A Simple Chemical Tuning of the Effective Concentration: Selection of Single-, Double-, and Triple-Stranded Binuclear Lanthanide Helicates

Emmanuel Terazzi,* Laure Guénée, Bernard Bocquet, Jean-François Lemonnier, Natalia Dalla Favera, and Claude Piguet*†

Dedicated to Professor Jean-Claude G. Bünzli on the occasion of his 65th birthday

Abstract: The replacement of terminal 2-benzimidazol-6-carboxypyrindine (two internal rotational degrees of freedom) with 2-benzimidazol-8-hydroxyquino line (one internal rotational degree of freedom) into segmental bis-tridentate ligands in going from \(L_2\) and \([L_3 - 2H]^2-\) to \([L_2 b - 2H]^2-\) does not significantly affect the structures of the resulting binuclear lanthanide triple-stranded helical complexes \([Ln_3(L_2 b - 2H)]\), \([Ln_3(L_3 - 2H)]\), and \([Ln_4(L_2 b - 2H)]\) (palindromic helices, intermetallic contact distance \(= 9 \, \text{Å}\), helical pitch \(= 1.4 \, \text{nm per turn}\)). However, their thermodynamic assemblies are completely different in solution, as evidenced by the spectacular decrease of the effective concentrations by two orders of magnitude for \([L_2 b - 2H]^2-\). This key parameter in the \([Ln_3(L_2 b - 2H)]\) \((n = 2, 3)\) complexes is further abruptly modulated along the lanthanide series \((\text{Ln} = \text{La to Lu})\), which provides an unprecedented tool for 1) tuning the number of ligand strands in the final helicates, 2) selectively coordinating lanthanides in the various complexes, and 3) controlling the ratio of lanthanide-containing polymers over discrete assemblies.

Keywords: effective concentration · helical structures · lanthanides · self-assembly · thermodynamics

Introduction

The assembly of the first binuclear lanthanide triple-stranded helicates \([Ln_2(L_1)]^{18+}\) \((\text{Ln}^{III} \, \text{is a trivalent lanthanide})\) were reported more than fifteen years ago. It relied on the well-established concept of a judicious matching between the binding possibilities of the ligands (segmental bis-tridentate and helical twist) and the stereochemical preferences of the metals (nine-coordinate, no ligand field).\(^{[1]}\) The subsequent systematic exploitation of this approach with the replaced segmental ligands \(L_2 - L_5\)—in which 1) the nature of the donor atoms of the tridentate binding sites were somehow varied, but 2) the two degrees of freedom produced by internal rotations about the central pyridine ring were retained—produced binuclear \([Ln_2(L_k)]^{18+}\) \((k = 1, 2)\), \([Ln_2(L_3 - 2H)]^{18+}\) \(^{[2]}\) , \([Ln_3(L_4)]^{18+}\), and \([Ln_4(L_5)]^{12+}\) \(^{[3]}\) triple-stranded helicates (Scheme 1). The metal-centered luminescence of these helicates and that of the closely related system \([Ln_2(L_6 - 2H)]^{18+}\) gave some valuable insights into the intimate mechanisms of intramolecular f–f energy-transfer processes.\(^{[1, 4]}\) The recent decoration of ligand \(L_3\) with water-solubilizing groups opened remarkable perspectives for the use of some derivatives of \([Ln_2(L_3 - 2H)]\) as bioprobes.\(^{[4]}\) Because of the transparency of biological tissue toward near-infrared (NIR) radiation, the field of lanthanide bioprobes evolved toward the design of novel ligands, which were able 1) to accommodate an efficient NIR emitter \((\text{Ln} = \text{Pr, Nd, Er, Yb})\), and 2) to extend the potential excitation light sources into the visible part of the electromagnetic spectrum.\(^{[8]}\) In this context, considerable efforts have been focused on the incorporation of the fused heterocyclic bidentate 8-hydroxyquinolone unit into tridentate binding ligands \(L_7 - L_10\), in which an additional donor group is connected at the 2-position of the pyridine ring (Scheme 2).\(^{[8, 12]}\) Upon deprotonation of the phenol ring and

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[2] Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200902026. This includes the synthesis of ligand \(L_{10b}\) and statistical factors for complexes used in nonlinear least-squares fits; tables of crystallographic data and geometrical analyses; tables of elemental analyses; ESIMS titrations and thermodynamic data; schemes and figures showing the synthetic, spectroscopic, crystallographic, and thermodynamic data; and cif files for the crystal structures of \(7\) and \(10\).
complexation with trivalent lanthanides, the saturated neutral [Ln(Lk-H)]3 complexes (k = 7–10) are readily formed as mixtures of head-to-head-to-head (HHH, C3-symmetrical) and head-to-head-to-tail (HHT, C1-symmetrical) isomers. A ligand-centered charge-transfer band develops in the visible domain, which can be exploited for sensitizing NIR lanthanide emitters.[10–12]

Though the isolation of a single isomer may result from lucky crystallization processes, or through selective interactions of the coordinated phenolate anions with cocrystallized alkaline cations,[10–12] more reliable strategies are to 1) connect three parallel tridentate binding units to a covalent tripod,[9,10] or 2) link two opposite tridentate binding units to a symmetrical spacer as found in ligands L11 and L12. The latter approach leads to the formation of two identical HHH nine-coordinated building blocks related by two-fold symmetry axes in the final binuclear helicates [Ln2(L11-2H)3] (Ln = Eu, Yb)[13] and [Ln2(L12a-2H)3] (Ln = La, Nd).[12]

The existence of neutral D3-symmetrical triple helices for [Ln2(L11-2H)3] has been established both in the solid state (Yb···Yb = 7.77 Å) and in solution. The stability constants in anhydrous acetonitrile [equilibrium shown in Eq. (1); log(βEu,L11-2H2,3) = 26.1(3) and log(βYb,L11-2H2,3) = 25.7(3)][13] although similar to those found for the charged helicates [Ln2(Lk-H)]3+ (k = 1, 2)[14] are alarmingly low and can be compared with log(βEu,L3-2H2,3) ≈ 51 (9.8 < pH < 10.4)[3] estimated for [L3-2H]+ in water, a solvent as competitive as acetonitrile for complexation with trivalent lanthanides.[17]

