Toward Programmed Molecular Lanthanide Probes and Sensors

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Abstract. The peculiar spectroscopic properties of the lanthanide metal ions (4f-block, Ln^{III}), and particularly Eu^{III} and Tb^{III}, make them suitable for the design of chemical luminescent probes and analytical sensors when Ln^{III} is introduced into organized molecular architectures possessing controlled and protected coordination sites. The tridentate receptors 2,6-bis(1-alkylbenzimidazol-2-yl)pyridine (L^i, i=2–7) play a crucial role since they react with Ln^{3+} to give mononuclear building blocks $[Ln(L^i)_3]^{3+}$ where the metal ion is protected by the wrapping of the aromatic ligands. In these ultraviolet to visible light-converting devices (Ln=Eu, Tb), the size of the internal cavity is controlled by the three closely packed strands which produce *i*) a promising discrimination between Ln^{III} according to their sizes and *ii*) efficient light-harvesting resulting form the strong absoprtion of ultraviolet light by the ligands. These building blocks have been introduced into more sophisticated homodinuclear triple-helical complexes $[Ln_2(L^8)_3]^{6+}$ and statistical mixtures containing the heterodinuclear directional visible to visible light-converting device $[EuTb(L^8)_3]^{6+}$. Improved molecular programming results form the use of acyclic segmental ligand possessing different binding units coded for one particular ion. The segmental ligands L^i (i=9,10) discriminate Fe^{II} and Ag^I to give the heterodinuclear double helicate $[FeAg(L^{10})_2]^{3+}$ and the heterotrinuclear organometallic [2]-catenate $[FeAg_2(L^9)_2]^{4+}$ where each metal ion occupies a coordination site satisfying its stereochemical requirements. The receptor L^{11} recognizes 3d- and 4f-block metal ions to give the heterodinuclear d-f triple-helical complexes $[LnZn(L^{11})_3]^{5+}$ where Zn^{II} occupies the *pseudo*-octahedral capping site and corresponds to a noncovalent tripod which properly organizes the strands for their coordination to Ln^{III}. In these new self-assembled lanthanide podates, predetermined structural and physical properties result form *i*) the judicious choice of the d-block ion associated with Ln^{III} and *ii*) the design of the tridentate unit bound to Ln^{III}. $[LnFe(L^{11})_3]^{5+}$ (Ln=La–Eu) display thermochromism and spin-crossover behavior while light emission can be increased by a factor 10^4 when going from $[EuZn(L^{11})_3]^{5+}$ to $[EuZn(L^{12})_3]^{5+}$. The design of tailored receptors for the preparation of stable lanthanide light-converting devices is discussed together with new characterization methods applied to complicated assembly processes in solution.

1. Self-Assembled Lanthanide Building Blocks

1.1. *Organized Lanthanide Luminescent Probes*

The coordination chemists generally consider the 4f-block ions (Ln^{III}) with limited interest since they display the same formal charge (3+) and very similar complexation properties [1]. However, the importance of Ln^{III} is related to their peculiar magnetic and spectroscopic properties (magnetic moments in complexes close to those predicted for the free ions [2], long lifetimes of the excited states, line-like emission bands and large *Stockes* shift [3]) resulting from the fact that excited states and ground states have the same $4f^n$-configuration and that 4f-orbitals are

shielded from the environment by 5s and 5p electrons [3]. The $4f^n$-configuration of a lanthanide ion gives rise to several terms arising from interelectronic repulsions ($\approx 10^4$ cm^{-1}), spin-orbit interactions ($\approx 10^3$ cm^{-1}), and ligand field effects ($\approx 10^2$ cm^{-1}) which are often considered as minor perturbations in contrast with the crucial role played by the ligand field in the coordination chemistry of d-block complexes [4]. The transitions between $4f^n$ electronic states are strictly parity forbidden [4] leading to very low probabilities for such transitions ($\varepsilon \approx 1$ M^{-1}·cm^{-1}), but long radiative lifetimes in the milisecond time scale [5]. In lanthanide complexes, the weak extinction coefficients of Ln^{III} may be overcome by using tailored receptors where light absorption is performed by allowed li-
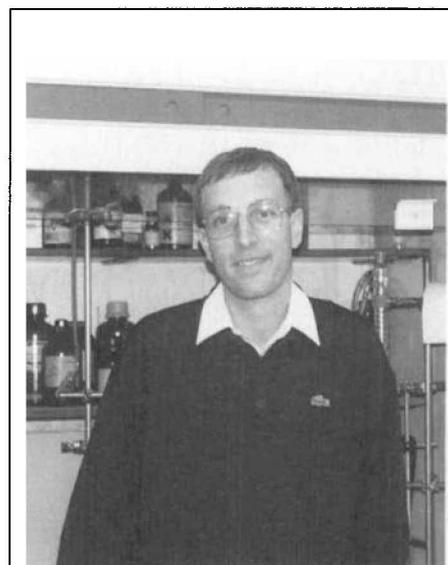
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gand-centered transitions ($\varepsilon \approx 10^3–10^5$ $M^{-1} \cdot cm^{-1}$), followed by energy transfer to Ln^{III} eventually leading to metal-centered luminescence (this overall process is called antenna effect [6]). However, non-radiative relaxation between the various J states of Ln^{III} may occur by interation of the electronic levels of Ln^{III} with suitable vibrational modes of the ligands which often limits the use of coordination complexes as luminescent probes [3][6]. Eu^{III} and Tb^{III} are of special interest in the lanthanide series because of their large energy gaps between their ground and first excited states which limit non-radiative relaxation *via* vibronic coupling and lead to strong emission in the visible (red for Eu^{III} and green for Tb^{III}) [3–6]. Taking advantage of the long lifetime and large *Stockes* shift of sensitized Eu^{III} and Tb^{III} luminescence, analytical sensors have been developed for fluoroimmunoassay [6], protein mapping [7], and DNA labelling [8] together with efficient ultraviolet to visible molecular light-converting devices based on the antenna effect [3][6]. To design an organized lanthanide luminescent probe, a unique combination of features must be realized: *i*) preparation of a receptor possessing suitable coordination sites for Ln^{III}, *ii*) presence of multiple strongly absorbing groups suitable for energy transfer, *iii*) protection of the included Ln^{III} from quenching due to interactions with solvent molecules [9] and/or high-energy vibrations from the ligating groups, and *iv*) high thermodynamic stability and kinetic inertness. When two different and suitable Ln^{III} may be introduced into an organized molecular edifice, new controlled intramolecular $Ln^1{\rightarrow}Ln^2$ energy transfers may occur which lead to directional photonic transfers and visible to visible light-converting devices (*Fig. 1*) [10].

