Supporting Information

Oxadiazolyl-Pyridinium as Cationic Scaffold for Fluorinated Ionic Liquid Crystals

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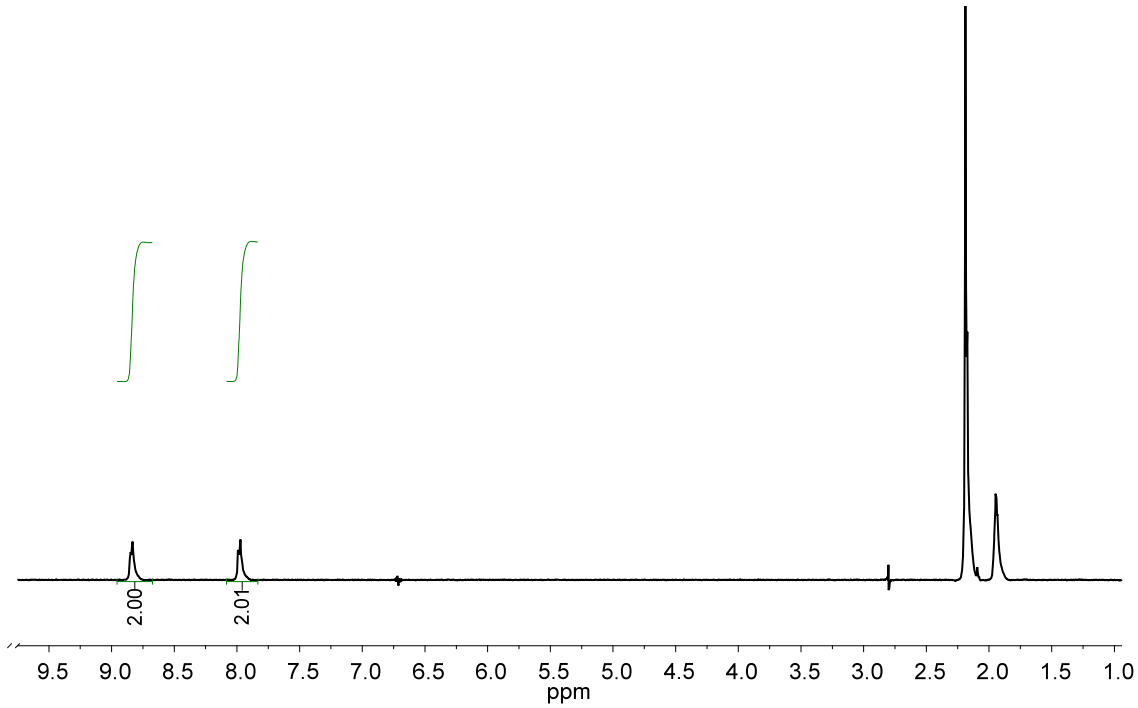
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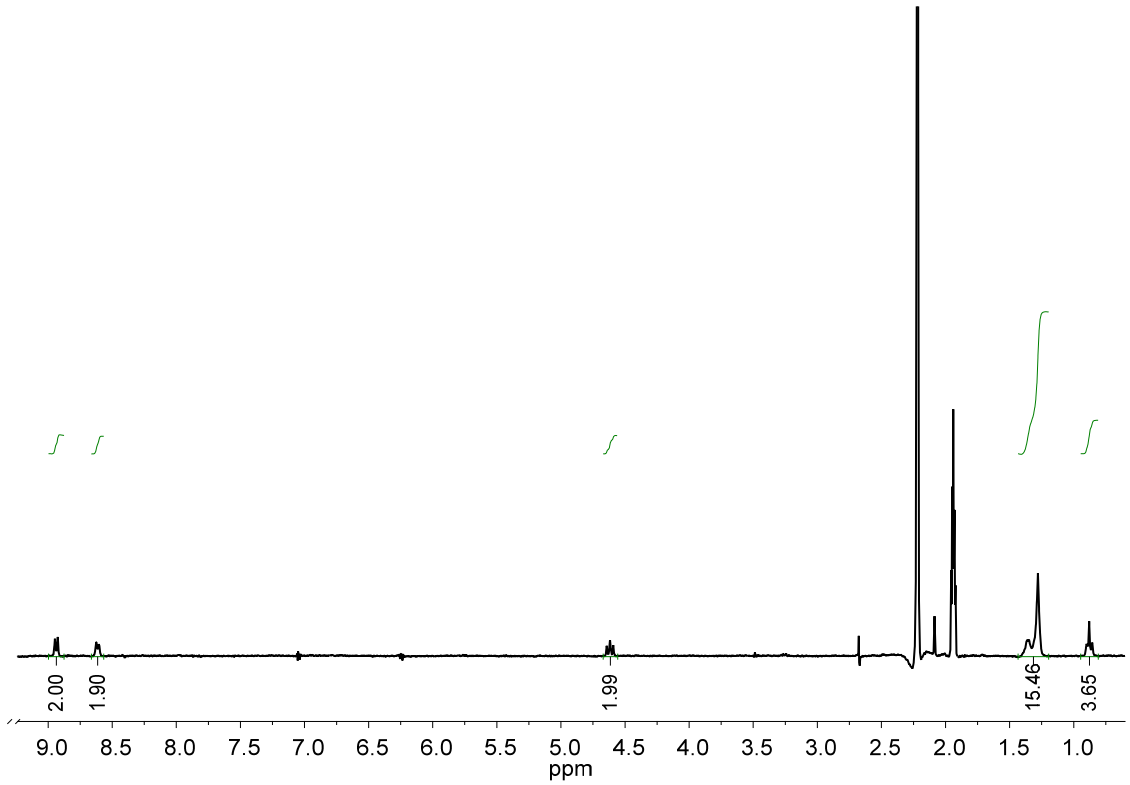
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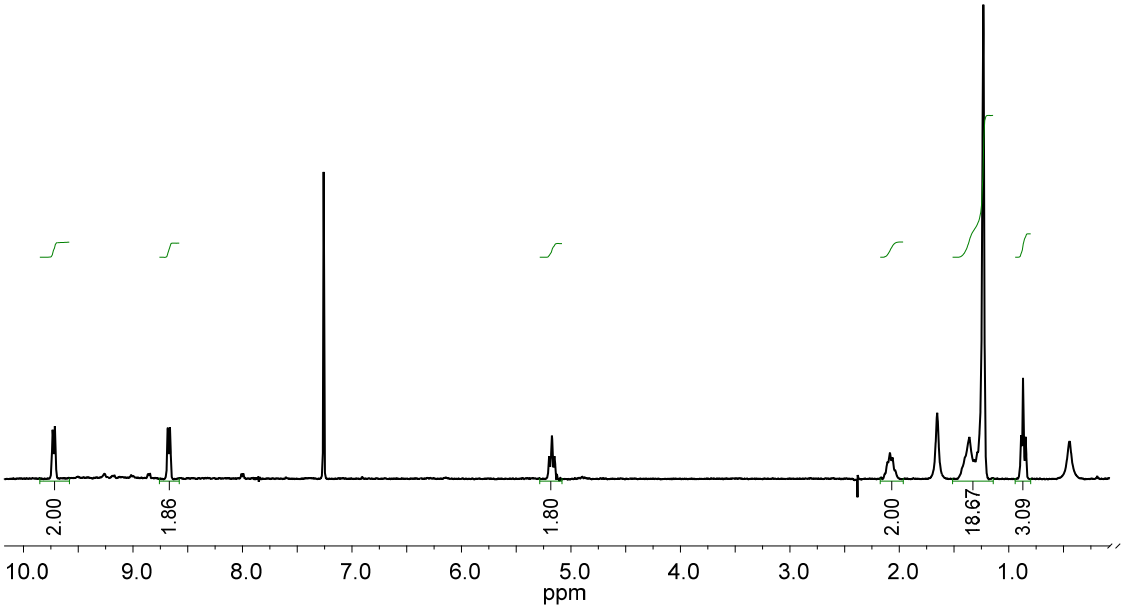
1. [1]H-NMR spectra of the synthesized compounds



