# Toward lanthanide-containing metallomesogens with tridentate ligands

**Homayoun Nozary,[a] Claude Piguet,*[a] Paul Tissot,[a] Gérald Bernardinelli,[b] Robert Deschenaux*[c] and Maria-Teresa Vilches[c]**

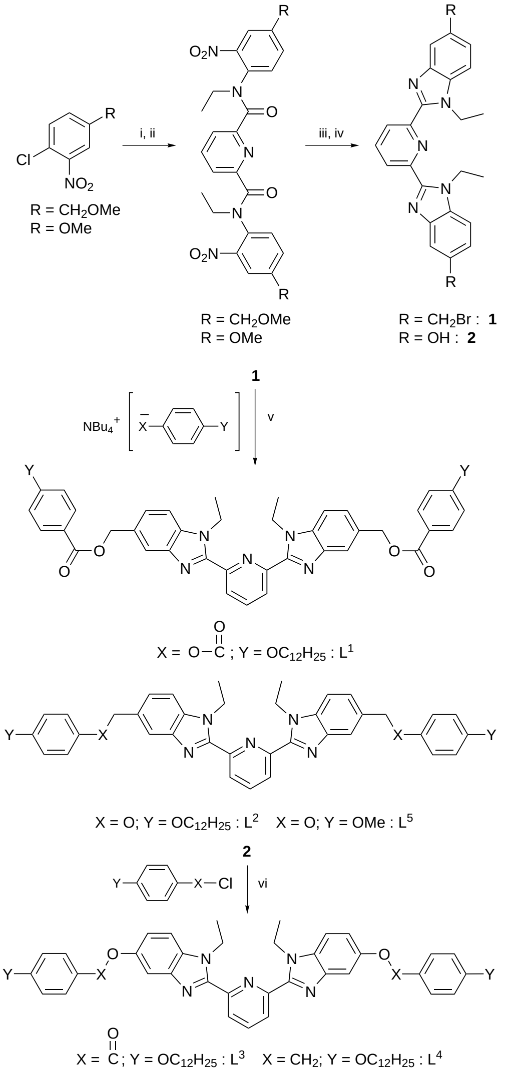
[a] *Department of Inorganic, Analytical and Applied Chemistry, University of Geneva, 30 quai E. Ansermet, CH-1211 Geneva 4, Switzerland*

[b] *Laboratory of X-ray Crystallography, University of Geneva, 24 quai E. Ansermet, CH-1211 Geneva 4, Switzerland*

[c] *Institute of Chemistry, University of Neuchâtel, Av. de Bellevaux 51, CH-2000 Neuchâtel, Switzerland*

**Tridentate aromatic receptors $L^1$–$L^4$ 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 $[LuL^2(NO_3)_3]$.**

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 prepared[7] and none with tridentate ligands, most likely as a consequence of their bent arrangement which results upon coordination.



**Scheme 1** *Reagents*: i, $EtNH_2$, EtOH; ii, pyridine-2,6-dicarbonyldichloride, $NEt_3$, $CH_2Cl_2$; iii, Fe, HCl–EtOH–$H_2O$; iv, $BBr_3$, $CH_2Cl_2$; v, $CH_2Cl_2$; vi, $NBu_4OH$, $CH_2Cl_2$

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 ($L^1$–$L^4$) 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 $L^1$, $L^2$ and $L^5$. Deprotonation of **2** with $NBu_4OH$ followed by alkylation or acylation provides the ligands $L^3$ and $L^4$.

$^1H$ NMR nuclear Overhauser enhancement effects (NOE) in solution suggest that the tridentate units adopt the expected *trans–trans* conformation in all free ligands $L^1$–$L^5$, which is confirmed in the solid state by the crystal structure of the non-mesogenic model compound $L^5$ [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 standard[10] 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 $L^2$ with stoichiometric amounts of $Ln(NO_3)_3$ (Ln = La, Lu) in acetonitrile produces quantitatively the complexes $[LnL^2(NO_3)_3]\cdot nH_2O$ (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 $H^{38}$–$H^{17}$) 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)

