Electronic Supplementary Material (ESI) for Dalton Transactions

Nematogenic tetracatenar lanthanidomesogens

Karel Goossens,*[a] Duncan W. Bruce,[b] Rik Van Deun,[c]
Koen Binnemans[a] and Thomas Cardinaels*[d]

[a] Department of Chemistry, KU Leuven, Celestijnenlaan 200F (PO box 2404), 3001 Heverlee (Belgium). Fax: +32 16 327992; Tel: +32 16 327431;
E-mail: karel.goossens@chem.kuleuven.be.

[b] Department of Chemistry, University of York, Heslington, York, YO10 5DD (United Kingdom).

[c] *f*-Element Coordination Chemistry Laboratory, Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 – building S3, 9000 Gent (Belgium).

[d] Institute for Nuclear Materials Sciences (SCK·CEN), Boeretang 200, 2400 Mol (Belgium). Fax: +32 14 321216; Tel: +32 14 333185;
E-mail: thomas.cardinaels@sckcen.be.

Supporting Information

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1. General experimental details

Elemental analyses (carbon, hydrogen and nitrogen) were obtained from a CE Instruments EA-1110 elemental analyser. The results in percentages were interpreted allowing a deviation of ±0.4%.

Optical textures of the mesophases were observed with an Olympus BX60 polarising optical microscope equipped with a LINKAM THMS600 heating stage and a LINKAM TMS93 programmable temperature controller. DSC traces were recorded under helium with a Mettler-Toledo DSC822e module. Heating/cooling rates are specified in the captions of the thermograms. Indium was used as a standard for temperature and enthalpy calibrations.

NIR luminescence spectra were recorded on an Edinburgh Instruments FLSP920 spectrofluorimeter, using a 450 W xenon lamp as the steady-state excitation source and a Hamamatsu R5509-72 NIR PMT detector. Emission spectra have been corrected for detector response.

Molecular models were obtained with the Chem3D software package from CambridgeSoft.

2. Synthesis

Ligands **6**-8, **6**-10 and **6**-12 were prepared as described elsewhere.[1]

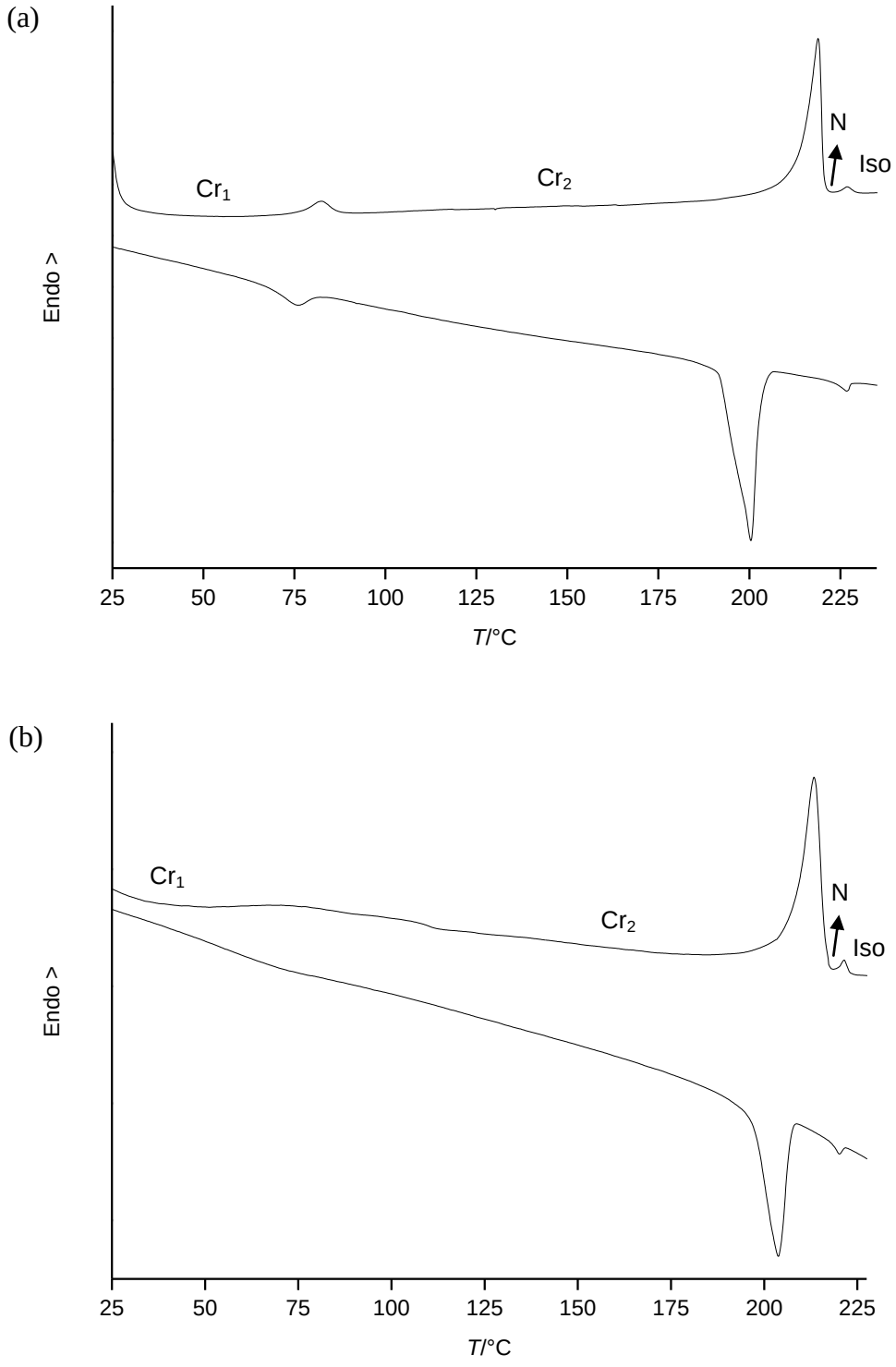
$Nd(tta)_3 \cdot 2H_2O$ was prepared according to a literature procedure for $Eu(tta)_3 \cdot 2H_2O$.[2] Calcd. for $C_{24}H_{12}F_9NdO_6S_3 \cdot 2H_2O$ (M = 843.80 g mol^{-1}): C 34.16, H 1.91. Found: C 34.39, H 2.03.