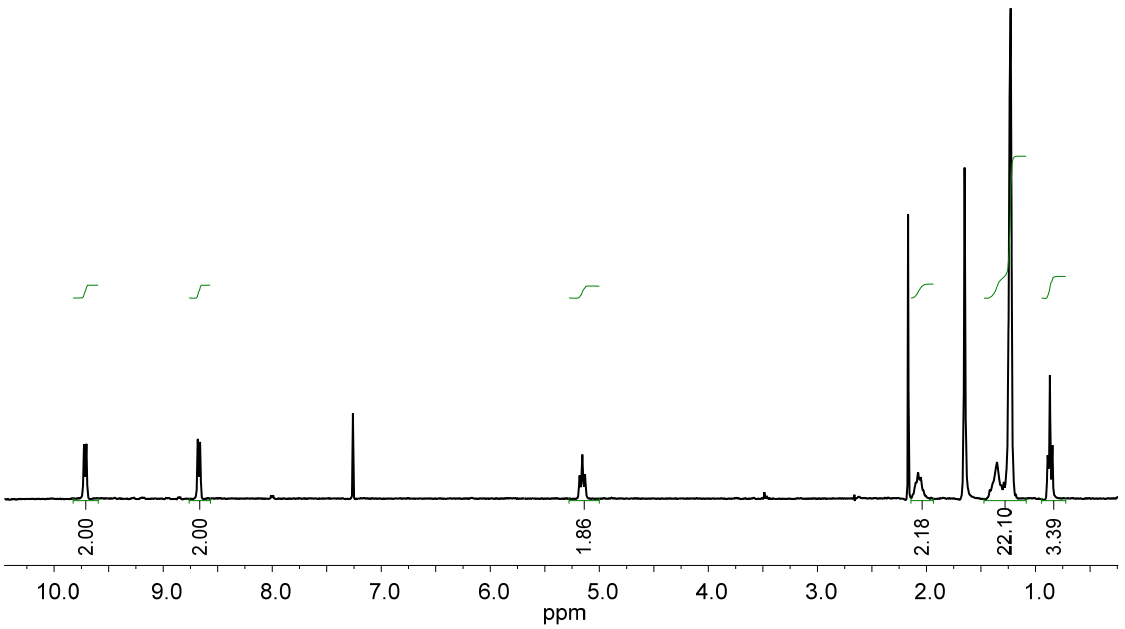
S1. [1]H-NMR spectrum of the 5-(Perfluoroheptyl)-3-(pyridin-4-yl)-1,2,4-oxadiazole precursor compound **1** in CD_3CN.



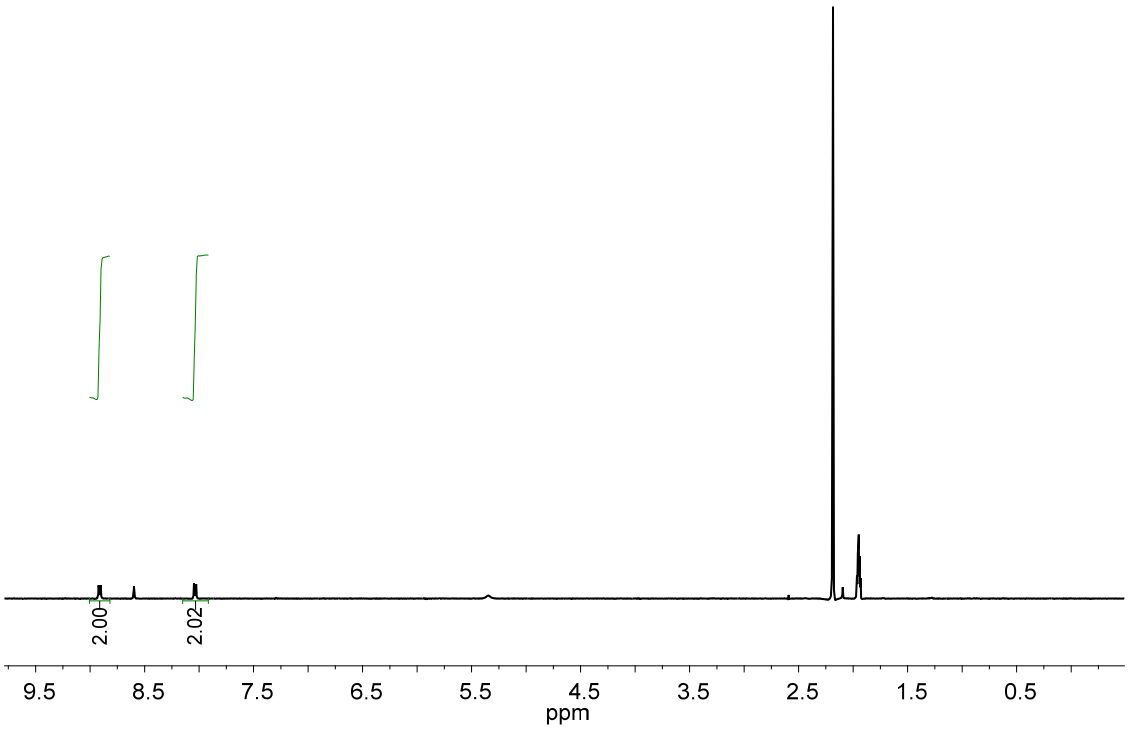
S2. [1]H-NMR spectrum of 1-decyl-4-(5-(perfluoroheptyl)-1,2,4-oxadiazol-3-yl) pyridin-1-ium iodide **1a** in CD_3CN.



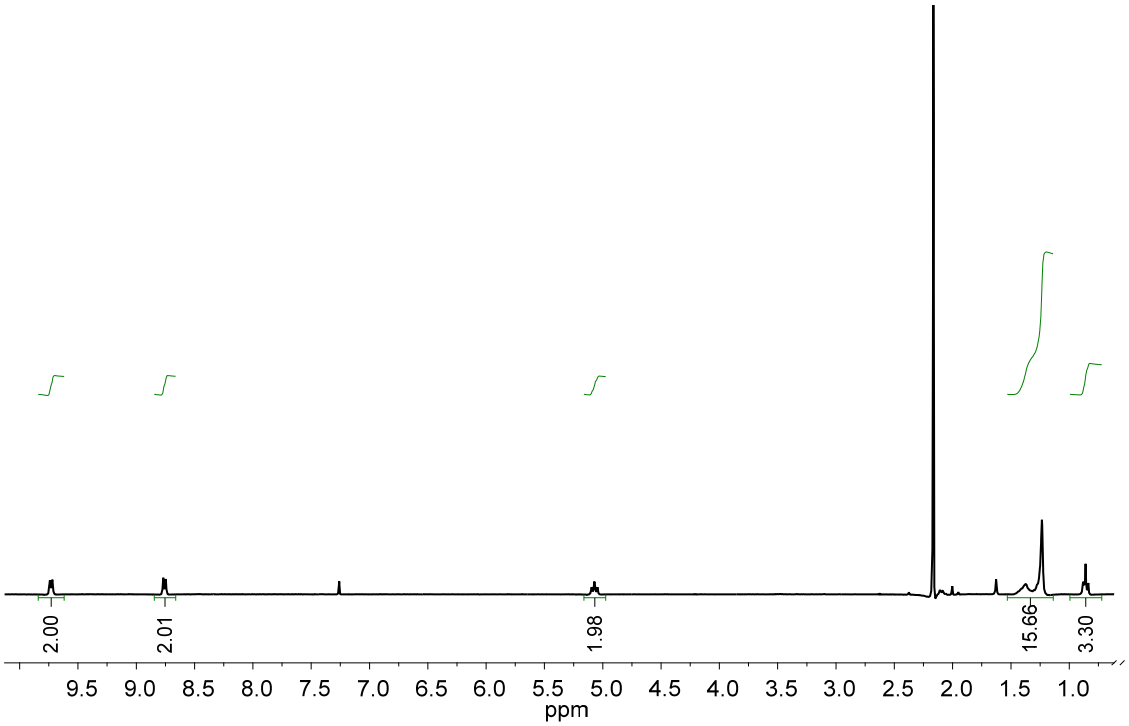
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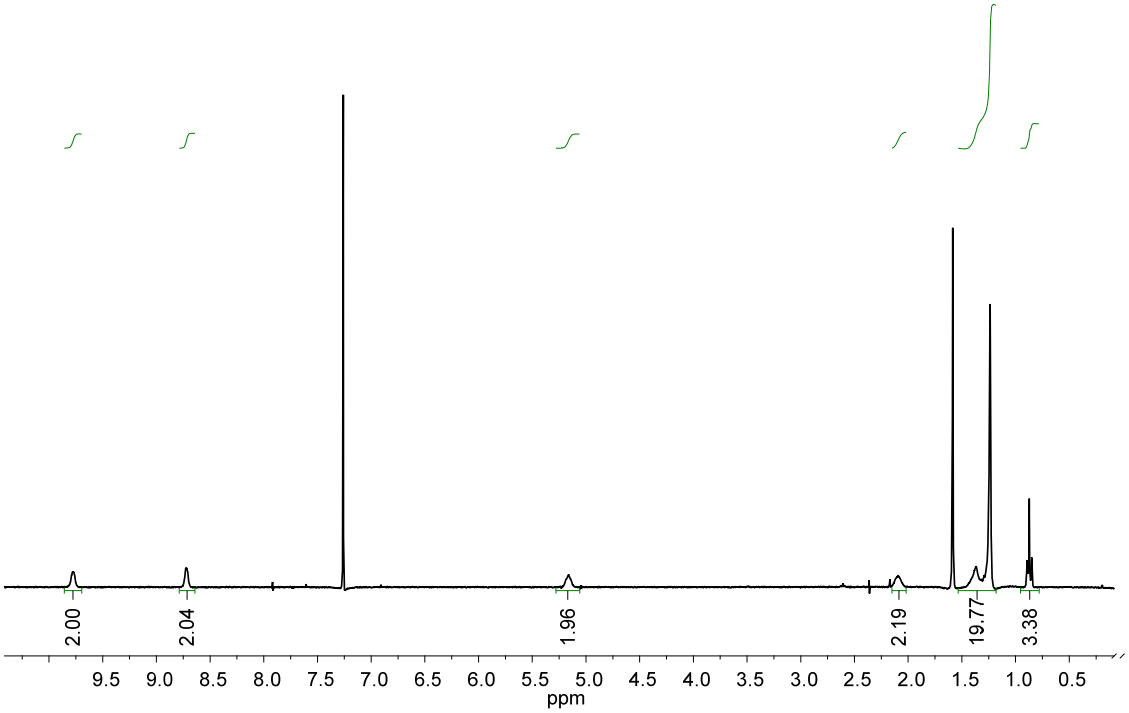