1.2. Self-Assembly of Supramolecular Complexes as a Tool

Ln^{III} display large and variable coordination numbers [11] with little stereochemical preferences [1]. The control of the coordination sphere around Ln^{III}, required for the development of organized lanthanide luminescent probes, thus mainly depends on the preorganization of the binding units of the receptor which limits the structural flexibility and increases the thermodynamic stability [12]. According to the 'Lock and Key' concept [13], podands [14], macrocyclic [15], and macrobicyclic cryptands [6] have been designed for the specific complexation of Ln^{III}, but the fine tuning of the coordination site and of the electronic properties is limited by the rigid
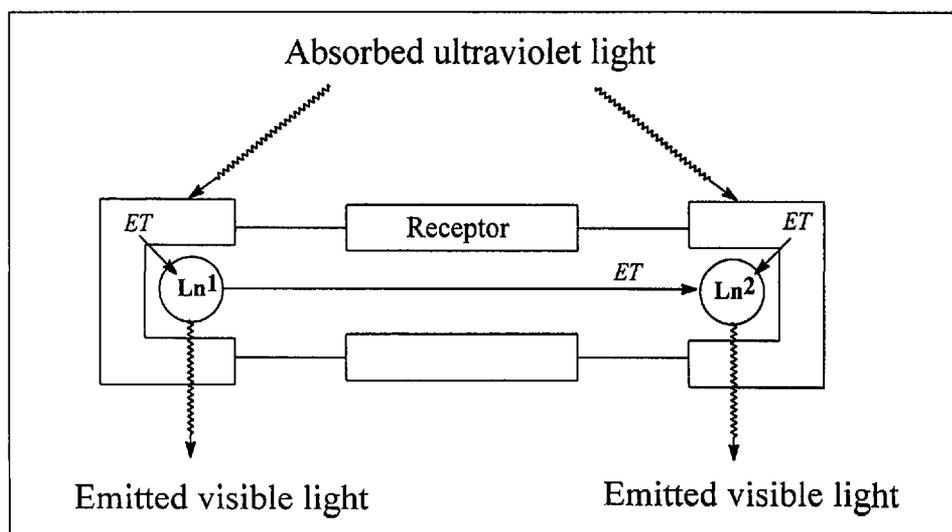
Fig. 1. *Schematic representation of an organized heterodinuclear lanthanide luminescent probe (ET:* energy transfer*)*

Scheme 1. *Self-Assembly Reactions of* L¹ *with Various 3d-Block Ions*
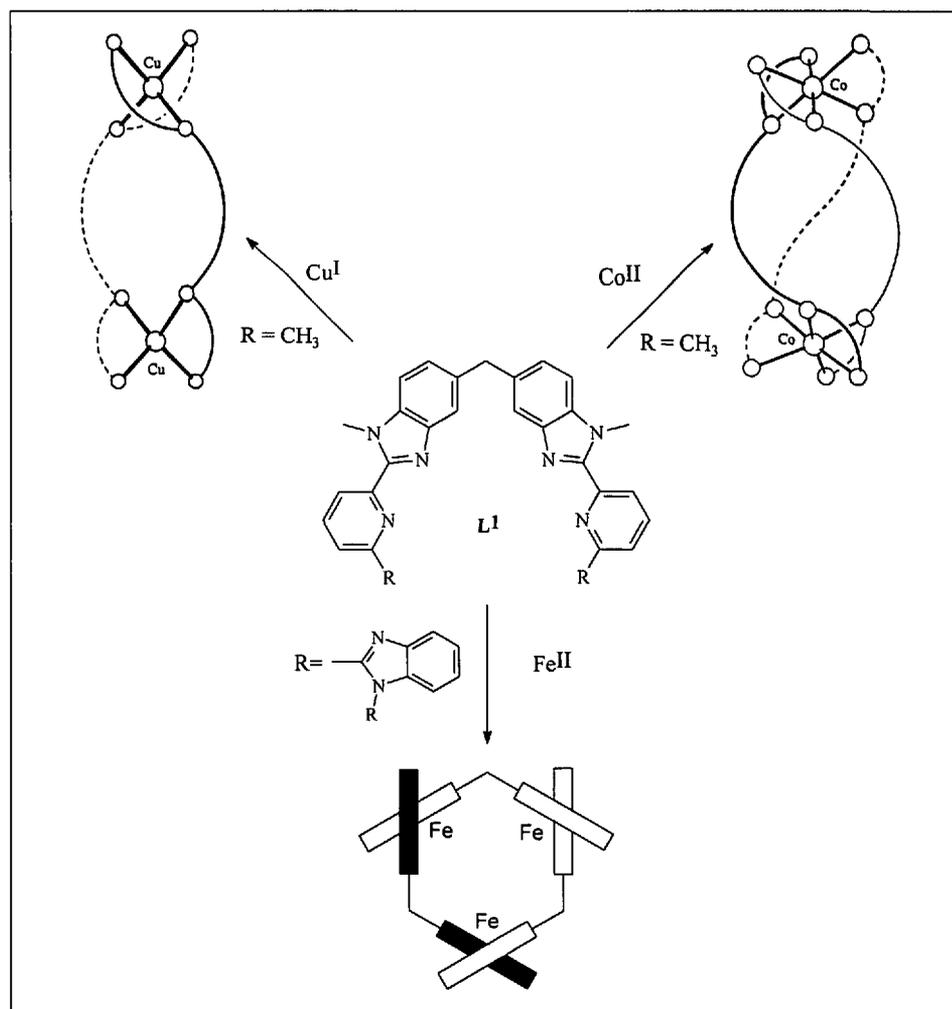
arrangement of the binding units and the tedious syntheses of macrobicyclic ligands. Inspired by the 'Induced Fit' concept [16], it has been shown that acyclic ligands with tailored coordination properties self-assemble [17] with d-block metal ions to give stable organized homopoly-

nuclear architectures [18]. Double- [18] [19] and triple-helical [20] and cylindrical [21] complexes have been investigated to unravel the mechanism of the assembly processes eventually leading to the design of extended homonuclear toroïdal complexes [22] [23], organometallic catenates

terpy

quinquepy

	R^1	R^2		R^1	R^2
L^2	H	Me	L^5	H	C$_6$H$_3$(OMe)$_2$
L^3	H	Et	L^6	H	Oct
L^4	H	Prop	L^7	Me	Et

L^8

Fig. 2. *Energy-level diagram and energy-transfer scheme for [Ln(L^2)(NO$_3$)$_3$(CH$_3$OH)] crystals at 77K* (reproduced with permission from [30])

Fig. 3. *ORTEP view of the X-ray crystal structure of the cation [Eu(L^2)$_3$]$^{3+}$ perpendicular to the C$_3$ axis.* H-atoms have been omitted.
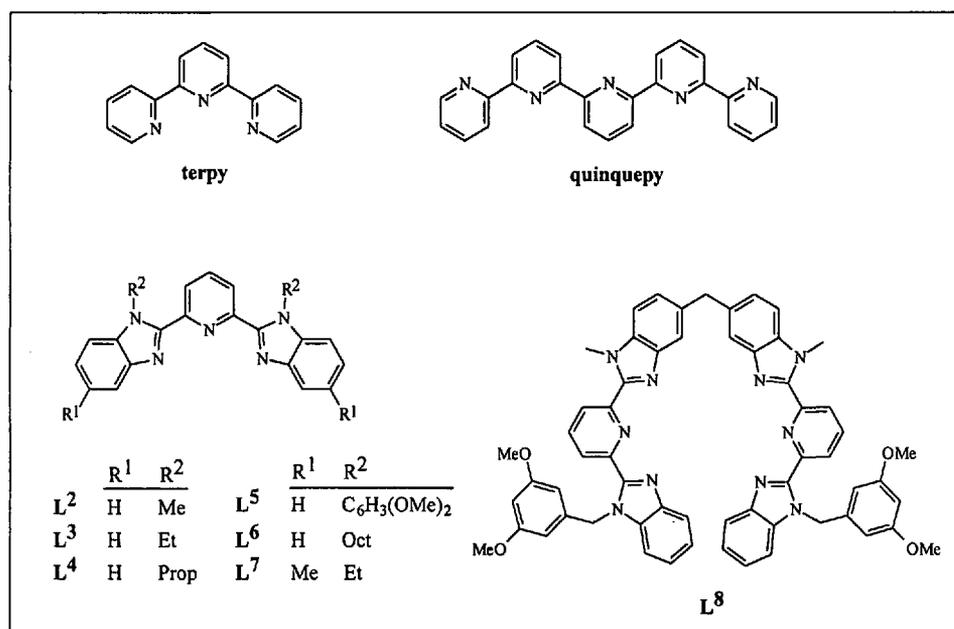
[24], and inorganic grids and racks [25]. One point appears to be essential, if these assembly processes are to give predictible and well-defined products: the binding possibilities of the receptor must be designed to closely match the stereochemical preferences of the metal ions which then control the final structure adopted by the complex. The pronounced stereochemical requirements of d-block ions make them suitable for being used in self-assembly reactions. For instance, the bis-bidentate ligand L^1 is designed to coordinate 'soft' 3d-ions and it reacts with spherical Cu^I to give stable double helicate where each Cu^I is *pseudo*-tetrahedrally coordinated by two bidentate units (*Scheme 1*) [20]. Upon reaction with Co^{II}, the same ligand produces a triple helicate where each metal ion is *pseudo*-octahedrally coordinated by three bidentate units (*Scheme 1*) [20]. Finally, the replacement of the Me groups bound to the 6-position of the pyridine rings in L^1 by terminal benzimidazole groups (as in L^8) leads to trinuclear toroïdal complexes where three Fe^{II} occupy the vertices of a triangle (*Scheme 1*) [22].