According to the concept that any metal–ligand assembly [equilibrium shown in Eq. (2)] can be modeled with the help of five microscopic thermodynamic parameters in Equation (3), we suspect that a thorough understanding of the thermodynamic process leading to [Ln2(L12)3]3+, [Ln2(L12-2H)3], and [Ln2(L12a-2H)3] may deliver some clues for programming selectivity and stability along the lanthanide series (αM,n,L is the statistical factor of the assembly,[15] fM,L is the absolute intermolecular affinity (including desolvation) of one site of the ligand for the entering metal, ceff is the effective concentration used to estimate the preorganization

3 [L11-2H]+ + 2 [Ln(CH3CN)3]+ ⇌ [Ln2(L11-2H)3] +18 CH3CN

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The reduction of the number of rotational degrees of freedom per tridentate binding unit in going from L1-L6 (n = 2, see curved arrows in Scheme 1) to L7-L12 (n = 1, see curved arrows in Scheme 2) is appealing, and ligand L12 is ideally suited for elucidating the effect produced by the fusion of the terminal phenol ring with the central pyridine ring in the 8-hydroxyquinoline moieties because the diphenylmethane spacers are identical in L1-L5 and L12.[17-19] Moreover, a preliminary NMR spectroscopy report by Bünzli and co-workers on the formation of [La2(L12a-2H)3] confirmed the formation of the binuclear triple helix in solution, but solubility problems and complicated behaviors along the lanthanide series prevented further characterizations except for the recording of photo-physical data in [Nd2(L12a-2H)]6.[20] These two points are encouraging for the investigation of unprecedented thermodynamic changes along the series. In this contribution, we thus focus on the exploration of the formation of the binuclear triple-stranded helicates [Ln6(L12b-2H)3], with the two following specifications in mind: 1) an analysis of the molecular structure of [Ln6(L12b-2H)3], followed by its comparison with [Ln6(L2)3]+ and [Ln6(L3-2H)3], and 2) a thermodynamic analysis of the formation of [Ln6(L12b-2H)3] and [Ln6(L2)3]+ along the lanthanide series.

Results and Discussion

Synthesis of the ligands: The segmental ligand L12b is obtained in a good global yield (48%) by means of a convergent six-step synthetic procedure (Scheme 3). An improved preparation of the precursor 3[20] starts with the O-benzyl protection of 8-hydroxyquinidine to give 1. A subsequent two-step oxidation using SeO2 followed by treatment with H2NSO3H/NaClO2 provides, successively, the aldehyde 2 and the carboxylic acid 3. The benzyl-protected ligand 7 is then obtained by condensation between precursors 3 and 5[21] followed by a double-reductive modified Philips coupling reaction.[22] Finally, 7 is deprotected by reaction with BBr3 and yields the bis-tridentate ligand L12b. Its 1H NMR spectrum confirms the existence of a dynamically averaged C2 symmetry on the NMR spectroscopic timescale (eight signals for the aromatic protons, two pairs of enantiotopic methylene protons in 1:2 ratio, and two signals for methyl groups) as previously reported for the analogous ligand L12a.[12] The parent monotopic tridentate ligand L10b (Scheme 2) is prepared by using the same synthetic strategy in three steps from 3 and 4[23] (yield 42%; see Scheme S1 in the Supporting Information).

For the two uncomplexed ligands L10b and L12b, the lack of a nuclear Overhauser enhancement (NOE) effect between the ethyl residues of the benzimidazole ring and the protons connected at the 3-position of the quinoline ring (see Scheme 2 for numbering) agrees with a trans arrangement of the N-donor atoms borne by the adjacent aromatic rings (Scheme 3). Slow evaporation of a solution of the precursor ligand 7 in CH2Cl2/MeOH gives colorless prisms, for
which the X-ray crystal structure, shown in Figure 1, confirms that the tridentate binding units adopt the expected trans conformation, which minimizes the global dipole momentum (i.e., the coordinating N-benzimidazole atom is trans to the N-quinoline atom with respect to the interannular C\(\text{C}/\text{C}_0\) bond). Because of the fused character of the hydroxyquinoline ring, the O-benzyl-protected quinoline atom is forced to adopt a constrained cis planar conformation with the adjacent N-quinoline atom, which contrasts with the more flexible trans–trans arrangement found for tridentate 2,6-disubstituted pyridine units in ligands L1–L6. Bond lengths and bond angles are standard (Tables S1–S3 in the Supporting Information), and the ligand possesses a pseudo-twofold axis along the c direction and passing through C26. Two intermolecular stacking interactions can be detected in the unit cell (Figure S1 and Table S3 in the Supporting Information).

Finally, the quantitative analysis of the helicity of the diphenylmethane spacer, defined as a five-atom crooked line (C19–C20–C26–C46–C45 in 7), by using Equation (4) gives a helicity index \(H\) of 0.13, which is diagnostic for a negligible helical preorganization of the ligand strand (\(L = 3.51\) Å is the end-to-end distance of the helix taken as the C19···C45 contact distance; \(A = 0.215\) Å\(^2\) is the area of the subtended figure produced by the projection of the five atoms onto a plane perpendicular to the helical axis defined by the line passing through two terminal atoms of the chain; and \(D = 5.82\) Å is the total length of the crooked line).

\[
H = \frac{6\sqrt{3\pi}LA}{D^2}
\]

Synthesis and structure of the complexes \([\text{Ln}_2(L12b\cdot2\text{H})_3]\) in the solid state: Reaction of the \(C_{3v}\)-symmetrical bis-tridentate ligand L12b (3 equiv) with \(\text{Ln}(\text{OTf})_3\cdotx\text{H}_2\text{O}\) (2 equiv; \(\text{Ln} = \text{La}, \text{Nd}, \text{Eu}; \text{OTf} = \text{CF}_3\text{SO}_3\)) in acetonitrile containing \(\text{K}_2\text{CO}_3\), followed by precipitation with diethyl ether, yields pure red-orange binuclear complexes \([\text{Ln}_2(L12b\cdot2\text{H})_3]\)·\(x\text{H}_2\text{O}\) (Table S4 in the Supporting Information). More than two

Figure 1. View of the crystal structure of the precursor ligand 7 with numbering scheme. Ellipsoids are represented at the 30% probability level.
hundred crystallization attempts provided some extremely fragile red crystals, from which an X-ray crystal structure of limited quality (see the Experimental Section) could be eventually obtained (Figure 2, Table 1; and Tables S5–S7 in the Supporting Information).

