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Lanthanide Metal Ions as Cornerstones in Functional Self-Assembled Supramolecular Complexes

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Abstract. The peculiar spectroscopic, magnetic, and chemical properties of lanthanide ions (4f block, Ln^{III}) are particularly attractive for the design of functional supramolecular devices if these ions can be selectively introduced into organized self-assembled architectures. The systematic investigation of a complete library of tridentate receptors leading to nine-coordinate tricapped trigonal prismatic sites upon coordination to Ln^{III} allows the elucidation of the factors governing the structural, thermodynamic, electronic, magnetic, and spectroscopic properties of the final complexes. The simultaneous use of Ln^{III} as cement between the molecular components of the supramolecular edifices and as functional vectors of the devices has been realized in self-assembled polynuclear d-f and f-f complexes. Predetermined properties may result from a judicious molecular programming of the nanometric architecture leading to fascinating applications in luminescence, magnetism, template syntheses, and liquid crystals.

1. Self-Assembled Metallosupramolecular Complexes

Solid-state semiconductors and analytical probes require ever increasing miniaturization of their components. The usual top-to-bottom approach has led to intense activity in the preparation and design of particles possessing nanometric sizes [1] whose properties are intermediate between those found in macroscopic materials and in molecules [2]. For the molecular chemist, the organization of nanometric objects results from the reverse approach (*i.e.*, a bottom-to-top process) where an elaborate supramolecular edifice arises from the sequential forma-

tion of chemical bonds between molecular components. The total syntheses of vitamin B₁₂ [3], palytoxin [4], and brevetoxin B [5] are among the most famous successes of organic chemistry based on covalent bonds, but this step-by-step approach has almost reached a limit, and one cannot envisage to produce more complicated and functional nanosystems with the exclusive repertoire of covalent bond-making tools. Non-covalent interactions, such as π - π or π - σ stacking [6], hydrogen bonds [7], coordination bonds [8], and donor-acceptor interactions [9], offer highly convergent alternative strategies where elaborated building blocks selectively assemble to give larger organized architectures, termed supermolecules [10]. During the last decade, the use of dative bonds between metal ions and preorganized ligands has received much attention for the design of organized molecular architectures. It has been recognized that a correct match between complementary components (*i.e.*, the ligands and the metal ions) leads to predictable three-dimensional supramolecular structures on the nanometric scale [8][10]. Pioneer works dedicated to poly-metallic helicates [11] and topologically nontrivial complexes, such as pseudo-rotxanes [12], knots [13], and catenates [14], have contributed to the understand-

ing of basic concepts in metallosupramolecular self-assembly and self-organization [10] which have been recently extended to polymetallic structures, such as racks [15], grids [16], boxes [17], intertwined macrocycles [18], and metallosupramolecular equivalents of coronands, cryptands [19], and clusters [20]. Since d-block ions provide strong and directional coordination bonds, they have been used intensively for the assembly of nanometric metallosupramolecular complexes. However, the intrinsic electronic, optical, and magnetic properties associated with d-block ions have been used only marginally for the development of functional supramolecular devices, except for a few significant contributions in magnetism [21] and luminescence [22]. In this context, the lanthanide ions (4f block, Ln^{III}) offer promising possibilities as cornerstones for the design of functional devices, since the fascinating magnetic and spectroscopic properties of the free ions are essentially maintained in their complexes as a result of the minute mixing of 4f-metal-centered and ligand-centered functions [23]. Eu^{III} and Tb^{III} derivatives play a major role as luminescent probes in time-resolved fluoroimmunoassays [24] and protein labeling [24][25], while Gd^{III} complexes are used as contrast agents in MRI (=Magnetic Resonance Imaging) [26]. However, the fine tuning and the optimization of the final properties of the devices require a precise control of the coordination sphere around the metal which is severely limited by *i)* the large and variable coordination numbers adopted by Ln^{III} and *ii)* the poor directionality of the Ln-ligand bonds [27]. In this short review, we present a supramolecular approach based on the *induced fit* concept [28] which allows the selective introduction of Ln^{III} into organized self-assembled functional devices (*Fig. 1*).

2. Mononuclear Lanthanide Building Blocks with Predetermined Properties

Compared to d-block metal ions which exhibit strong and directional coordination bonds, 4f-block lanthanide ions appear to offer more limited perspectives as 'cement' between organic strands. In order to improve the structural control around Ln^{III}, we have investigated a series of tridentate chelating units L^{1–11} which wrap about the metal ions leading to mononuclear triple-helical complexes possessing a well-defined pseudo-tricapped trigonal prismatic site whose size can be tuned *via* secondary intramolecular interstrand in-

