hz), 7.50 (d, 4H, H-aryl, J = 8.6 Hz). δ_C (75 MHz, CD_2Cl_2): 13.91, 19.51, 21.87, 24.13, 26.22, 26.44, 29.21, 29.52, 31.62, 48.95, 65.07, 65.33, 68.05, 68.31, 114.96, 118.02, 122.27, 127.70, 133.24, 133.29, 158.60. Calcd. for $C_{33}H_{48}F_6N_2O_6S_2$ (746.86): C 53.07, H 6.48, N 3.75. Found: C

53.12, H 6.17, N 3.70. ESI-MS (methanol, m/z): 466.8, $[M - [NTf_2]^-]^+$; 1212.5, $[M + M - [NTf_2]^-]^+$. **5b**: Yield: 77% (0.17 g). δ_H (300 MHz, $CDCl_3$): 0.88 (t, 3H, CH_3, *J* = 7.4 Hz), 1.28-1.46 (m, 26H, CH_2), 1.74-1.81 (m, 6H, $O-CH_2-C\mathbf{H}_2$ en $N-CH_2-C\mathbf{H}_2$), 2.26 (m, 4H, pyrr.H-3 and H-4), 3.04 (s, 3H, $N-CH_3$), 3.26-3.32 (m, 2H, $N-CH_2$), 3.50-3.51 (m, 4H, pyrr. H-2 and H-5), 3.98 (t, 4H, $O-CH_2$, *J* = 6.5 Hz), 6.94 (d, 4H, H-aryl, *J* = 8.5 Hz), 7.46 (d, 4H, H-aryl, *J* = 8.5 Hz). δ_C (75 MHz, $CDCl_3$): 14.53, 21.94, 23.09, 24.26, 26.38, 26.47, 26.54, 29.34, 29.56, 29.62, 29.67, 29.73, 29.82, 29.99, 32.30, 48.86, 64.98, 65.23, 68.42, 68.51, 74.39, 115.15, 118.10, 122.37, 128.01, 133.61, 133.67, 158.62. Calcd. for $C_{37}H_{60}F_6N_2O_6S_2$ (831.02): C 56.37, H 7.28, N 3.37. Found: C 56.00, H 7.33, N 3.32. ESI-MS (methanol, m/z): 550.7, $[M - [NTf_2]^-]^+$; 1380.3, $[M + M - [NTf_2]^-]^+$. **6b**: Yield: 62% (0.18 g). δ_H (300 MHz, $CDCl_3$): 1.00 (t, 3H, CH_3, *J* = 7.3 Hz), 1.51-1.56 (m, 2H, CH_2), 1.79-1.91 (m, 6H, $N-CH_2-C\mathbf{H}_2$, pyrr. H-3 and H-4), 2.25-2.26 (m, 4H, $O-CH_2-C\mathbf{H}_2$), 3.05 (s, 3H, $N-CH_3$), 3.41-3.52 (m, 6H, $N-CH_2$, pyrr. H-2 and H-5), 4.03-4.07 (m, 4H, $O-CH_2$), 6.94-6.99 (m, 4H, H-aryl), 7.23 (d, 2H, H-aryl, *J* = 8.5 Hz), 7.51 (d, 2H, H-aryl, *J* = 8.4 Hz), 7.57 (d, 2H, H-aryl, *J*= 8.6 Hz), 8.14 (d, 2H, H-aryl, *J* = 8.9 Hz). δ_C (75 MHz, $CDCl_3$): 13.78, 19.16, 21.13, 21.67, 26.07, 31.11, 48.65, 63.73, 64.51, 66.81, 68.00, 114.29, 114.83, 121.45, 122.07, 127.61, 128.19, 132.26, 133.27, 138.21, 150.11, 158.13, 163.57, 165.05. Calcd. for $C_{34}H_{40}F_6N_2O_8S_2$ (782.81): C 52.17, H 5.15, N 3.85. Found: C 52.04, H 4.92, N 3.49. ESI-MS (methanol, m/z): 502.5, $[M - [NTf_2]^-]^+$; 1284.2, $[M + M - [NTf_2]^-]^+$. **7b**: Yield: 84% (0.17 g). δ_H (300 MHz, $CDCl_3$): 0.89 (t, 3H, CH_3, *J* = 7.4 Hz), 1.28-1.52 (m, 14H, CH_2), 1.80-2.00 (m, 6H, $O-CH_2-C\mathbf{H}_2$ and $N-CH_2-C\mathbf{H}_2$), 2.25-2.26 (m, 4H, pyrr. H-3 and H-4), 3.05 (s, 3H, $N-CH_3$), 3.41-3.53 (m, 6H, $N-CH_2$ and pyrr. H-2 and H-5), 4.02-4.08 (m, 4H, $O-CH_2$), 6.96-6.98 (m, 4H, H-aryl), 7.24 (d, 2H, H-aryl, *J* = 8.6 Hz), 7.51 (d, 2H, H-aryl, *J* = 8.5 Hz), 7.57 (d, 2H, H-aryl, *J* = 8.6 Hz), 8.14 (d, 2H, H-aryl, *J* = 8.7 Hz). δ_C (75 MHz, $CDCl_3$): 14.09, 20.94, 21.56, 22.66, 25.79, 25.97, 29.10, 29.30, 29.36, 29.54, 31.88, 48.46, 64.32, 64.62, 66.68, 68.36, 114.34, 114.85, 118.26, 121.40, 121.46, 122.13, 127.59, 128.15, 132.27, 133.16, 138.56, 150.14, 158.18, 163.63, 165.13. Calcd. for $C_{40}H_{52}F_6N_2O_8S_2$ (866.97): C 55.41, H 6.05, N 3.23. Found: C 55.49, H 6.11, N 3.24. ESI-MS (methanol, m/z): 586.5, $[M - [NTf_2]^-]^+$; 1452.2, $[M + M - [NTf_2]^-]^+$. **8b**: Yield: 90% (0.19 g). δ_H (300 MHz, $CDCl_3$): 1.00 (t, 3H, CH_3, *J* = 7.4 Hz), 1.32-1.53 (m, 14H, CH_2), 1.77-1.84 (m, 6H, N-CH_2-C**H**$_2$, pyrr. H-3 and H-4), 2.29 (m, 4H, O-CH_2-C**H**$_2$), 3.28 (s, 3H, N-CH_3), 3.62-3.68 (m, 2H, N-CH_2), 3.82-3.84 (m, 4H, pyrr. H-2 and H-5), 3.98-4.08 (m, 4H, O-CH_2), 6.96-6.99 (m, 4H, H-aryl), 7.24 (d, 2H, H-aryl, *J* = 8.6 Hz), 7.51 (d, 2H, H-aryl, *J* = 8.8 Hz), 7.58 (d, 2H, H-aryl, *J* = 8.6 Hz), 8.15 (d, 2H, H-aryl, *J* = 8.9 Hz). δ_C (75 MHz, $CDCl_3$): 14.23, 19.59, 21.90, 24.24, 26.32, 26.53, 29.34, 29.44, 29.57, 29.64, 31.53, 48.78, 64.94, 65.22, 68.43, 114.72, 115.27, 118.13, 121.83, 122.37, 122.49, 123.63, 128.00, 128.46, 128.71, 132.70, 133.03, 133.12, 138.88, 150.42, 158.20, 164.01, 165.56. Calcd. for $C_{40}H_{52}F_6N_2O_8S_2$ (866.97): C 55.41, H 6.05, N 3.23. Found: C 54.99, H 5.79, N 3.14. ESI-MS (methanol, m/z): 586.5, $[M - [NTf_2]^-]^+$; 1452.8, $[M + M - [NTf_2]^-]^+$. **9b**: Yield: 42% (0.13 g). δ_H (300 MHz, $CDCl_3$): 0.89 (t, 3H, CH_3, *J* = 7.4 Hz), 1.28-1.52 (m, 26H, CH_2), 1.74-1.85 (m, 6H, O-CH_2-C**H**$_2$ and N-CH_2-C**H**$_2$), 2.26 (m, 4H, pyrr. H-3 and H-4), 3.04 (s, 3H, N-CH_3), 3.27-3.32 (m, 2H, N-CH_2), 3.50-3.51 (m, 4H, pyrr. H-2 and H-5), 3.98-4.07 (m, 4H, O-CH_2), 6.95-6.99 (m, 4H, H-aryl), 7.24 (d, 2H, H-aryl, *J* = 8.7 Hz), 7.51 (d, 2H, H-aryl, *J* = 8.5 Hz), 7.58 (d, 2H, H-aryl, *J* = 8.7 Hz), 8.15 (d, 2H, H-aryl, *J* = 8.9 Hz). δ_C (75 MHz, $CDCl_3$): 14.53, 23.09, 24.24, 26.32, 26.38, 26.55, 29.34, 29.50, 29.56, 29.64, 29.71, 29.76, 29.95, 30.10, 32.29, 48.80, 64.94, 65.19, 68.44, 68.76, 74.39, 114.72, 115.27, 118.10, 121.82, 122.37, 122.47, 128.00, 128.45, 132.69, 133.03, 150.40, 159.16, 164.01, 165.57. Calcd. for $C_{46}H_{64}F_6N_2O_8S_2$ (951.13): C 58.05, H 6.78, N 2.95. Found: C 57.71, H 6.81, N 2.89. ESI-MS (methanol, m/z): 670.7, $[M - [NTf_2]^-]^+$; 1620.2, $[M + M - [NTf_2]^-]^+$.