Two independent neutral binuclear triple-stranded helical complexes possessing opposite helicities A-[Nd₃(L₁₂b-2H₃)₃] (multiplicity: 8) and B-[Nd₃(L₁₂b-2H₃)₃] (multiplicity: 4) are found in the unit cell, together with interstitial solvent molecules, thus leading to the complete chemical formula \{A-[Nd₃(L₁₂b-2H₃)₃]\}[B-[Nd₃(L₁₂b-2H₃)₃]]·8CH₃CN·4H₂O (10) with Z = 4. Although B-[Nd₃(L₁₂b-2H₃)₃] is located on a crystallographic twofold axis passing through C19e, the metric of the two independent complexes is very similar (Table 1; Tables S5–S7 in the Supporting Information); they show pseudo-D₃ symmetrical binuclear triple-stranded helicates. The two metal cations Nd³⁺ are nine-coordinated in pseudo-tricapped trigonal prismatic sites, with each \(\text{H₃N} \cdot \text{H₂O} \) site being defined by three oxygen atoms of the terminal phenol rings (upper tripod, average Nd–Oₚhen = 2.40(1) Å), three capping nitrogen atoms of the quinolines (average Nd–N₂ₕin = 2.65(1) Å), and three nitrogen atoms of the benzimidazole rings (lower tripod, average Nd–N₂ₕin = 2.72(1) Å; Table 1, Figure 2; and Scheme S2 in the Supporting Information). The Nd–O and the Nd–N bond lengths are comparable to those reported for the mononuclear complex \(\text{HHT-[Nd(L₁₀-H₃)]} \) (R = Me in Scheme 2; average Nd–Oₚhen = 2.406(8) Å, average Nd–N₂ₕin = 2.64(2) Å, and average Nd–N₂ₕin = 2.73(6) Å).[15] This logically leads to the calculation of similar nine-coordinate ionic radii randomly distributed around the values of 1.163 Å that are expected for unconstrained nine-coordinate Nd³⁺.[20] We thus deduce that 1) the different relative orientations of the three 2-benzimidazol-8-hydroxyquinoline binding units bound to Nd³⁺ (H₃N or HHT), and 2) the incorporation of the benzimidazole ring into the diphenylmethane spacer in [Nd₃(L₁₂b-2H₃)] has no major structural effect in the final complexes. However, the average bond valences,[27,28] which reflects the strength of the Ln–donor interactions,[29] provide evidence for stronger interactions for the terminal oxygen atoms in [Nd₃(L₁₂b-2H₃)] at the cost of some weaker interactions with the nitrogen atoms of the benzimidazole rings, thus maintaining the bond-valence sum within the acceptable range of \(V_{\text{Ln}} = 3.0 ± 0.2 \) (Table 1).[30] Comparison with \([\text{TB}_3(L₃-2H₃)],\) in which the terminal-fused hydroxyquinoline rings are replaced with pyridine–carboxylate units (Schemes 1 and 2), shows the opposite trend with a smaller difference between \(V_{\text{La},\text{O}}\) and \(V_{\text{La},\text{N}_\text{bim}}\) (Table 1). An analysis

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**Figure 2.** Perspective view with numbering scheme of the molecular structure of A-[Nd₃(L₁₂b-2H₃)] in the crystal structure of 10. Ellipsoids are represented at 30% probability level. The three strands are represented with different grayscale intensities (the respective strands are named a, b, and c for A-[Nd₃(L₁₂b-2H₃)], and d, e, and f for B-[Nd₃(L₁₂b-2H₃)].)

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**Table 1.** Ln–Ln distances, average Ln–N and Ln–O bond lengths [Å], bond valences \(V_{\text{Ln},\text{O}}\) and \(V_{\text{Ln},\text{N}_\text{bim}}\) bond-valence sums \(V_{\text{Ln}}\) and geometric analysis of the coordination polyhedra in A-[Nd₃(L₁₂b-2H₃)] and B-[Nd₃(L₁₂b-2H₃)] helicates and related complexes.

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[a] \(V_{\text{Ln},\text{O}} = \sum_{\text{Ln–O}} v_{\text{Ln–O}}\), in which \(d_{\text{LnN}}\) is the Ln-donor atom j distance. The bond-valence parameters \(R_{\text{Ln–N}}\) and \(R_{\text{Ln–O}}\) are taken from ref.[28] and \(b = 0.37\) Å.[27] [b] \(V_{\text{Ln}} = \sum v_{\text{Ln–O}}\). Each value is the average of three bond lengths and the number in parentheses corresponds to the standard deviation of the average. The original uncertainties affecting each bond length are given in Table S5 in the Supporting Information. [d] Bzim = benzimidazole and Quin = quinoline.
of the geometries, shapes and helicities of these two complex shows very similar characteristics (Tables S8 and S9, and Figures S2 and S3 in the Supporting Information). Consequently, the Nd–Nd contact distance in the [Nd(L12b–2H)]+ (9.02–9.05 Å) is almost identical to those found in [Tb(L3–2H)]+ and [Tb(L2)]+ (Table 1), thus leading to approximate palindromic helices (length ~1.4 nm, diameter ~1.1 nm, pitch ~1.4 nm per turn).