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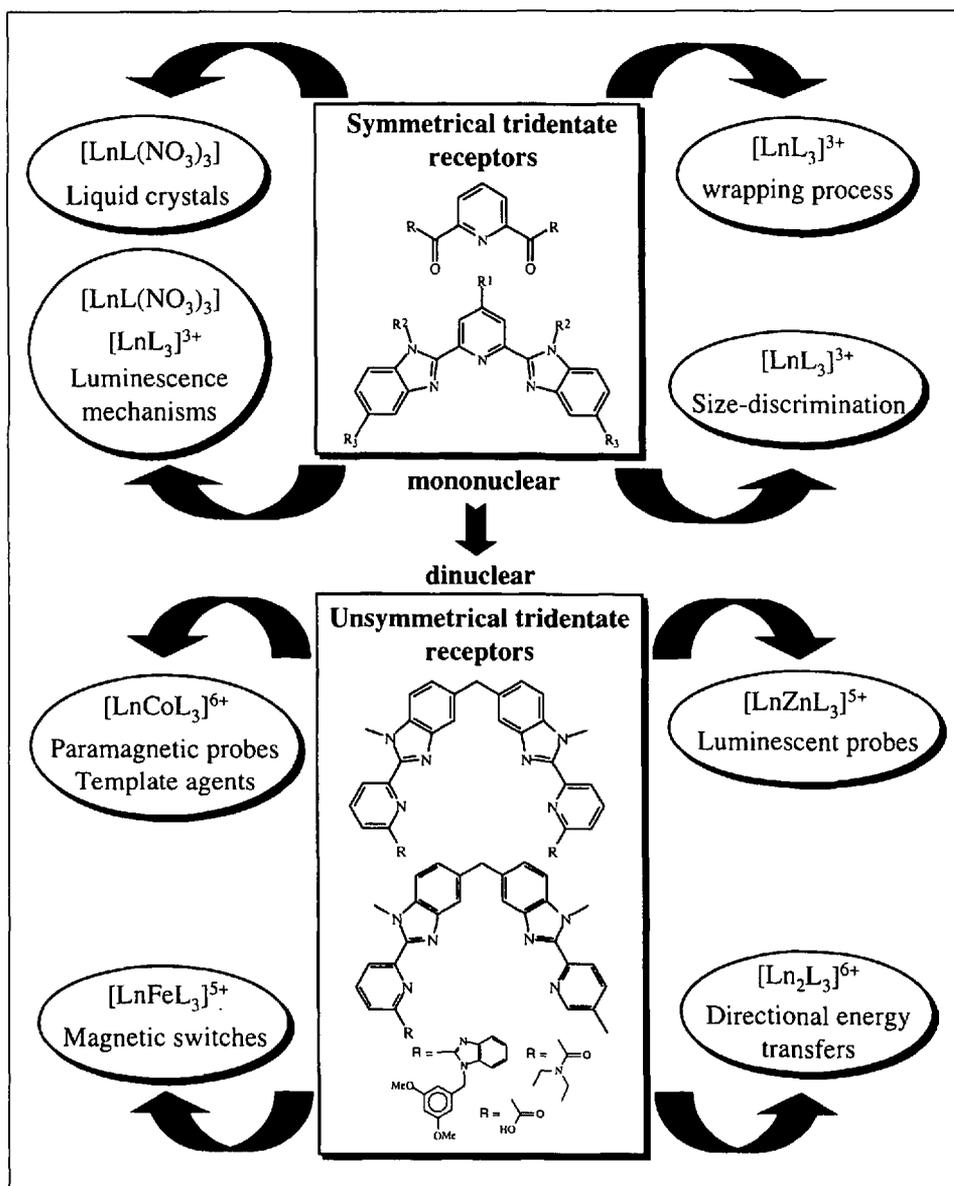


Fig. 1. Self-assembled lanthanide devices with tridentate receptors

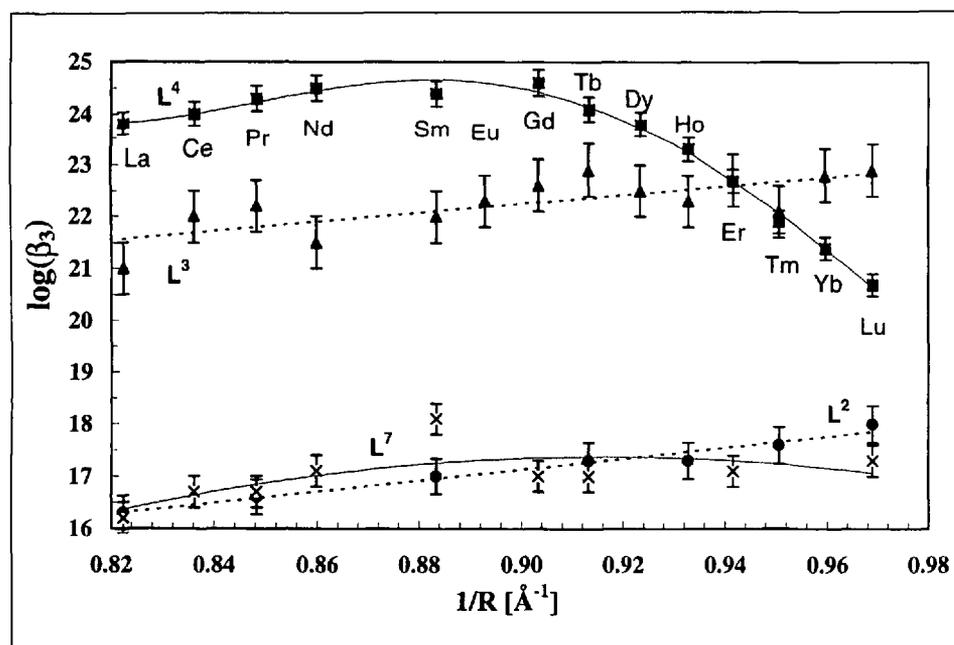


Fig. 2. Cumulative stability constants $\log(\beta_3)$ for complexes $[\text{Ln}(\text{L}^i)_3]^{3+}$ ($i = 2, 3, 4,$ and 7) in acetonitrile at 25° vs. the reciprocal of the ionic radii of nine-coordinate Ln^{III}

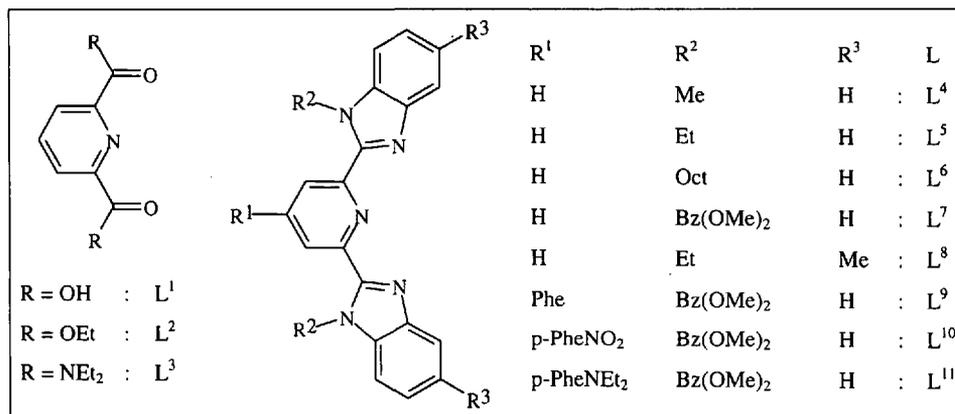
teractions. As early as in 1961, Grenthe [29] showed that dipicolinate ($\text{L}^1\text{-2H}$)²⁻ reacts with Ln^{III} to give stable and strongly luminescent triple-helical mononuclear complexes $[\text{Ln}(\text{L}^1\text{-2H})_3]^{3-}$ in water. A minor decrease of the cumulative stability constant $\log(\beta_3)$ for small Ln^{III} reveals weak repulsive secondary electrostatic interactions between the negatively charged terminal carboxylate groups of the different strands which are brought close together by the wrapping process. In order *i*) to induce significant steric interactions between the termini of the strands and *ii*) to allow the incorporation of these tridentate binding units into extended ligand strands, we have replaced the carboxylic groups of L^1 by neutral ester groups leading to L^2 [30] and bulky amide groups leading to L^3 [31]. As a result of the weak fractional negative charge borne by the carbonyl groups of ester side arms, L^2 coordinates only weakly to Ln^{III} . Poorly stable (Fig. 2) and kinetically labile triple-helical complexes $[\text{Ln}(\text{L}^2)_3]^{3+}$ are formed in acetonitrile which are of limited interest as building blocks despite their attracting emission properties with Eu^{III} [30]. The diamide derivative L^3 appears to be more promising because the triple-helical complexes $[\text{Ln}(\text{L}^3)_3]^{3+}$ are more stable and display a smooth increase in stability with decreasing lanthanide ionic radii in agreement with the expected electrostatic effects [31]. Paramagnetic NMR data in solution reveals that a regular D_3 -symmetrical triple-helical structure is adopted for the smaller Ln^{III} ions ($\text{Ln} = \text{Tb-Lu}$), but a significant distortion of the central pyridine ring is required to adapt the internal cavity for the coordination of larger Ln^{III} ions in $[\text{Ln}(\text{L}^3)_3]^{3+}$ [31]. Although secondary interstrand interactions arising from the wrapping process (electrostatic for $[\text{Ln}(\text{L}^1\text{-2H})_3]^{3-}$ and steric for $[\text{Ln}(\text{L}^3)_3]^{3+}$) have only minor effects on the structural, thermodynamic, kinetic, and electronic properties of the final complexes, they clearly demonstrate that one can take advantage of the *induced fit* concept [28] for the design of lanthanide building blocks with predetermined properties.