*Synthesis of compounds **1c**-**9c***

*Compounds **1c**-**7c**:* 2-Thenoyltrifluoroacetone (4 eq.) was dissolved in ethanol (20 mL), and NaOH (4 eq., 1 mol L^{-1} aqueous solution) was added. The mixture was stirred for 10 min. Then the appropriate bromide salt (compounds **1a**-**7a**) (1 eq.) was added. The mixture was heated to 60 or 65 °C and stirred until a clear solution was formed. A saturated aqueous solution of $EuCl_3{\cdot}6H_2O$ (1 eq.) was added dropwise and the mixture was stirred for 1.5 h at 60 or 65 °C with exclusion of light. A pale yellow precipitate was formed, filtered off and washed with water and with warm ethanol. The pure product was dried *in vacuo* at 50 °C. **1c**: Yield: 33% (0.11 g). Calcd. for $C_{61}H_{57}EuF_{12}N_2O_9S_4$ (1470.32): C 49.83, H 3.91, N 1.91. Found: C 49.57, H 3.71, N 1.92. ESI-MS (methanol, m/z): 433.5, $[M - [Eu(tta)_4]^-]^+$; 221.6, $[tta]^-$ (observed in negative mode); 1037.0, $[Eu(tta)_4]^-$ (observed in negative mode). **3c**: Yield: 46% (0.14 g). Calcd. for $C_{63}H_{64}EuF_{12}NO_{10}S_4$ (1503.39): C 50.33, H 4.29, N 0.93. Found: C 49.98, H 3.99, N 0.93. ESI-MS (methanol, m/z): 466.8, $[M - [Eu(tta)_4]^-]^+$; 221.6, $[tta]^-$ (observed in negative mode); 1037.0, $[Eu(tta)_4]^-$ (observed in negative mode). **5c**: Yield: 28% (0.10 g). Calcd. for $C_{69}H_{76}EuF_{12}NO_{10}S_4$ (1587.55): C 52.20, H 4.83, N 0.88. Found: C 52.22, H 5.04, N 0.97. ESI-MS (methanol, m/z): 550.7, $[M - [Eu(tta)_4]^-]^+$; 221.6, $[tta]^-$ (observed in negative mode); 1037.0, $[Eu(tta)_4]^-$ (observed in negative mode). **6c**: Yield: 22% (0.11 g). Calcd. for $C_{64}H_{56}EuF_{12}NO_{12}S_4{\cdot}H_2O$ (1557.35): C 49.36, H 3.75, N 0.90. Found: C 49.47, H 3.74, N 1.00. ESI-MS (methanol, m/z): 502.3, $[M - [Eu(tta)_4]^-]^+$; 221.6, $[tta]^-$ (observed in negative mode); 1037.0, $[Eu(tta)_4]^-$ (observed in negative mode). **7c**: Yield: 36% (0.15 g). Calcd. for $C_{70}H_{68}EuF_{12}NO_{12}S_4$ (1623.49): C 51.79, H 4.22, N 0.86. Found: C 51.53, H 4.17, N 0.95. ESI-MS (methanol, m/z): 586.4, $[M - [Eu(tta)_4]^-]^+$; 221.6, $[tta]^-$ (observed in negative mode); 1037.0, $[Eu(tta)_4]^-$ (observed in negative mode).

Compounds 8c-9c: Unfortunately, we did not succeed in obtaining complexes **8c** and **9c** in sufficient purity. Different synthetic routes were tested: (i) mixing Htta, NaOH (1 mol L^{-1} aqueous solution), **8a/9a**, and $EuCl_3 \cdot 6H_2O$ in warm ethanol (with exclusion of light); (ii) mixing **8a/9a** and 2 equivalents of $[Na][Eu(tta)_4]$ in dry dichloromethane or in dry dichloromethane/ethanol (3:2) (with exclusion of light); (iii) mixing **8a/9a** and 2 equivalents of $[Ag][Eu(tta)_4]$ in dry dichloromethane/ethanol (3:2) (with exclusion of light) ($[Ag][Eu(tta)_4]$ does not dissolve well in pure dichloromethane); (iv) mixing **8a/9a** and 2 equivalents of $[NH_4][Eu(tta)_4]$ in dry dichloromethane (with exclusion of light) (both $[NH_4][Eu(tta)_4]$ and **8a/9a** are soluble in dichloromethane). Although compounds **8a** and **9a** are soluble in ethanol at temperatures above approximately 60 °C, method (i) did not work (unreacted **8a/9a** was recovered after filtration), while complexes **1c-7c** could be obtained in this way. Method (ii) probably failed because the interaction of the Na^+ cation with the metal-containing anion, $[Eu(tta)_4]^-$, is too strong. Method (iii) unfortunately led to a mixture of the desired complex with remaining starting bromide (as confirmed by CHN elemental analysis), which could not be separated. Method (iv) afforded luminescent products that yielded satisfactory CHN and MS results. However, examination by POM and DSC revealed that these products were not entirely pure: between 40 and 50 °C part of the sample liquefied, but this liquid did not mix with the rest of the sample at the melting point, indicating two different products. In any way, these (impure) products were not liquid-crystalline. Solubility differences between compounds **6a** and **7a**, and **8a** and **9a**, respectively, seem to be a major reason why no pure **8c** and **9c** could be obtained. Attempts to fully exhange the bromide anion of compounds **8a** and **9a** for a 2-thenoyltrifluoroacetonate anion ($[\text{tta}]^-$) failed. Otherwise, these 2-thenoyltrifluoroacetonate pyrrolidinium salts could be mixed with $\text{Eu(tta)}_3{\cdot}2\text{H}_2\text{O}$ to obtain the desired complexes.

