Supplementary Material (ESI) for Chemical Communications

Encoding calamitic mesomorphism in thermotropic lanthanidomesogens.

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Electronic Supporting Information (ESI)

(13 pages)

Experimental Section

Solvents, Starting Materials, and Syntheses.

Chemicals were purchased from Fluka AG and Aldrich, and used without further purification unless otherwise stated. The synthons **1**,[1] **4**,[2] and **5** [3] were prepared according to literature procedures. Silicagel (Acros, 0.035-0.07 mm) was used for preparative column chromatography. The nitrate salts $Ln(NO_3)_3{\cdot}xH_2O$ (Ln = Lu, Tb, Gd and Eu, x =1-4) were prepared from the corresponding oxides (Rhodia, 99.99%).[4] The Ln content of solid salts was determined by complexometric titrations with Titriplex III (Merck) in the presence of urotropine and xylene orange.[5] Acetonitrile and dichloromethane were distilled over calcium hydride.

Preparation of synthon 2

To a solution of 4-carboxybenzaldehyde (0.32 g, 2.12 mmol), DCC (1.09 g, 5.30 mmol) and 4-DMAP (catalytic) in CH_2Cl_2 (100 ml), **1** (1.00 g, 2.12 mmol) was added. After 15 minutes stirring at room temperature, the solution was refluxed for 16 hours. The solvent was evaporated, and the solid residue purified by column chromatography (CH_2Cl_2/MeOH 100:0 and then 99.6: 0.4) to give **2** (0.42 g, yield: 33%).

^{1}H NMR in $CDCl_3$: 1.30-1.56 (12H, m) ; 1.78-1.88 (4H, m) ; 4.07 (2H, t, J^3=6.4 Hz) ; 4.38 (2H, t, J^3=6.8 Hz) ; 7.00 (2H, d, J^3=9.2 Hz) ; 7.34 (2H, d, J^3=8.4 Hz) ; 7.66 (2H, d, J^3=8.4 Hz) ; 7.71 (2H, d, J^3=8.4 Hz) ; 7.76 (2H, d, J^3=8.4 Hz) ; 7.97 (2H, d, J^3=8.0 Hz) ; 8.17 (2H, d, J^3=8.8 Hz) ; 8.22 (2H, d, J^3=8.0 Hz) ; 10.13 (1H, s). ^{13}C NMR in $CDCl_3$: (C_{prim}) 26.02 ; 28.67 ; 29.12 ; 29.26 ; 29.35 ; 29.46 ; 29.49 ; 65.77 ; 68.36 (C_{sec}) 114.38 ; 122.59 ; 127.71 ; 128.37 ; 129.53 ; 130.17 ; 132.38 ; 132.68 (C_{tert}) 111.00 ; 118.92 ; 121.24 ; 135.49 ; 136.72 ; 139.10 ; 144.88 ; 151.60 ; 163.71 ; 164.85 ; 165.65 ; 191.69 (C_{quat}). ESI-MS (CH_2Cl_2/MeOH 9:1): m/z = 626.5 ($[M+Na]^+$).

Preparation of synthon 3

2 (0.35 g, 0.58 mmol), $NaClO_2$ (0.20 g, 2.19 mmol) and H_2NSO_3H (0.21 g, 2.19 mmol) were dissolved in a THF/H_2O (1:1) mixture (100 ml). The solution was stirred at room temperature for 2 hours. THF was evaporated under vacuum. The aqueous phase was extracted with hot CH_2Cl_2 (100

ml) in order to avoid precipitation. The organic phase was dried with anhydrous Na_2SO_4 and filtered. Evaporation to dryness gave **3** (0.35 g, yield: 97%).

^{1}H NMR in d^6-DMSO : 1.26-1.47 (12H, m) ; 1.69-1.77 (4H, m) ; 4.08 (2H, t, J^3=6.4 Hz) ; 4.30 (2H, t, J^3=6.4 Hz) ; 7.13 (2H, d, J^3=8.8 Hz) ; 7.42 (2H, d, J^3=8.8 Hz) ; 7.85 (2H, d, J^3=8.4 Hz) ; 7.91-7.97 (4H, m) ; 8.07 (4H, s) ; 8.09 (2H, d, J^3=8.8 Hz) 13.36 (1H, br). ^{13}C NMR in $CDCl_3$: (C_{prim}) 26.01 ; 28.66 ; 29.11 ; 29.24 ; 29.34 ; 29.44 ; 29.47 ; 65.71 ; 68.36 (C_{sec}) 114.38 ; 122.60 ; 127.72 ; 128.37 ; 129.64 ; 130.18 ; 132.39 ; 132.68 (C_{tert}) 111.00 ; 118.92 ; 121.22 ; 132.80 ; 135.11 ; 136.73 ; 144.90 ; 151.59 ; 163.71 ; 164.89 ; 165.76 ; 170.47 (C_{quat}). ESI-MS (CH_2Cl_2/MeOH 9:1): *m/z* = 642.5 ($[M+Na]^+$).