In order to tune ligand-ligand interactions in the final complexes, we have synthesized a complete library of semirigid aromatic tridentate binding units L^{4-11} [32] [33]. Contrary to terpyridine derivatives which produce only poorly stable and dynamically labile 1:3 complexes in solution [34], the related ligand L^4 reacts with large Ln^{III} ($\text{Ln} = \text{La-Tb}$) to give stable and inert triple-helical complexes $[\text{Ln}(\text{L}^4)_3]^{3+}$ in acetonitrile [33][35][36]. As a result of the three strong intramolecular interstrand

stacking interactions between pairs of benzimidazole rings (Fig. 3), the contraction of the internal cavity required for complexing the smaller Ln^{III} ions is severely limited, thus providing an unprecedented selectivity for the midrange Ln^{III} ions ($\Delta \log K_3$ (Gd–Lu) \approx 4; Fig. 2) [36]. The bulky 3,5-dimethoxybenzyl groups (R² = Bz(OMe)₂) in L⁷ hinders the wrap-

ping process and removes the interstrand stacking interactions in [Ln(L⁷)₃]³⁺. A severe decrease in stability results together with an almost complete loss of selectivity along the lanthanide series (Fig. 2). The introduction of donor groups in 4-position of the pyridine ring leading to L¹¹ reinforces the coordinating ability of the N(pyridine)-atom and restores the selec-

tivity for midrange Ln^{III} ions in [Ln(L¹¹)₃]³⁺ ($\Delta \log K_3$ (Gd–Lu) \approx 3). An electron-attracting nitro group in L¹⁰ produces the opposite effect and prevents the formation of 1:3 complexes [36]. Electronic properties are also affected by the various substituents bound to the ligand backbone: paramagnetic NMR contact shifts in [Ln(L^{1-2H})₃]³⁺ [37] and [Ln(Lⁱ)₃]³⁺ (i = 3,4) [31][36] show an increased unpaired spin density delocalized onto the central pyridine ring in the order [L^{1-2H}]²⁻ \ll L³ < L⁴, while the luminescence studies of the complexes [EuLⁱ(NO₃)₃] (i = 4–11) demonstrate that the emission properties can be finely tuned by a judicious choice of the substituents [38].



3. Self-Assembly of Dinuclear d-f and f-f Metallosupramolecular Complexes

The introduction of two or more metallic building blocks into an organized supramolecular architecture broadens the level of structural and electronic control [39]. The use of the rigid and constrained diphenylmethane spacer to connect binding units led to the preparation of symmetrical (L¹²⁻¹³) and unsymmetrical (L¹⁴⁻¹⁵) ditopic segmental ligands [40] coded for the self-assembly of dinuclear 4f-4f [Ln₂(Lⁱ)₃]⁶⁺ (i = 12,13) [41] and 3d-4f [LnM(Lⁱ)₃]⁵⁺ (i = 14,15) supramolecular complexes, respectively (Fig. 4) [42–44]. The detailed thermodynamic studies of the assembly of [Ln₂(Lⁱ)₃]⁶⁺ (i = 12,13) strongly suggest that a negatively cooperative process occurs which is tentatively attributed to the high positive charge (3+)

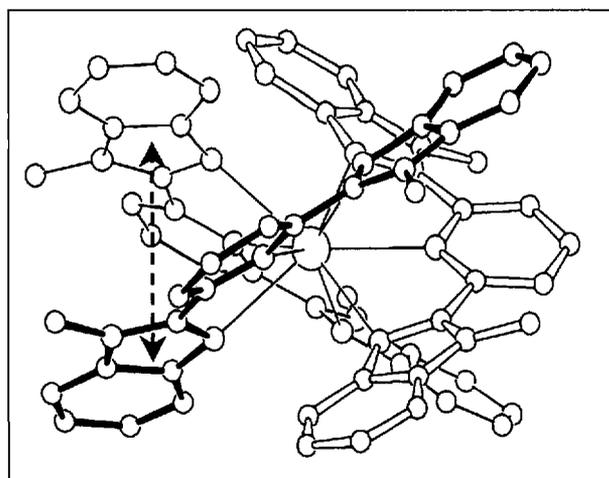


Fig. 3. ORTEP view of the X-ray crystal structure of the cation [Eu(L⁴)₃]³⁺ perpendicular to the C₃ axis with one interstrand stacking interaction highlighted