*Synthesis of compounds **1d**-**9d***

A warm solution of $\text{UO}_2\text{Br}_2{\cdot}x\text{H}_2\text{O}$ (1 eq.) in ethanol (7.5 mL) was added dropwise to a stirred solution of the appropriate bromide salt (2 eq.) in ethanol (15 mL) (compounds **1a**-**3a**, **6a** and **7a**) or ethanol/1-butanol (2:1) (15 mL) (compounds **5a**, **8a** and **9a**) at 60 °C. The reaction mixture was stirred for 2 h at 70 °C. The yellow precipitate was filtered off while the reaction mixture was still moderately hot, and washed with (warm) ethanol. After further purification (see below), the yellow solid was dried *in vacuo* at 50 °C. ^{1}H and ^{13}C NMR spectra of the uranyl complexes that dissolve in CDCl_3 or CD_2Cl_2 (not reported here) are similar to those obtained for the parent halide salts in CDCl_3 or CD_2Cl_2. **1d**: After filtration, the crude product was stirred for 30 min. in ethanol at 70 °C, and filtered off while the suspension was still moderately hot. Yield: 33% (0.15 g). Calcd. for $\text{C}_{58}\text{H}_{82}\text{Br}_4\text{N}_4\text{O}_4\text{U}$ (1456.94): C 47.81, H 5.67, N 3.85. Found: C 47.62, H 5.52, N 3.71. **2d**: After filtration, the crude product was recrystallized from ethanol. Yield: 27% (0.13 g). Calcd. for $\text{C}_{50}\text{H}_{72}\text{Br}_4\text{N}_2\text{O}_6\text{U}$ (1354.76): C 44.33, H 5.36, N 2.07. Found: C 44.23, H 5.50, N 2.04. **3d**: After filtration, the crude product was stirred for 30 min. in ethanol at 70 °C, and filtered off while the suspension was still moderately hot. Yield: 40% (0.14 g). Calcd. for

$C_{62}H_{96}Br_4N_2O_6U$ (1523.08): C 48.89, H 6.35, N 1.84. Found: C 49.17, H 6.38, N 1.79. **5d**: After filtration, the crude product was stirred for 30 min. in 1-butanol at 70 °C, and filtered off while the suspension was still moderately hot. Yield: 22% (0.12 g). Calcd. for $C_{74}H_{120}Br_4N_2O_6U$ (1691.40): C 52.55, H 7.15, N 1.66. Found: C 52.41, H 7.51, N 1.57. **6d**: After filtration, the crude product was stirred for 30 min. in chloroform at 50 °C, and filtered off while the suspension was still moderately hot. Yield: 27% (0.12 g). Calcd. for $C_{64}H_{80}Br_4N_2O_{10}U$ (1594.97): C 48.19, H 5.06, N 1.76. Found: C 48.29, H 4.97, N 1.82. **7d**: After filtration, the crude product was stirred for 30 min. in chloroform at 50 °C, and filtered off while the suspension was still moderately hot. Yield: 24% (0.14 g). Calcd. for $C_{76}H_{104}Br_4N_2O_{10}U$ (1763.29): C 51.77, H 5.94, N 1.59. Found: C 51.65, H 5.79, N 1.68. **8d**: After filtration, the crude product was stirred for 30 min. in 1-butanol at 70 °C, and filtered off while the suspension was still moderately hot. Then it was stirred for 30 min. in chloroform at 50 °C, and filtered off. Yield: 47% (0.15 g). Calcd. for $C_{76}H_{104}Br_4N_2O_{10}U$ (1763.29): C 51.77, H 5.94, N 1.59. Found: C 51.42, H 5.57, N 1.69. **9d**: After filtration, the crude product was recrystallized from chloroform. Yield: 36% (0.13 g). Calcd. for $C_{88}H_{128}Br_4N_2O_{10}U$ (1931.61): C 54.72, H 6.68, N 1.45. Found: C 54.30, H 6.29, N 1.48.

Single Crystal X-ray Diffraction

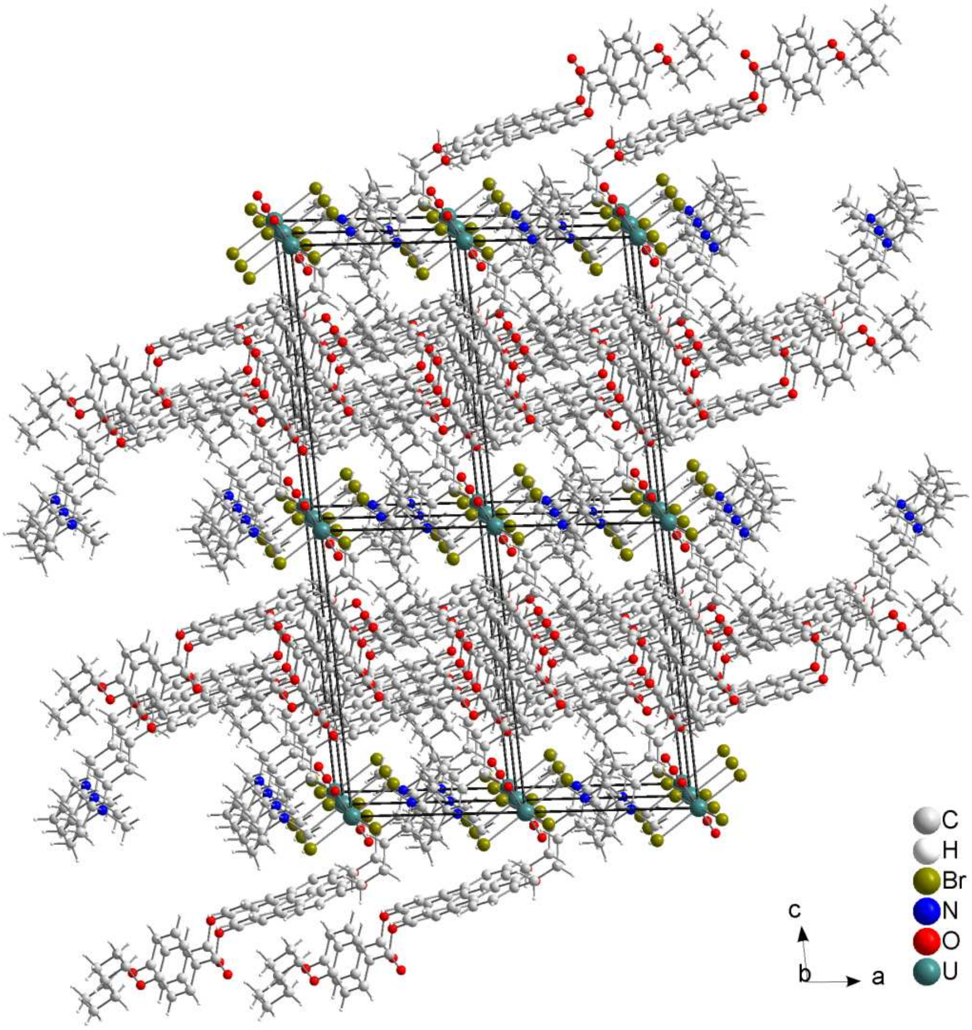


Figure S1. Packing in the crystal structure of compound **6d**, plotted for a 2 × 2 × 2 supercell.