Preparation of synthon 6

5 (1.00 g, 0.67 mmol), $NaClO_2$ (0.23 g, 2.50 mmol) and H_2NSO_3H (0.24 g, 2.50 mmol) were dissolved in a THF / H_2O (2:1) mixture (50 ml). The solution was stirred at room temperature for 2 hours. THF was evaporated under vacuum. The aqueous phase was extracted with CH_2Cl_2 (100 ml). The organic phase was dried with anhydrous Na_2SO_4 and filtered. Evaporation to dryness followed by precipitation (dissolution in CH2Cl2 and precipitation by pouring the solution into MeOH) gave **6** (1.01 g, yield: 100%).

^{1}H NMR in $CDCl_3$: 1.37-1.49 (36H, m) ; 1.77-1.90 (12H, m) ; 4.06 (6H, t, J^3=6.8 Hz) ; 4.38 (6H, t, J^3=6.8 Hz) ; 6.97 (4H, d, J^3=8.8 Hz) ; 6.98 (2H, d, J^3=9.2 Hz) ; 7.33 (4H, d, J^3= 8.8 Hz) ; 7.64 (4H, d, J^3=8.8 Hz) ; 7.71 (4H, d, J^3=8.4 Hz) ; 7.74 (4H, d, J^3=8.8 Hz) ; 8.09 (2H, d, J^4=1.2 Hz) ; 8.14-8.20 (10H, m) ; 8.62 (1H, t, J^4=1.2 Hz). ^{13}C NMR in $CDCl_3$: (C_{prim}) 25.98 ; 26.01 ; 28.67 ; 29.11 ; 29.26 ; 29.36 ; 29.45 ; 29.49 ; 65.70 ; 65.81 ; 68.37 ; 68.40 (C_{sec}) 114.40 ; 114.47 ; 122.60 ; 127.37 ; 127.70 ; 127.95 ; 128.36 ; 129.62 ; 130.15 ; 132.38 ; 132.47 ; 132.67 (C_{tert}) 100.01 ; 110.98 ; 118.91 ; 120.76 ; 121.19 ; 132.35 ; 132.99 ; 135.01 ; 136.68 ; 144.86 ; 151.11 ; 151.60 ; 163.73 ; 163.89 ; 164.59 ; 164.88 ; 165.15 ; 165.78 ; 170.42 (C_{quat}). ESI-MS (CH_2Cl_2/MeOH 9:1): *m/z* = 1538.8 ($[M+Na]^+$).

Preparation of L3.

4 (0.097 g, 0.24 mmol) was added to a solution of **3** (0.30 g, 0.48 mmol), EDCI (0.19 g, 0.97 mmol) and 4-DMAP (catalytic) in CH_2Cl_2 (50 ml). After 15 minutes stirring at room temperature, the solution was refluxed for 12 hours under an inert atmosphere. The solvent was evaporated and the organic residue redissolved in CH_2Cl_2 (100 ml). The organic phase was washed with water (3 x 100 ml), dried with anhydrous Na_2SO_4, filtered and evaporated under vacuum. The residue was purified by column chromatography (CH_2Cl_2/MeOH 100:0, 99.5:0.5, 99.3:0.7 and finally 99:1) to give L3 (0.30 g, yield: 77%).