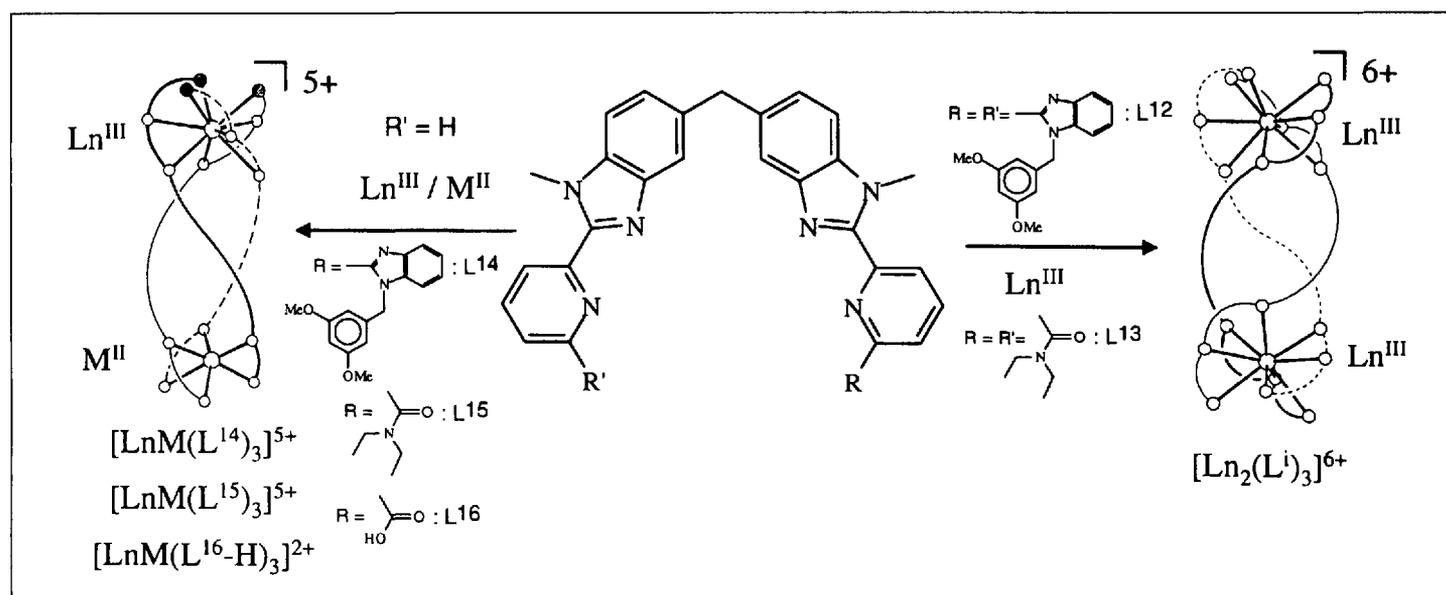


Fig. 4. Self-assembly of dinuclear f-f triple-stranded helicates [Ln₂(Lⁱ)₃]⁶⁺ (i = 12,13) and dinuclear d-f non-covalent podates [LnM(Lⁱ)₃]⁵⁺ (i = 14,15) and [Ln₂(L^{16-H})₃]²⁺

borne by the entering cations [41]. The recent observation that the homotopic triple-stranded helicates $[\text{Ln}_2(\text{L}^{13})_3]^{6+}$ react with an excess of Ln^{III} to give the double-stranded side-by-side complexes $[\text{Ln}_2(\text{L}^{13})_2]^{6+}$ demonstrates that a close control of stoichiometric conditions is crucial if these self-assembly processes are to give predictable products [41].

The synthesis of the heterodinuclear non-covalent lanthanide podates $[\text{LnM}(\text{L}^i)_3]^{5+}$ ($i=14,15$) requires a higher degree of molecular programming because two different metal ions must be selectively recognized by the binding units of the segmental ligands during the self-assembly process. Careful speciations and thermodynamic investigations show that the tridentate 2,6-bis(benzimidazol-2-yl)pyridine unit of L^{14} exhibits a significant affinity for both 3d- and 4f-block ions, which restricts the quantitative formation of the desired head-to-head non-covalent podate $(\text{HHH})\text{-}[\text{LnM}(\text{L}^{14})_3]^{5+}$ ($\text{M} = \text{Fe}, \text{Zn}$) to a total ligand concentration larger than 0.01 M, a too large value for the development of molecular devices and analytical probes [42][43]. The replacement of the terminal benzimidazole group in L^{14} by a carboxamide group leading to L^{15} significantly improves the selectivity of the tridentate binding unit for 4f-block ions, and $(\text{HHH})\text{-}[\text{LnM}(\text{L}^{15})_3]^{5+}$ ($\text{M} = \text{Fe}, \text{Zn}$) is formed quantitatively for total ligand concentrations around 10^{-4} M in acetonitrile [42][43]. Recent advances in that field have shown that negatively charged carboxylate groups significantly increases the stability of the final complex in strongly coordinating solvents, thus allowing the preparation of non-covalent lanthanide podates $(\text{HHH})\text{-}[\text{LnZn}(\text{L}^{16}\text{-H})_3]^{2+}$ in water at low concentration [44].

4. Functional Lanthanide-Containing Supramolecular Devices

4.1. Luminescent Probes

The use of Eu^{III} and Tb^{III} as long-lived luminescent stains is restricted by the faint oscillator strength of the Laporte-forbidden f-f transition [45][46]. Complexation of Ln^{III} to aromatic ligands may overcome this limitation *via* an energy-conversion process, termed the *antenna effect* and consisting of three steps: 1) Efficient light-harvesting *via* allowed ligand-centered transitions, 2) energy transfer to Ln^{III} , and 3) long-lived metal-centered emission [46]. Detailed photophysical investigations of this light-converting process in mononuclear building blocks $[\text{Ln}(\text{L}^i)(\text{NO}_3)_3]$ ($i=4-11$) [38] and $[\text{Ln}(\text{L}^i)_3]^{3+}$ ($i=2-11$) [31][33][35][47] lead to the conclusion that *i*) tridentate bis(benzimidazol-2-yl)pyridine units provide low-lying LMCT (=Ligand-to-Metal Charge Transfer) states which quench the Eu^{III} luminescence in triple-helical complexes, *ii*) carboxamide and carboxylic side arms improve the emission quantum yield and the affinity for Ln^{III} , and *iii*) unsymmetrical tridentate binding units allow the fine tuning of the ligand-centered electronic levels. A global consideration of these results led us to develop the non-covalent lanthanide podates $[\text{EuZn}(\text{L}^i)_3]^{5+}$ ($i=14,15$) and $[\text{EuZn}(\text{L}^{16}\text{-H})_3]^{2+}$, where Zn^{II} acts as a pure structural organizer since no low-lying excited states are associated with its filled electronic configuration ($3d^{10}$). The first synthesized podate $[\text{EuZn}(\text{L}^{14})_3]^{5+}$ exhibits very weak emission properties (quantum yield relative to $[\text{Eu}(\text{terpy})_3]^{3+}$, $\Phi_{\text{rel}} = 10^{-4}$) as a result of the inadequate bis(benzimidazol-2-yl)pyridine units bound to Eu^{III} [42]. However,