Interestingly, reaction of the L12b (3 equiv) with Ln(OTf)3·xH2O (2 equiv: Ln = Y, Lu; x = 1–3) in acetonitrile containing K2CO3 failed to give pure bimetallic complexes [Ln(L12b–2H)3·xH2O], which are systematically contaminated with 15–25% of the highly insoluble complexes [Ln(L12b–2H)3(OTf)2] that possess Ln/L12: 2:2 stoichiometry (Table S4 in the Supporting Information).

### Speciation, stability, and structure of the complexes [Ln(L12b–2H)]:

The fent solvent of both free ligand L12b and of its complexes [Ln(L12b–2H)] in water or in polar organic solvent represents a severe handicap for the characterization of the assembly processes operating in solution. After considerable effort, we found that titrations of the deprotonated ligand [L12b–2H]+ (obtained from reaction of L12b with 2 equiv of (nBu)4NOH with increasing quantities of Ln(OTf)3·xH2O (Ln = La, Nd, Eu, Y; x = 1–3) can be performed at 10–45% in CH2Cl2/CH3OH (1:1), or up to 2 × 10–5:1 in DMSO, although the free deprotonated ligand rapidly (within one hour) decomposes in the latter solvent. Monitoring the titrations with electrospray ionization mass spectrometry (ESIMS) for Ln/L12b in the range 0.1 to 2.0 displays similar results in both solvents and ionization mass spectrometry (ESIMS) for Ln/L12b in acetonitrile (Ln = Sm, Eu, Y; Figure 3a) but very significant for small lanthanides (Ln = Y, Lu; Figure 3b). Factor analyses suggest the formation of, respectively, three (large LnIII) or four (small LnII) absorbing species during the titration processes, and the spectrophotometric data can be satisfactorily fitted with the equilibria shown in Equations (5) and (6) for Ln = La, Nd, Eu, and Equations (5)–(7) for Ln = Y, Lu, by using nonlinear least-squares techniques.[30]

3[L12b–2H]+ + 2Ln2+ = [Ln(L12b–2H)3]+ (5)

2[L12b–2H]+ + 2Ln2+ = [Ln(L12b–2H)2]+2+ (6)

[L12b–2H]+ + 2Ln2+ = [Ln(L12b–2H)2]+ (7)

The associated cumulative constants log(β3) and log(β2) collected in Table 2 are of the same magnitude as those previously reported for [Ln(L1–2H)3]+ (Table 3 in the Supporting Information). For the smaller lanthanides (Ln = Sm, Eu; Figure 2; Table S5 in the Supporting Information). Interestingly, the stabilities of [Ln(L12b–2H)3]+ and [Ln(L12b–2H)2]+ for Ln = Nd and Lu are comparable, but the possibility for the smaller lanthanide to form the stable [Ln(L12b–2H)2]+ complex limits the formation of the triple helix (Figure 4), which partly explains the difficulties encountered in isolating pure neutral complexes along the second part of the lanthanide series.

1H NMR spectroscopic data are especially hard to obtain because of the poor sensitivity of this technique, which usually requires concentrations in the millimolar range. Solubility of both ligands and complexes in CDCl3/CD3OH (1:1) is not sufficient, but reliable 1H NMR spectra can be recorded for saturated solutions of [Ln(L12b–2H)]3 in CD2CN with the larger lanthanides (Ln = La, Nd, Eu, Y), whereas titrations cannot be envisioned because of precipitation of [Ln(L12b–2H)3](OTf)2 in an excess of metal. The 1H NMR spectra of both diamagnetic (Ln = La, Y; Figure 5) and fast-relaxing paramagnetic (Ln = Nd, Eu; Figure S6 in the Supporting Information) [Ln(L12b–2H)3] complexes display eight signals for the aromatic protons, which are diagnostic for D3 (helical) or C3h symmetry (side-by-side).[30] The concomitant observation of singlets (i.e., A2 spin systems) for the enantiotopic methylene protons of the diphenylmethane spacer (H9; Figure 5) requires three twofold axes perpendicular to the threefold axis and thus confirms the formation of the expected D3-symmetrical triple helix.[31] A complete assignment is obtained by means of 2D-COSY and 2D-NOESY spectroscopies for the diamagnetic complexes, although some ambiguities remain for the paramagnetic an...
alogues since the increased nuclear relaxation severely limits the use of these two-dimensional techniques (Figure S6 in the Supporting Information).

In the more coordinating [D₆]DMSO solvent, the stability constants are severely reduced and we observe a significant amount of free ligand in slow exchange with [Ln₂(L₁₂b-2H)₃] for Ln/L₁₂b = 0.67 and a total ligand concentration of 2/C₁₄₈₁₀/C₀₃ m (Ln = La, Nd, Eu, Y, Lu; Figures S7–S11 in the Supporting Information). However, the addition of an excess of metal does not produce immediate precipitation and we can record the ¹H NMR spectroscopic signatures for the successive formation of [Ln₂(L₁₂b-2H)₂]⁺ and [Ln₂(L₁₂b-2H)₄]⁺. For large diamagnetic (Ln = La) or paramagnetic (Ln = Nd, Eu) lanthanides, the broadened signals due to intermediate chemical exchange on the NMR spectroscopic timescale, combined with lanthanide-induced relaxation, prevent a detailed analysis. On the other hand, the ¹H NMR spectroscopic titrations with small diamagnetic cations (Ln = Y, Lu; Figures S10 and S11) show the stepwise replacement of the D₃-symmetrical [Ln₂(L₁₂b-2H)₃] helicate with [Ln₂(L₁₂b-2H)₃]⁺ existing as a mixture of double-stranded (D₂ symmetry characterized by enantiotopic H₉,₉′ and diastereotopic H₁₀,₁₀′ methylene protons)[34] and side-by-side (C₂ᵥ symmetry characterized by two diastereotopic pairs of methylene protons for H₉,₉′ and H₁₀,₁₀′, Scheme 4a)[34] a situation previously documented for related binuclear lanthanide complex with bis-bidentate Schiff base ligands.[36] The ultimate complex [Ln₂(L₁₂b-2H)₄]⁺ displays ¹H NMR spectroscopic singlet signals for all methylene probes H₉,₉′ and H₁₀,₁₀′, which is in line with an average extended planar C₂ᵥ symmetry of the ligand strand (Scheme 4b) previously established for the related complexes [Ln₂(L₂)(NO₃)₆].[25]