For the synthesis of neodymium(III) complex **7**-8, ligand **6**-8 (0.046 mmol, 0.050 g) and $Nd(tta)_3 \cdot 2H_2O$ (0.046 mmol, 0.039 g) were dissolved in 10 mL of toluene. The mixture was heated to 115 °C for 3 hours, after which the solvent was removed under reduced pressure. The crude product was dissolved in a minimal amount of toluene, and *n*-hexane was added until precipitation occurred. The yellow-orange precipitate was filtered off, washed with *n*-hexane and dried *in vacuo* at 50 °C. Yield: 80% (0.070 g). Calcd. for $C_{100}H_{100}F_9N_2NdO_{10}S_3$ (M = 1901.29 g mol^{-1}): C 63.17, H 5.30, N 1.47 (as a comparison: calcd. for the ligand **6**-8: C 83.47, H 8.11, N 2.56). Found: C 63.02, H 5.43, N 1.39.

Neodymium(III) complex **7**-10 was prepared in a similar way as **7**-8. The precipitate obtained by adding *n*-hexane to a solution of the complex in a minimal amount of toluene proved to be difficult to filter off. Therefore, after leaving it for 10 minutes in a freezer, the toluene/*n*-hexane mixture was centrifuged (3500 rpm). Then the supernatant was removed. The residue was dissolved again in a minimal amount of toluene, and *n*-hexane was added until the appearance of a precipitate, after which it was left in a freezer for 10 minutes. Then the mixture was again subjected to centrifugation. This procedure was repeated three more times. The final yellow-orange precipitate was dried *in vacuo* at 50 °C. Yield: 78% (0.017 g). Calcd. for $C_{108}H_{116}F_9N_2NdO_{10}S_3$ (M = 2013.50 g mol^{-1}): C 64.42, H 5.81, N 1.39. Found: C 64.75, H 5.99, N 1.63.

Neodymium(III) complex **7**-12 was prepared in a similar way as **7**-10. Yield: 66% (0.057 g). Calcd. for $C_{116}H_{132}F_9N_2NdO_{10}S_3$ (M = 2125.72 g mol^{-1}): C 65.54, H 6.26, N 1.32. Found: C 65.47, H 6.51, N 1.62.