the introduction of carboxamide groups in L^{15} provides the non-covalent podate $[\text{EuZn}(\text{L}^{15})_3]^{5+}$ whose quantum yield is improved by a factor 10^3 ($\Phi_{\text{rel}} = 0.29$) in acetonitrile. The recent analogue $[\text{EuZn}(\text{L}^{16}\text{-H})_3]^{2+}$ is even more luminescent ($\Phi_{\text{rel}} = 1.00$) and stable in water at concentrations up to 10^{-6} M without any significant amount of decomplexation or interactions with solvent molecules in the first coordination sphere of Eu^{III} [44]. The latter complex demonstrates that these nanometric lanthanide podates can work as light-converting devices in strongly coordinating solvent such as water, a crucial step for the design of luminescent probes in biological media. The introduction of spectroscopically active Fe^{II} in the non-covalent tripod has little effect on the structural and thermodynamic characteristics of the final complexes, but it strongly affects the photophysical properties of the complex *via* an efficient intramolecular $\text{Eu}^{\text{III}} \rightarrow \text{Fe}^{\text{II}}$ energy-transfer process which completely quenches the Eu -centered luminescence in the dark red podates $[\text{EuFe}(\text{L}^i)_3]^{5+}$ ($i=14,15$) [43]. Compared to the strongly luminescent analogue $[\text{EuZn}(\text{L}^{15})_3]^{5+}$, the replacement of Zn^{II} by Fe^{II} corresponds to a YES/NO logic gate, a prerequisite for the design of molecular devices performing logic operations if the switching process can be addressed *via* an external signal (electrochemical, optical, or magnetic) [48]. Finally, the existence of isolated pairs of lanthanide metal ions in the triple-stranded helicates $[\text{Ln}_2(\text{L}^i)_3]^{6+}$ ($i=12,13$) is crucial to unravel the intimate mechanisms of f-f energy transfers which find applications in directional light-conversion [41] and four-level lasers [49]. The heterodinuclear complex $[\text{EuTb}(\text{L}^{12})_3]^{6+}$ studied in a statistical mixture of homo- and heteropairs represents one of the first fully characterized intramolecular $\text{Tb} \rightarrow \text{Eu}$ energy transfer (dipole-dipolar mechanism, yield 76%) within a well-defined supramolecular edifice [41]. As expected from our previous work on non-covalent lanthanide podates [42], the binding of carboxamide groups to Eu^{III} in $[\text{Eu}_2(\text{L}^{13})_3]^{6+}$ indeed improves both emission output and resistance toward hydrolysis [41].

4.2. Magnetic Probes

The large intramolecular intermetallic distances (8.8–9.0 Å) in $[\text{LnM}(\text{L}^i)_3]^{5+}$ ($i=14,15$) combined with the absence of short unsaturated intermetallic bridges ensure that no significant 3d-4f magnetic coupling operates [50] which is confirmed by the magnetically isolated spin-crossover ($^1\text{A} \rightleftharpoons ^5\text{T}$) behavior observed for Fe^{II} in

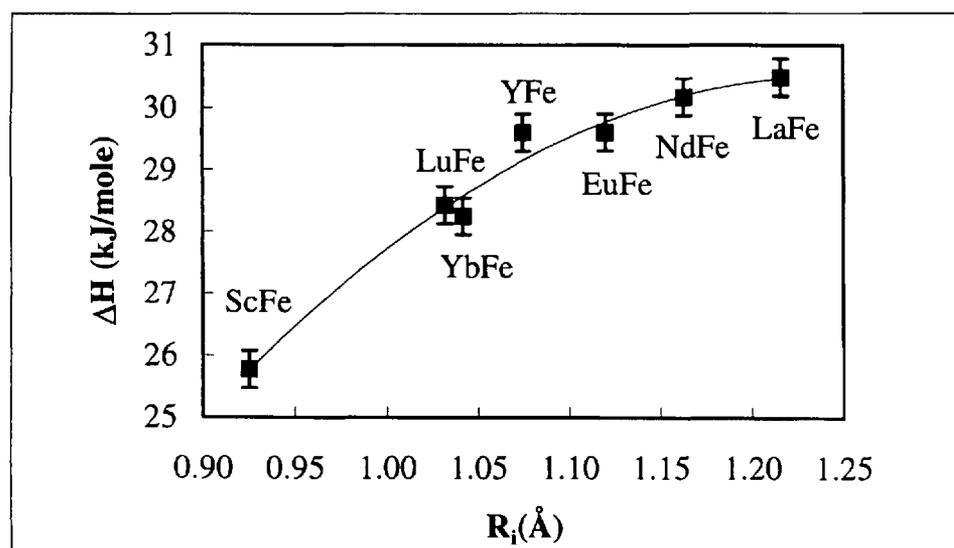


Fig. 5. Enthalpic contributions ($\Delta H_{s,c}$) to the Fe^{II} spin-crossover equilibria ($^1\text{A} \rightleftharpoons ^5\text{T}$) for $[\text{LnFe}(\text{L}^{15})_3]^{5+}$ in acetonitrile vs. the ionic radii of nine-coordinate Ln^{III}