A receptor adapted to Ln^{III} should thus possess the following characteristics: *i*) polydentate binding units to fit large coordination numbers and to maximize the stabilizing chelate effect [12], *ii*) judicious spacers between the binding units to favor polynuclear coordination, and *iii*) strongly absorbing units and efficient energy-transfer capabilities to maximize the antenna effect.

1.3. *Mononuclear Lanthanide Building Blocks*

2,2':6',2''-terpyridine (terpy) reacts with Ln^{III} to give stable 1:1 and 1:2 complexes [27], but the thermodynamically unstable D_3-symmetrical 1:3 complexes [Ln(terpy)$_3$]$^{3+}$ can be only prepared in absence of coordinating counter anions [28][29]. The analogous tridentate ligands L^i (i = 2–7) possess extended aromatic benzimidazole side arms bound to the central pyridine ring which are expected *i*) to increase light-harvesting, *ii*) to stabilize and control the final structure of the 1:3 complexes [Ln(L^i)$_3$]$^{3+}$ (i = 2–7) by intramolecular π-stacking interactions, and *iii*) to protect Ln^{III} from external interactions. The ligands L^i (i = 2, 6) react with Ln(NO$_3$)$_3$ to give 1:1 complexes [Ln(L^2)(NO$_3$)$_3$ (CH$_3$OH)] and [Ln(L^6)(NO$_3$)$_3$] (Ln = La–Lu) whose X-ray crystal structures (Ln = Eu) show the ligands to be meridionally tricoordinated to Eu^{III}, three bidentate nitrate anions (and one methanol molecule for L^2) occupying the other coordination
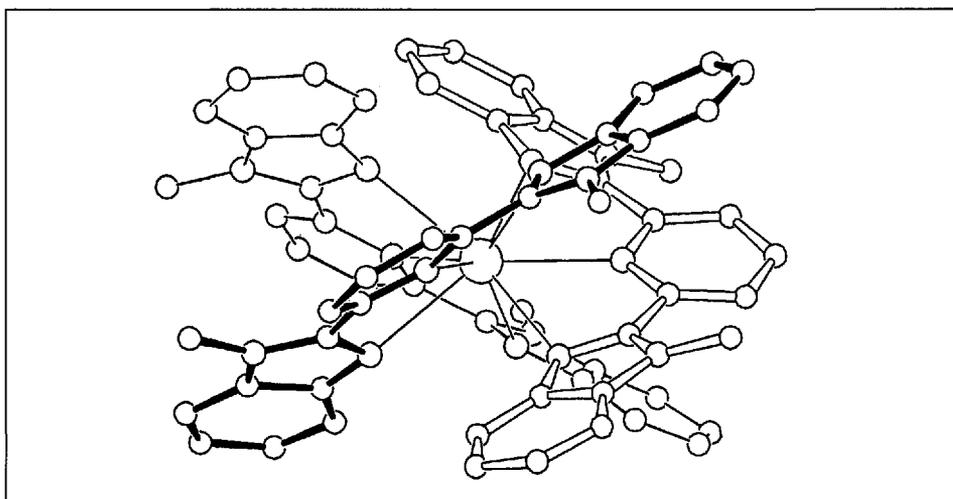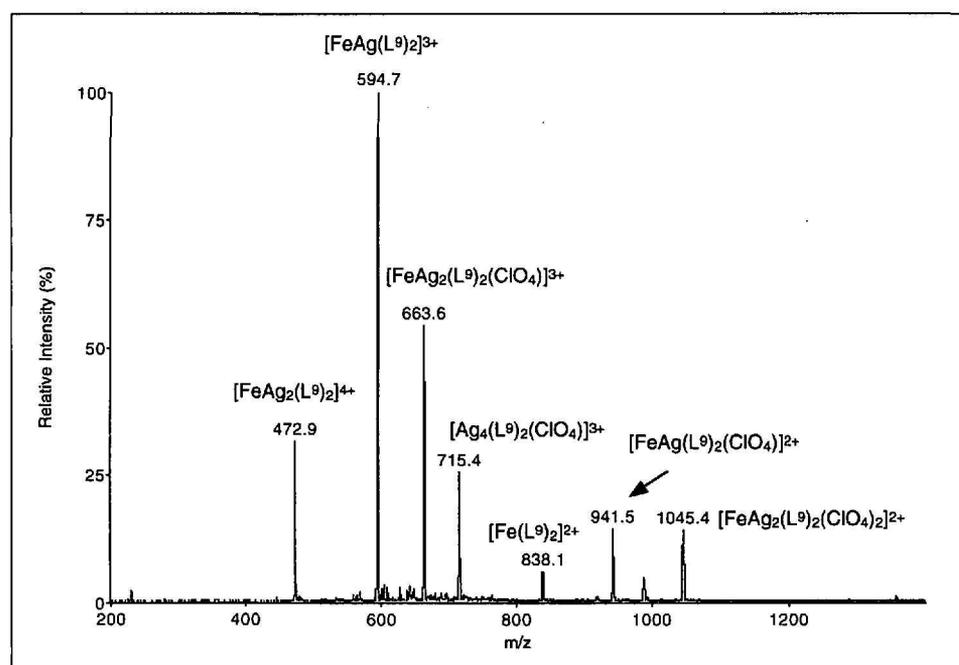
Fig. 4. *ES-MS spectrum of [FeAg₂(L⁹)₂]⁴⁺ in CH₃CN (total ligand concentration 10⁻⁴ M)*

Scheme 2. *Self-Assembly of [Eu₂(L⁸)₃]⁶⁺ in CH₃CN*

The intramolecular energy transfers depicted in *Fig. 2* also occur for $[Ln(L^i)_3]^{3+}$ (i = 2–7), but only a weak luminescence is observed for Ln = Eu, Tb. The quantum yields in acetonitrile indicate that $[Eu(L^i)_3]^{3+}$ (i = 2–7) are less luminescent than $[Eu(terpy)_3]^{3+}$ by a factor of 10^3–10^4 (*Table*) [32]. Neither low-lying LMCT states [10], nor solvent interactions can explain this result, but the significant increase in luminescence observed upon partial decomplexation of the ligands (resulting from addition of water or from the use of bulky substituents as in $[Eu(L^5)_3]^{3+}$; *Table*) leads to the conclusion that efficient radiationless processes are associated with the close packing of the ligands in the mononuclear lanthanide building blocks [32].

