Lanthanide luminescent mesomorphic complexes with macrocycles derived from diaza-18-crown-6

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Electronic Supplementary Information (5 pages)

R	H ^{1,1'} free		H ^{1,2} _{bound} ^a				H ^{2,2'} free	
	7.45	ppm	7.35 ppm		7.25 ppm		7.16 ppm	
	L3	L4	L3	L4	L3	L4	L3	L4
0.0	3.98	4.0	0	0	0	0	3.95	4.00
0.1	3.74	3.86	0.27	0.12	0.33	0.18	3.73	3.91
0.2	3.48	3.50	0.52	0.43	0.56	0.50	3.47	3.58
0.3	3.20	3.17	0.82	0.76	0.87	0.84	3.19	3.24
0.4	2.79	2.85	1.08	1.09	1.13	1.20	2.71	2.88
0.5	2.57	2.55	1.43	1.41	1.47	1.48	2.56	2.59
0.6	2.23	2.22	1.78	1.75	1.81	1.80	2.22	2.25
0.7	1.90	1.90	2.12	2.00	2.15	2.11	1.90	1.94
0.8	1.58	1.59	2.42	2.34	2.47	2.47	1.60	1.64
0.9	1.31	1.28	2.67	2.65	2.69	2.76	1.32	1.32
1.0	1.05	1.01	2.97	2.93	2.97	3.01	1.05	1.02
1.2	0.48	0.49	3.41	3.43	3.49	3.50	0.49	0.56
1.5	0.16	0.34	3.82	3.69	3.88	3.79	0.15	0.27
2.0	0	0.22	3.93	3.68	4.02	3.90	0	0.14
3.0	0	0.16	3.92	3.80	4.02	3.99	0	0.07
4.0	0	0.1	3.93	3.85	4.08	4.02	0	0.00

Table S1 Integrated intensity of the resonances from the aromatic protons of the free and complexed ligands L3 and L4, versus $R = [La]_{tot}/[L]_{tot}$ in deuterated THF at 298 K.

^a Assignment of protons H¹ and H² uncertain

Complex	$E(^{1}\pi\pi^{*})$ /	$E(^{3}\pi\pi^{*})$ /	Complex	$E(^{1}\pi\pi^{*})$ /	$E(^{3}\pi\pi^{*})$ /
	cm ⁻¹	cm ⁻¹		cm ⁻¹	cm ⁻¹
$La(CF_3SO_3)_3L1$	26 520	20 660	$Tb(NO_3)_3L3$	29 410	b
Eu(CF ₃ SO ₃) ₃ L1	26 520	21 280	EuCl ₃ L3	30 500	b
	20 740 sh			29 970 sh	
$La(NO_3)_3L2$	29 500	20 530	$Eu(CF_3SO_3)_3L3$	а	b
$Eu(NO_3)_3L2$	а	b	$La(NO_3)_3L4$	29 580	21 400
$La(NO_3)_3L3$	30 500 sh	21 400	$Nd(NO_3)_3L4$	а	20 920
	29 770				
	28 780 sh				
$Nd(NO_3)_3L3$	29 290	20 910	$Eu(NO_3)_3L4$	а	Ь
$Eu(NO_3)_3L3$	29 590	b	Eu(NO ₃) ₃ L5	27 320	20 200
				23 700 sh	
				22420 sh	
				20 580 sh	

Table S2. Energy of the singlet and triplet states of the ligands in the complexes (solid state samples, 77 K).

Table S3. SAXS pattern of Eu(NO₃)₃L3 in its hexagonal columnar phase (Col_H).

$2 heta_{ m obs}/^0$	$d_{\rm obs}$	d_{calc}	Intensity ^a	hk
3.49	25.3	25.15	S	10
6.08	14.5	14.5	VW	11
7.05	12.5	12.55	VW	20
9.6	4.6		d	diffuse

^a s = intense ; vw = very weak; d = very weak and diffuse



Figure S1. Plot of the integrated intensity of the resonances from bound ligand assigned to $H^{1,1'}+H^{2,2'}$ versus the ratio $R = [La]_{tot}/[L]_{tot}$, in deuterated THF at 298 K.



Figure S2. Absorption spectra of the ligands at 298 K.



Figure S3. Emission spectra of the complexes at 77 K (solid state samples, excitation on ligand bands).



Figure S4. Thermogravimetric analysis of the $Eu(NO_3)_3L3 \cdot 0.5H_2O$ complex showing the loss of water and the decomposition above 200 °C