$[\text{LnFe}(\text{L}^i)_3]^{5+}$ ($i = 14, 15$) [43]. However, the size of Ln^{III} bound in the nine-coordinate site systematically affects the enthalpic (ΔH_{sc}) and entropic parameters (ΔS_{sc}) of the spin-state equilibria (Fe^{II} low spin (diamagnetic) \rightleftharpoons Fe^{II} high spin (paramagnetic)), thus implying a mechanical coupling between the metallic sites *via* the ligand backbone. According to the observed systematic increase of ΔH_{sc} with increasing Ln^{III} ionic radius (Fig. 5), we deduce that the average 0.2-Å elongation of the Fe–N bond associated with low-spin \rightarrow high-spin transition is favored when the small Ln^{III} occupies the tricapped trigonal prismatic site [43]. A strong thermochromism, resulting from different Fe^{II} ligand-field (d-d) and charge-transfer (MLCT) transitions in the two spin states, comes with the magnetic changes leading to fascinating possibilities for the design of thermally and optically addressable magnetic switches [43]. Finally, we take advantage of the straightforward separation of contact and dipolar contributions to the lanthanide-induced paramagnetic NMR shifts for the electronic and structural characterization of C_3 -symmetrical (HHH)- $[\text{LnZn}(\text{L}^i)_3]^{5+}$ ($i = 14, 15$) in solution [42], respectively. Extension of this technique to other diamagnetic d-block ions such as Co^{III} (d^6 low spin) in $[\text{LnCo}(\text{L}^{15})_3]^{6+}$ and to dinuclear 3d-4f complexes $[\text{LnCo}(\text{L}^{15})_3]^{5+}$ possessing two magnetically uncoupled paramagnetic centers (Ln^{III} and Co^{II}) is currently under investigation in our laboratories [51].

4.3. Template Agents

Although the stability and the organization of the final non-covalent lanthanide podates $[\text{LnM}(\text{L}^{15})_3]^{5+}$ result mainly from the strong bonds between 3d-block metals and heterocyclic nitrogen donor atoms, Ln^{III} still exerts a minor, but crucial synergistic effect onto the d-block site which contributes to the high selectivity of the assembly process [42][43]. The removal of Ln^{III} from the labile self-assembled podates induces thermodynamic and structural rearrangements leading to intricate mixtures of homopolynuclear d-block complexes. However, the oxidation of the labile paramagnetic Co^{II} in $[\text{LaCo}(\text{L}^{15})_3]^{5+}$ into kinetically inert Co^{III} in $[\text{LaCo}(\text{L}^{15})_3]^{6+}$ prevents any structural rearrangement upon the release of Ln^{III} leading to a facial nonadentate receptor $\text{fac-}[\text{Co}(\text{L}^{15})_3]^{3+}$ which is highly preorganized for the selective recognition of Ln^{III} (Fig. 6) [51]. In this synthetic strategy, La^{III} acts as a template agent leading to the quantitative formation of the self-assembled podate $[\text{LaCo}(\text{L}^{15})_3]^{5+}$. The subsequent oxidative

post-processing ‘locks’ the final d-block tripod, thus allowing further transformations within the supramolecular architecture.

4.4. Liquid Crystals

Despite the fascinating luminescent and magnetic properties expected for lanthanide-containing mesogenic complexes, the weak stability and selectivity of Ln-ligands bond severely limits the preparation of mesophases based on 4f-block complexes [52]. As tridentate binding units have been shown to improve the chelate effect upon coordination to Ln^{III} , we have synthesized extended ligands L^{17-19} possessing semirigid lipophilic tails connected to a central bis(benzimidazol-2-yl)pyridine unit. The usual *trans-trans* arrangement of the nitrogen donor atoms in the benzimidazole-pyridine moieties provides a linear disposition of the semirigid lipophilic tails connected to the 5-position of the benzimidazole ring leading to rod-like molecules in the solid state and in solution [53]. Thermal analyses combined with polarized microscopy indeed show that L^{17-19} melt around 131–144° to give calamitic smectic (S_A and S_C) mesophases where the ligands maintain their *I*-shaped arrangement [53]. Complexation to $\text{Ln}(\text{NO}_3)_3$ induces the expected conformational change *trans-trans* \rightarrow *cis-cis* of the central tridentate unit leading to *U*-shaped arrangement of the ligand strand in $[\text{Ln}(\text{L}^{17})(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$ and $[\text{Ln}(\text{L}^{20})(\text{NO}_3)_3]$. This deep change of the molecular shape in the complexes combined with the increased reactivity of nitrate anions at high temperature have prevented the observation of stable mesophases for $[\text{Ln}(\text{L}^{17})(\text{NO}_3)_3] \cdot \text{H}_2\text{O}$.

5. Conclusions

Semirigid tridentate binding units containing a central pyridine ring are suitable receptors for the recognition and selective complexation of Ln^{III} for four reasons: 1) the significant entropic chelate effect ensures a sufficient stability which overcomes the weak Ln–N(heterocyclic) bonds; 2) the wrapping of three ligands produces tricapped trigonal prismatic sites which satisfy the lanthanide stereochemical preferences and induces secondary tunable intramolecular interstrand interactions; 3) the aromatically centered $\pi\pi^*$ excited states act as efficient relays for collecting UV light and transferring it to Eu^{III} and Tb^{III} , and 4) a complete library of tridentate binding units results from a judicious substitution of the substituents in

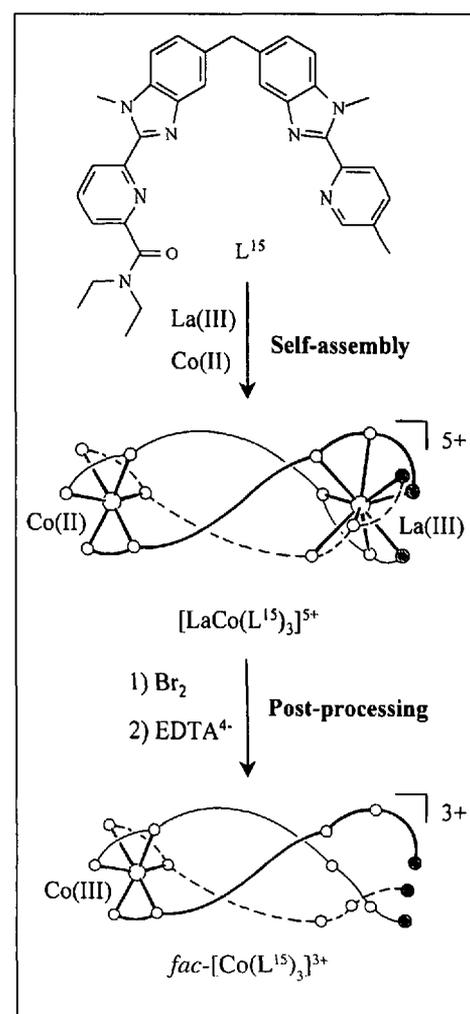
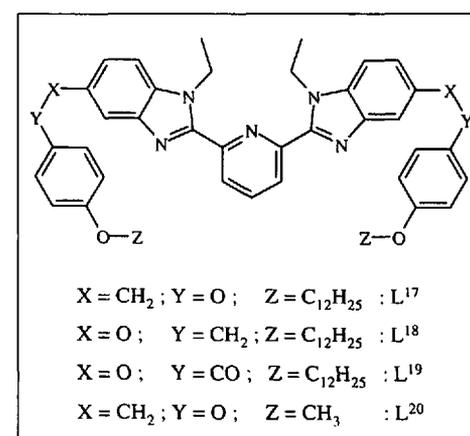