^{1}H NMR in $CDCl_3$: 1.39-1.47 (16H, m) ; 1.43 (6H, t, J^3=7.2 Hz) ; 1.47-1.52 (8H, m) ; 1.81-189 (8H, m) ; 4.08 (4H, t, J^3=6.8 Hz) ; 4.41 (4H, t, J^3=6.8 Hz) ; 4.83 (4H, q, J^3=7.2 Hz) ; 7.02 (4H, d, J^3=8.8 Hz) ; 7.26 (2H, dd, J^3=8.8 Hz, J^4=2.0 Hz) ; 7.35 (4H, d, J^3=8.8 Hz) ; 7.54 (2H, d, J^3=8.8 Hz) ; 7.66 (4H, d, J^3=8.8 Hz) ; 7.70 (4H, d, J^3=8.4 Hz) ; 7.74 (2H, d, J^4=2.0 Hz) ; 7.75 (4H, d, J^3=8.4 Hz) ; 8.11 (1H, t, J^3=8.0 Hz) ; 8.17 (4H, d, J^3=9.2 Hz) ; 8.22 (4H, d, J^3=8.4 Hz) ; 8.37 (4H, d, J^3=8.4 Hz) ; 8.38 (2H, d, J^3=8.0 Hz). ^{13}C NMR in $CDCl_3$: 15.53 (C_{prim}) 26.02 ; 26.04 ; 28.69 ; 29.12 ; 29.28 ; 29.36 ; 29.47 ; 29.50 ; 40.13 ; 65.73 ; 68.37 (C_{sec}) 110.67 ; 112.92 ; 114.39 ; 118.05 ; 122.60 ; 126.13 ; 127.71 ; 128.37 ; 129.71 ; 130.23 ; 132.38 ; 132.67 ; 138.38 (C_{tert}) 111.00 ; 118.92 ; 121.22 ; 133.34 ; 134.89 ; 136.72 ; 144.89 ; 146.78 ; 151.59 ; 163.71 ; 164.87 ; 165.04 ; 165.83 (C_{quat}). ESI-MS (CH_2Cl_2/MeOH 9:1): *m/z* = 1603.8 ($[M+H]^+$). Anal Calcd for $C_{99}H_{91}N_7O_{14}\cdot 1.3\ H_2O$: C, 73.14; H, 5.80; N, 6.03. Found : C, 73.15; H, 5.84; N 5.91.

Preparation of L4.

4 (0.040 g, 0.10 mmol) was added to a solution of **6** (0.30 g, 0.20 mmol), EDCI (0.076 g, 0.40 mmol) and 4-DMAP (catalytic) in CH_2Cl_2 (50 ml). After 15 minutes stirring at room temperature, the solution was refluxed for 12 hours under an inert atmosphere. The solvent was evaporated and the organic residue redissolved in CH_2Cl_2 (100 ml). The organic phase was washed with water (4 x 100 ml), dried with anhydrous Na_2SO_4, filtered and then evaporated under vacuum. The residue was purified by column chromatography (CH_2Cl_2:MeOH 100:0 and finally 99.5:1.5). The product was

dissolved in a minimum volume of CH_2Cl_2 and poured into acetone. Pure L4 was filtered and dried under vacuum at 100 °C (0.024 g, yield: 70%).

^{1}H NMR in $CDCl_3$: 1.31-1.57 (72H, m) ; 1.45 (6H, t, J^3=7.2 Hz) ; 1.77-1.91 (24H, m) ; 4.04-4.09 (12H, m) ; 4.36-4.42 (12H, m) ; 4.85 (4H, q, J^3=7.2 Hz) ; 7.00 (8H, d, J^3= 8.8 Hz) ; 7.01 (4H, d, J^3=8.4 Hz) ; 7.28 (2H, dd, J^3=8.8 Hz, J^4=2.0 Hz) ; 7.33 (8H, d, J^3=8.4 Hz) ; 7.54 (2H, d, J^3=8.8 Hz) ; 7.64 (8H, d, J^3=8.4 Hz) ; 7.71 (8H, d, J^3=8.4 Hz) ; 7.74 (2H, d, J^4=2.0 Hz) ; 7.75 (8H, d, J^3=8.4 Hz) ; 8.08 (2H, d, J^4=1.2 Hz) ; 8.11 (1H, t, J^3=8.0 Hz) ; 8.18 (12H, d, J^3=8.8 Hz) ; 8.23 (4H, d, J^3=8.4 Hz) ; 8.37 (4H, d, J^3=8.4 Hz) ; 8.40 (2H, d, J^3=8.0 Hz). ^{13}C NMR in $CDCl_3$: 0.98 (C_{prim}) 15.45 ; 25.90 ; 25.92 ; 25.96 ; 25.97 ; 28.61 ; 28.63 ; 29.04 ; 29.18 ; 29.22 ; 29.28 ; 29.31 ; 29.37 ; 29.41 ; 29.44 ; 40.02 ; 65.64 ; 65.70 ; 68.31 ; 68.35 (C_{sec}) 110.56 ; 112.92 ; 114.33 ; 114.41 ; 117.87 ; 122.52 ; 125.95 ; 127.28 ; 127.64 ; 127.87 ; 128.29 ; 129.65 ; 130.16 ; 132.31 ; 132.39 ; 132.61 ; 138.25 (C_{tert}) 110.96 ; 118.83 ; 120.73 ; 121.17 ; 134.07 ; 136.64 ; 143.18 ; 144.82 ; 150.97 ; 151.06 ; 151.56 ; 163.66 ; 163.84 ; 164.51 ; 164.78 ; 164.97 ; 165.05 ; 165.76 (C_{quat}). Anal Calcd for $C_{209}H_{209}N_9O_{34}\cdot 1.39\ H_2O$: C, 73.49; H, 6.25; N, 3.69. Found : C, 73.49; H, 6.23; N 3.57.