Thermal Behavior

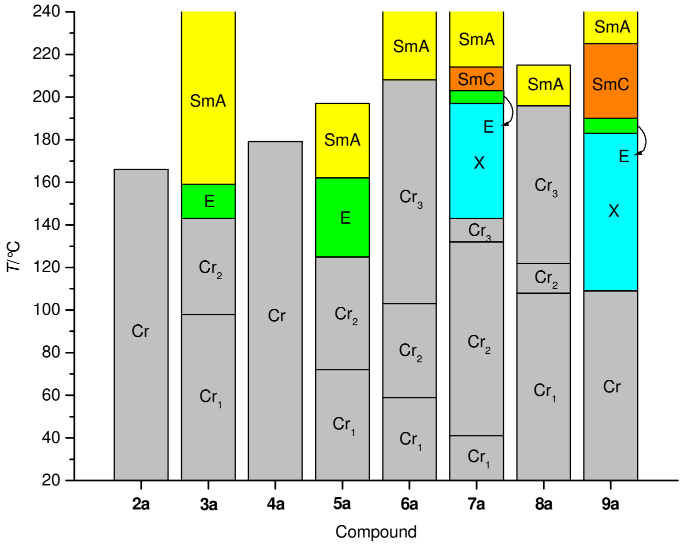


Figure S2. Stack column graph showing the evolution of the transition temperatures in the series **2a-9a**. Values are taken from Table 1, for transitions between enantiotropic mesophases. Abbreviations: Cr, Cr_1, Cr_2 and Cr_3 = crystalline phase; X = unidentified highly ordered smectic phase; E = crystal smectic E phase; SmC = smectic C phase; SmA = smectic A phase.

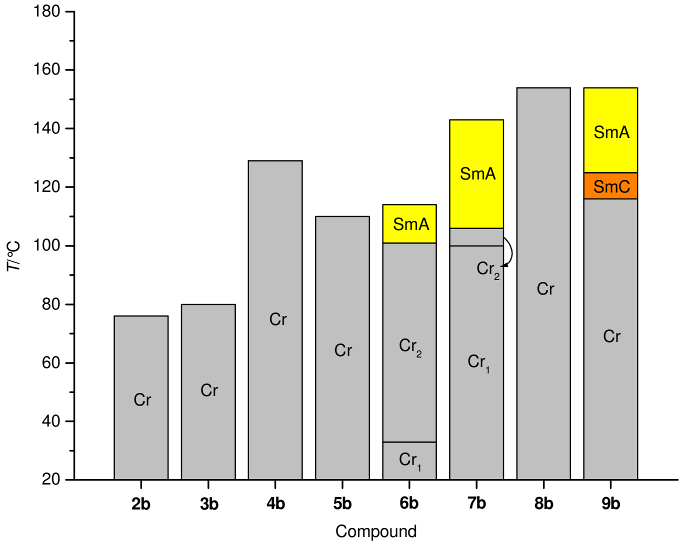


Figure S3. Stack column graph showing the evolution of the transition temperatures in the series **2b**-**9b**. Values are taken from Table 1, for transitions between enantiotropic mesophases. Abbreviations: Cr, Cr_1 and Cr_2 = crystalline phase; SmC = smectic C phase; SmA = smectic A phase.

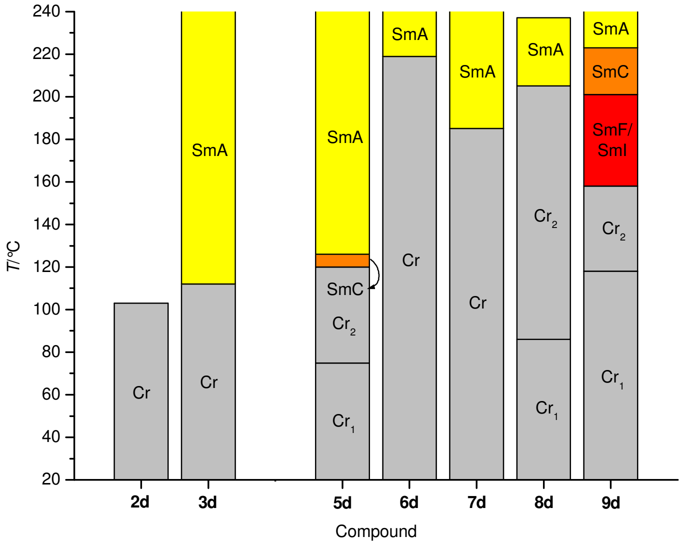


Figure S4. Stack column graph showing the evolution of the transition temperatures in the series **2d**-**9d**. Values are taken from Table 1, for transitions between enantiotropic mesophases. Abbreviations: Cr, Cr_1 and Cr_2 = crystalline phase; SmI = smectic I phase, SmF = smectic F phase; SmC = smectic C phase; SmA = smectic A phase.

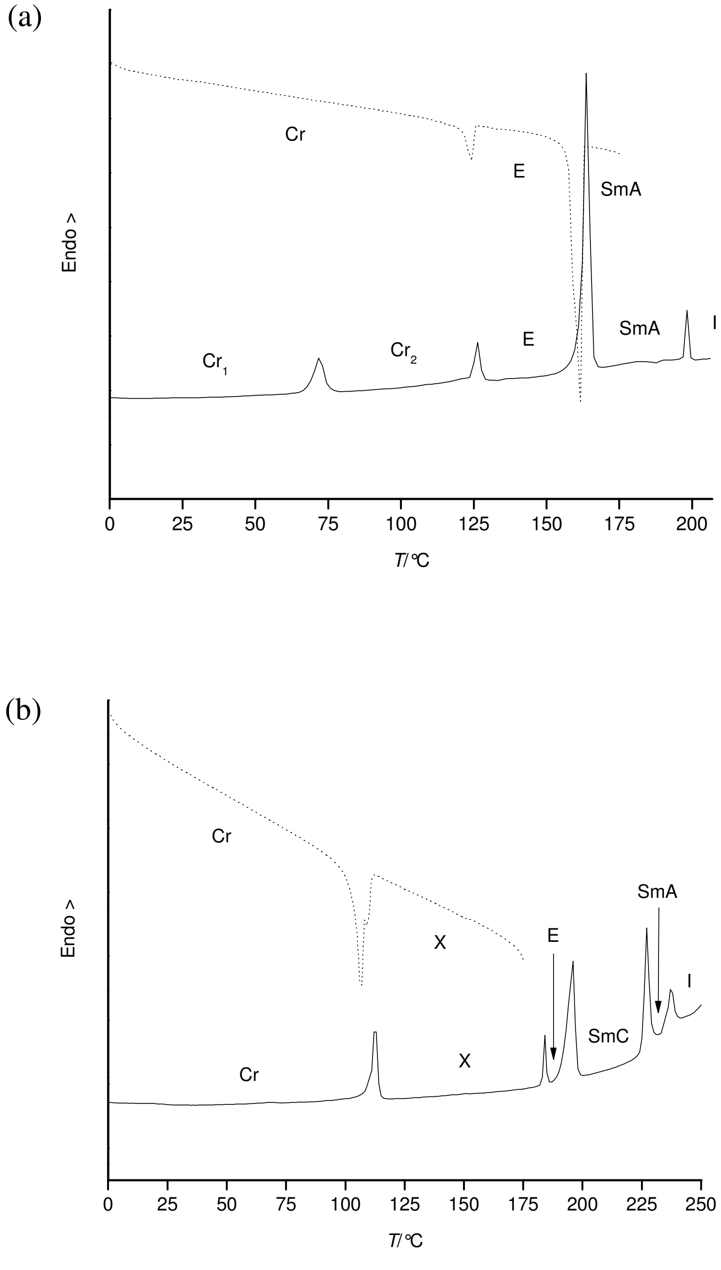


Figure S5. DSC traces of (a) **5a** and (b) **9a** (heating/cooling rate of 10 °C min^{-1}; He atmosphere). The first cooling run is shown by a dashed line; the second heating run is shown by a solid line. Abbreviations: Cr, Cr_1 and Cr_2 = crystalline phase; X = unidentified highly ordered smectic phase; E = crystal smectic E phase; SmC = smectic C phase; SmA = smectic A phase; I = isotropic liquid. Endothermic peaks point upwards.