1.4. Dinuclear Triple-Helical Lanthanide Building Blocks

According to the criteria established for the assembly of supramolecular polynuclear complexes [34] (see *Sect. 1.2*), dinuclear triple-helical lanthanide complexes might be anticipated, if Ln^{III} is reacted with a linear receptor containing two tridentate binding units. The segmental ligand L^8, which possesses two coordinating units analogous to L^2-connected by a methylene spacer, has been synthesized for this purpose. ElectroSpray Mass-Spectrometry (ES-MS), spectrophotometric and ¹H-NMR studies show that L^8 reacts with $Ln(ClO_4)_3$ in acetonitrile to give the stable homodinuclear D_3-triple-helical complexes $[Ln_2(L^8)_3]^{6+}$ (Ln = La–Lu, *Scheme 2*) [35]. The X-ray crystal structure of $[Eu_2(L^8)_3]^{6+}$ confirms the NMR data and shows the three ligands wrapped about the

sites leading to low symmetrical coordination spheres around Eu^{III} [30]. An almost quantitative intramolecular $L^2(^3\pi\pi^*) \rightarrow Ln^{III}$ energy transfer, associated with the strong ultraviolet absorption of the aromatic receptor ($\varepsilon \approx 30'000$ M^{-1}·cm^{-1}) are responsible for the strong red Eu^{III} emission observed at room temperature for $[Eu(L^2)(NO_3)_3(CH_3OH)]$. The Tb^{III} complexes are less luminescent because of a back-transfer taking place between the $^5D_4(Tb)$ level and the feeding triplet state $(^3\pi\pi^*)$ of the ligand which have similar energies as shown in the energy-level diagram of *Fig. 2*.

When the poorly complexing ClO_4^- anion is used as counteranion, spectrophotometric and ¹H-NMR studies show that the D_3-symmetrical cations $[Ln(L^i)_3]^{3+}$ (Ln = La–Tb, i = 2–7) are quantitatively formed in acetonitrile [31][32]. The X-ray crystal

structure of $[Eu(L^2)_3](ClO_4)_3$ [31] confirms the NMR data: the complex consists of a mononuclear *pseudo*-D_3 cation $[Eu(L^2)_3]^{3+}$ with the three ligands helically wrapped around Eu^{III} producing a *pseudo*-tricapped trigonal prismatic arrangement of the nine coordinated donor N-atoms (*Fig. 3*) [31]. Three strong intramolecular stacking interactions between benzimidazole rings belonging to different strands stabilize the structure, but produce a close packing of the substituents bound to the N-atoms of the benzimidazole rings (R^2) [31][32]. A contraction of the structure to produce smaller cavities adapted to the heavier lanthanide ions is, therefore, difficult to achieve, which leads to the selective complexation of large Ln^{III} as demonstrated by a 10^3 increase in stability when going from $[Lu(L^2)_3]^{3+}$ to $[Tb(L^2)_3]^{3+}$ in acetonitrile [33].

Table. *Quantum Yields at 295 K for Anhydrous Acetonitrile Solutions Relative to $[Eu(terpy)_3]^{3+}$*

Compound	Conc./M	η_{rel}
$[Eu(terpy)_3]^{3+}$	10^{-3}	1.0
$[Eu(L^2)_3]^{3+}$	10^{-3}	6.3×10^{-5}
$[Eu(L^3)_3]^{3+}$	10^{-3}	6.2×10^{-4}
$[Eu(L^4)_3]^{3+}$	10^{-3}	4.8×10^{-4}
$[Eu(L^5)_3]^{3+}$	10^{-3}	2.2×10^{-3}
$[Eu(L^7)_3]^{3+}$	10^{-3}	5.9×10^{-4}
$[EuZn(L^{11})_3]^{5+}$	10^{-3}	$< 1.0 \times 10^{-4}$
$[EuZn(L^{12})_3]^{5+}$	10^{-3}	0.13
$[EuZn(L^{12})_3]^{5+}$	10^{-4}	0.29

pseudo-C_3 axis passing through the metal ions (Eu–Eu distance: 8.876 Å) [36]. The coordination spheres around each Eu(III) are very similar and correspond to *pseudo*-tricapped trigonal prisms. The structure of $[Eu_2(L^8)_3]^{6+}$ may be roughly derived from the packing of two mononuclear $[Eu(L^2)_3]^{3+}$ building blocks along the helical axis (*Scheme 2*).

According to ES-MS and ^{1}H-NMR results [35], the stoichiometric mixing of L^8 (3 equiv.) with $Ln^1(ClO_4)_3$ (1 equiv.) and $Ln^2(ClO_4)_3$ (1 equiv.) in acetonitrile ($Ln^1 \neq Ln^2$; Ln^1 = La, Eu, Tb, Lu; Ln^2 = Eu, Tb, Lu) leads to the self-assembly of only three complexes: the two homodinuclear $[(Ln^1)_2(L^8)_3]^{6+}$ and $[(Ln^2)_2(L^8)_3]^{6+}$ species and the heterodinuclear $[Ln^1Ln^2(L^8)_3]^{6+}$ complex. With the exception of the La/Eu pair, we observe a systematic deviation from the expected statistical distribution, which is an indication that the organization of the ligands around the first metal ion leads to the formation of a second coordination site more favorable for the coordination of a second lanthanide ion of similar size [35]. The energy-transfer scheme depicted in *Fig. 2* still holds for $[Ln_2(L^8)_3]^{6+}$ (Ln = Eu, Tb), but a new intramolecular directional Tb→Eu energy transfer with 76% yield is evidenced in the heterodinuclear complex $[EuTb(L^8)_3]^{6+}$. The dinuclear complexes $[Ln^1Ln^2(L^8)_3]^{6+}$ represent one of the few cases [10] where a pair of different Ln^{III} ions is incorporated into a building block governing the coordination spheres around the metal ions, the distance between them, their protection from external interactions, and the intramolecular energy transfers as depicted in *Fig. 1*.

