Thermodynamics of Dimerization in Solution as a Rational Tool for Inducing Nematic versus Smectic Organizations in Lanthanidomesogens

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Supporting Information

(16 pages)

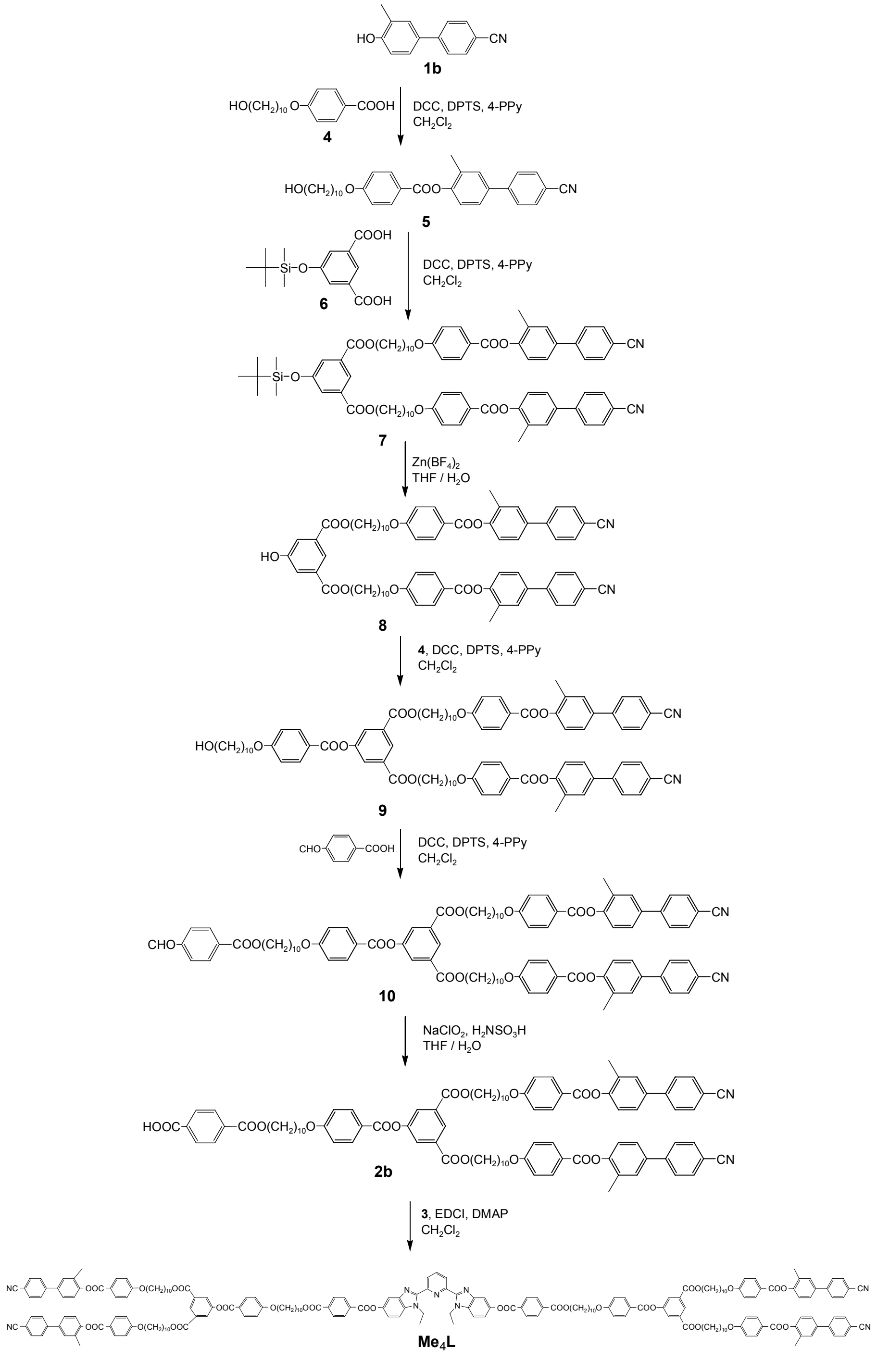
Experimental

Synthesis of Me_4L

Abbreviations used: DCC (*N*,*N'*-dicyclohexylcarbodiimide), DMAP (4-(Dimethylamino)pyridine), 4-PPy (4-Pyrrolidinopyridine), EDCI (*N*-(3-Dimethylaminopropyl)-*N'*-ethylcarbodiimide), DPTS (4-(Dimethylamino)pyridinium 4-toluenesulfonate).

Synthons **1b**[1], **3**[2], **4**[3], and **6**[4] (Scheme S1) as well as DPTS[5] were prepared according to published procedures.

Scheme S1 Synthesis of ligand Me_4L.



Preparation of Synthon 5

To a solution of **1b** (1.08 g; 5.16 mmol) in 100 ml dry CH_2Cl_2 stirred at 0 °C was added **4** (1.52 g; 5.16 mmol), DCC (2.06 g; 10 mmol), DPTS (1.52 g; 5.16 mmol) and a spatula tip of 4-Pyrrolidinopyridine. The reaction mixture was allowed to heat slowly to room temperature and stirred for 48 hours. After filtration the solution was evaporated to dryness and the residue was purified by column chromatography (silica; $CH_2Cl_2/CH_3OH = 100/0 \rightarrow 99/1$) to yield 2.28 g (91 %) of **5**.