Preparation of the Complexes [Ln(L*i*)(NO$_3$)$_3$] (Ln = Lu, Tb, Gd and Eu, *i* = 3, 4)

L1 (1.0 equivalent, typically 100 mg) in dichloromethane (5 mL) was added to one equivalent $Ln(NO_3)_3\cdot xH_2O$ (Ln = Lu, Tb, Gd and Eu, 1.0 equivalent) in acetonitrile (5 mL). After 1 h. stirring at RT, the dichloromethane was evaporated and the white precipitate was filtered, washed with CH_3CN and dried to give 80-90 % of [Ln(L*i*)(NO$_3$)$_3$] (Ln = Lu, Tb, Gd and Eu, *i* = 3, 4) containing variable quantities of co-crystallized water molecules. All the complexes were characterized by IR spectra and elemental analyses (Table S1).

Spectroscopic and Analytical Measurements.

^{1}H and ^{13}C NMR spectra were recorded at 25 °C on a Bruker Avance 400 MHz spectrometer. Chemical shifts are given in ppm with respect to TMS. Diffusion experiments were recorded at 400-MHz-proton-Larmor frequency at room temperature. The sequence corresponds to Bruker pulse program *ledbpgp2s* [6] using stimulated echo, bipolar gradients and longitudinal eddy current

delay as z filter. The four 2 ms gradients pulses have sine-bell shapes and amplitudes ranging linearly from 2.5 to 50 G/cm in 16 steps. The diffusion delay was 100 ms and the number of scan 16. The processing was done using a line broadening of 5 Hz and the diffusion rates calculated using the Bruker processing package. Pneumatically-assisted electrospray (ESI-MS) mass spectra were recorded from 10^{-4} mol·dm^{-3} solutions on a Finnigan SSQ7000 instrument. 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 SA-XRD patterns were obtained with three different experimental set-ups. In all cases, a linear monochromatic Cu-Kα beam (λ = 1.5405 Å) was obtained using a sealed-tube generator (900 W) equipped with a bent quartz monochromator. In the first set, the transmission Guinier geometry was used, whereas a Debye-Scherrer-like and a flat film geometry were used in the second and third experimental set-ups, respectively. In all cases, the crude powder was filled in Lindemann capillaries of 1 mm diameter and 10 mm wall-thickness. An initial set of diffraction patterns was recorded on an image plate; periodicities up to 80 Å can be measured, and the sample temperature controlled to within ±0.3 °C from 20 to 350 °C. The second set of diffraction patterns was recorded with a curved Inel CPS 120 counter gas-filled detector linked to a data acquisition computer; periodicities up to 60 Å can be measured, and the sample temperature controlled to within ±0.05 °C from 20 to 200°C. Finally, the last set of diffraction patterns was recorded on image plate, and periodicities up to 350 Å can be measured, and the sample temperature controlled to within ±0.01 °C from 20 to 200°C. In each case, exposure times were varied from 1 to 24 h. Elemental analyses were performed by Dr. H. Eder from the microchemical Laboratory of the University of Geneva.

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Table S1 Elemental Analyses for the Complexes [Ln(L*i*)$(NO_3)_3$], (*i* = 3, 4, Ln = Lu, Tb, Gd and Eu).

Compd	%C found	%H found	%N found	%C calc	%H calc	%N calc
[Lu(L3)$(NO_3)_3$]·2.1 H_2O	59.40	4.85	6.97	59.39	4.85	6.97
[Eu(L3)$(NO_3)_3$]	61.15	4.98	7.08	61.27	4.73	7.22
[Lu(L4)$(NO_3)_3$] 3.6 H_2O	65.78	5.61	4.29	65.78	5.71	4.40
[Tb(L4)$(NO_3)_3$] 3.6 H_2O	66.08	5.71	4.18	66.07	5.73	4.42
[Gd(L4)$(NO_3)_3$] 3.6 H_2O	66.09	5.76	4.41	66.09	5.73	4.42
[Eu(L4)$(NO_3)_3$] 2.7 H_2O	66.15	5.71	4.28	66.15	5.71	4.28

Table S2 ^{1}H NMR shifts for the aromatic protons in the ligands L1, L3 and L4, and in their complexes [Ln(L*i*)$(NO_3)_3$] (CD_2Cl_2, 293 K).