2. Molecular Programming Controlled by Segmental Ligands

2.1. *Heterodinuclear d-d Complexes as Model Compounds*

During the electrochemical investigations of the double-helical complexes $[Cu_2(quinquepy)_2]^{n+}$ (*Formulae*), *Barley et al.* [37] and later *Potts et al.* [38] have realized that a mixed-valence Cu^{II}/Cu^I dinuclear double helicate could be prepared. In this complex, the pentadentate quinquepyridine ligand is separated into two nucleating regions: a bipyridine unit coordinated to the *pseudo*-tetrahedral Cu^I and a terpyridine unit bound to the *pseudo*-octahedral Cu^{II}. Extension of this work [39] has led to the synthesis of the heterodinuclear double-helical complex $[CoAg(quinquepy)_2]^{3+}$ where Co^{II} is coordinated by two terpyridine units and Ag^I lies in the
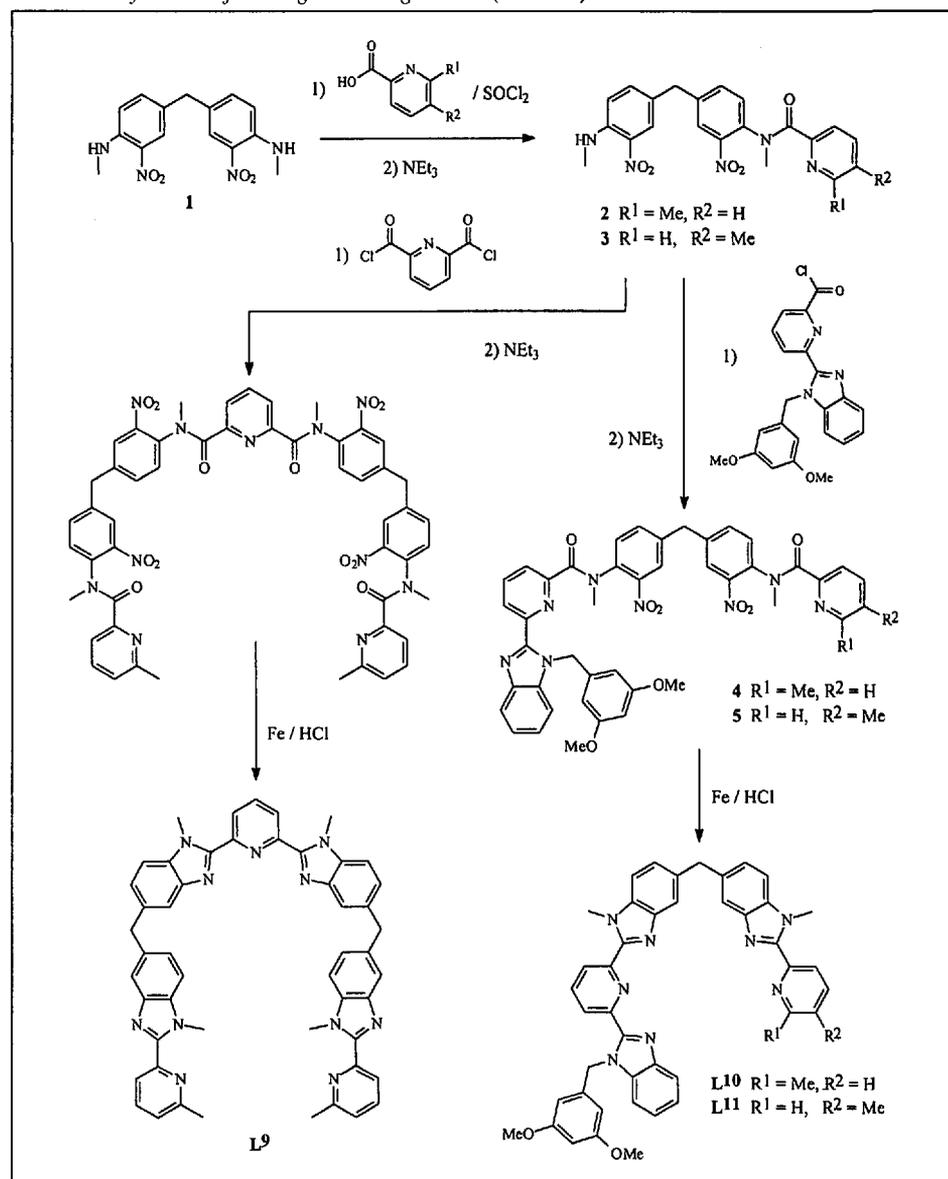
pseudo-tetrahedral site produced by the remaining bidentate units. However, the lack of spacer between the pyridine rings in quinquepy and other oligopyridines prevents a close control of their binding mode as demonstrated by the rich and varied chemistry of oligopyridine ligands [19]. The introduction of suitable spacers between the various coordinating units removes any ambiguities concerning their binding modes and gives segmental ligands possessing different units along the strand. The recent development of a modified *Phillips*-type coupling reaction [40] has allowed us to prepare symmetrical and unsymmetrical segmental ligands possessing aromatic bidentate and tridentate units coded for the recognition of one particular metal ion (*Scheme 3*) [40].

The ligand L^{10} possesses a bidentate unit analogous to 6-methyl-2,2'-bipyridine and designed for the formation of *pseudo*-tetrahedral complexes, while the

tridentate unit is coded for the coordination of *pseudo*-octahedral metal ions [41]. On adding a stoichiometric mixture of Fe^{II} (octahedral cation) and Ag^I (tetrahedral ion), we expect the formation of the heterodinuclear double-helical complex $[FeAg(L^{10})_2]^{3+}$ where each cation occupies a site satisfying its stereochemical preferences. Contrary to our expectation, both Fe^{II} and Ag^I display considerable affinity for the tridentate units leading to stable homonuclear complexes $[Fe(L^{10})_2]^{2+}$ and $[Ag_2(L^{10})_2]^{2+}$ which limit the quantitative formation of the double-helical heterodinuclear complex $[FeAg-(L^{10})_2]^{3+}$ to suitable external conditions: *i*) large ligand concentrations (> 0.02M) and *ii*) an accurate stoichiometric ratio $L^{10}:Fe^{II}:Ag^I = 2:1:1$. A detailed characterization of the assembly process (see *Sect. 2.2*) implies the existence of four different complexes according to *Eqns. 1– 4* [41].

Scheme 3. *Synthesis of the Segmental Ligands* L^i (i = 9–11)

$$Fe^{2+} \quad + \quad 2\,L^{10} \quad \leftrightarrow \quad [Fe(L^{10})_2]^{2+} \qquad \log(\beta_1) = 14.0(7) \qquad (1)$$

$$2\,Fe^{2+} \quad + \quad 2\,L^{10} \quad \leftrightarrow \quad [Fe_2(L^{10})_2]^{4+} \qquad \log(\beta_2) = 17.0(1) \qquad (2)$$

$$2\,Ag^+ \quad + \quad 2\,L^{10} \quad \leftrightarrow \quad [Ag_2(L^{10})_2]^{2+} \qquad \log(\beta_3) = 14.5(5) \qquad (3)$$

$$Fe^{2+} + Ag^+ \quad + \quad 2\,L^{10} \quad \leftrightarrow \quad [FeAg(L^{10})_2]^{3+} \qquad \log(\beta_4) = 18.0(9) \qquad (4)$$
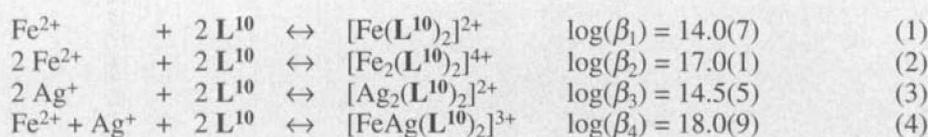
Such complicated equilibria are common for multi-components assemblies between tailored receptors and labile metal ions [42] and this apparently lessens the magical attraction of self-assembly reactions. However, the judicious choice of the experimental conditions offers the possibility to finely control the thermodynamic processes leading to new programmed systems when a dependable speciation can be obtained in solution.

2.2. The Characterization Problem

The final organized supramolecular architectures are stabilized by reversible noncovalent interactions and are thus in equilibrium with their components. This poses a unique challenge for the speciation in solution and for structural characterization. For instance, let us consider the assembly processes of the segmental ligand L^9 with Fe^{II} and Ag^I. First, relative and absolute stoichiometries between the three components must be gauged. One common approach uses the method of continuous variations applied to the electronic absorption spectrum of the ligand which is modified upon complexation to metal ions [43]. Spectrophotometric data resulting from titrations of L^9 with Fe^{II} and Ag^I can be fitted using non-linear least-squares methods [20][43] to chemical equilibria analogous to those depicted in *Eqns. 1–4*, but implying the homonuclear complexes $[Fe(L^9)_2]^{2+}$ and $[Fe_2(L^9)_2]^{4+}$ and the heteronuclear complexes $[FeAg(L^9)_2]^{3+}$ and $[FeAg_2(L^9)_2]^{4+}$ [41]. However, this method is limited to the speciation of compounds displaying different electronic spectra and fails to investigate the homonuclear complexes with Ag^I, because only negligible variations of molar extinctions occur when L^9 is titrated with Ag^I. Secondly, the chemical model suggested by the spectrophotometric investigations is checked with ES-MS. The principle of this very powerful technique of characterization, recently applied to supramolecular complexes [22][44], is simple: a solution containing the complexes is sprayed into the mass spectrometer under conditions in which the neutral solvent molecules are evaporated and separated, and the desolvated ionic species are then introduced directly into the instrument without prior steps of isolation and ionization [22]. The determination of the m/z values allows the accurate assignment of relative stoichi-

ometries to the various ionic species in solution, while the measurement of isotopic pattern (for small z values, $z \le 3$) and the observation of adduct ions with counterions (for large z values, $z \ge 3$) lead to dependable absolute stoichiometries for each complexes [22]. The ES-MS spectrum of a solution containing 10^{-4} M of L^9

and a stoichiometric ratio $L^9{:}Fe^{II}{:}Ag^I = 2{:}1{:}2$ (*Fig. 4*) confirms the spectrophotometric results and displays the expected homo- and heterodinuclear complexes [41]. In contrast to spectrophotometry, titrations of L^9 with Ag^I may be monitored with ES-MS and show the successive formation of four homonuclear complexes $[Ag_n(L^9)_2]^{n+}$ $(n = 1–4)$ [41].