3. Thermal behaviour: differential scanning calorimetry (DSC)



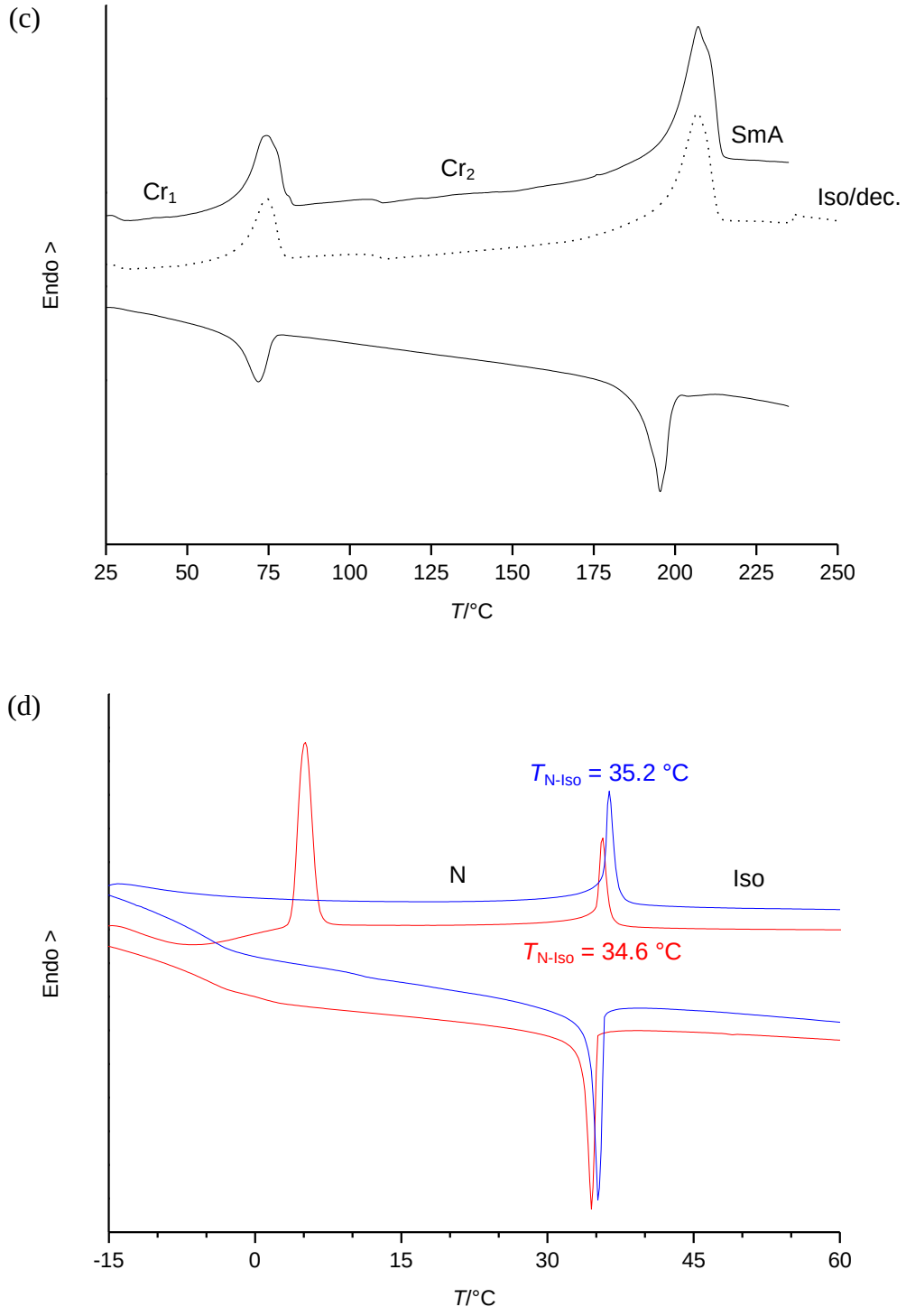


Figure S1. DSC traces of (a) compound **7**-8 (2nd heating/cooling cycle, 1st heating run up to 235 °C); (b) compound **7**-10 (2nd heating/cooling cycle, 1st heating run up to 235 °C); (c) compound **7**-12 (solid line: 2nd heating/cooling cycle (between 0 °C and 235 °C), dashed line: 3rd heating run); (d) the commercially available liquid crystal K15 (= 4-pentyl-4'-cyanobiphenyl, 5CB; red line, 2nd heating/cooling cycle) and compound

7-12 doped (1 wt.%) into K15 (blue line, 2nd heating/cooling cycle). The heating/cooling rate was 10 °C min.$^{-1}$, and the measurements were performed under a helium atmosphere. Abbreviations: Cr, Cr_1, Cr_2 = crystalline phase; SmA = smectic A phase; N = nematic phase; Iso = isotropic liquid phase; dec. = thermal decomposition. Endothermic peaks point upwards. The bottom figure shows the slight increase in clearing point ($T_{N\text{-}Iso}$) by doping 5CB with 1 wt.% of the high-clearing compound **7**-12.