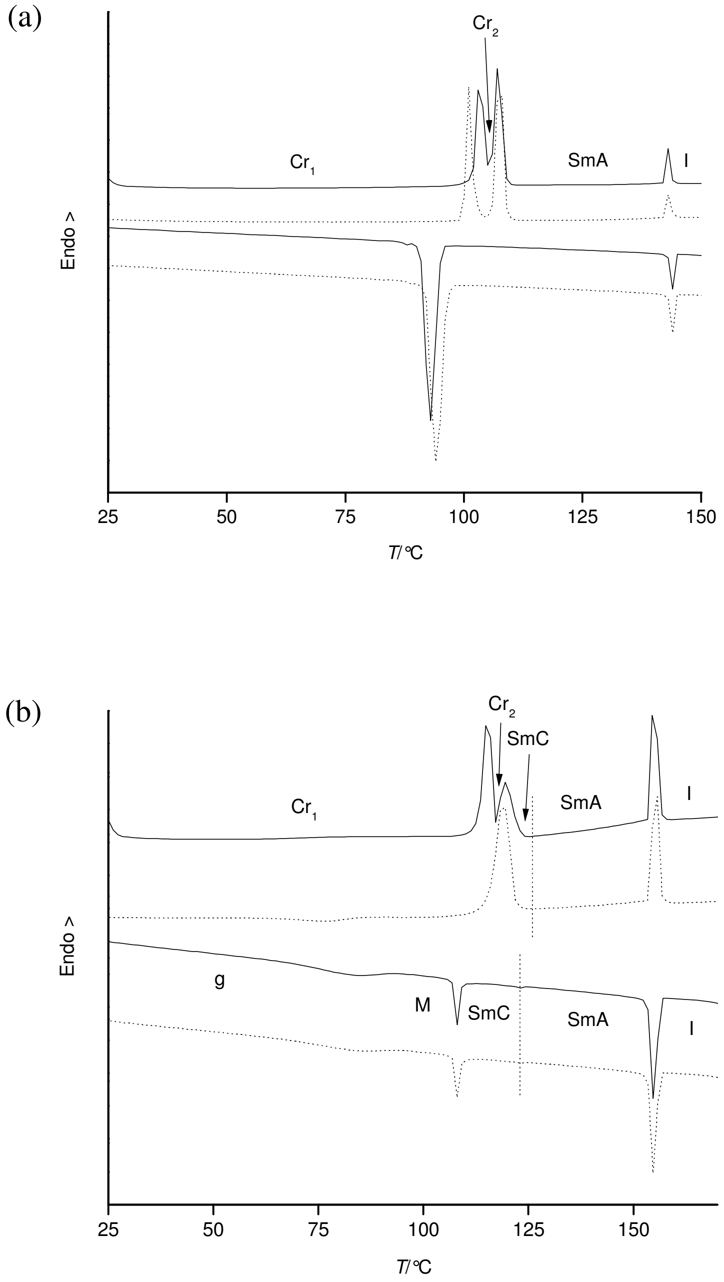


Figure S6. DSC traces of (a) **7b** and (b) **9b** (heating/cooling rate of 10 °C min^{-1}; He atmosphere). The first heating/cooling cycle is shown by a solid line; the second heating/cooling cycle is shown by a dashed line. Abbreviations: g = glass; Cr$_1$ and Cr$_2$ = crystalline phase; M = unidentified smectic phase; SmC = smectic C phase; SmA = smectic A phase; I = isotropic liquid. Endothermic peaks point upwards. For compound **9b**, the SmC → SmA transition was hardly detected by DSC.

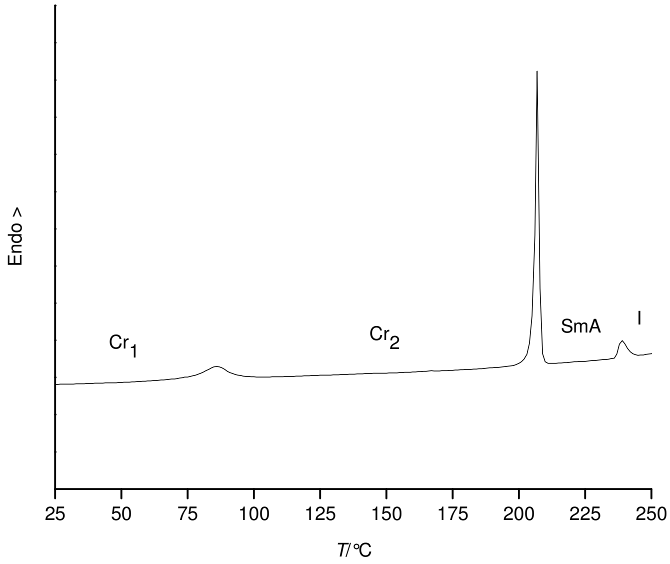
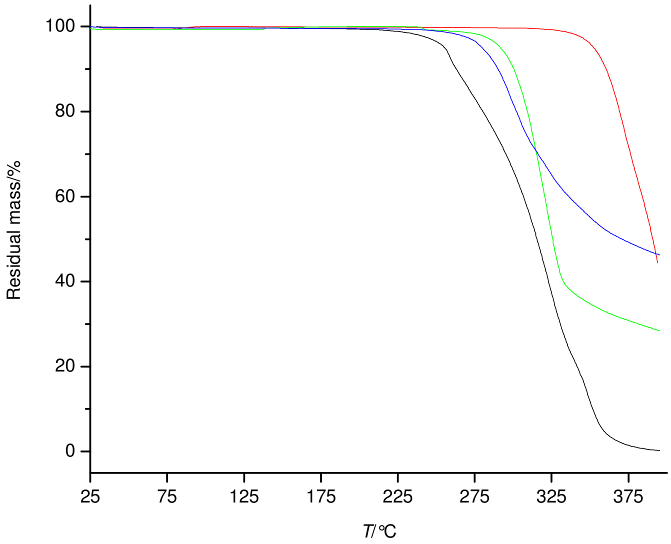
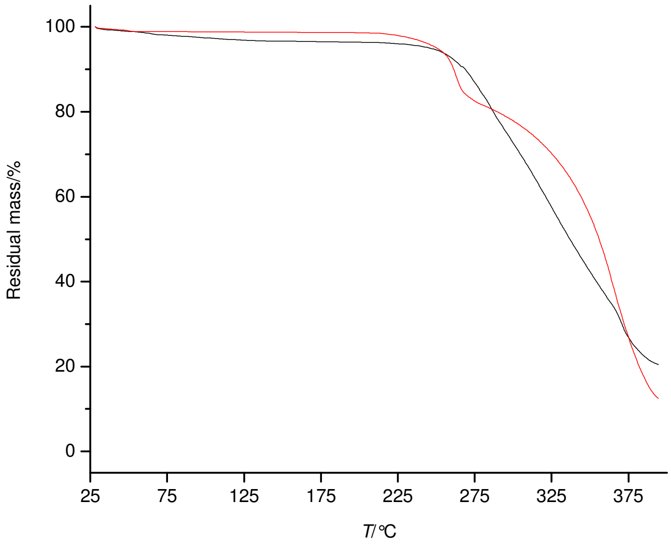


Figure S7. DSC trace of **8d** (heating/cooling rate of 10 °C min^{-1}; He atmosphere): second heating run. Abbreviations: Cr$_1$ and Cr$_2$ = crystalline phase; SmA = smectic A phase; I = isotropic liquid. Endothermic peaks point upwards.