^{1}H NMR ($CDCl_3$): δ 8.18 (d, 2H, $^3J = 9.0$ Hz), 7.73 (d, 2H, $^3J = 8.6$ Hz), 7.68 (d, 2H, $^3J = 8.7$ Hz), 7.49 (d, 1H, $^4J = 1.8$ Hz), 7.46 (dd, 1H, $^3J = 8.3$ Hz, $^4J = 2.2$ Hz), 7.25 (d, 1H, $^3J = 8.5$ Hz), 6.99 (d, 2H, $^3J = 9.0$ Hz), 4.06 (t, 2H, $^3J = 6.5$ Hz), 3.65 (t, 2H, $^3J = 6.5$ Hz), 2.31 (s, 3H), 1.79-1.87 (m, 2H), 1.53-1.61 (m, 2H), 1.44-1.52 (m, 2H), 1.30-1.40 (m, 10H).

MS: *m/z*: 277.4 $(HO(CH_2)_{10}OC_6H_4CO]^+$, 486.5 ($[M+H]^+$), 503.5 ($[M+H_2O]^+$), 508.6 ($[M+Na]^+$), 989.0 ($[2M+H_2O]^+$), 994.0 ($[2M+Na]^+$).

Elemental analysis: Calculated for $C_{31}H_{35}NO_4 \cdot 0.18H_2O$: C 76.16; H 7.29; N 2.87. Found C 76.07; H 7.23; N 2.83.

Preparation of Synthon 7

To a suspension of **6** (0.70 g; 2.35 mmol) in 50 ml freshly distilled CH_2Cl_2 stirred in an ice bath was added first a solution of DCC (3.00 g; 14.5 mmol), DPTS (0.30 g; 1.02 mmol) and a spatula tip of 4-PPy in 25 ml CH_2Cl_2, then a solution of **5** (2.28 g; 4.70 mmol) in 25 ml CH_2Cl_2. After stirring for 30 minutes the ice bath was removed and the solution was stirred for 17 hours. After filtration the solution was evaporated to dryness. The crude product was purified by column chromatography (silica; $CH_2Cl_2/CH_3OH = 100/0 \rightarrow 99.5/0.5$) to yield 2.21 g (79 %) of **7**.

^{1}H NMR ($CDCl_3$): δ 8.28 (t, 1H, $^4J = 1.5$ Hz), 8.17 (d, 4H, $^3J = 9.0$ Hz), 7.72 (d, 4H, $^3J = 8.7$ Hz), 7.67 (d, 4H, $^3J = 8.9$ Hz), 7.67 (d, 2H, $^4J = 1.5$ Hz), 7.48 (d, 2H, $^4J = 1.8$ Hz), 7.46 (dd, 2H, $^3J = 8.2$ Hz, $^4J = 2.3$ Hz), 7.24 (d, 2H, $^3J = 8.2$ Hz), 6.99 (d, 4H, $^3J = 8.9$ Hz), 4.33 (t, 4H, $^3J = 6.8$ Hz), 4.05 (t, 4H, $^3J = 6.6$ Hz), 2.30 (s, 6H), 1.74-1.87 (m, 8 H), 1.30-1.53 (m, 24 H), 1.00 (s, 9H), 0.24 (s, 6H).

MS: *m/z*: 1253.4 ($[M+Na]^+$).

Elemental analysis: Calculated for $C_{76}H_{86}N_2O_{11}Si \cdot 0.33H_2O$: C 73.75; H 7.06; N 2.27. Found C 73.75; H 7.08; N 2.33.

Preparation of Synthon 8

A solution of **7** (2.24 g; 1.82 mmol) and $Zn(BF_4)_2 \cdot 6H_2O$ (8.00 g; 23.0 mmol) in 160 ml THF and 40 ml H_2O was stirred at 60 °C for 15 hours. The THF was evaporated and the aqueous phase was extracted with 4×40 ml CH_2Cl_2. The combined organic phases were dried over Na_2SO_4, filtered and evaporated. The solid residue was purified by column chromatography (silica; CH_2Cl_2/CH_3OH = 100/0 → 99/1) to yield 2.01 g (99 %) of **8**.

^{1}H NMR ($CDCl_3$): δ 8.26 (t, 1H, ^4J = 1.4 Hz), 8.17 (d, 4H, ^3J = 9.0 Hz), 7.72 (d, 4H, ^3J = 8.6 Hz), 7.70 (d, 2H, ^4J = 1.4 Hz), 7.67 (d, 4H, ^3J = 8.6 Hz), 7.48 (d, 2H, ^4J = 2.2 Hz), 7.45 (dd, 2H, ^3J = 8.2 Hz, ^4J = 2.3 Hz), 7.24 (d, 2H, ^3J = 8.3 Hz), 6.99 (d, 4H, ^3J = 9.0 Hz), 5.61 (s, 1H), 4.33 (t, 4H, ^3J = 6.7 Hz), 4.05 (t, 4H, ^3J = 6.6 Hz), 2.30 (s, 6H), 1.73-1.87 (m, 8 H), 1.30-1.53 (m, 24 H).

MS: *m/z*: 1116.1 ($[M-H]^-$).

Elemental analysis: Calculated for $C_{70}H_{72}N_2O_{11}\cdot 0.18H_2O$: C 75.02; H 6.51; N 2.51. Found C 75.02; H 6.58; N 2.43.