Compd	H1	H2	H6	H7	H9
L1	8.05	8.32	7.48	7.18	7.64
[Lu(L1)$(NO_3)_3$]	8.51	8.23	7.56	7.41	8.12
L3	8.11	8.38	7.54	7.26	7.74
[Lu(L3)$(NO_3)_3$]	8.53	8.24	7.68	7.46	7.77
L4	8.11	8.40	7.54	7.28	7.74
[Lu(L4)$(NO_3)_3$]	8.53	8.23	7.68	7.45	7.76

Table S3 Indexation at a given temperature (T/°C) for the Reflections Detected in the Liquid-Crystalline Phases by SA-XRD for the Complexes [Ln(L4)$(NO_3)_3$] (Ln = Lu, Tb, Eu and Gd).

	T /°C	$d_{00l(\mathrm{mes})}$/Å	I /au	00l	A / Å$^{2\,a}$
[Lu(L4)$(NO_3)_3$]	100	128.0	S	001	46.5
	Heating	64.0	S	002	
		8.9	Br		
		4.5	Br		
	120	126.2	S	001	47.8
	Heating	63.1	S	002	
		8.9	Br		
		4.5	Br		
	140-160	Cryst.			
	Heating				
	190	110.4	S	001	57.3
	Heating	55.2	S	002	
		4.5	Br		

	T /°C	$d_{00l(\mathrm{mes})}$/Å	I /au	00l	A / Å$^{2\,a}$
[Tb(L4)$(NO_3)_3$]	100	128.0	S	001	46.5
	Heating	64.0	S	002	
		4.5	Br		
	120	125.4	S	001	48.1
	Heating	62.7	S	002	
		4.5	Br		
	140	121.0	S	001	50.5
	Heating	60.5	S	002	
		4.5	Br		
	160	111.8	S	001	55.5
	Heating	55.9	S	002	
		4.5	Br		
	180	107.0	S	001	58.7
	Heating	53.5	S	002	
		4.5	Br		

	T /°C	$d_{00l(\mathrm{mes})}$/Å	I /au	00l	A / Å$^{2\,a}$
[Gd(L4)(NO$_3$)$_3$]	100	130.0	S	001	45.8
	Heating	65.0	S	002	
		4.5	Br		
	120	126.2	S	001	47.8
	Heating	63.1	S	002	
		4.5	Br		
	140	119.4	S	001	51.2
	Heating	59.7	S	002	
		4.5	Br		
	160	112.6	S	001	55.1
	Heating	56.3	S	002	
		4.5	Br		

	T /°C	$d_{00l(\mathrm{mes})}$/Å	I /au	00l	A / Å$^{2\,a}$
[Eu(L4)(NO$_3$)$_3$]	100	123.6	S	001	48.1
	Heating	61.8	S	002	
		4.5	Br		
	120	125.4	S	001	48.1
	Heating	62.7	S	002	
		4.5	Br		
	140	121.0	S	001	50.5
	Heating	60.5	S	002	
		4.5	Br		
	160	117.0	S	001	53.0
	Heating	58.5	S	002	
		4.5	Br		
	180	105.2	S	001	59.7
	Heating	52.6	S	002	
		4.5	Br		

[a] Molecular area $A = V/d_{001}$ with $V = MM_{\mathrm{complex}}\cdot\lambda\cdot10^{-24}/d\cdot N_{\mathrm{av}}$, ($MM_{\mathrm{complex}}$, molecular weight of the complex, N_{av}, Avogadro's number,and $\lambda = V_{CH2}(T)/V_{CH2}(T^0)$, where $V_{CH2}(T) = 0.02023T + 26.5616$ (T in °C), and $T^0 = 25$°C, T temperature of the experiment).[13]