4. Polarising optical microscopy (POM) textures

*Neodymium(III) complex **7**-8*

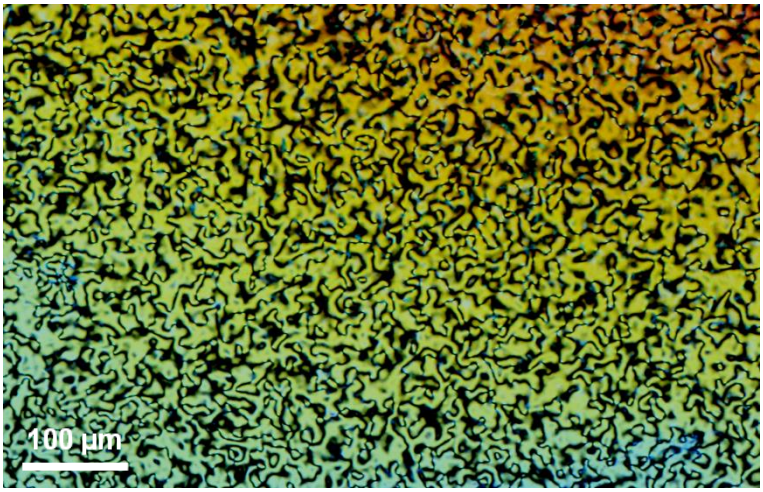


Figure S2. Schlieren texture of the nematic phase of complex **7**-8 at 215 °C on cooling from the isotropic liquid.

*Neodymium(III) complex **7**-8: 1 wt.% solution in 5CB*

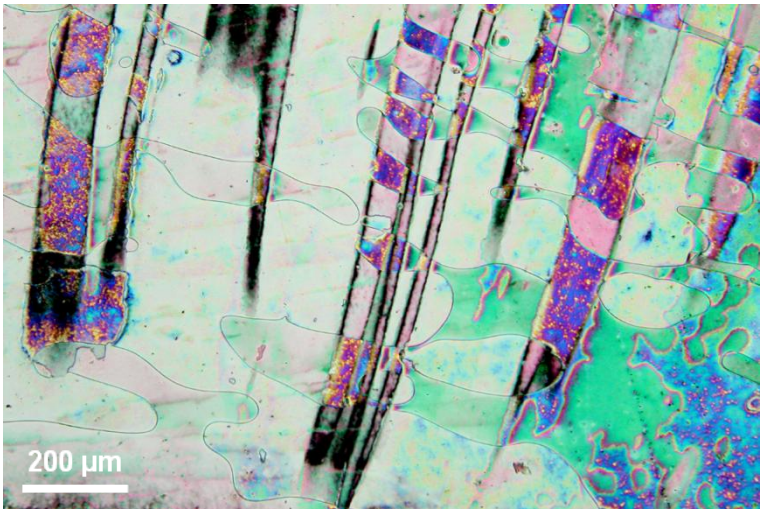


Figure S3. Marble and thread-like texture of the nematic phase of a 1 wt.% solution of complex **7**-8 in 5CB, at 28 °C.

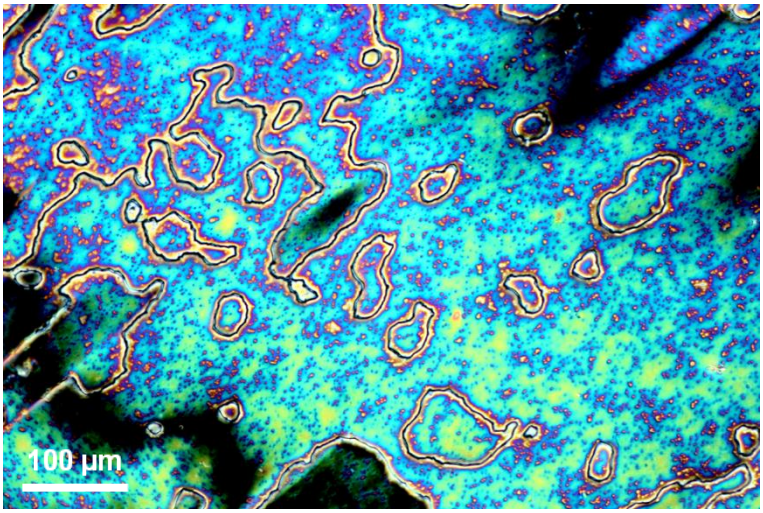


Figure S4. Thread-like texture of the nematic phase of a 1 wt.% solution of complex **7**-8 in 5CB, at 28 °C.