Fig. 6. Template synthesis of $\text{fac-}[\text{Co}(\text{L}^{15})_3]^{3+}$ using self-assembly with post-processing



the 2- and 6-positions of the pyridine ring. Despite the weak luminescence associated with low-lying LMCT states in mononuclear triple-helical complexes $[\text{Ln}(\text{L}^i)_3]^{3+}$, the elucidation of the factors governing thermodynamic, structural, and electronic properties in these simple complexes is crucial for the design of larger supramolecular edifices where Ln^{III} acts simultaneously as *i*) cement between the sophisticated components and *ii*) active site in final functional device. When one consid-

ers the versatile coordination behavior of Ln^{III} and the limited electronic predictions related to second-order effects involving 4f states [46], this bottom-to-top approach represents a fascinating challenge in metallosupramolecular chemistry. Although our attempts to develop functional devices based on self-assembled lanthanide complexes are still in their beginning, the preliminary successful applications as luminescent probes, magnetic sensors, and template agents reported in this review bring the goal of tailored nanometric functional devices in the realms of possibility.

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- [1] J.F. You, G.C. Papaefthymiou, R.H. Holm, *J. Am. Chem. Soc.* **1992**, *114*, 2697; A. Henglein, *Chem. Rev.* **1989**, *89*, 186 and refs. cit. therein.
- [2] H. Weller, *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 41, and refs. cit. therein.
- [3] R.B. Woodward, *Pure Appl. Chem.* **1973**, *33*, 145.
- [4] E.M. Suh, Y. Kishi, *J. Am. Chem. Soc.* **1994**, *116*, 11205.
- [5] K.C. Nicolaou, *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 589.
- [6] C.A. Hunter, J.K.M. Sanders, *J. Am. Chem. Soc.* **1990**, *112*, 5525; H. Adams, F.J. Carven, C.A. Hunter, J.C. Morales, E.M. Seward, *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1542.
- [7] M.M. Conn, J. Rebek, Jr., *Chem. Rev.* **1997**, *97*, 1647; R. Taylor, O. Kennard, *J. Am. Chem. Soc.* **1982**, *104*, 5063; G. Desiraju, *Acc. Chem. Res.* **1996**, *29*, 441.
- [8] D.S. Lawrence, T. Jiang, M. Levett, *Chem. Rev.* **1995**, *95*, 2229.
- [9] D.B. Amabilino, J.F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725; D. Philp, J.F. Stoddart, *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1154.
- [10] J.-M. Lehn, 'Supramolecular Chemistry', VCH, Weinheim, 1995; M.C.T. Fyfe, J.F. Stoddart, *Acc. Chem. Res.* **1997**, *30*, 393.
- [11] For recent reviews see: C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005; A.F. Williams, *Chem. Eur. J.* **1997**, *3*, 15.
- [12] P.N.W. Baxter, H. Sleiman, J.-M. Lehn, K. Rissanen, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1294; D.J. Cardenas, P. Gavina, J.-P. Sauvage, *J. Am. Chem. Soc.* **1997**, *119*, 2656.
- [13] C. Dietrich-Bücheker, G. Rapenne, J.-P. Sauvage, *Chem. Commun.* **1997**, 2053, and refs. cit. therein.
- [14] C. Piguet, G. Bernardinelli, A.F. Williams, B. Bocquet, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 582; D. J. Cardenas, J.-P. Sauvage, *Inorg. Chem.* **1997**, *36*, 2777.
- [15] G.S. Hanan, C.R. Arana, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **1996**, *2*, 1292.
- [16] P.N.W. Baxter, J.-M. Lehn, B.O. Kneisel, D. Fenske, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1978.
- [17] P.J. Stang, B. Olenyuk, *Acc. Chem. Res.* **1997**, *30*, 502, and refs. cit. therein.
- [18] D.P. Funeriu, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **1997**, *3*, 99.
- [19] R.W. Saalfrank, A. Dresel, V. Seitz, S. Trummer, F. Hampel, M. Teichert, D. Stalke, C. Stadler, J. Daub, V. Schünemann, A.X. Trautwein, *Chem. Eur. J.* **1997**, *3*, 2058; F. Birkelbach, T. Weyermüller, M. Lengen, M. Gerdan, A.X. Trautwein, K. Wieghardt, P. Chaudhuri, *J. Chem. Soc., Dalton Trans.* **1997**, 4529.
- [20] R.W. Saalfrank, I. Bernt, E. Uller, F. Hampel, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2482, and refs. cit. therein.
- [21] S. Turner, O. Kahn, L. Rabardel, *J. Am. Chem. Soc.* **1996**, *118*, 6428; R.L. Oushoorn, K. Boubekur, P. Batail, O. Guillou, O. Kahn, *Bull. Soc. Chim. Fr.* **1996**, *133*, 777.
- [22] V. Balzani, *Tetrahedron* **1992**, *48*, 10443; V. Balzani, F. Bolletta, M.T. Gandolfi, A. Juris, M. Maestri, M.F. Manfrin, L. Moggi, N. Sabbatini, *Coord. Chem. Rev.* **1993**, *125*, 75; M.D. Ward, *Chem. Soc. Rev.* **1997**, *26*, 365.