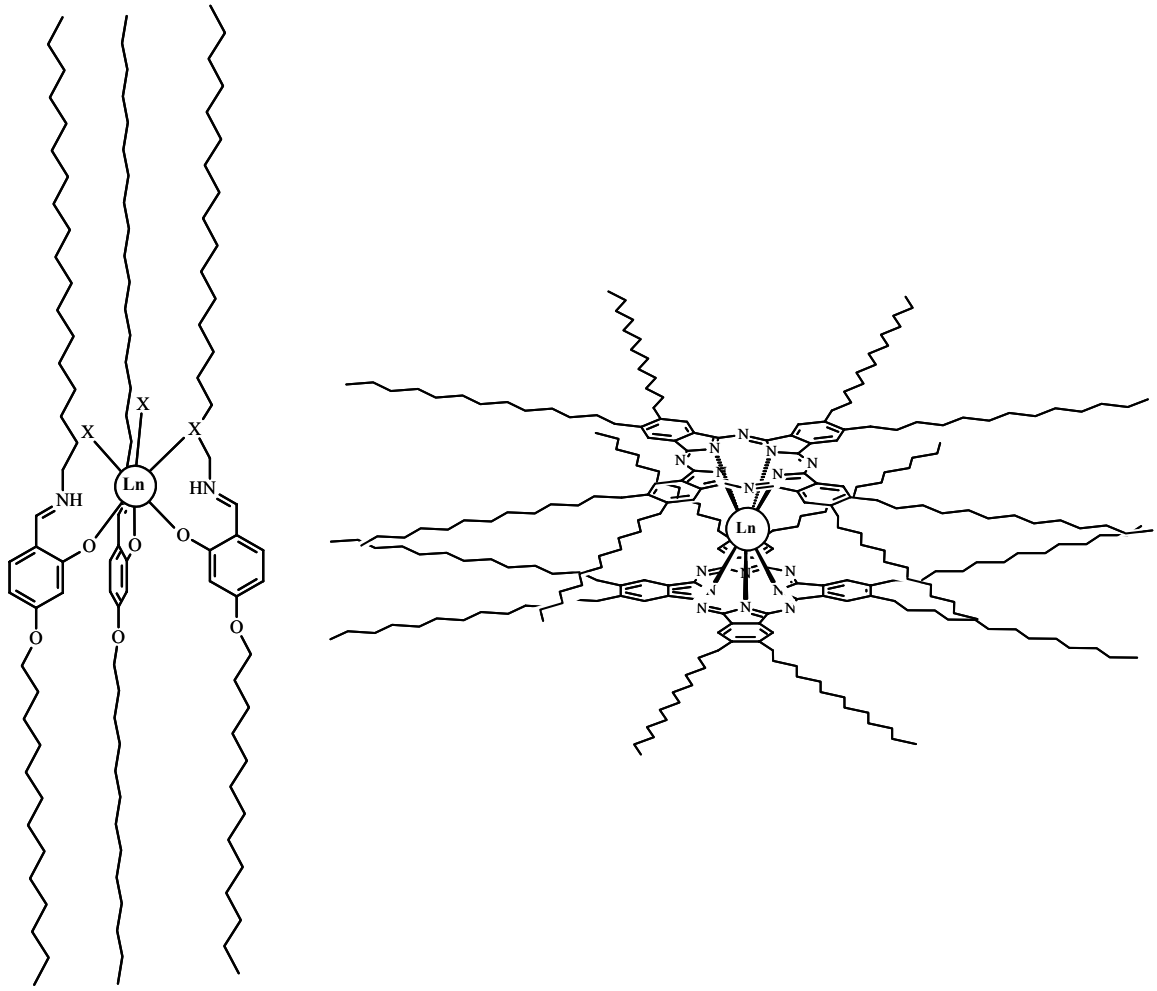

Figure S1 Two examples of lanthanidomesogens obtained for complexes, in which the trivalent lanthanide is embedded within aromatic polarizable cavities.