According to the speciations obtained by ES-MS and spectrophotometry, we can determine suitable experimental conditions for which the heterotrinuclear complex $[FeAg_2(L^9)_2]^{4+}$ is formed quantita-
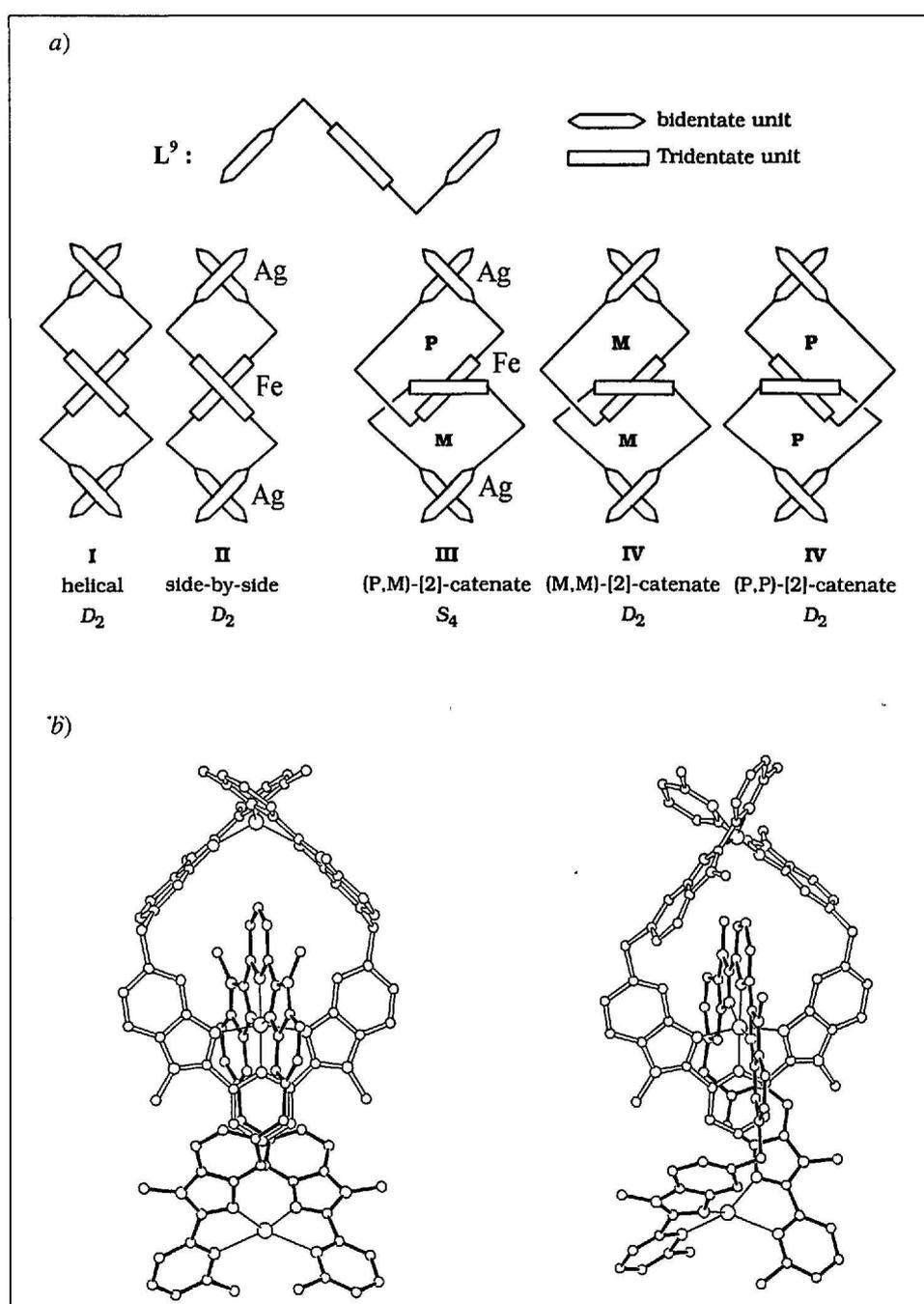
Fig. 5. a) *Possible structure for $[FeAg_2(L^9)_2]^{4+}$ in CH_3CN and* b) *ORTEP views of the X-ray crystal structures of the two diastereomeric forms of $[FeAg_2(L^9)_2]^{4+}$. The heterochiral (P,M)-meso- form* **III** *is shown on the left and one enantiomer (M,M) of the homochiral form* **IV** *on the right. H-atoms are omitted (reproduced with permission from [46]).*

tively (concentration of $L^9 \geq 0.02M$, L^9:Fe^{II}:Ag^I = 2:1:2). Structural characterization is then performed with modern NMR techniques. Detailed ^{1}H-NMR studies using 2D-COSY and 2D-NOESY correlation spectroscopies together with intramolecular diastereotopic methylene probes [45] show that [FeAg$_2$(L^9)$_2$]$^{4+}$ belongs to D_2 or S_4 point groups which are compatible with either helical (I), side-by-side (II), or interlocked [2]-catenate complexes (III, IV, *Fig. 5a*) [41]. Weak interstrand Nuclear *Overhauser* Effects (NOE) preclude structures I and II, and definitely establish that [FeAg$_2$(L^9)$_2$]$^{4+}$ adopts the unusual organometallic [2]-catenate structure [46]. Variable-temperature NMR measurements show that dynamic processes take place in acetonitrile which rapidly interconvert the heterochiral cate-

nate III with its homochiral diastereomer IV on the NMR time scale at 295 K [46]. We were able to isolate single crystals displaying two different morphologies (hexagonal prisms and pellets), but corresponding to the same formula: [FeAg$_2$(L^9)$_2$](PF$_6$)$_4$. The X-ray crystal structures confirm the formation of the two possible diastereomeric organometallic [2]-catenates (*Fig. 5b*) [46].

A complete and accurate structural information can be readily obtained from the X-ray crystal structure, but a total reliance on the crystal structure shows two major limitations: *1*) it is quite often impossible to grow suitable crystals for these large supramolecular assemblies, and even when it is possible, disordered solvent molecules and counterions can give considerable problems in the resolution and

refinement of the structure [26]; *2*) the crystallization process, itself a form of self-assembly [47], may affect significantly the external conditions leading to structures in the solid state not relevant to the species observed in solutions. Therefore, the detailed investigation of the assembly processes in solution is crucial for programming heteronuclear edifices with segmental ligands. Subsequent attempts to crystallize supramolecular complexes for X-ray diffraction studies will take advantage of suitable experimental conditions maximizing the quantity of the desired species in solution.