Preparation of Synthon 9

To a solution of **4** (0.53 g; 1.79 mmol) in freshly distilled CH_2Cl_2 stirred in an ice bath was added **8** (2.00 g; 1.79 mmol), DPTS (0.53 g; 1.79 mmol), DCC (0.83 g; 4.00 mmol) and a spatula tip of 4-PPy. The ice bath was removed and the solution was stirred at room temperature for 72 hours. After filtration the solution was evaporated to dryness and the crude product was purified by column chromatography (silica; CH_2Cl_2/CH_3OH = 100/0 → 99/1) to yield 2.44 g (98 %) of **9**.

^{1}H NMR ($CDCl_3$): δ 8.60 (t, 1H, ^4J = 1.4 Hz), 8.17 (d, 4H, ^3J = 9.0 Hz), 8.14 (d, 2H, ^3J = 9.0 Hz), 8.06 (d, 2H, ^4J = 1.4 Hz), 7.72 (d, 4H, ^3J = 9.0 Hz), 7.67 (d, 4H, ^3J = 9.0 Hz), 7.48 (d, 2H, ^4J = 2.3 Hz), 7.45 (dd, 2H, ^3J = 8.7 Hz, ^4J = 2.3 Hz), 7.24 (d, 2H, ^3J = 8.4 Hz), 6.98 (d, 6H, ^3J = 8.7 Hz), 4.35 (t, 4H, ^3J = 6.6 Hz), 4.04 (t, 6H, ^3J = 6.6 Hz), 3.64 (t, 2H, ^3J = 6.5 Hz), 2.30 (s, 6H), 1.74-1.86 (m, 10 H), 1.54-1.61 (m, 2 H), 1.29-1.52 (m, 36 H).

MS: *m/z*: 1411.1 ($[M+H_2O]^+$).

Elemental analysis: Calculated for $C_{87}H_{96}N_2O_{14}\cdot 0.64H_2O$: C 74.36; H 6.98; N 1.99. Found C 74.36; H 7.14; N 2.20.

Preparation of Synthon 10

To a solution of 4-carboxybenzaldehyde (74 mg; 0.49 mmol) and **9** (670 mg; 0.49 mmol) in 100 ml freshly distilled CH_2Cl_2 stirred in an ice bath was added DPTS (30 mg; 0.10 mmol), DCC (300 mg; 1.45 mmol) and a spatula tip of 4-PPy. After 30 minutes the ice bath was removed and the solution was stirred for 24 hours at room temperature. The solution was filtered and evaporated and the crude product was purified by column chromatography (silica; CH_2Cl_2/CH_3OH = 100/0 → 99.5/0.5). Yield: 700 mg (96 %).

^{1}H NMR ($CDCl_3$): δ 10.10 (s, 1H) 8.59 (t, 1H, ^4J = 1.5 Hz), 8.20 (d, 2H, ^3J = 8.4 Hz), 8.17 (d, 4H, ^3J = 8.9 Hz), 8.14 (d, 2H, ^3J = 9.0 Hz), 8.06 (d, 2H, ^4J = 1.6 Hz), 7.95 (d, 2H, ^3J = 8.3 Hz), 7.72 (d, 4H, ^3J = 8.6 Hz), 7.67 (d, 4H, ^3J = 8.5 Hz), 7.48 (d, 2H, ^4J = 2.3 Hz), 7.46 (dd, 2H, ^3J = 8.4 Hz, ^4J = 2.3 Hz), 7.24 (d, 2H, ^3J = 8.4 Hz), 6.99 (d, 4H, ^3J = 8.9 Hz), 6.98 (d, 2H, ^3J = 9.0 Hz), 4.36 (t, 2H,

^3J = 6.7 Hz), 4.35 (t, 4H, ^3J = 6.7 Hz), 4.05 (t, 6H, ^3J = 6.5 Hz), 2.30 (s, 6H), 1.74-1.87 (m, 12 H), 1.30-1.52 (m, 36 H).

MS: *m/z*: 1543.1 ($[M+H_2O]^+$).

Elemental analysis: Calculated for $C_{95}H_{100}N_2O_{16}\cdot 0.91H_2O$: C 73.98; H 6.65; N 1.82. Found C 73.98; H 6.60; N 1.86.

Preparation of Synthon 2b

A solution of **10** (0.64 g; 0.42 mmol), $NaClO_2$ (0.20 g; 2.2 mmol) and H_2NSO_3H (0.21 g; 2.3 mmol) in 25 ml THF and 25 ml H_2O was stirred at room temperature for 2 hours. After evaporation of the THF the aqueous phase was extracted with 2 × 50 ml CH_2Cl_2. The combined organic phases were dried over Na_2SO_4, filtered and evaporated. Yield: 0.64 g (99 %).

^1H NMR ($CDCl_3$): δ 8.59 (t, 1H, ^4J = 1.5 Hz), 8.11-8.19 (m, 10H), 8.06 (d, 2H, ^4J = 1.5 Hz), 7.72 (d, 4H, ^3J = 8.6 Hz), 7.67 (d, 4H, ^3J = 8.6 Hz), 7.48 (d, 2H, ^4J = 2.2 Hz), 7.46 (dd, 2H, ^3J = 8.3 Hz, ^4J = 2.2 Hz), 7.24 (d, 2H, ^3J = 8.3 Hz), 6.98 (d, 4H, ^3J = 9.0 Hz), 6.98 (d, 2H, ^3J = 9.0 Hz), 4.35 (t, 6H, ^3J = 6.7 Hz), 4.04 (t, 6H, ^3J = 6.6 Hz), 2.30 (s, 6H), 1.74-1.89 (m, 12 H), 1.29-1.53 (m, 36 H).