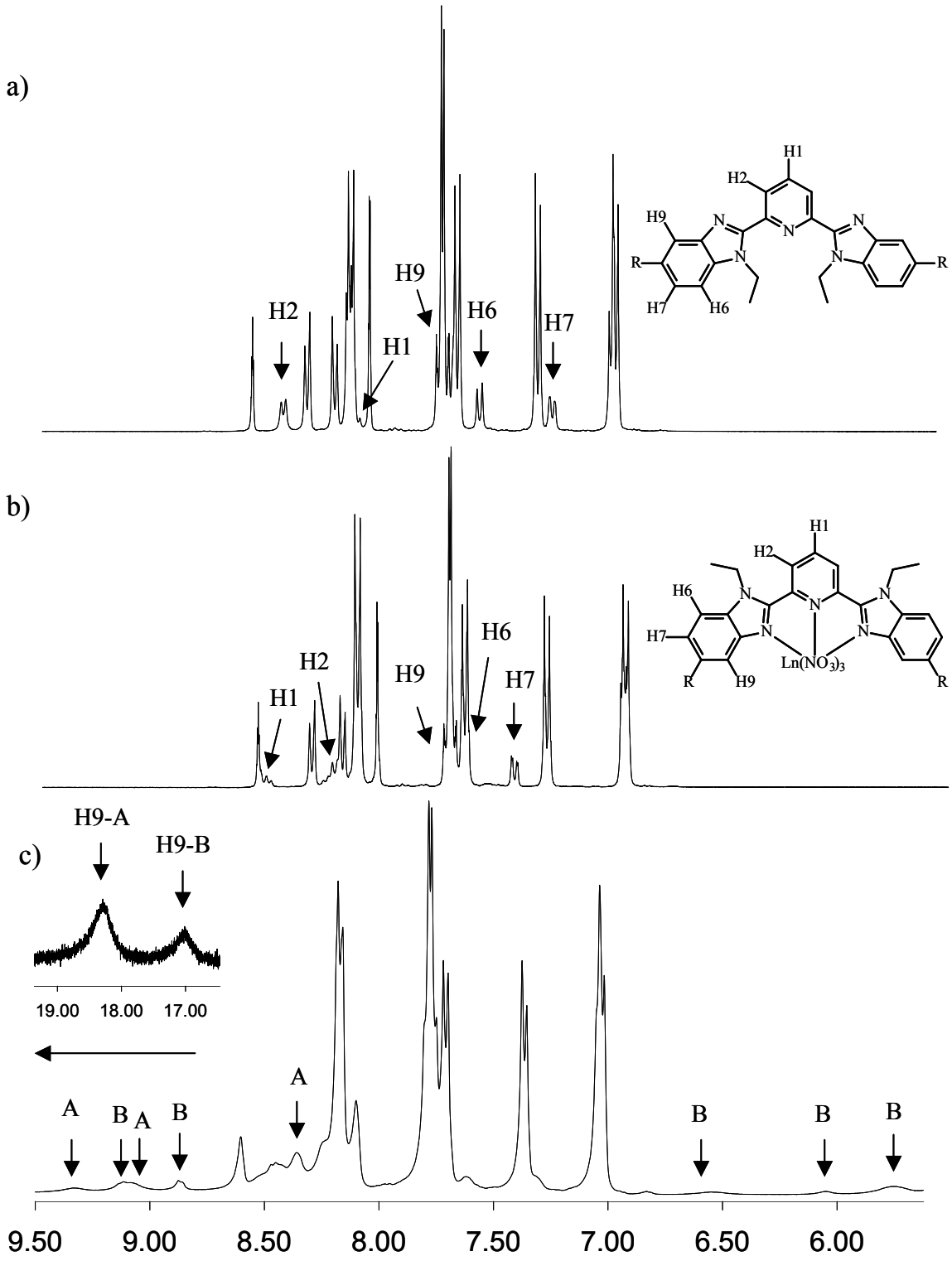

Figure S2 : ^{1}H NMR spectra of a) L4, b) [Lu(L4)$(NO_3)_3$] and c) [Eu(L4)$(NO_3)_3$].

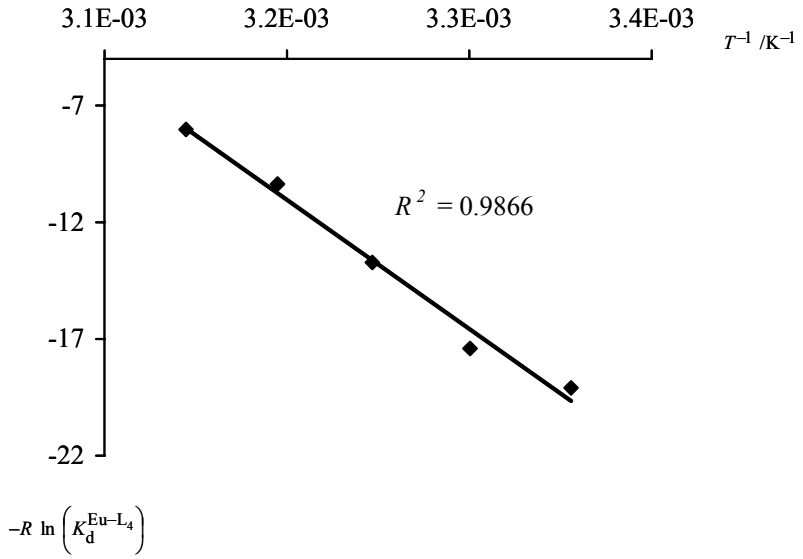

Figure S3 Van't Hoff plot $-R\cdot\ln(K_d^{Eu,L4})$ versus T^{-1}, from which the thermodynamic parameters $\Delta H_d^{Eu,L4}$ = -55(4) kJ·mol^{-1} and $\Delta S_d^{Eu,L4}$ = -166(11) J·mol^{-1}·K^{-1} can be determined