(a)


Residual mass/%
100
80
60
40
20
0
25
75
125
175
225
275
325
375
T/℃

(b)


Residual mass/%
100
80
60
40
20
0
25
75
125
175
225
275
325
375
T/℃

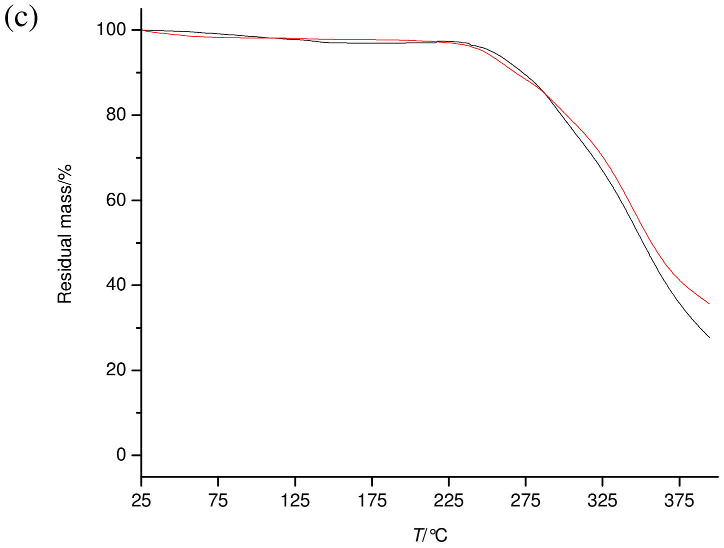


Figure S8. Thermograms of selected pyrrolidinium salts (heating rate of 10 °C min^{-1}; N_2 atmosphere). (a) **3a** (black line), **3b** (red line), **3c** (green line) and **3d** (blue line); (b) **6a** (black line) and **7a** (red line); (c) **8a** (black line) and **9a** (red line). For compound **3c**, the weight loss between 275 °C and 370 °C corresponds to the gradual decomposition of the metal-containing anion, $[Eu(tta)_4]^-$.

Polarizing Optical Microscopy Textures

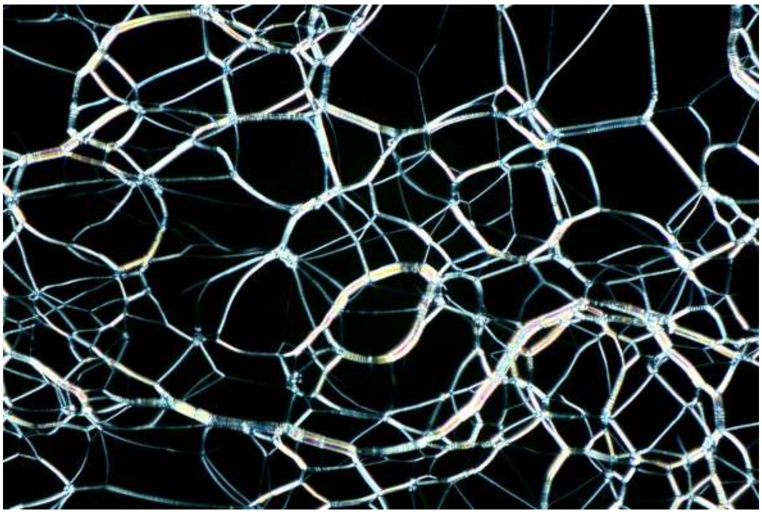


Figure S9. Oily streak texture of the SmA phase of **7a** at 220 °C (200× magnification).

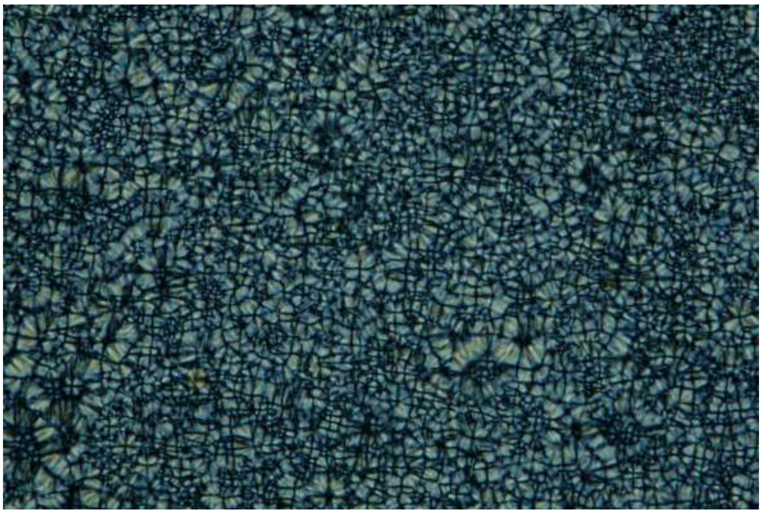


Figure S10. Focal conic texture of the SmA phase of **5a** at 176 °C (500× magnification).

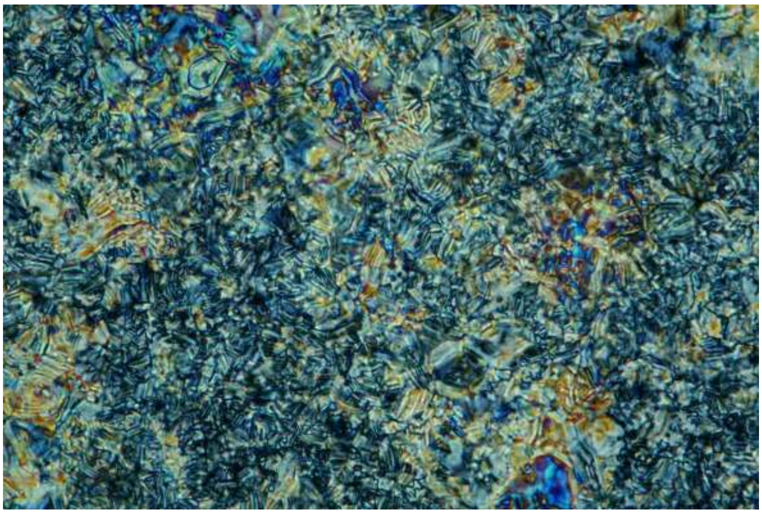


Figure S11. Non-characteristic paramorphotic texture of the crystal smectic E phase of **5a** at 156 °C (bulk of the sample), obtained on cooling from the SmA phase shown in Figure S10 (500× magnification).

Powder X-ray Diffraction

Table S1. Bragg reflections collected from the X-ray diffractograms of the different enantiotropic mesophases.