**Thermodynamic modeling and rationalization of the formation of the complexes [Ln₂(L₁₂b-2H)ₙ]⁺⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻��****

Figure 3. Variation of the absorption spectra and corresponding variations of molar extinctions at seven different wavelengths observed for the spectrophotometric titrations of [L₁₂b-2H]²⁻ (2 × 10⁻³ m in CH₂Cl₂/MeOH 1:1) with a) Nd(OTf)₃ and b) Y(OTf)₃ (Ln/L₁₂b = 0.1–3.0).
Table 2. Experimental and computed cumulative formation constants 
log(β_{L12b}^{Ln}) and log(β_{L12b}^{Ln/u}) obtained by spectrophotometry according to the 
equilibria in Equations (5)–(7) and (11)–(13) for the complexes 
[Ln(L12b-2H)]^{3+} [N2O] and [Ln(L10b-2H)]^{3+} [N2O] (Ln=La, Nd, Eu, Y, 
and Lu; CH2Cl2/MeOH 1:1, 298 K).

<table>
<thead>
<tr>
<th>Ln^{III}</th>
<th>La</th>
<th>Nd</th>
<th>Eu</th>
<th>Y</th>
<th>Lu</th>
</tr>
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<tbody>
<tr>
<td>N_{0}/[^{15}A]</td>
<td>1.216</td>
<td>1.163</td>
<td>1.120</td>
<td>1.075</td>
<td>1.032</td>
</tr>
<tr>
<td>log(β_{L12b}^{Ln})</td>
<td>23.1(6)</td>
<td>24.8(5)</td>
<td>27.0(8)</td>
<td>26.5(5)</td>
<td>24.0(4)</td>
</tr>
<tr>
<td>calcld[8]</td>
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<td>24.8</td>
<td>27.0</td>
<td>26.8</td>
<td>24.3</td>
</tr>
<tr>
<td>calcld[9]</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>26.5</td>
<td>24.0</td>
</tr>
<tr>
<td>log(β_{L12b}^{Ln/u})</td>
<td>17.0(5)</td>
<td>18.7(4)</td>
<td>20.2(7)</td>
<td>20.9(4)</td>
<td>18.6(3)</td>
</tr>
<tr>
<td>calcld[8]</td>
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<td>18.7</td>
<td>20.2</td>
<td>20.9</td>
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<tr>
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<td>–</td>
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<td>18.6</td>
</tr>
<tr>
<td>log(β_{L12b}^{Ln})</td>
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<td>≤ 11</td>
<td>≤ 12</td>
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<td>11.7(2)</td>
</tr>
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<td>12.0</td>
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<td>–</td>
<td>–</td>
<td>13.0</td>
<td>11.7</td>
</tr>
<tr>
<td>log(β_{L12b}^{Ln/u})</td>
<td>20.3(5)</td>
<td>19.7(5)</td>
<td>20.1(6)</td>
<td>23.1(9)</td>
<td>23.5(9)</td>
</tr>
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<td>19.7</td>
<td>20.1</td>
<td>23.4</td>
<td>23.7</td>
</tr>
<tr>
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<td>–</td>
<td>–</td>
<td>23.1</td>
<td>23.5</td>
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<tr>
<td>log(β_{L12b}^{Ln})</td>
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<td>16.3</td>
</tr>
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<tr>
<td>log(β_{L12b}^{Ln/u})</td>
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<td>7.6(6)</td>
<td>7.9(3)</td>
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<td>8.7(7)</td>
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<td>calcld[9]</td>
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</tr>
<tr>
<td>AF_{u}[10]</td>
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<td>0.0017</td>
<td>0.0006</td>
<td>0.0171</td>
<td>0.0180</td>
</tr>
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<td>calcld[8]</td>
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<td>–</td>
<td>–</td>
<td>0.0050</td>
<td>0.0025</td>
</tr>
</tbody>
</table>

[a] Ionic radii for nine-coordinate trivalent lanthanides. [b] The quoted errors correspond to those estimated during the nonlinear least-square fits. [c] Computed with Equations (8)–(10) and (14)–(16) and parameters of Table 3 (first fitting process). [d] Computed with Equations (8)–(9) and (14)–(17) and parameters of Table 3 (second fitting process). [e] Willcott agreement factor; see text and references.[10]

Equations (8)–(10), in which the three experimentally accessible thermodynamic constants β_{L12b}^{Ln}, β_{L12b}^{Ln/u}, and β_{L12b}^{Ln} require a minimal set of four microscopic parameters for 
their modeling (β_{L12b}^{Ln} is the affinity, including desolvation, of Ln^{III} for the tridentate binding site in [L12b-2H]); u^{Ln,L} and u^{L,L} are the average Boltzmann factors for intramolecular 
homo-component interactions operating within the final assemblies; and e^{eff} is the average effective concentration characterizing the macrocyclization processes responsible 
for the formation of discrete double-stranded or triple-stranded helicates), together with a statistical factor calculated 
by using the method of symmetry-numbered, first introduced by Benson (detailed calculations are given in the Supporting Information).[14,17]

\[
\begin{align*}
\beta_{L12b}^{Ln} & = 96(f_{L12b}^{Ln})(e^{eff})(u^{Ln,L})(u^{L,L}) \\
\beta_{L12b}^{Ln/u} & = 72(f_{L12b}^{Ln})(e^{eff})(u^{L,L})(u^{Ln,L}) \\
\beta_{L12b}^{Ln} & = 36(f_{L12b}^{Ln})(e^{eff})(u^{Ln,L})
\end{align*}
\]