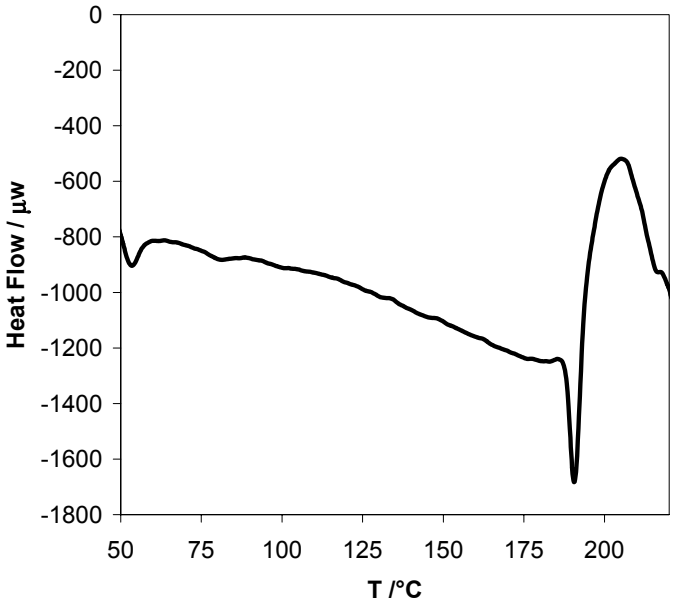

Figure S4 DSC trace recorded for the complex [Eu(L4)$(NO_3)_3$] during a single heating process.

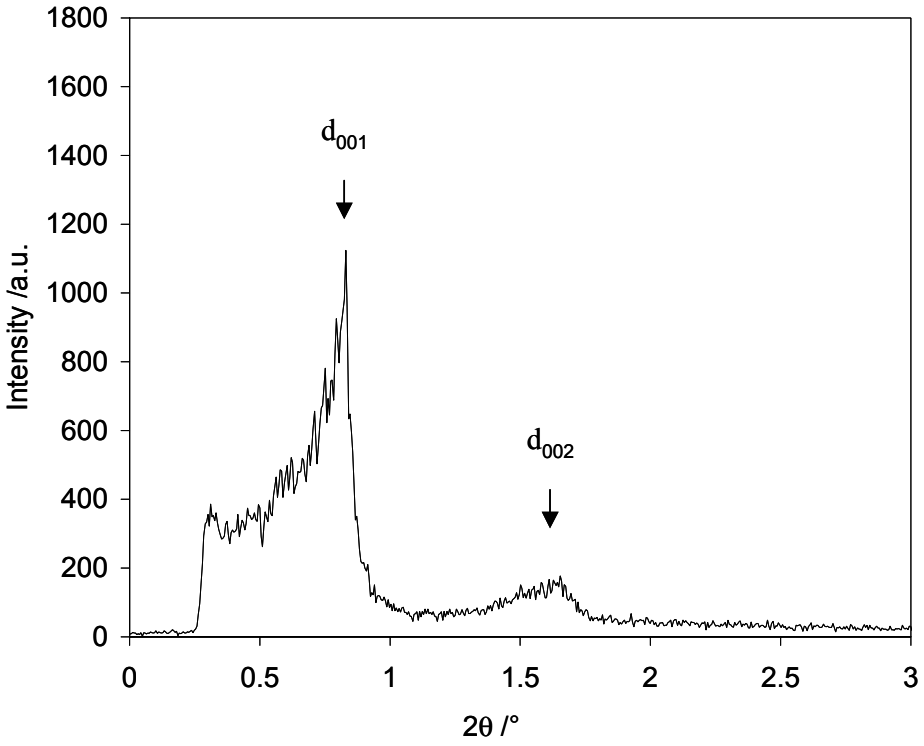

Figure S5 SA-XRD profile in liquid crystalline phase, and associated indexation for [Eu(L4)$(NO_3)_3$] at 160°C.