Neodymium(III) complex 7-10

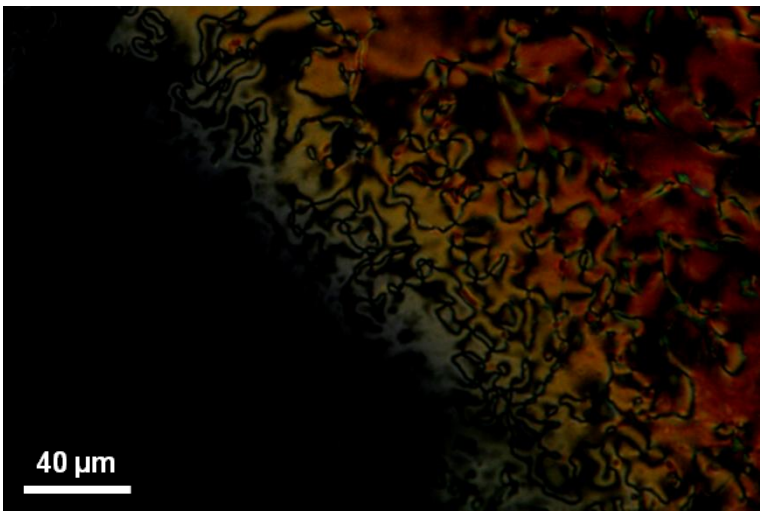


Figure S5. Schlieren texture of the nematic phase of complex **7**-10 at 212 °C on cooling from the isotropic liquid.

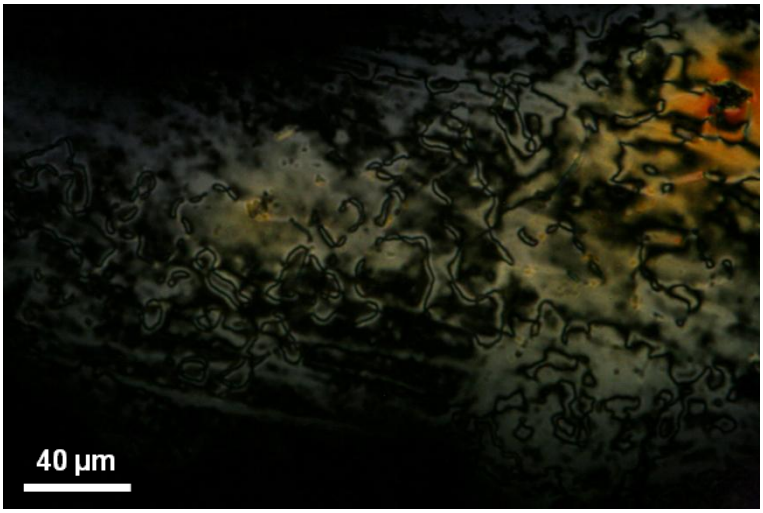


Figure S6. Schlieren texture of the nematic phase of complex **7**-10 at 212 °C on cooling from the isotropic liquid.

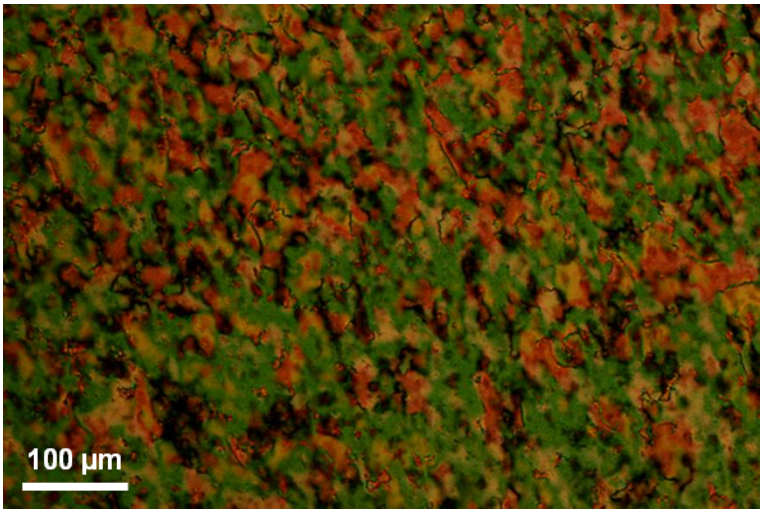


Figure S7. Marble texture of the nematic phase of complex **7**-10 at 212 °C on cooling from the isotropic liquid.