The collection of a sufficient number of experimental stability 
constants forced us to perform additional spectrophotometric 
titration of the simple tridentate ligands [L10b-2H]^{-} 
with Ln(OTf)_{3}·xH_{2}O (2×10^{-4} M in CH_{2}Cl_{2}/CH_{3}OH (1:1, 
298 K); these eventually give three additional macroconst-
ants β_{L10b}, β_{L10b}^{Ln} and β_{L10b}^{Ln/u}, which correspond to 
the equilibria in Equations (11)–(13) after nonlinear least-
squares fits of the data (Table 2).[10]

\[
\begin{align*}
3[L10b-2H]^{-} + Ln^{3+} & \rightleftharpoons [Ln(L10b-2H)]^{2+} \\
2[L10b-2H]^{-} + Ln^{3+} & \rightleftharpoons [Ln(L10b-2H)]^{+} \\
[L10b-2H]^{-} + Ln^{3+} & \rightleftharpoons [Ln(L10b-2H)]^{2+} + Ln^{3+}
\end{align*}
\]

To limit the number of adjustable microscopic parameters, we have set 1) u^{L10b} = u^{L10b} = u^{Ln,L}; which implies statistical distributions of the microspecies 
HHT-[Ln(L10b-2H)]^{2+} = 1, and HHT-[Ln(L10b-2H)]^{+}/HHT-[Ln(L10b-2H)]^{2+} = 0.33 (justified by the similar Nd–N and 
Nd–O bond lengths and bond valences found in HHT-
[Nd(L10b-2H)] and (HHHT)-[Nd(L12b-2H)] in the solid state), and 2) \( \frac{u^{Ln,L}}{u^{Ln,L}} = \frac{u^{Ln,L}}{u^{Ln,L}} \) (i.e., the tridentate binding 
units in [L10b-2H]^{-} and [L12b-2H]^{-} have similar affinities for Ln^{III}). Application of the site-binding model [Equa-
tion (3) eventually gives Equations (14)–(16).

\begin{align*}
\rho_{1,3}^{\text{La.L12b}} &= 16(f_{\text{La.L12b}}^L)^3(u_{L,1,1})^3 & (14) \\
\rho_{1,2}^{\text{La.L12b}} &= 12(f_{\text{La.L12b}}^L)^2(u_{L,1,1})^2 & (15) \\
\rho_{1,1}^{\text{La.L12b}} &= 6(f_{\text{La.L12b}}^L) & (16)
\end{align*}

Simultaneous multilinear least-squares fits of Equations (8)–(10) and (14)–(16) for each lanthanide yield the sets of four microscopic thermodynamic descriptors collected in Table 3 (rows 1–8) and shown in Figure 6a, which satisfactorily reproduce the experimental data, as ascertained by the small computed values of the Willcott agreement factors (0.0006 ≤ AF_{\text{La}} ≤ 0.0180, Table 2) [38].

The main driving force of the complexation processes results from intermolecular metal–ligand connection processes, which do not significantly vary along the lanthanide series (−44 ≤ ΔG_{\text{inter}}^{\text{La.L12b}} ≤ −39 kJ mol⁻¹). The interligand interactions also poorly change along the lanthanide series, but contribute to a global destabilization (ΔE^{\text{ex}} ≥ 0) when the metals are stepwise saturated with tridentate binding units. The concave behavior of ΔE^{\text{ex}} on, which shows a minimum intermetallic repulsion for mid-range Ln III (Figure 6a), is responsible for the parallel extra stabilization of the binuclear [Ln₂(L12b-2H)₃]⁶⁻ complexes (n = 2, 3) in the middle of the series (Table 2; Figure S5 in the Supporting Information).

However, the most striking point concerns the very low effective concentrations [39] (−9 ≤ log(ε_{\text{eff}}) ≤ −6), which is at least two orders of magnitude smaller than 1) log(ε_{\text{eff}}) = −4.1(4) reported for [Lu₂(Lk)₆]⁶⁺ in acetonitrile (k = 1, 2, Scheme 1; n = 2, 3), [19] and 2) log(ε_{\text{eff}}) = −0.3(4), estimated from thermodynamic and kinetic data collected for [Eu₃(L₃-2H)₆]³⁻ in water at pH 6.15. [15] Moreover, log(ε_{\text{eff}}) in [Ln₂(L12b-2H)₆]⁶⁻ abruptly decreases in going from Ln = Eu to Ln = Y, which translates into an inversion of the sign of the free-energy change characterizing intramolecular macrocyclization processes (ΔG_{\text{inter}}^{\text{La.L12b}} > 0) is favorable for large Ln III, but ΔG_{\text{inter}}^{\text{La.L12b}} > 0 is unfavorable for small Ln III, Figure 6a). Although this factor may explain the limited stability of macro(bicyclic double-stranded and triple-stranded binuclear helicates with respect to the noncy-
Table 3. Fitted microscopic thermodynamic parameters for \([\text{ Ln(L12b-H)}_3]^\text{+}\) and \([\text{ Ln(L12b-2H)}_3]^\text{+}\) (Ln = La, Nd, Eu, and Lu; CH3Cl/CH3OH 1:1, 298 K).\(^{[1]}\)