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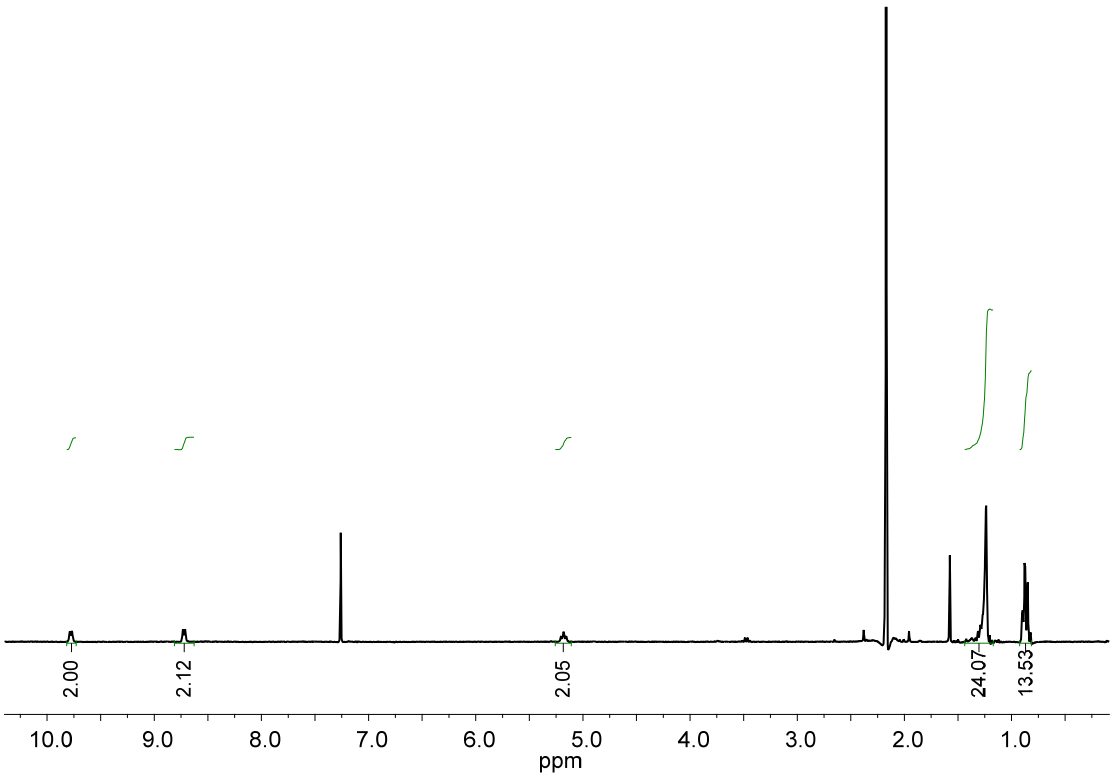
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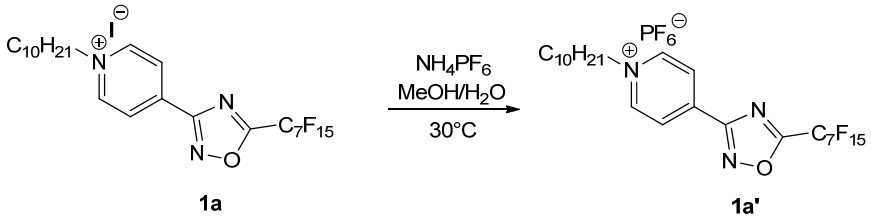
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*1. Synthesis and Aanalytical Data for **1a'***

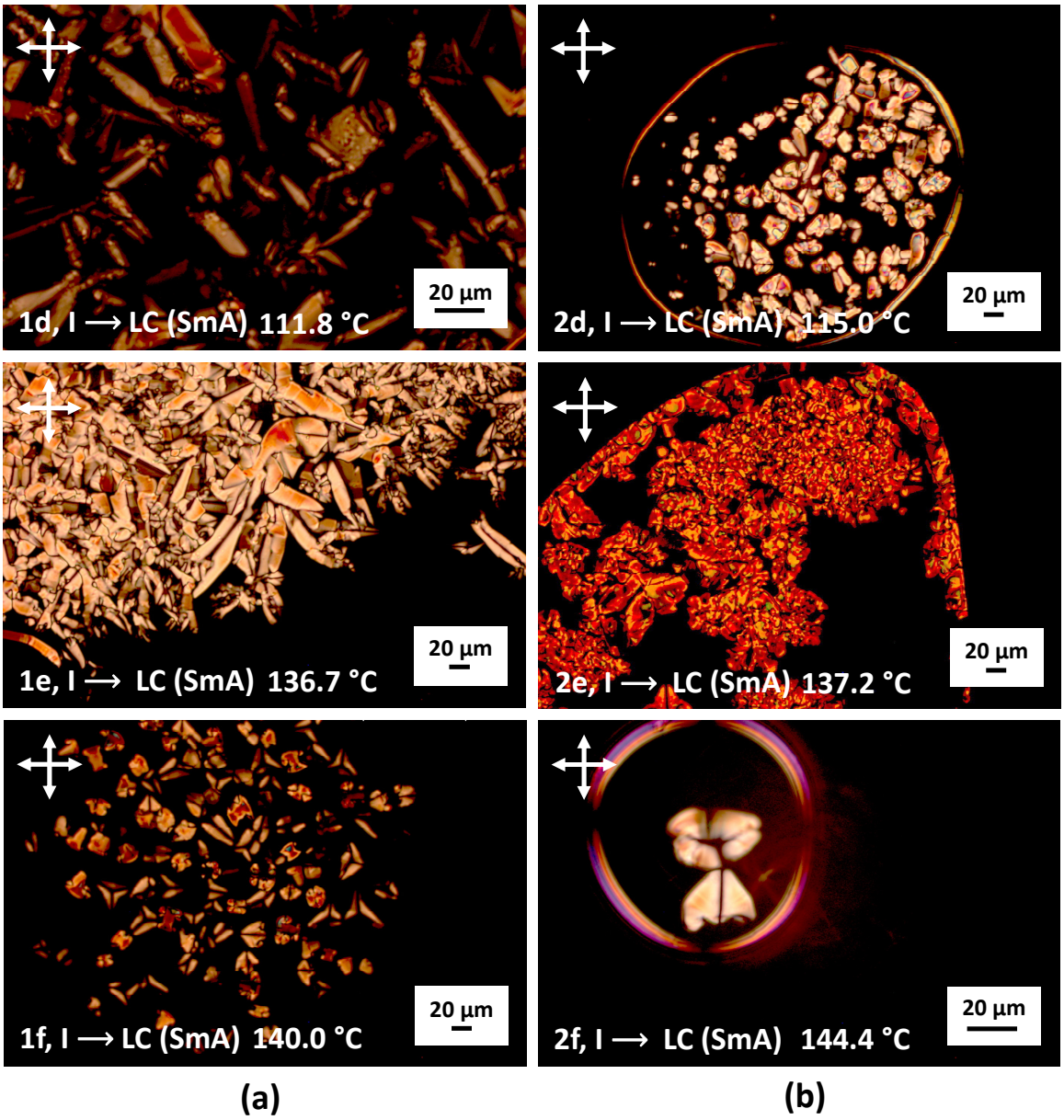
The metathesis from **1a** with iodide as counter ion has been realized in methanol