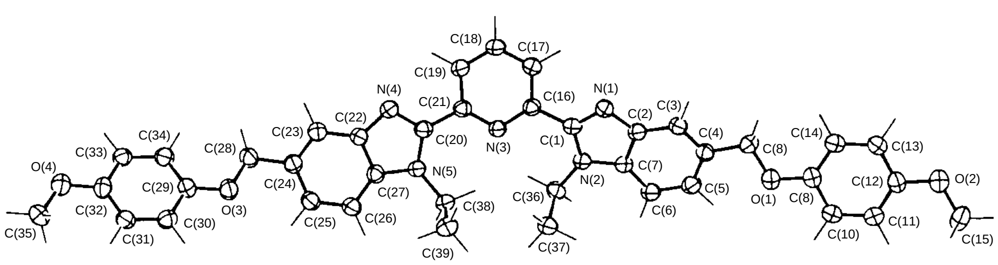


**Fig. 1** ORTEP[15] view of the ligand $L^5$ with ellipsoids represented at 50% probability level

**Table 1** Phase-transition temperatures and enthalpy and entropy changes for ligands $L^1$–$L^4$ and complex $[LuL^2(NO_3)_3]\cdot H_2O$

| Compound | Transition[a] | $T$/°C | $\Delta H$/kJ mol$^{-1}$ | $\Delta S$/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] | — |
|  | $S_A$–I | 188 | 17 | 37 |
| $L^3$ | K–$S_C$ | 131 | 35 | 86 |
|  | $S_C$–$S_A$ | 217 | —[c] | — |
|  | $S_A$–N | 223 | —[d] | — |
|  | N–I | 226 | 7[e] | 14[e] |
| $L^4$ | K–$S_A$ | 144 | 28 | 66 |
|  | $(S_C–S_A)$[b] | 107[f] | — | — |
|  | $S_A$–I | 193 | 18 | 39 |
| $[LuL^2(NO_3)_3]$ | 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 $N_2$); 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 $L^1$ (three-atom spacers) does not show mesogenic behaviour. However, the ligands $L^2$–$L^4$, 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 $L^3$. Interestingly, the mesomorphic behaviour of $L^2$ is essentially retained in the lanthanide complexes. In $[LaL^2(NO_3)_3]\cdot 3H_2O$, the melting process (130 °C) is associated with a fast decomposition which prevents an unambigous characterization of the mesophase(s), but the analogous complex $[LuL^2(NO_3)_3]\cdot H_2O$ melts at 133 °C to give a stable $S_A$ phase which isotropizes at 188 °C. Although the temperatures of the $K \rightarrow S_A$ and $S_A \rightarrow I$ transitions are similar for $L^2$ and its complex $[LuL^2(NO_3)_3]\cdot H_2O$, the enthalpy and entropy changes are significantly larger for the latter compound.

In conclusion, two-atom spacers as in $L^2$–$L^4$ 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.

We gratefully thank Mrs Hélène Lartigue, Dr J.-P. Rivera and C. Fouillet for their technical assistance. C. P. thanks the Werner Foundation for a fellowship. This work is supported through grants from the Swiss National Science Foundation.

## Footnotes and References

* E-mail: claude.piguet@chiam.unige.ch

† *Crystal data* for $L^5$: $C_{39}H_{37}N_5O_4$, $M$ = 639.8, triclinic, space group $P\bar{1}$, $a$ = 10.315(1), $b$ = 11.8767(7), $c$ = 14.170(1) Å, $\alpha$ = 105.076(5), $\beta$ = 108.972(6), $\gamma$ = 95.109(5)°, $U$ = 1556.2(2) Å$^3$ (by least-squares refinement of 24 reflections, $57 \leqslant 2\theta \leqslant 76°$), $Z$ = 2, $D_c$ = 1.37 g cm$^{-3}$, $F(000)$ = 676. Yellow prisms. Crystal dimensions 0.15 × 0.20 × 0.37 mm, $\mu$(Cu-K$\alpha$) = 0.721 mm$^{-1}$. *Data Collection and Processing*: Stoe STADI4 diffractometer, $T$ = 200 K, $\omega$–$2\theta$ scan, scan width = 1.05 + 0.35 tan$\theta$, scan speed 0.06° s$^{-1}$, Cu-K$\alpha$ radiation ($\lambda$ = 1.5418 Å); 3741 reflections measured ($3 \leqslant 2\theta \leqslant 105°$, $-10 < h < 10$, $-12 < k < 11$, $0 < l < 14$), 3561 unique reflections ($R_{int}$ for equivalent reflections = 0.017) of which 3091 were observable $[|F_o| > 4\sigma(F_o)]$. 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 effects[12] ($A^*_{min}$ = 1.102, $A^*_{max}$ = 1.186). The structure was solved by direct methods using MULTAN 87;[13] all other calculations used XTAL[14] system and ORTEP II[15] programs. Full-matrix least-squares refinements (on $F$) using weights of $w = 1/[\sigma^2(F_o) + 0.0001(F_o^2)]$ 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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*Received in Cambridge, UK, 7th August 1997; 7/05776H*