<table>
<thead>
<tr>
<th>Fitted parameters (first fit)(^{[b]})</th>
<th>La</th>
<th>Nd</th>
<th>Eu</th>
<th>Y</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\log(f_{\text{L12b}}^{\text{La-H}}))</td>
<td>7.44(6)</td>
<td>6.87(5)</td>
<td>7.14(2)</td>
<td>7.1(4)</td>
<td>7.7(3)</td>
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<tr>
<td>(\Delta G_{\text{int}}^{\text{La-H}}) [kJ mol(^{-1})]</td>
<td>-42.4(4)</td>
<td>-39.2(3)</td>
<td>-40.7(1)</td>
<td>-41(2)</td>
<td>-44(2)</td>
</tr>
<tr>
<td>(\log(c^{\text{La}}))</td>
<td>-6.8(1)</td>
<td>-6.4(1)</td>
<td>-5.83(4)</td>
<td>-8.5(8)</td>
<td>-8.98(8)</td>
</tr>
<tr>
<td>(\Delta G_{\text{int}}^{\text{Eu-H}}) [kJ mol(^{-1})]</td>
<td>-3.6(6)</td>
<td>-2.7(5)</td>
<td>-7.5(2)</td>
<td>8(3)</td>
<td>7.5(3)</td>
</tr>
<tr>
<td>(\log(c^{\text{Eu}}))</td>
<td>-1.09(8)</td>
<td>-0.70(6)</td>
<td>-0.86(2)</td>
<td>-0.3(4)</td>
<td>-0.2(4)</td>
</tr>
<tr>
<td>(\Delta E_{\text{el}}^{\text{La-H}}) [kJ mol(^{-1})]</td>
<td>7.2(5)</td>
<td>4.0(4)</td>
<td>4.3(1)</td>
<td>2(1)</td>
<td>1.2(1)</td>
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<tr>
<td>(\Delta E_{\text{el}}^{\text{Eu-H}}) [kJ mol(^{-1})]</td>
<td>-3.5(2)</td>
<td>-1.5(2)</td>
<td>-0.99(6)</td>
<td>-2.5(8)</td>
<td>-4.9(8)</td>
</tr>
<tr>
<td>(\Delta E_{\text{el}}^{\text{La-H}}) [kJ mol(^{-1})]</td>
<td>20(1)</td>
<td>9(1)</td>
<td>5.6(4)</td>
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</tr>
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</table>

<table>
<thead>
<tr>
<th>Fitted parameters (second fit)(^{[c]})</th>
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<th>Nd</th>
<th>Eu</th>
<th>Y</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
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<td>(\log(f_{\text{L12b}}^{\text{La-H}}))</td>
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</table>

\[a\] The uncertainties correspond to those found during the multilinear least-square fits. \[b\] First fit: \(f_{\text{L12b}}^{\text{La-H}}, c^{\text{La}}, c^{\text{Eu}}, c^{\text{Y}}, c^{\text{Lu}}\) by using Equations (8)–(10) and (14)–(16). \[c\] \(\Delta G_{\text{int}}^{\text{La-H}} = -RT \ln(a_{\text{L12b-H}}^{\text{La-Ln}})\), \(\Delta G_{\text{int}}^{\text{Eu-H}} = -RT \ln(a_{\text{L12b-H}}^{\text{Eu-Ln}})\), \(\Delta G_{\text{int}}^{\text{La-H}} = -RT \ln(a_{\text{L12b-H}}^{\text{La-Ln}})\). \[d\] \(\Delta E_{\text{el}}^{\text{La-H}}\) (La and Eu) by using Equations (8)–(9) and (14)–(17).

A second round of multilinear least-squares fits of Equations (8), (9), and (14)–(17) for Ln = Y, Lu obviously improves the quality of the fit, but indeed confirms the counterintuitive sequence \(\Delta E_{\text{el}}^{\text{La-H}} > \Delta E_{\text{el}}^{\text{Eu-H}}\) (Table 3, rows 9–18; Figure S12 in the Supporting Information), which may now rationalize the low stability constants observed for \([\text{ Ln(L12b-2H)}_3]^\text{+}\) with large Ln\(^{III}\). From this complete thermodynamic picture for the formation of \([\text{ Ln(L12b-2H)}_3]^\text{+}\) it is tempting to assign the huge decrease of \(\log(c^{\text{Eu}})\) in going from \(\text{L2 (Ln = Lu)}^{[19]}\) to \([\text{L3-2H]}^{2+} (Ln = Eu)^{[13]}\) to \([\text{L12b-2H)}_3]^\text{+}\) (Ln = La, Nd, Eu, Y, Lu) to the replacement of flexible terminal pyridine-carboxyamide (or late) groups with fused ten-membered rigid aromatic 8-hydroxyquinolines.

The uncertainties correspond to those found during the multilinear least-square fits. First fit: \(f_{\text{L12b}}^{\text{La-H}}, c^{\text{La}}, c^{\text{Eu}}, c^{\text{Y}}, c^{\text{Lu}}\) by using Equations (8)–(10) and (14)–(16). First fit: \(f_{\text{L12b}}^{\text{La-H}}, c^{\text{La}}, c^{\text{Eu}}, c^{\text{Y}}, c^{\text{Lu}}\) by using Equations (8)–(9) and (14)–(17).

For this complete thermodynamic picture for the formation of \([\text{ Ln(L12b-2H)}_3]^\text{+}\) it is tempting to assign the in the Supporting Information). Despite the use of two different solvents for imporous solubility reasons, we have indeed selected two systems (CH3Cl/CH3OH (1:1) and CH3CN) with similar polarities, which allow a direct comparison of the different parameters. We immediately notice that the absolute magnitude of the various thermodynamic parameters are similar, whereas their variation along the lanthanide series differ in both systems (Figure 6). However, the larger and most striking discrepancy unambiguously concerns the gradual increase of the effective concentration along the series for \(\text{L2 (Ln = Lu)}^{[19]}\) to \([\text{L3-2H]}^{2+} (Ln = Eu)^{[13]}\) and \([\text{Ln(L13)}_3]^\text{+} (n = 1–3)\) in acetonitrile along the lanthanide series. Equations (8), (9), and (14)–(16) still apply for fitting the experimental stability constants (Table S15 in the Supporting Information) to give the microscopic parameters shown in Figure 6b (Table S16).