MS: *m/z*: 1540.3 ($[M-H]^-$).

Elemental analysis: Calculated for $C_{95}H_{100}N_2O_{17}\cdot 1.92H_2O$: C 72.38; H 6.64; N 1.78. Found C 72.38; H 6.75; N 1.70.

Preparation of Me_4L

A solution of **2b** (1.46 g; 0.95 mmol), **3** (189 mg; 0.47 mmol), EDCI·HCl (400 mg; 2.1 mmol) and DMAP (250 mg; 2.05 mmol) in 100 ml freshly distilled CH_2Cl_2 was refluxed under N_2 for 17 hours. The solution was extracted three times with 80 ml H_2O + 10 ml sat. NH_4Cl. The combined aqueous phases were extracted with 50 ml CH_2Cl_2 and the organic extracts were dried over Na_2SO_4, filtered and evaporated to dryness. The crude product was purified by column chromatography (silica; $CH_2Cl_2/CH_3OH = 100/0 \rightarrow 99/01$). Yield: 830 mg (51 %).

^1H NMR ($CDCl_3$): δ 8.59 (t, 2H, ^4J = 1.5 Hz), 8.35 (d, 2H, ^3J = 8.1 Hz), 8.33 (d, 4H, ^3J = 8.6 Hz), 8.20 (d, 4H, ^3J = 8.5 Hz), 8.16 (d, 8H, ^3J = 8.9 Hz), 8.14 (d, 4H, ^3J = 8.8 Hz), 8.08 (t, 1H, ^3J = 7.9 Hz), 8.05 (d, 4H, ^4J = 1.5 Hz), 7.72 (d, 8H, ^3J = 8.4 Hz), 7.71 (d, 2H, ^4J = 2.3 Hz), 7.67 (d, 8H, ^3J = 8.4 Hz), 7.52 (d, 2H, ^3J = 9.0 Hz), 7.48 (d, 4H, ^4J = 2.1 Hz), 7.46 (dd, 4H, ^3J = 8.3 Hz, ^4J = 2.2 Hz), 7.25 (dd, 2H, ^3J = 9.0 Hz, ^4J = 2.3 Hz), 7.24 (d, 4H, ^3J = 8.3 Hz), 6.98 (d, 12H, ^3J = 9.0 Hz), 4.82 (q, 4H, ^3J = 7.2 Hz), 4.38 (t, 4H, ^3J = 6.7 Hz), 4.35 (t, 8H, ^3J = 6.8 Hz), 4.05 (t, 4H, ^3J = 6.6 Hz), 4.04 (t, 8H, ^3J = 6.6 Hz), 2.30 (s, 12H), 1.74-1.87 (m, 24 H), 1.30-1.52 (m, 78 H).

MS: *m/z*: 1724.3 ($[M+2H]^{2+}$).

Elemental analysis: Calculated for $C_{213}H_{217}N_9O_{34}\cdot 0.22H_2O$: C 74.13; H 6.35; N 3.65. Found C 74.14; H 6.41; N 3.53.

Preparation of [Ln(Me$_4$L)(NO$_3$)$_3$]·nH$_2$O complexes

The water content of Ln(NO$_3$)$_3$·nH$_2$O salts was determined prior to use by complexometric titration with Na$_2$H$_2$EDTA in the presence of urotropine using xylene orange as indicator.

In a typical preparation 100-150 mg of **Me$_4$L** was dissolved in 5 ml CH$_2$Cl$_2$. One equivalent of Ln(NO$_3$)$_3$·nH$_2$O (Ln = Pr, Eu, Lu) in 5 ml CH$_3$CN was added and the solution was stirred for 1 hour. After evaporation of the solvent, the complex was washed with CH$_3$CN and dried in vacuum overnight at 60 °C. Yields were 72-89 %.

Elemental analysis: Calculated for [Eu(**Me$_4$L**)(NO$_3$)$_3$]·1.84H$_2$O: C 67.00; H 5.83; N 4.40. Found: C 67.02; H 5.93; N 4.26. Calculated for [Lu(**Me$_4$L**)(NO$_3$)$_3$]·0.61H$_2$O: C 66.99; H 5.76; N 4.40. Found: C 67.00; H 5.81; N 4.30.

References

1 Y. L. Bennani, R. Faghih, W. J. Dwight, A. Vasudevan, S. E. Conner, U.S. Pat. Appl. Publ. **2002**, Ser. No. 902,925, CODEN: USXXCO US 2002137931 A1 20020926.

2 Nozary, H.; Piguet, C.; Tissot, P.; Bernardinelli, G.; Bünzli, J.-C. G.; Deschenaux, R.; Guillon, D., *J. Am. Chem. Soc.* **1998,** 120, (47), 12274-12288.

3 Dardel, B.; Guillon, D.; Heinrich, B.; Deschenaux, R., *J. Mater. Chem.* **2001,** 11, 2814-2831.

4 Miller, T. M.; Kwock, E. W.; Neenan, T. X., *Macromol.* **1992,** 25, 3143-3148.

5 Moore, J. S.; Stupp, S. I., *Macromol.* **1990,** 23, 65-70.

Spectroscopic and Analytical Measurements.