2.3. Structurally Programmed Heterodinuclear d-f Complexes

The structural programming of heterodinuclear d-f complexes requires the shift of the Me groups from the 6-position of the pyridine ring in L^{10} to the 5-position in L^{11}, thus creating a segmental ligand with a bidentate unit suitable for efficient facial *pseudo*-octahedral coordination of d-block ions [26] and a tridentate unit coded for *pseudo*-tricapped trigonal prismatic coordination of Ln^{III} [31–36]. The recognition of d- and f-block ions indeed occurs and L^{11} reacts with Zn(ClO$_4$)$_2$ and Ln(ClO$_4$)$_3$ (Ln = La–Lu) to give only one heterodinuclear C_3-triple-helical complex [LnZn(L^{11})$_3$]$^{5+}$ in acetonitrile [48]. Spectrophotometric, ES-MS and ^{1}H-NMR studies of the self-assembly process have established that several equilibria occur between the heterodinuclear complex and its homonuclear precursors (*Fig. 6*) [48]. However, suitable experimental conditions (total ligand concentration $\geq 10^{-2}$ M, stoichiometric ratio Ln^{III}:Zn^{II}:L^{11} = 1:1:3) lead to [LnZn(L^{11})$_3$]$^{5+}$ as being the only significant species in solution (>95%). Separation of contact and pseudo-contact contribution to the paramagnetic ^{1}H-NMR shifts and photophysical studies of [LnZn-(L^{11})$_3$]$^{5+}$ (Ln = La–Lu) show that the d-block metal ion lies in a *pseudo*-octahedral capping site produced by the three bidentate binding units which controls the structure of the resulting facial *pseudo*-tricapped trigonal prismatic site occupied by Ln^{III} [49]. [LnZn(L^{11})$_3$]$^{5+}$ may be thus roughly derived from the packing along the C_3 axis of a mononuclear lanthanide building blocks analogous to [Ln(L^2)$_3$]$^{3+}$ with a facial *pseudo*-octahedral 3d-complex [49]. The Zn^{II} complex may be considered as a noncovalent tripod which leads to a new type of podates where the structural and physical properties of the lanthanide building blocks are controlled by the stereochemical and electronic properties of the d-block tripod [49].
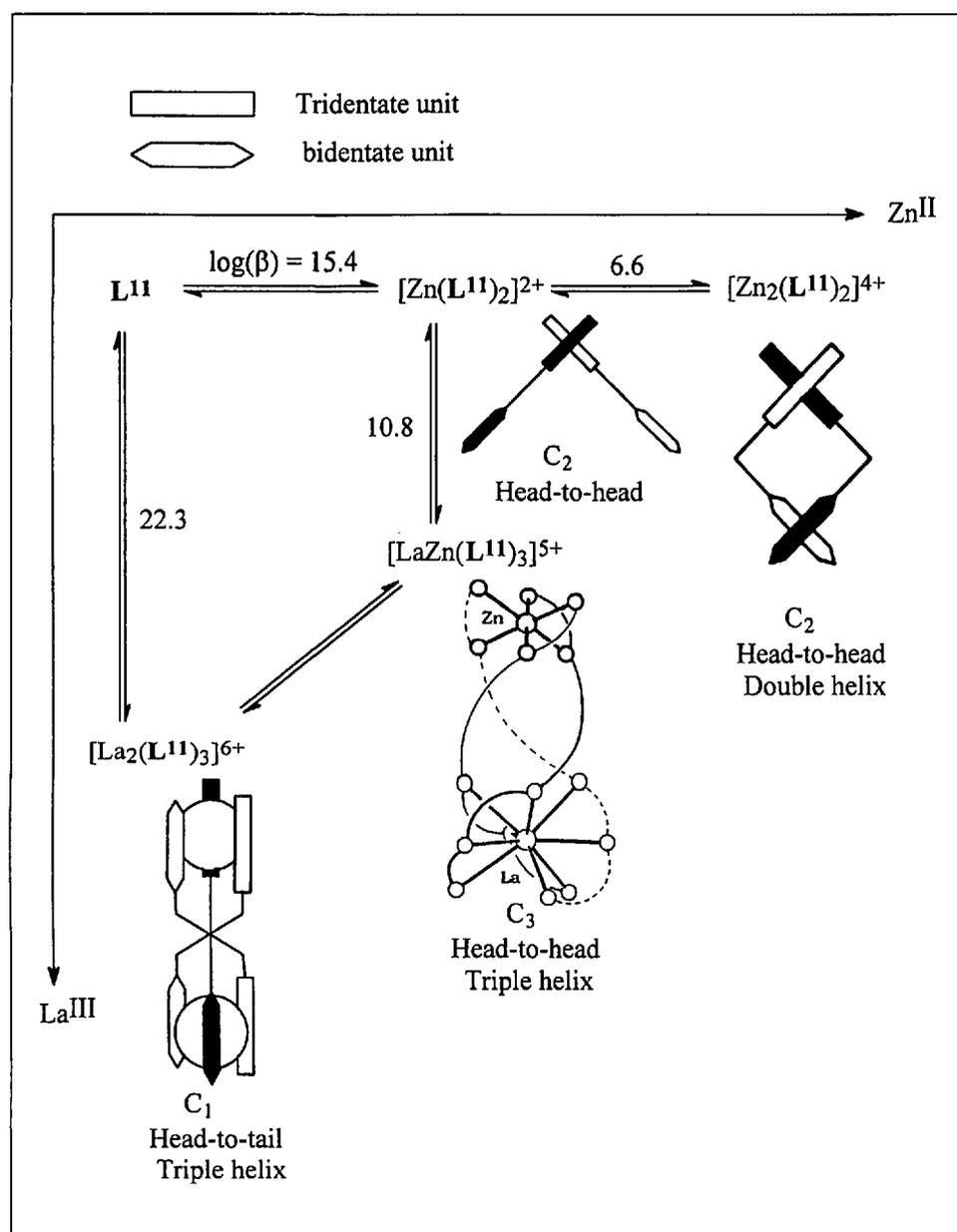
Fig. 6. *Equilibria of* L^{11} *with* La^{III} *and* Zn^{II} *in* CH$_3$CN. Stability constants are given as $log(\beta)$ (reproduced with permission from [48]).

3. Noncovalent Lanthanide Podates with Predetermined Properties

3.1. *The Influence of the Noncovalent d-block Tripod*

Stereochemically, magnetically, and spectroscopically active d-block ions (M) may be introduced into the noncovalent tripod of the heterodinuclear d-f complexes $[LnM(L^{11})_3]^{5+}$. Fe^{II} appears to be particularly suitable since its spin-state, spectroscopic, and magnetic properties are very sensitive to the coordinated unit [50]. Recently, we have prepared the heterodinuclear triple-helical complexes [LnFe-$(L^{11})_3]^{5+}$ for the large Ln^{III} (Ln = La–Eu) in acetonitrile [51]. The sterically more demanding noncovalent Fe^{II} tripod, compared with Zn^{II} tripod, distorts the structure and prevents the structural contraction required for the complexation of the heavy Ln^{III} in the heterodinuclear edifices [51]. New magnetic properties are associated with the formation of the heterodinuclear complexes $[LnFe(L^{11})_3]^{5+}$ (Ln = La–Eu) which display partial thermal Fe^{II} spin-crossover behavior ($^1A \leftrightarrow ^5T$) in acetonitrile. In the complexes $[LnFe(L^{11})_3]^{5+}$, Fe^{II} is essentially diamagnetic (d^6, low-spin) at low temperature (243 K) and a smooth spin transition produces *ca.* 40% of high-spin Fe^{II} at 333 K (*Fig.* 7) for all the Ln^{III} studied [51].

Thermochromism results [50][51] together with a new intramolecular Eu→Fe energy transfer responsible for the complete quenching of the Eu-centred luminescence in $[EuFe(L^{11})_3]^{5+}$. If we consider the spectroscopic and magnetic properties, $[LnFe(L^{11})_3]^{5+}$ are complementary to $[LnZn(L^{11})_3]^{5+}$ for structural investigations: the Zn^{II} tripod allows the detailed study of the lanthanide coordination site by using Ln^{III} as luminescent probes and NMR-paramagnetic shift reagents [49], while the Fe^{II} tripod allows the characterization of the *pseudo*-octahedral site occupied by the d-block ion which acts as a spectrosopic and magnetic probe [51].