Compd.	$d_{\text{meas.}}$/Å[a]	I[b]	hkl[c]	$d_{\text{calc.}}$/Å[a]	Parameters of smectic phase[d,e,f,g]
3a	42.29	VS	001	42.15	E: T = 150 °C
	21.07	M	002	21.08	V_{M} = 993 Å^3
	–[h]		003		A_{M} = 47.2 Å^2
	10.54	VW	004	10.54	a = 7.48 Å
	8.42	W	005	8.43	b = 6.09 Å
	7.01	M	006	7.03	c = 42.15 Å
	6.02	W	007	6.02	L = 31.75 Å
	5.28	W	008	5.27	d/L = 1.33
	4.73[i]	VW	110 [j]	4.72	
	4.68	VW	009 [j]	4.68	
	4.31	VW	114	4.31	
	3.74	VW	200 [j]	3.74	
	3.67	VW	202	3.68	
	3.52	VW	204	3.52	
	3.28	VW	206	3.30	
	49.63	VS	001	49.63	SmA: T = 180 °C
	24.81	W	002	24.81	V_{M} = 1013 Å^3
					A_{M} = 40.8 Å^2
					L = 31.75 Å
					d/L = 1.56
5a	52.68	VS	001	52.32	E: T = 145 °C
	26.11	M	002	26.16	V_{M} = 1142 Å^3
	17.46	S	003	17.44	A_{M} = 43.6 Å^2
	–[h]		004		a = 8.24 Å
	10.43	M	005	10.46	b = 5.58 Å
	8.72	M	006	8.72	c = 52.32 Å
	7.48	M	007	7.47	L = 38.77 Å
	6.54	M	008	6.54	d/L = 1.35
	5.80	W	009	5.81	
	4.62	W	110	4.62	
	4.58	VW	111	4.60	
	4.34	VW	114	4.36	
	4.22	VW	115	4.23	
	4.12	VW	200 [k]	4.12	
	4.02	VW	203	4.01	
	3.49	VW	208	3.49	

	57.75	VS	001	57.83	SmA: $T = 170$ °C $V_M = 1162$ Å^3 $A_M = 40.2$ Å^2 $L = 38.77$ Å $d/L = 1.49$
	29.01	W	002	28.92	
	19.25	W	003	19.28	
6a	50.04	VS	001	50.04	SmA: $T = 210$ °C $V_M = 1102$ Å^3 $A_M = 44.0$ Å^2 $L = 30.63$ Å $d/L = 1.63$
7a	46.92	VS	001	46.58	X: $T = 170$ °C[l] $V_M = 1228$ Å^3 $A_M = 52.8$ Å^2 $L = 38.40$ Å
	23.27	M	002	23.29	
	15.56	W	003	15.53	
	–[h]		004		
	9.30	W	005	9.32	
	7.75	W	006	7.76	
	6.63	W	007	6.65	
	5.81	W	008	5.82	
	5.16	VW	009	5.18	
	4.31	VW			
	4.22	VW			
	3.98	VW			
	3.61	VW			
	3.36	VW			
	3.24	VW			
	51.77	VS	001	51.47	E: $T = 200$ °C $V_M = 1253$ Å^3 $A_M = 48.6$ Å^2 $L = 38.40$ Å $d/L = 1.34$
	25.77	M	002	25.73	
	17.16	W	003	17.16	
	–[h]		004		
	10.29	W	005	10.29	
	8.59	W	006	8.58	
	7.33	W	007	7.35	
	6.41	W	008	6.43	
	5.70	VW	009	5.72	
	4.49	VW			
	3.88	VW			
	3.01	VW			
	59.46	VS	001	59.62	SmC: $T = 205$ °C $V_M = 1257$ Å^3 $A_M = 42.2$ Å^2 $L = 38.40$ Å
	29.87	M	002	29.81	
	19.88	W	003	19.87	
	67.48	VS	001	67.56	SmA: $T = 220$ °C $V_M = 1269$ Å^3 $A_M = 37.6$ Å^2 $L = 38.40$ Å $d/L = 1.76$
	33.73	W	002	33.78	
	22.57	VW	003	22.52	

9a	60.06	VS	001	60.00	X: T = 160 °C[l] V_{M} = 1373 Å^3 A_{M} = 45.8 Å^2 L = 45.41 Å
	30.02	M	002	30.00	
	20.02	S	003	20.00	
	–[h]		004		
	–[h]		005		
	9.98	W	006	10.00	
	8.56	W	007	8.57	
	7.50	W	008	7.50	
	6.67	W	009	6.67	
	4.62	M			
	4.57	M			
	4.19	M			
	4.16	M			
	3.09	W			
	57.75	VS	001	58.19	E: T = 188 °C V_{M} = 1399 Å^3 A_{M} = 48.0 Å^2 a = 8.33 Å b = 5.60 Å c = 58.19 Å L = 45.41 Å d/L = 1.28
	29.15	M	002	29.10	
	19.37	S	003	19.40	
	–[h]		004		
	–[h]		005		
	9.69	W	006	9.70	
	8.33	M	007	8.31	
	7.28	M	008	7.27	
	6.48	W	009	6.47	
	4.65	M	110[m]	4.65	
	4.59	M	112	4.59	
	4.41	W	114	4.43	
	4.16	W	200[m]	4.16	
	3.73	VW	207	3.72	
	3.62	VW	208	3.61	
	3.51	VW	209	3.50	
	3.16	VW			
	65.28	VS	001	65.12	SmC: T = 205 °C V_{M} = 1415 Å^3 A_{M} = 43.4 Å^2 L = 45.41 Å
	32.63	M	002	32.56	
	21.60	M	003	21.71	
	67.48	VS	001	67.26	SmA: T = 216 °C[n] V_{M} = 1425 Å^3 A_{M} = 42.4 Å^2 L = 45.41 Å d/L = 1.48
	33.54	M	002	33.63	
	22.41	M	003	22.42	
6b	43.51	VS	001	43.51	SmA: T = 105 °C V_{M} = 1378 Å^3 A_{M} = 63.4 Å^2 L = 30.63 Å d/L = 1.42
	21.76	VW	002	21.76	

7b	61.28 30.95	VS W	001 002	61.59 30.80	SmA: T = 125 °C V_{M} = 1548 Å^3 A_{M} = 50.2 Å^2 L = 38.40 Å d/L = 1.60
9b	53.62 27.05	VS S	001 002	53.86 26.93	SmC: T = 120 °C V_{M} = 1692 Å^3 A_{M} = 62.8 Å^2 L = 45.41 Å
	54.60 27.29	VS S	001 002	54.59 27.30	SmA: T = 135 °C V_{M} = 1710 Å^3 A_{M} = 62.6 Å^2 L = 45.41 Å d/L = 1.20
3d	50.89 25.66	VS W	001 002	51.11 25.55	SmA: T = 140 °C V_{M} = 2748 Å^3 A_{M} = 53.8 Å^2 L = 31.75 Å d/L = 1.61
5d	61.28 30.64 20.42	VS VW W	001 002 003	61.28 30.64 20.43	SmC: T = 123 °C V_{M} = 3014 Å^3 A_{M} = 49.2 Å^2 L = 38.77 Å
	63.89 31.94 21.14	VS VW W	001 002 003	63.73 31.87 21.24	SmA: T = 140 °C V_{M} = 3052 Å^3 A_{M} = 47.9 Å^2 L = 38.77 Å d/L = 1.64
6d	45.49	VS	001	45.49	SmA: T = 225 °C V_{M} = 3046 Å^3 A_{M} = 67.0 Å^2 L = 30.63 Å d/L = 1.49
7d	63.89	VS	001	63.89	SmA: T = 195 °C V_{M} = 3302 Å^3 A_{M} = 51.7 Å^2 L = 38.40 Å d/L = 1.66