^{1}H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. TG were performed with a thermogravimetric balance Seiko TG/DTA 320 (under N$_2$). DSC traces were obtained with a Seiko DSC 220C differential scanning calorimeter from 3-5 mg samples (5 °C min^{-1}, under N$_2$). The characterizations of the mesophases were performed with a polarizing microscope Leitz Orthoplan-Pol with a Leitz LL 20x/0.40 polarizing objective, and equipped with a Linkam THMS 600 variable-temperature stage. The SAXS patterns were obtained with three different experimental setups, and in all cases, the crude powder was filled in Lindemann capillaries of 1 mm diameter. 1) a STOE transmission powder diffractometer system STADI P using a focused monochromatic CuKα1 beam obtained from a curved Germanium monochromator (Johann-type) and collected on a curved Image-Plate Position Sensitive Detector (IP-PSD). A calibration with silicon and copper laurate standards, for high and low angle domains respectively, was preliminary performed. Sample capillaries were placed in the high temperature attachment for measurements in the range of desired temperatures (from -40 up to 170°C) within ± 0.05°C. Periodicities up to 50 Å could be measured. The exposure times were varied from 1 to 4 h. 2) A curved counter Inel CPS 120 using a linear monochromatic CuKα_1 beam obtained with a sealed-tube generator (900 W) and a bent quartz monochromator, for which the sample temperature was controlled within ±0.05°C; periodicities up to 60 Å could be measured. 3) An Image Plate; the cell parameters were calculated from the position of the reflection at the smallest *Bragg* angle, which was in all cases the most intense. Periodicities up to 90 Å could be measured, and the sample temperature was controlled within ± 0.3°C. The exposure times were varied from 1 to 24 h depending on the specific reflections being sought (weaker reflections obviously taking longer exposure times). Elemental analyses were performed by Dr. H. Eder from the microchemical Laboratory of the University of Geneva.

Table S1 SAXS reflections measured for the complex [Eu(**Me_4L**)$(NO_3)_3$].

T / °C	$d_{hkl\,(\text{mes})}$ / Å	*I* /a.u.	00*l*	$d_{hkl\,(\text{calc})}$ / Å	Phase
30	119.38	VS(Sh)	001	117.62	*d* = 117.62 Å
Heating	57.93	S(Sh)	002	58.81	g
	-	-	-	-	
	4.50	S(Br)	-	-	
60	120.19	VS(Sh)	001	117.62	*d* = 117.62 Å
Heating	57.93	S(Sh)	002	58.81	g
	-	-	-	-	
	4.50	S(Br)	-	-	
120	110.42	VS(Sh)	001	109.74	*d* = 109.74 Å
Heating	54.53	S(Sh)	002	54.87	SmA
	-	-	-	-	
	4.50	S(Br)	-	-	
140°C	-	-	-	-	-
Heating	-	-	-	-	N
	-	-	-	-	
	4.50	S(Br)	-	-	
150°C	-	-	-	-	-
Heating	-	-	-	-	I
	-	-	-	-	
	4.50	S(Br)	-	-	
137°C	-	-	-	-	-
Cooling	-	-	-	-	N
	-	-	-	-	
	4.50	S(Br)	-	-	
120°C	110.42	VS(Sh)	001	109.57	*d* = 109.57 Å
Cooling	54.36	S(Sh)	002	54.59	SmA
	-	-	-	-	
	4.50	S(Br)	-	-	
70°C	126.20	VS(Sh)	001	120.46	*d* = 120.46 Å
Cooling	57.36	S(Sh)	002	60.23	g

	-	-	-	-	
	4.50	S(Br)	-	-	
30°C	126.20	VS(Sh)	001	120.28	d = 120.28 Å
Cooling	57.18	S(Sh)	002	60.14	g
	-	-	-	-	
	4.50	S(Br)	-	-	

$d_{hkl(\mathrm{mes})}$ and $d_{hkl(\mathrm{calc})}$ are the measured and calculated diffraction spacing; d is the lattice parameter of the smectic phase ($d = \langle d_{001} \rangle_{(\mathrm{calc})}$). I corresponds to the intensity of the reflections (VS : very strong, S : strong ; Br and Sh stand for broad and sharp, respectively). $d_{001(\mathrm{calc})}$ is calculated according the formula: $\langle d_{001} \rangle_{(\mathrm{calc})} = \frac{1}{2}(d_{001(\mathrm{exp})} + 2\, d_{002(\mathrm{exp})})$ and $d_{002(\mathrm{calc})}$ is calculated according the formula: $\langle d_{002} \rangle_{(\mathrm{calc})} = \frac{1}{2}\,(d_{001(\mathrm{calc})})$.

Table S2 SAXS reflections measured for the complex [Lu(**Me$_4$L**)(NO$_3$)$_3$].

T /°C	$d_{hkl\,(\mathrm{mes})}$ /Å	I /a.u.	00l	$d_{hkl\,(\mathrm{calc})}$ /Å	Phase
30	90.14	S(Br)	-	-	d = 63.15 Å
Heating	63.15	S(Sh)	001	-	g
	9.80	S(Br)	-	-	
	4.35	S(Br)			
	4.50	S(Br)	-	-	
60	88.34	S(Br)	-	-	d = 63.10 Å
Heating	63.10	S(Sh)	001	-	g
	9.80	S(Br)	-	-	
	4.35	S(Br)			
	4.50	S(Br)	-	-	
120	100.39	S(Br)	-	-	d = 58.89 Å
Heating	58.89	S(Sh)	001	-	SmA
	9.80	S(Br)	-	-	
	4.35	S(Br)			
	4.50	S(Br)	-	-	
137°C	9.80	S(Br)	-	-	-
Heating	4.35	S(Br)	-	-	N
	-	-	-		
	4.50	S(Br)	-		
140°C	-	-	-	-	-
Heating	-	-	-	-	I
	-	-	-	-	
	4.50	S(Br)	-	-	
137°C	9.80	S(Br)	-	-	-
Cooling	4.35	S(Br)	-	-	N
	-	-	-	-	
	4.50	S(Br)	-	-	
120°C	98.16	S(Br)	-	-	d = 57.93 Å
Cooling	57.93	S(Sh)	001	-	SmA
	9.80	S(Br)	-	-	
	4.35	S(Br)			

