

Toward lanthanide-containing metallomesogens with tridentate ligands

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Tridentate aromatic receptors L¹–L⁴ containing the 2,6-bis(benzimidazol-2-yl)pyridine chelating unit are designed to exhibit thermotropic calamitic liquid-crystalline phases; the mesomorphic behaviour is essentially retained in the complex [LnL²(NO₃)₃].

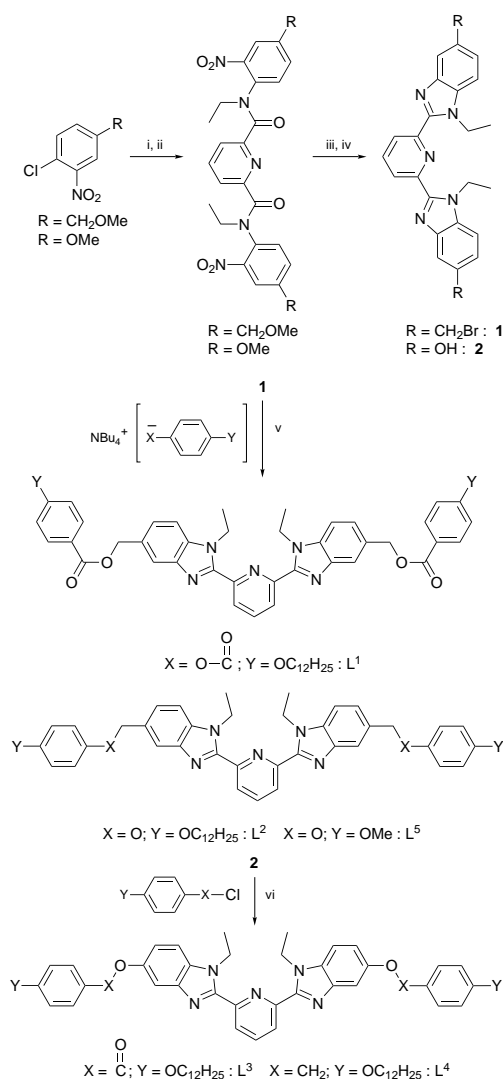
We have recently launched into a research program aimed at developing lanthanide building blocks with tailored tridentate binding units.¹ It is now possible to finely control and tune the

thermodynamic, structural, electronic and magnetic properties of the resulting mononuclear 1 : 1 and 1 : 3 complexes.^{2–4} The incorporation of these building blocks into extended organized polynuclear architectures has been demonstrated,^{4–6} but this approach is severely limited by the large amount of structural information required by segmental ligands for the selective recognition of 4f-block metal ions.^{5,6} An alternative approach could take advantage of the molecular order associated with liquid-crystalline phases. Only a few lanthanide-containing metallomesogens have been prepared⁷ and none with tridentate ligands, most likely as a consequence of their bent arrangement which results upon coordination.

We report here on the design of semi-rigid tridentate receptors tailored for the preparation of calamitic lanthanide-containing liquid crystals. Substituted 2,6-bis(1'-ethylbenzimidazol-2'-yl)pyridine binding units (L¹–L⁴) have been selected for their peculiar electronic and structural properties which fit the Ln^{III} stereochemical preferences, leading to stable complexes with predetermined properties.^{3,8} Semi-rigid lipophilic substituents have been connected to the 5-positions of the benzimidazole rings in order (i) to extend the rigid core and the axial anisotropy, (ii) to improve intermolecular interactions and (iii) to limit the stability of the crystalline phase owing to flexible lipophilic chains. The spacers between the tridentate unit and the *para*-substituted phenyl side-arms are crucial since they must be flexible enough to allow the ligands to adopt suitable conformations in the free form (*trans–trans*)⁵ and in the complexes (*cis–cis*), and rigid enough to ensure a rod-like shape compatible with the formation of calamitic mesophases. The synthons **1** and **2** are obtained in satisfying yields (28 and 38%, respectively) according to a multistep strategy based on the recently developed cyclisation of unsymmetrical benzimidazole rings from *N*-(2-nitroaryl)arenecarboxamide (Scheme 1).⁹ Nucleophilic substitutions using **1** as electrophile give L¹, L² and L⁵. Deprotonation of **2** with NBu₄OH followed by alkylation or acylation provides the ligands L³ and L⁴.