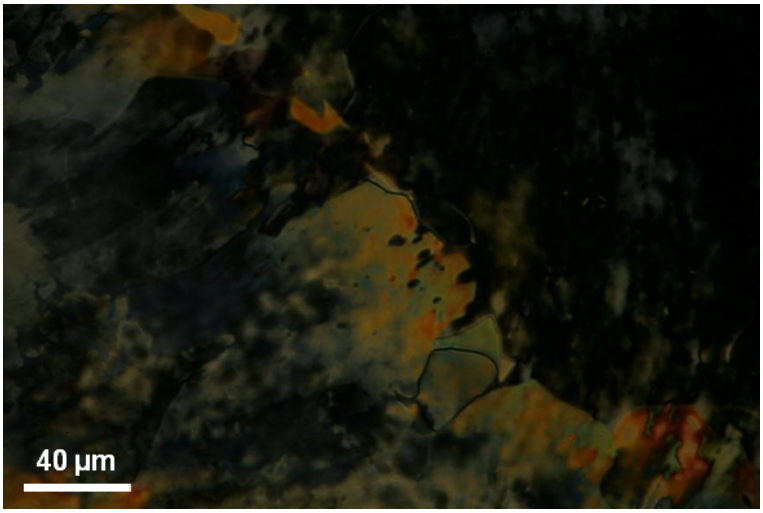
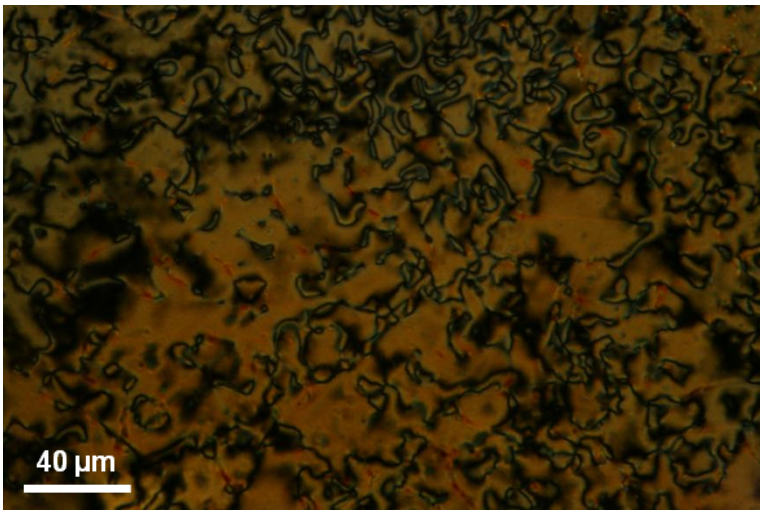
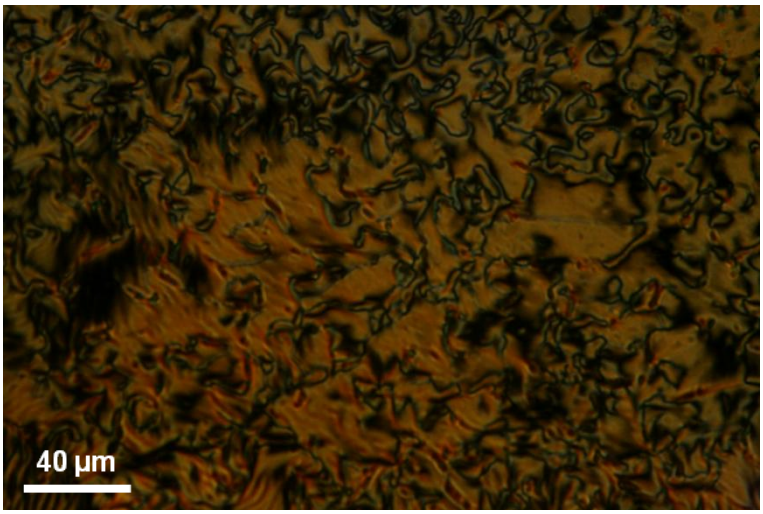


Figure S8. Marble and thread-like texture of the nematic phase of complex **7**-10 at 212 °C on cooling from the isotropic liquid.

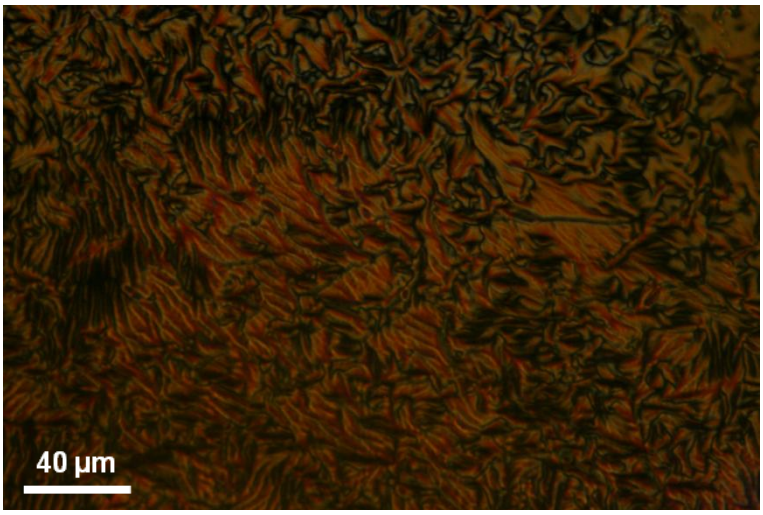
(a)