	4.50	S(Br)	-	-	
70°C	91.67	S(Br)	-	-	$d = 62.65$ Å
Cooling	62.65	S(Sh)	001	-	g
	9.80	S(Br)	-	-	
	4.35	S(Br)			
	4.50	S(Br)	-	-	
30°C	92.50	S(Br)	-	-	$d = 61.10$ Å
Cooling	61.10	S(Sh)	001	-	g
	9.80	S(Br)	-	-	
	4.35	S(Br)			
	4.50	S(Br)	-	-	

$d_{hkl(\mathrm{mes})}$ and $d_{hkl(\mathrm{calc})}$ are the measured and calculated diffraction spacing. I corresponds to the intensity of the reflections (VS : very strong, S : strong ; Br and Sh stand for broad and sharp, respectively). d is the lattice parameter of the smectic phase ($d = \langle d_{001} \rangle_{(\mathrm{exp})}$)

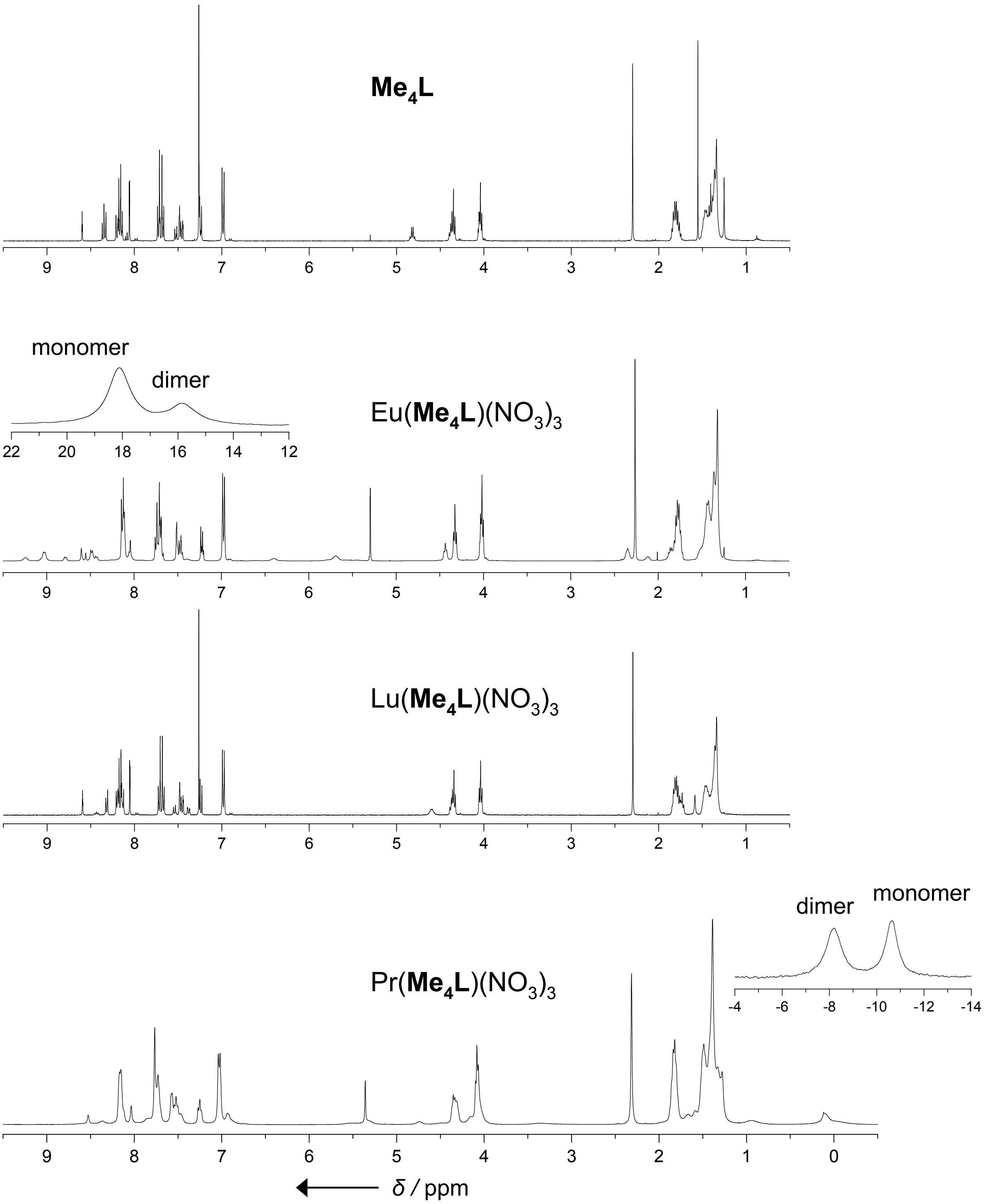


Figure S1 ^{1}H NMR spectra of **Me$_4$L** and of its complexes.