¹H NMR nuclear Overhauser enhancement effects (NOE) in solution suggest that the tridentate units adopt the expected *trans–trans* conformation in all free ligands L¹–L⁵, which is confirmed in the solid state by the crystal structure of the non-mesogenic model compound L⁵ [N(4) is *trans* to N(3) and N(1) is *trans* to N(3), Fig. 1].[†] All C–C, C–N and C–O bonds are standard¹⁰ and the C_{ar}–C–O–C_{ar} atoms of the two spacers adopt all-*trans* conformations leading to an approximate rod-like shape of the receptor (Fig. 1). Reaction of L² with stoichiometric amounts of Ln(NO₃)₃ (Ln = La, Lu) in acetonitrile produces quantitatively the complexes [LnL²(NO₃)₃]*n*H₂O (Ln = La, *n* = 3; Ln = Lu, *n* = 1) where Ln^{III} is nine-coordinated by the tridentate aromatic unit which adopts the *cis–cis* conformation (NOE effects observed between H³⁸–H¹⁷) and three bidentate nitrate anions as similarly reported for the analogous complexes with unsubstituted 2,6-bis(1'-alkylbenzimidazol-2'-yl)pyridine ligands.^{8,11}

The thermal and liquid-crystal properties were investigated by a combination of differential scanning calorimetry (DSC)



Scheme 1 Reagents: i, EtNH₂, EtOH; ii, pyridine-2,6-dicarbonyldichloride, NEt₃, CH₂Cl₂; iii, Fe, HCl–EtOH–H₂O; iv, BBr₃, CH₂Cl₂; v, CH₂Cl₂; vi, NBu₄OH, CH₂Cl₂

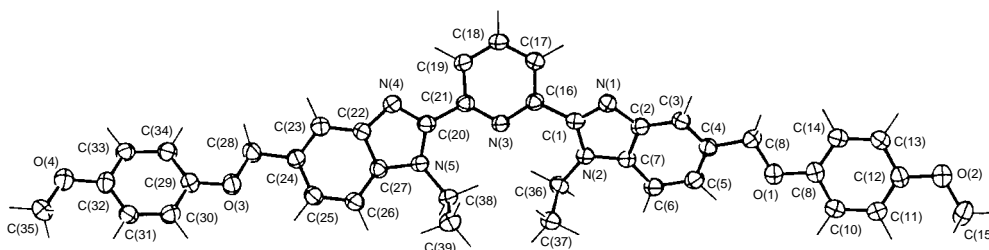


Fig. 1 ORTEP¹⁵ view of the ligand L⁵ with ellipsoids represented at 50% probability level

Table 1 Phase-transition temperatures and enthalpy and entropy changes for ligands L¹–L⁴ and complex [LuL²(NO₃)₃·H₂O]

Compound	Transition ^a	T/°C	ΔH/kJ mol ⁻¹	ΔS/J mol ⁻¹ K ⁻¹
L ¹	K–I	107	80	211
L ²	K–S _A	132	50	122
	(S _C –S _A) ^b	98	— ^c	—
L ³	S _A –I	188	17	37
	K–S _C	131	35	86
	S _C –S _A	217	— ^c	—
	S _A –N	223	— ^d	—
L ⁴	N–I	226	7 ^e	14 ^e
	K–S _A	144	28	66
	(S _C –S _A) ^b	107 ^f	—	—
[LuL ² (NO ₃) ₃]	S _A –I	193	18	39
	K–S _A	133	72	176
	(S _C –S _A) ^b	98	— ^c	—
	S _A –I	188	23	50