(b)



(c)



(d)

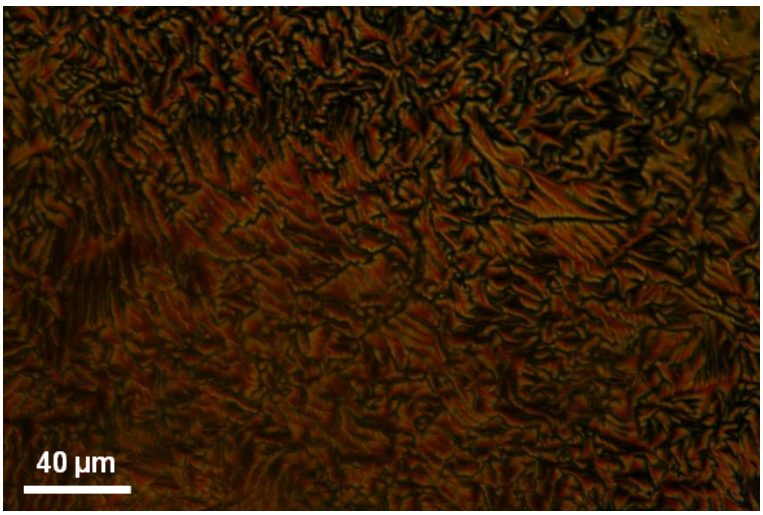


Figure S9. Gradual formation of the monotropic SmA phase of complex **7**-10 on cooling from the nematic phase: (a) at 212 °C; (b) at 207 °C; (c) at 205 °C ; (d) at 202 °C (the nematic schlieren texture changes into a paramorphotic texture).

Neodymium(III) complex 7-12

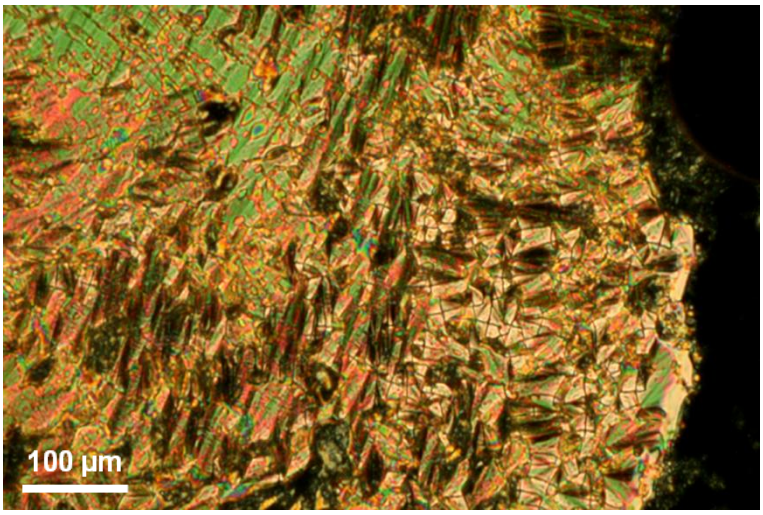


Figure S10. Focal conic fan texture of the SmA phase of complex **7**-12 at 202 °C on cooling from the isotropic liquid (on the right-hand side, a homeotropically aligned area is seen below the air bubble).

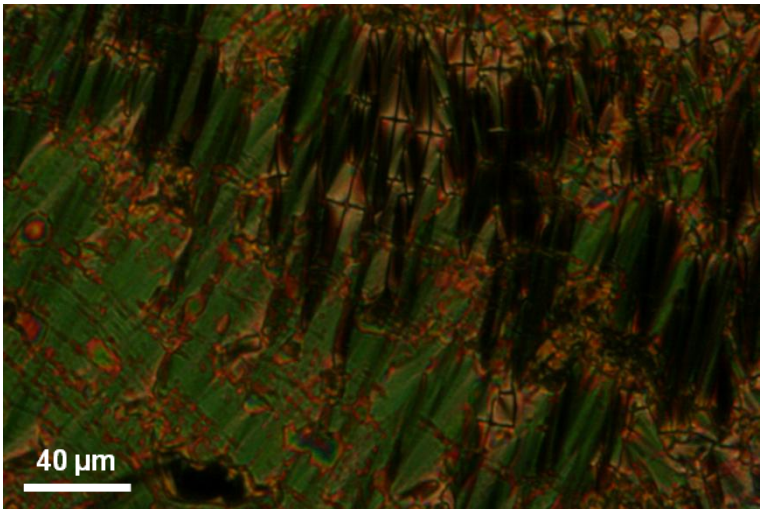


Figure S11. Focal conic fan texture of the SmA phase of complex **7**-12 at 206 °C on cooling from the isotropic liquid.