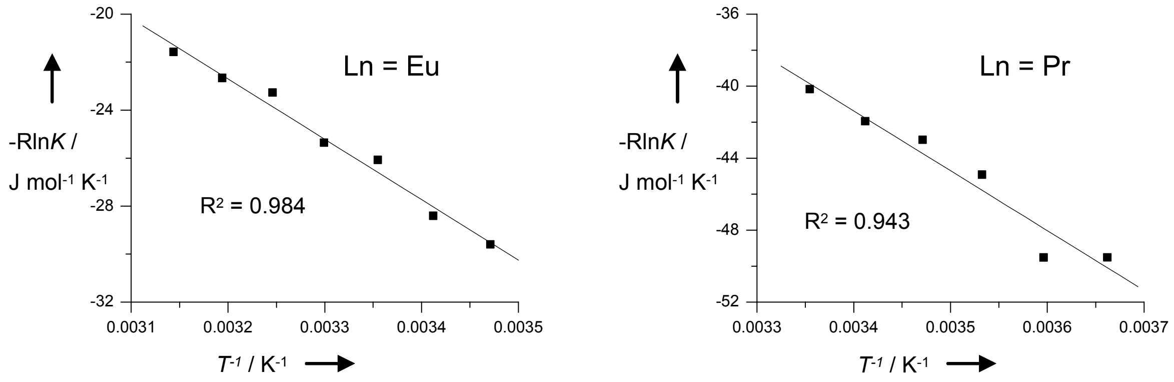


Figure S2 van't Hoff plots for equilibrium 1.

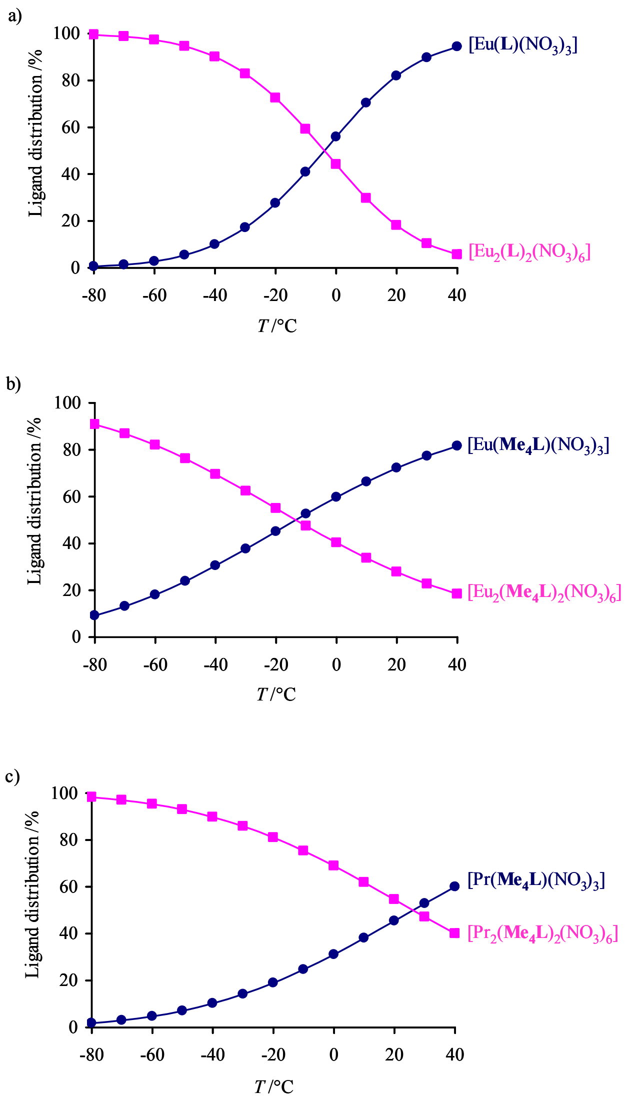


Figure S3 Ligand distribution for equilibrium 1 for the complexes a) [Eu(**L**)$(NO_3)_3$], b) [Eu(**Me$_4$L**)$(NO_3)_3$] and c) [Pr(**Me$_4$L**)$(NO_3)_3$] (CD_2Cl_2, total ligand concentration: 0.01 M).