8d	48.82	VS	001	48.82	SmA: $T = 210$ °C $V_M = 3335$ Å^3 $A_M = 68.3$ Å^2 $L = 38.23$ Å $d/L = 1.28$
9d	57.75	VS	001	57.70	SmF/SmI: $T = 170$ °C $V_M = 3557$ Å^3 $A_M = 61.7$ Å^2 $L = 45.41$ Å
	28.59	W	002	28.85	
	19.25	S	003	19.23	
	–[h]		004		
	11.55	M	005	11.54	
	9.63	M	006	9.62	
	8.26	M	007	8.24	
	7.23	W	008	7.21	
	6.41	W	009	6.41	
	5.48	VW	110	5.48	
	4.53	VW	$h_{\text{hexagonal}}$		
	3.91	VW	200	3.87	
	3.49	VW	210	3.46	
	61.28	VS	001	61.92	SmC: $T = 210$ °C $V_M = 3653$ Å^3 $A_M = 59.0$ Å^2 $L = 45.41$ Å
	31.27	VW	002	30.96	
	20.85	W	003	20.64	
	15.32	VW	004	15.48	
	63.89	VS	001	63.89	SmA: $T = 230$ °C $V_M = 3701$ Å^3 $A_M = 57.9$ Å^2 $L = 45.41$ Å $d/L = 1.41$

[a] $d_{\text{meas.}}$ and $d_{\text{calc.}}$ are the measured and calculated diffraction spacings, respectively. [b] I is the intensity of the reflections: VS, very strong; S, strong; M, medium; W, weak; VW, very weak; br, broad reflection. [c] *hkl* are the Miller indices of the reflections. $h_{\text{hexagonal}}$ denotes the wide-angle reflection that was indexed as the (10) reflection on a two-dimensional hexagonal lattice. [d] T is the temperature at which the X-ray diffractogram was recorded. [e] V_M is the molecular volume, A_M is the molecular area (for the bromide and bis(trifluoromethylsulfonyl)imide salts: $A_M = 2V_M/d$; for the tetrabromouranyl salts: $A_M = V_M/d$). [f] a, b and c are the dimensions of the orthorhombic unit cell in the crystal smectic E phase. Because indexation of the powder X-ray diffractogram of **7a** at 200 °C was not straightforward, no values are given for a, b and c. [g] L is the calculated length of the relevant pyrrolidinium cation in its most extended conformation (estimated with Chem3D; the structure of the pyrrolidinium cation was energy-minimized *via* an MM2 calculation within Chem3D). [h] Not detected because of overlap with the diffraction signal produced by the covering foil, used in the experimental set-up (this signal occurs at $2\theta = 5.7\text{-}7.6$ Å). [i] This reflection partly overlaps with the (009) reflection. [j] The (111) and (201) reflections are probably not fully resolved from the (110) and (009) reflections, and from the (200) reflection, respectively. [k] The (201) reflection is probably not fully resolved from the (200) reflection. [l] Some additional, extremely weak wide-angle reflections were visible in the powder X-ray diffractogram, but these are not reported here. [m] The (111) and (201) reflections are probably not fully resolved from the (110) and (200) reflections, respectively. [n] During the temperature scan of the X-ray diffraction measurement, the SmA phase was observed at somewhat lower temperatures than indicated by DSC (Table 1). This might point to a slight decomposition of the sample at high temperatures.

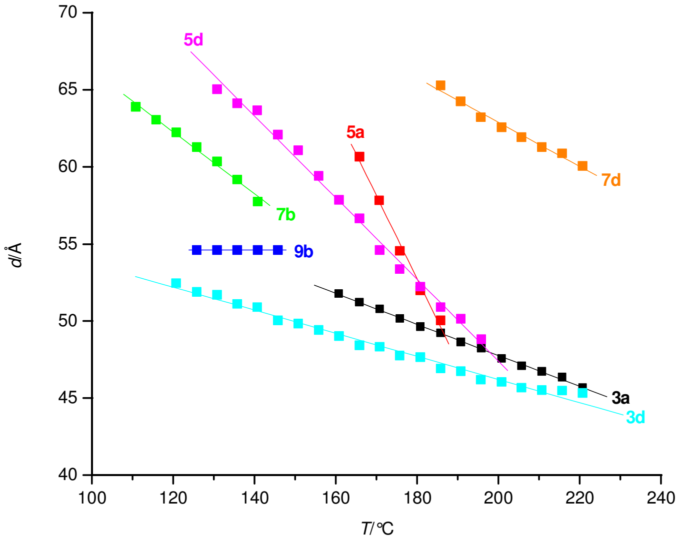


Figure S12. Evolution of the layer thickness, *d*, of the SmA phases shown by selected compounds, as a function of the temperature.

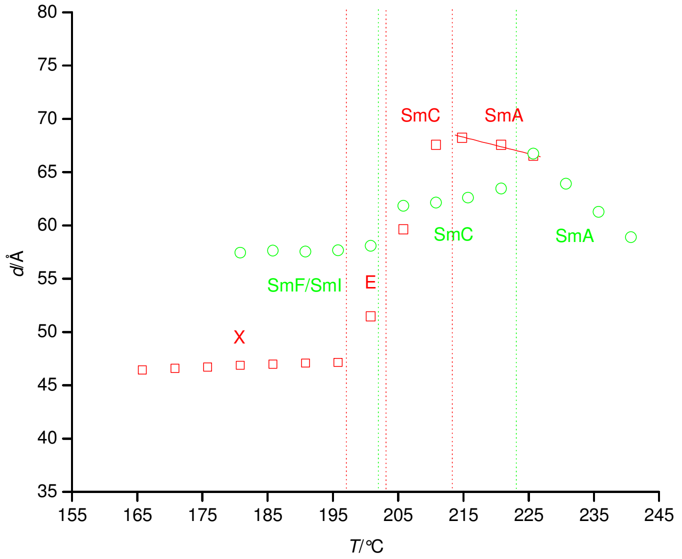


Figure S13. Evolution of the layer thickness, *d*, of the different mesophases shown by **7a** (red symbols) and **9d** (green symbols) as a function of the temperature (linear fit of the SmA layer thickness data for **7a**: $d = -0.15(\pm 0.03)T + 101.5(\pm 0.6)$).

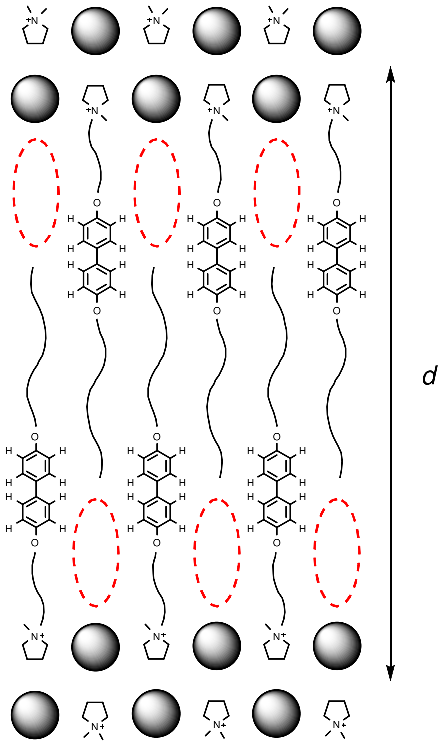


Figure S14. Hypothetical structural model for the SmA phase exhibited by compound **3a**, discarded because of an inefficient space-filling (indicated by the dashed ellipses). Bromide anions are represented by grey spheres, but cations are not displayed in space-filling mode.

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