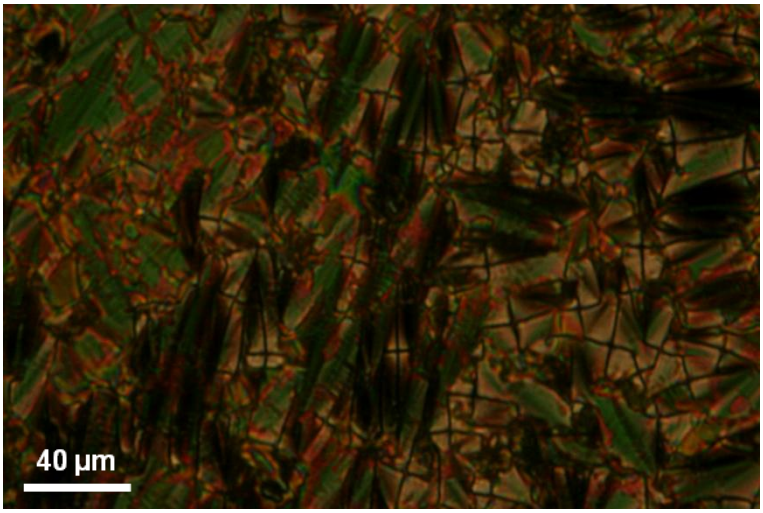


Figure S12. Focal conic fan texture of the SmA phase of complex **7**-12 at 206 °C on cooling from the isotropic liquid.

5. Additional spectroscopic data

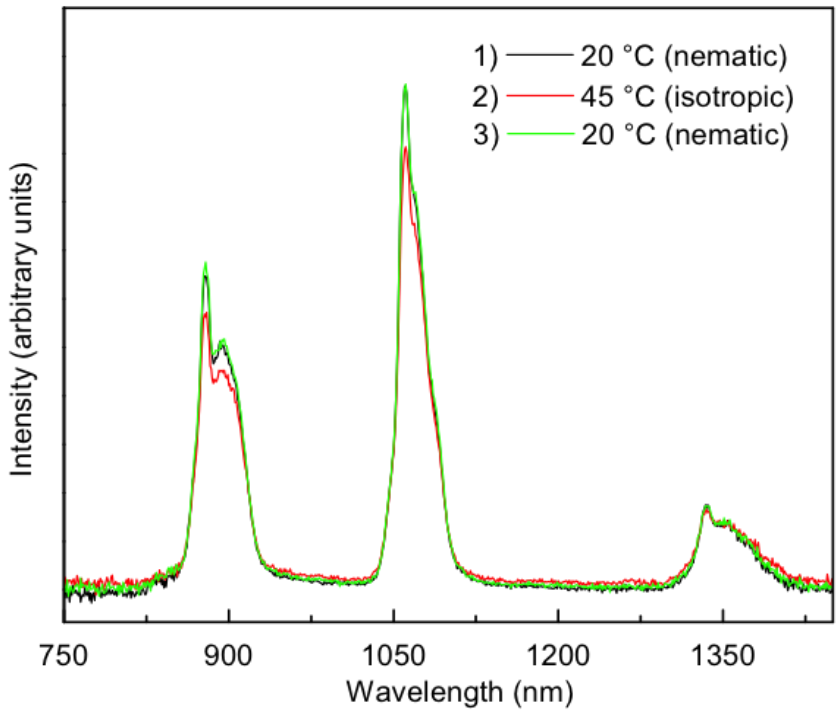


Figure S13. NIR luminescence spectrum of **7**-12 (1 wt.%) doped into 5CB: the black curve represents the virgin sample, prepared at room temperature (nematic phase); the red curve represents the same sample, heated to 45 °C (isotropic phase); the green curve represents the sample cooled from 45 °C back to room temperature (nematic phase).

6. References

1 T. Cardinaels, J. Ramaekers, P. Nockemann, K. Driesen, K. Van Hecke, L. Van Meervelt, G. Wang, S. De Feyter, E. Fernandez Iglesias, D. Guillon, B. Donnio, K. Binnemans and D. W. Bruce, *Soft Matter*, 2008, **4**, 2172-2185.

2 K. Binnemans, P. Lenaerts, K. Driesen and C. Görller-Walrand, *J. Mater. Chem.*, 2004, **14**, 191-195.