3.2. *The Influence of the Binding Unit*

The two binding units of L^{11} differ only in their denticity, the ligating atoms (imine nitrogen) and the chelate bite angle remaining constant, which leads to a limited selectivity for the recognition of d- and f-block ions. Solution studies show that only 45% of $[EuZn(L^{11})_3]^{5+}$ are formed for a total ligand concentration of 10^{-4} M and that a quantitative formation requires ligands concentrations in the range 0.02–0.05M [48][49]. The replacement of the terminal benzimidazole group of L^{11} by a *N,N'*-diethylcarboxamide group in L^{12}
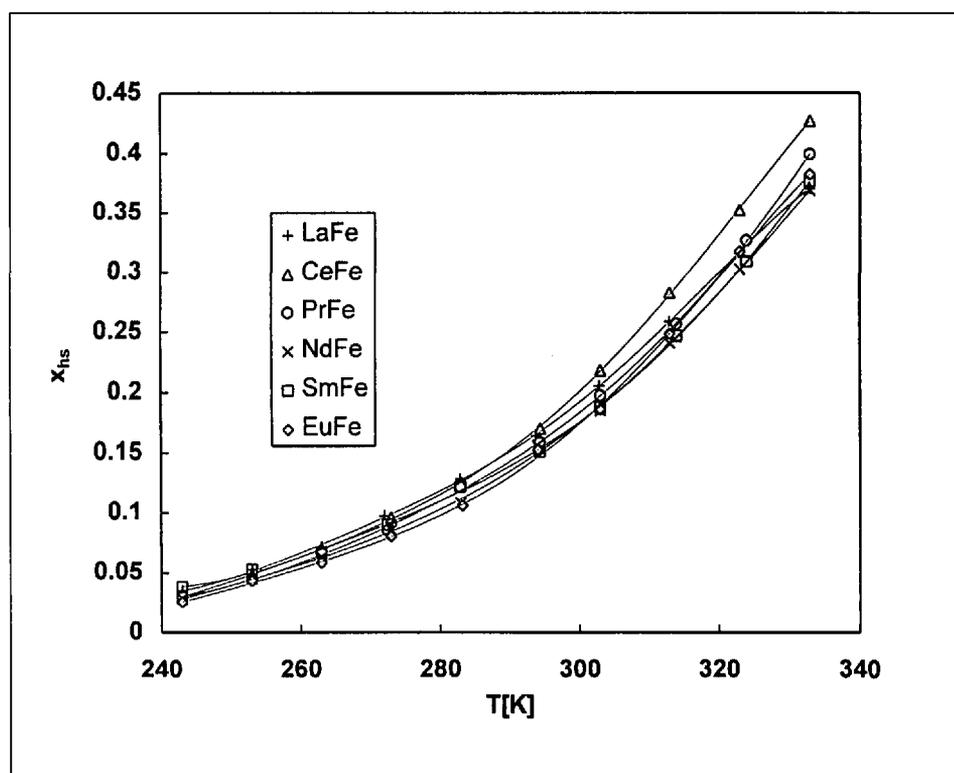
Fig. 7. *Mole fraction of high-spin* Fe^{II} (^5T) *for* $[LnFe(L^{11})_3]^{5+}$ (Ln = La–Eu) *in* CH_3CN *between 243 and 333 K* (reproduced with permission from [51])

improves the selectivity of the assembly leading to the quantitative formation of the analogous heterodinuclear C_3-triple-helical complex $[EuZn(L^{12})_3]^{5+}$ for a total ligand concentration of 10^{-4} M (*Fig.* 8a) [52]. Contrary to the systematic isolation of amorphous powders for the complexes with the lipophilic ligand L^{11}, crystalline materials are obtained with L^{12} allowing X-ray diffraction studies. The crystal structure of the cation $[EuZn(L^{12})_3]^{5+}$ confirms the head-to-head triple-helical structure previously suggested from solution studies (*Fig.* 8b) [52]. Despite the reduced steric hindrance produced by the carboxamide groups in $[EuZn(L^{12})_3]^{5+}$ (compared to the benzimidazole groups in $[EuZn(L^{11})_3]^{5+}$), Eu^{III} lies in a *pseudo*-tricapped trigonal prismatic site very similar to that found for the mononuclear building block $[Eu(L^2)_3]^{3+}$ (see *Sect. 1.3*). Photophysical studies indicate that an efficient protection of the lanthanide occurs in $[EuZn(L^{12})_3]^{5+}$ leading to a strong metal-centred red emission in the solid state and in solution. Quantum-yield measurements in acetonitrile show that [EuZn-$(L^{12})_3]^{5+}$ is *i*) strongly resistant to water hydrolysis and *ii*) more luminescent than the analogous complex $[EuZn(L^{11})_3]^{5+}$ by a factor 10^3–10^4 (*Table*) which demonstrates the crucial role played by the design of the binding unit for the control of the physical properties of the final complex [52].

4. Conclusions

The tridentate aromatic binding units derived from 2,6-bis(1-alkyl-benzimidazol-2-yl)pyridine units (L^2–L^7) correspond to primary receptors for the design of lanthanide building blocks where Ln^{III} is protected from external interactions by the wrapped ligands. Stable and organized cations $[Ln(L^i)_3]^{3+}$ (i = 2–7) are obtained in one step from their components and these complexes act as ultraviolet to visible light-converting devices (Ln = Eu, Tb), even though the closely packed arrangement of the strands severely limits the quantum yields in solution. Using selective self-assembly reactions as a tool, the dinuclear f-f triple-helical complexes $[Ln_2(L^8)_3]^{6+}$ result from the reaction of the more sophisticated symmetrical ligand L^8 with $Ln(ClO_4)_3$ in acetonitrile. In these complexes, two mononuclear building blocks are closely packed along the helical axis restricting the energy-transfer processes to intramolecular processes as depicted in *Fig.* 1. The intramolecular Tb→Eu energy transfer exhibited in $[EuTb(L^8)_3]^{6+}$ represents a promising possibility for directional visible to visible light-converting devices, if pure heterodinuclear f-f complexes may be synthesized [10][34]. As a first step toward this goal, the segmental ligands L^{11} and L^{12} have been shown to react with equimolar mixtures of Ln^{III} and d-block ions (M =

Zn, Fe) to give pure C_3-triple-helical complexes $[LnM(L^i)_3]^{5+}$ (i = 11, 12) where M^{II} is *pseudo*-octahedrally coordinated by the three bidentate binding units leading to a noncovalent tripod which controls the entropically driven [34][42] formation of 'facial' *pseudo*-tricapped trigonal prismatic lanthanide podates. This approach is relevant to biological recognition and regulation processes where the tailored active site results from specific preorganization of the polypeptidic backone using non-

covalent interactions [53]. In this new generation of noncovalent podates, a close control of the structural and physical properties of the lanthanide site results from the judicious choice of i) the d-block ion in the noncovalent tripod and ii) the design of the binding units. Structurally controlled ($[LnZn(L^{11})_3]^{5+}$), magnetically active ($[LnFe(L^{11})_3]^{5+}$), and strongly luminescent ($[EuZn(L^{12})_3]^{5+}$) heterodinuclear d-f complexes may be selectively prepared which offers fascinating possibilities for

the development of new luminescent materials, and biological and analytical sensors with switchable properties [3–8]. Further research in this field includes i) the development of new segmental ligands suitable for the recognition of different 4f-block ions and the preparation of directional light-converting devices and ii) the introduction of covalent tripodal spacers associated with noncovalent tripods to properly organize the lanthanide building blocks in assembled multi-components luminescent materials.

Fig. 8. a) *Self-Assembly of the heterodinuclear d-f triple-helical complex $[EuZn(L^{12})_3]^{5+}$ in CH_3CN and* b) *ORTEP view of the X-ray crystal structure of the cation $[EuZn(L^{12})_3]^{5+}$ perpendicular to the pseudo-C_3 axis. H-atoms have been omitted.*

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