and addition of the new desired counterion, here ammonium hexafluorophosphate ([PF6-]). The salt **1a** has been dissolved in a minimum amount of methanol (3-10 ml) and ammonium hexafluorophosphate (5 mole eq.) was added. The mixture was heated up to 30 – 35 °C and stirred for 0.5 h. Water was added dropwise until a permanent precipitate was formed. The mixture was stirred for 1 h. The solid was filtered under vacuum and washed with water. Filtration and washing with water yielded the desired product **1a'** (S1). Detection of the new counterion hexafluorophosphate has been done via HPLC-MS in negative mode. Complete conversion from iodide to hexafluorophosphate has been guaranteed by HPLC-MS as no residues of the precursor counterions were detected.



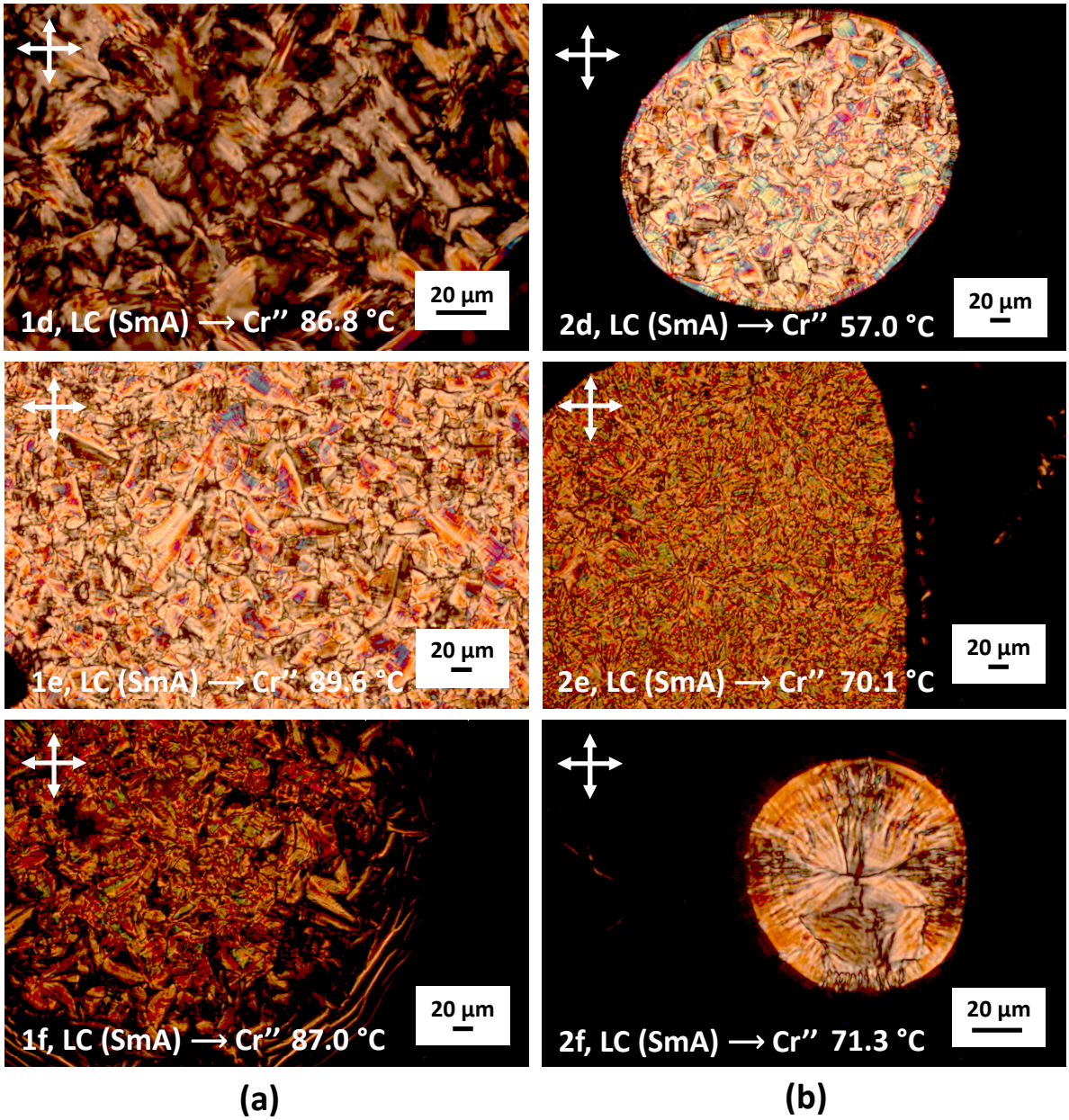
S9. Scheme of the synthesis of the perfluoroheptyl 1,2,4-oxadiazolylpyridinium