- [23] G. Blasse, *Struct. Bonding* **1976**, *26*, 45.
- [24] I. Hemmilä, T. Stahlberg, P. Mottram, 'Bio-analytical Applications of Labeling Technologies', 2nd edn., Wallac Oy, Turku, 1995; G. Mathis, *Clin. Chem.* **1995**, *41*, 1391.
- [25] J.-C.G. Bünzli, J.-M. Pfefferlé, *Helv. Chim. Acta* **1994**, *77*, 323.
- [26] R.B. Lauffer, in 'MRI Clinical Magnetic Resonance Imaging', 2nd edn., Eds. R.E. Edelman, M.B. Zlatkin, J.R. Hesselink, and W.B. Saunders Co., Philadelphia, 1996, Vol. 1, Ch. 5; S. Aime, M. Bolta, M. Fasano, E. Terreno, *Chem. Soc. Rev.* **1998**, *27*, 19.
- [27] G.R. Choppin, in 'Lanthanide Probes in Life, Chemical and Earth Sciences', Eds. J.-C.G. Bünzli, G.R. Choppin, Elsevier, Amsterdam, 1989, Chapt. 1.
- [28] C. Piguet, *Chimia* **1997**, *51*, 240; D.E. Koshland, *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2375.
- [29] I. Grenthe, *J. Am. Chem. Soc.* **1961**, *83*, 360.
- [30] F. Renaud, C. Piguet, G. Bernardinelli, J.-C.G. Bünzli, G. Hopfgartner, *Chem. Eur. J.* **1997**, *3*, 1660.
- [31] F. Renaud, C. Piguet, G. Bernardinelli, J.-C.G. Bünzli, G. Hopfgartner, *Chem. Eur. J.* **1997**, *3*, 1646.
- [32] C.G. Bochet, C. Piguet, A.F. Williams, *Helv. Chim. Acta* **1993**, *76*, 372.
- [33] C. Piguet, J.-C.G. Bünzli, G. Bernardinelli, C.G. Bochet, P. Froidevaux, *J. Chem. Soc., Dalton Trans.* **1995**, 83.
- [34] R.D. Chapman, R.T. Loda, J.P. Riehl, R.W. Schwartz, *Inorg. Chem.* **1984**, *23*, 1652.
- [35] C. Piguet, A.F. Williams, G. Bernardinelli, J.-C.G. Bünzli, *Inorg. Chem.* **1993**, *32*, 4139.
- [36] S. Petoud, J.-C.G. Bünzli, F. Renaud, C. Piguet, K.J. Schenk, G. Hopfgartner, *Inorg. Chem.* **1997**, *36*, 5750.
- [37] C.N. Reilley, B.W. Good, J.F. Desreux, *Anal. Chem.* **1975**, *47*, 2110.
- [38] C. Piguet, A.F. Williams, G. Bernardinelli, E. Moret, J.-C.G. Bünzli, *Helv. Chim. Acta* **1992**, *75*, 1697; S. Petoud, J.-C.G. Bünzli, K.J. Schenk, C. Piguet, *Inorg. Chem.* **1997**, *36*, 1345.
- [39] C. Piguet, *Chimia* **1996**, *50*, 144; J.-C.G. Bünzli, S. Petoud, C. Piguet, *J. Alloys Compounds* **1997**, *249*, 14; C. Piguet, J.-C.G. Bünzli, *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 165.
- [40] C. Piguet, B. Bocquet, G. Hopfgartner, *Helv. Chim. Acta* **1994**, *77*, 931.
- [41] C. Piguet, J.-C.G. Bünzli, G. Bernardinelli, G. Hopfgartner, A.F. Williams, *J. Am. Chem. Soc.* **1993**, *115*, 8197; N. Martin, J.-C.G. Bünzli, V. McKee, C. Piguet, G. Hopfgartner, *Inorg. Chem.* **1998**, *37*, 577.
- [42] C. Piguet, E. Rivara-Minten, G. Hopfgartner, J.-C.G. Bünzli, *Helv. Chim. Acta* **1995**, *78*, 1541; C. Piguet, J.-C.G. Bünzli, G. Bernardinelli, G. Hopfgartner, S. Petoud, O. Schaad, *J. Am. Chem. Soc.* **1996**, *118*, 6681.
- [43] C. Piguet, E. Rivara-Minten, G. Hopfgartner, J.-C.G. Bünzli, *Helv. Chim. Acta* **1995**, *78*, 1651; C. Piguet, E. Rivara-Minten, G. Bernardinelli, J.-C.G. Bünzli, G. Hopfgartner, *J. Chem. Soc., Dalton Trans.* **1997**, 421.
- [44] C. Edder, C. Piguet, J.-C.G. Bünzli, G. Hopfgartner, *J. Chem. Soc., Dalton Trans.* **1997**, 4657.
- [45] J.-C.G. Bünzli, in 'Lanthanide Probes in Life, Chemical and Earth Sciences', Eds. J.-C.G. Bünzli and G.R. Choppin, Elsevier Publishing Co, Amsterdam, 1989, Chapt. 7.
- [46] J.-C.G. Bünzli, P. Froidevaux, C. Piguet, *New J. Chem.* **1995**, *19*, 661 and refs. cit. therein.
- [47] S. Petoud, J.-C.G. Bünzli, C. Piguet, R. Thummel, in preparation.
- [48] A.P. de Silva, H.Q.N. Gunaratne, C.P. McCoy, *Nature (London)* **1993**, *364*, 42; P. Ghosh, P.K. Bharadwaj, J. Roy, S. Ghosh, *J. Am. Chem. Soc.* **1997**, *119*, 11903.
- [49] R. Reisfeld, C. K. Jørgensen, 'Lasers and Excited States of Rare Earths', in 'Inorg. Chem. Concepts', Vol. 1, Springer Verlag, Berlin-Heidelberg-New York, 1977.
- [50] I. Ramade, O. Kahn, Y. Jeannin, F. Robert, *Inorg. Chem.* **1997**, *36*, 930, and refs. cit. therein.
- [51] S. Rigault, C. Piguet, G. Bernardinelli, G. Hopfgartner, *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 169.
- [52] Y. Galymetdinov, A.M. Athanassopoulou, O. Kharitonova, E.A. Soto-Bustamante, I.K. Ovchinnikov, W. Hasse, *Chem. Mater.* **1996**, *8*, 922; I. Bikhantaev, Y. Galymetdinov, O. Kharitonova, I.K. Ovchinnikov, D.W. Bruce, D.A. Dunmur, D. Guilter, B. Heinrich, *Liq. Cryst.* **1996**, *20*, 489.
- [53] H. Nozary, C. Piguet, P. Tissot, G. Bernardinelli, R. Deschenaux, M.-T. Vilches, *Chem. Commun.* **1997**, 2101.