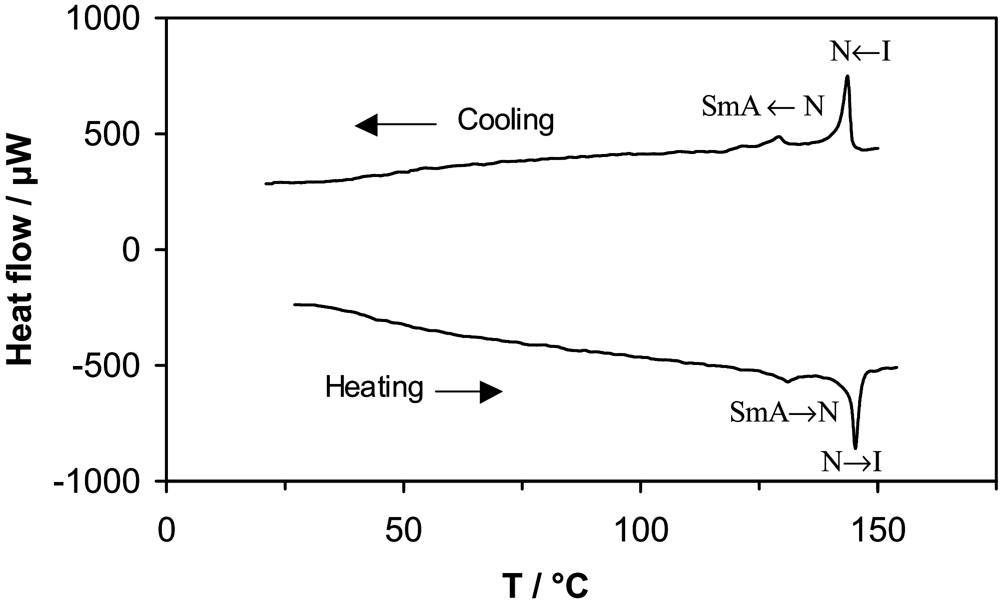
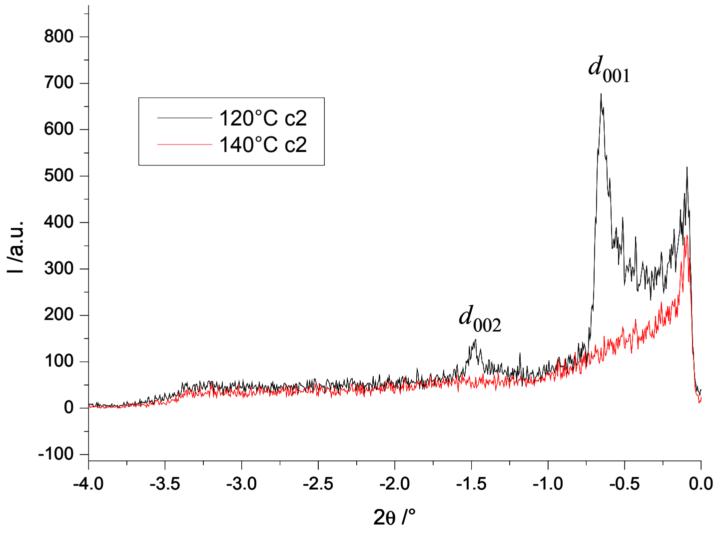


Figure S4 DSC trace of [Lu(**Me$_4$L**)(NO$_3$)$_3$] (5°C/min under N2).

a)



b)

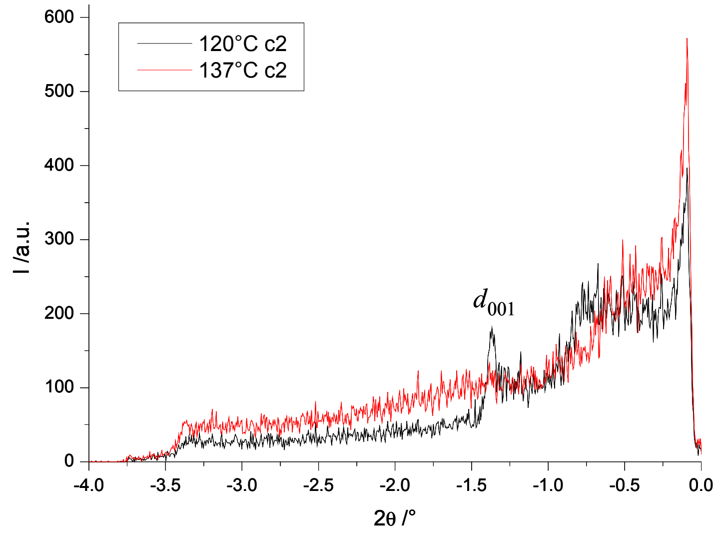


Figure S5 SAXS profiles showing the SmA → N phase transition for a) [Eu(**Me$_4$L**)(NO$_3$)$_3$] and b) [Lu(**Me$_4$L**)(NO$_3$)$_3$].

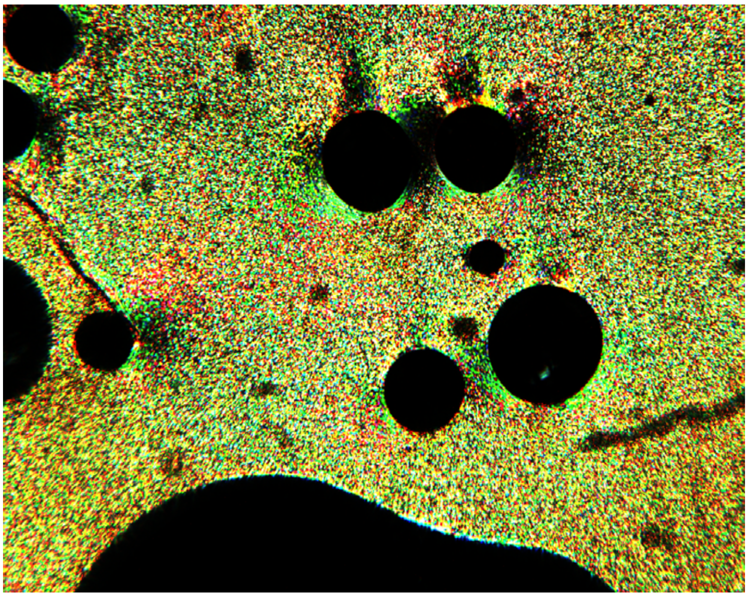


Figure S6 Birefringent texture observed by POM for [Eu(**Me$_4$L**)(NO_3)$_3$] in the nematic mesophase at 141 °C.