salt **1a'** with hexafluorophosphate as counter ion from the precursor salt **1a**.

1-decyl-4-(5-(perfluoroheptyl)-1,2,4-oxadiazol-3-yl) pyridin-1-ium hexafluorophosphate (1a'):
Orange solid. Yield: 70 %. MS analysis: Calc.: 144.9647 g mol^{-1}, exp.: 144.9645 g mol^{-1}.

*2. Polarized Optical Microscopy Images of compounds **1d-f** and **2d-f***



S10. Polarized optical microscopy images of the salts (**a**) **1d** at 111.8 °C, **1e** at 136.7 °C, **1f** at 140.0 °C and (**b**) **2d** at 115.0 °C, **2e** at 137.2 °C, **2f** at 144.4 °C observed by polarized optical microscopy analysis under crossed polarizers showing the 1st transition from the isotropic liquid to the liquid crystalline phase (I ⟶ LC (SmA)) upon cooling with 10 °C min^{-1}. Abbreviation: I, isotropic phase; LC, liquid crystalline phase; SmA, smectic A phase.



S11. Polarized optical microscopy images of the salts (**a**) **1d** at 86.8 °C, **1e** at 89.6 °C, **1f** at 87.0 °C and (**b**) **2d** at 57.0 °C, **2e** at 70.1 °C, **2f** at 71.3 °C observed under crossed polarizers showing the 2nd transition from the liquid crystalline phase to a crystalline solid-state (LC (SmA) ⟶ Cr'') upon cooling with 10 °C min^{-1}. Abbreviation: LC, liquid crystalline phase; SmA, smectic A phase; Cr'', crystalline solid-state.