^a K = crystal, S_C = smectic C phase, S_A = smectic A phase, N = nematic phase, I = isotropic fluid; temperatures are given as the onset of the peak (Seiko DSC 220C differential scanning calorimeter, 5 °C min⁻¹, under N₂); the liquid crystalline phases were identified from their optical textures: S_C = broken focal-conic fan and *schlieren* textures; S_A = focal-conic fan texture and homeotropic zones; N = *schlieren* and marbled textures.
^b Monotropic transition. ^c Second-order transition determined by polarized optical microscopy. ^d Masked by isotropization. ^e Cumulated enthalpies and entropies. ^f Approximate value: the S_C phase formed during the crystallization process.

and polarized optical microscopy (Table 1). The ligand L¹ (three-atom spacers) does not show mesogenic behaviour. However, the ligands L²–L⁴, which possess two-atom spacers, display interesting mesomorphism: they all present disordered smectic C and smectic A phases. An additional nematic phase is obtained for L³. Interestingly, the mesomorphic behaviour of L² is essentially retained in the lanthanide complexes. In [LuL²(NO₃)₃·3H₂O], the melting process (130 °C) is associated with a fast decomposition which prevents an unambiguous characterization of the mesophase(s), but the analogous complex [LuL²(NO₃)₃·H₂O] melts at 133 °C to give a stable S_A phase which isotropizes at 188 °C. Although the temperatures of the K → S_A and S_A → I transitions are similar for L² and its complex [LuL²(NO₃)₃·H₂O], the enthalpy and entropy changes are significantly larger for the latter compound.

In conclusion, two-atom spacers as in L²–L⁴ are suitable for the incorporation of bent tridentate units into rod-like shape receptors exhibiting thermotropic calamitic behaviours. A fine tuning of the thermal properties results from the nature of the spacer, while metallic size effects are responsible for the larger stability of the Lu complex as previously reported for other lanthanide-containing metallomesogens.⁷ The introduction of spectroscopically and magnetically active Ln^{III} into smectic phases is currently under investigation.

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Footnotes and References

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† Crystal data for L⁵: C₃₉H₃₇N₅O₄, M = 639.8, triclinic, space group P $\bar{1}$, a = 10.315(1), b = 11.8767(7), c = 14.170(1) Å, α = 105.076(5), β = 108.972(6), γ = 95.109(5)°, U = 1556.2(2) Å³ (by least-squares refinement of 24 reflections, 57 ≤ 2θ ≤ 76°), Z = 2, D_c = 1.37 g cm⁻³, F(000) = 676. Yellow prisms. Crystal dimensions 0.15 × 0.20 × 0.37 mm, μ(Cu-Kα) = 0.721 mm⁻¹. Data Collection and Processing: Stoe STAD14 diffractometer, T = 200 K, ω–2θ scan, scan width = 1.05 + 0.35 tanθ, scan speed 0.06° s⁻¹, Cu-Kα radiation (λ = 1.5418 Å); 3741 reflections measured (3 ≤ 2θ ≤ 105°, –10 < h < 10, –12 < k < 11, 0 < l < 14), 3561 unique reflections (R_{int} for equivalent reflections = 0.017) of which 3091 were observable [|F_o| > 4σ(F_o)]. Two reference reflexions were measured every 45 min and showed no variation in intensity. Structure analysis and refinement: data were corrected for Lorentz, polarization and absorption effects¹² (A*_{min} = 1.102, A*_{max} = 1.186). The structure was solved by direct methods using MULTAN 87;¹³ all other calculations used XTAL¹⁴ system and ORTEP II¹⁵ programs. Full-matrix least-squares refinements (on F) using weights of w = 1/[σ²(F_o) + 0.0001(F_o)²] gave final values R = 0.044, R_w = 0.049, for 434 variables and 3091 contributing reflections. All non-H atoms were refined with anisotropic displacement parameters. H-atoms were placed in calculated positions and contributed to F_c calculations. CCDC 182/599.

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