For this complete thermodynamic picture for the formation of \([\text{ Ln(L12b-2H)}_3]^\text{+}\) it is tempting to assign the
binuclear lanthanide helicates [Ln(L12b-2H)] and shown that it is similar to those of [Ln(L3-2H)] and [Ln(L2)], in the solid state and in solution, despite the fusion of the terminal aromatic rings in L12b. On the other hand, the thermodynamic assembly process is specific for each ligand strand, and is strongly influenced by the choice of the solvent. In weakly polar organic solvents, the free-energy changes in the connection of Ln^3+ to an N2O tridentate and Ln2( )2H)3+ are strongly influenced by the choice of the solvent, as a function of the inverse of nine-coordinate ionic radii for the assemblies of a) [Ln(L10b-H)]1−n+[ and [Ln(L12b-2H)] n=1−3, CH2Cl2/CH3OH (1:1, 298 K), and b) [Ln(L1)], n+ and [Ln(L2)], n+ (n=1−3, CH3CN, 298 K). The dotted lines are only guides for the eyes.

**Conclusion**

Reconsidering the specifications mentioned in the introduction, we have indeed established the structure of the triple-stranded binuclear helicates [Ln(L12b-2H)] and shown that it is similar to those of [Ln(L3-2H)] and [Ln(L2)], in the solid state and in solution, despite the fusion of the terminal aromatic rings in L12b. On the other hand, the thermodynamic assembly process is specific for each ligand strand, and is strongly influenced by the choice of the solvent. In weakly polar organic solvents, the free-energy changes in the connection of Ln^3+ to an N2O tridentate binding site are similar for [L12b-2H]3+ or L2 (ΔG^L2/L12b = ΔG^L2/L12b ≈ −42 kJ mol−1), and we deduce that the huge contribution of charge neutralization to the entropy of complexation (through the relaxation of the organization of the solvent molecules), is mainly restricted to water or to highly polar solvents, in which the formation of ionic pairs is negligible. For the Ln^3+[L12b-2H]2− system, we must consider that the respective counterions, TFO−/(nBu)4N+, have non-negligible interactions with their respective partners, and that their release into solution during the metal–ligand complexation process limits the classical charge-neutralization process described in water. This behavior may explain the decrease in stability by twenty-five orders of magnitude in going from [Ln(L3-2H)] (measured in water) to [Ln(L12b-2H)] (measured in CH2Cl2/CH3OH) or [Ln(L11-2H)] (measured in CH3CN). Beyond this crucial factor, the comparison of the assembly of the negatively charged segmental ligand [L12b-2H]2− with that of its neutral analogue L2, performed in solvents of comparable polarities, shows that the effective concentration plays a leading role. Firstly, it decreases by approximately two orders of magnitude in going from L2 to [L12b-2H]2− because of the reduction of the total number of rotational degrees of freedom within the tridentate binding units that possess fused hydroxyquinoline groups. This eventually disfavors the macrocyclization processes that lead to [Ln(L12b-2H)]3+. Secondly, the effective concentration decreases along the lanthanide series for [L12b-2H]2−, whereas it increases for L2, which produces opposite contributions to the quantities of linear over macrocyclic complexes formed along the series. This intimate dependence of the effective concentration on minor changes in the number of rotational degrees of freedom within the tridentate binding unit opens novel possibilities for rationally programming segmental ligands that favor the thermodynamic formation of discrete polynuclear complexes, or infinite coordination polymers[40] with a predetermined number of bridging ligands—a strong point for the design of single-stranded lanthanide polymers extending along one direction and working as organic light-emitting diodes (OLEDs)[25]. Finally, both ΔE^L2 and ΔE^L1a,n may bring some additional help for the fine thermodynamic tuning of the target assemblies. However, their physical origin arising from a balance between opposite and huge coulombic (repulsive) and solvation (attractive) interactions strongly limits their intuitive chemical programming[18,19]. In [Ln(L12b-2H)], the bowl-shaped curve found for ΔE^L1a,n is responsible for some variable contributions to the anti-cooperative processes, which eventually provides an extra stabilization for mid-range lanthanides, a remarkable behavior that could be exploited for producing heterometallic f−f systems that show some planned deviations from statistics.[41]

**Experimental Section**

**General**: Chemicals were purchased from Fluka AG and Aldrich and used without further purification unless otherwise stated. Starting synths 4[21] 5[21] and ligands L2[23] and L13[29] were prepared according to literature procedures. The syntheses of intermediates 1, 2, and 3 were inspired from the literature[26] but the modifications and improvements brought in this work justified a novel description of those three steps. The trifluoromethanesulfonate salts Ln(CF3SO3)x·H2O were prepared from the corresponding oxide (Aldrich, 99.99 %)[27] by the Ln contents of solid salts were determined by complexometric titrations with Titrplex III (Merck) in the presence of urotropine and xylene orange.[31] Acetoni-
trile and dichloromethane were distilled over calcium hydride. Methanol was distilled over Mg(OCH₃)₂. Silicon gel plates Merck 60 F254 were used for thin-layer chromatography (TLC) and Fluka silicon gel 60 (0.04–0.063 mm) was used for preparative column chromatography.

Preparation of 8: 8-Hydroxyquinoline (16.53 g, 103.84 mmol), benzyl bromide (261.64 g, 155.75 mmol), anhydrous K₂CO₃ (28.70 g, 207.66 mmol), and a catalytic amount of KI were suspended in acetonitrile (150 mL) and heated at reflux until complete consumption of the starting material (12 h, TLC: CH₂Cl₂/MeOH 98:2). The reaction mixture was evaporated to dryness and the residue dissolved in CH₂Cl₂/H₂O 1:1 (300 mL). The organic layer was separated and dried over anhydrous MgSO₄, filtered, and evaporated to dryness. The white solid was purified by column chromatography (silica gel, CH₂Cl₂/MeOH 98:2) to yield 7 (3.05 g, 4.54 mmol, 79%) as a white solid. When required, 7 can be crystallized from CH₂CN or by slow evaporation from a CH₂Cl₂/MeOH mixture. X-ray quality crystals can be obtained by slow evaporation from a CH₂Cl₂/MeOH mixture. X-ray quality crystals can be obtained by slow evaporation from a CH₂Cl₂/MeOH mixture. X-ray quality crystals can be obtained by slow evaporation from a CH₂Cl₂/MeOH mixture.

Preparation of 6: A large excess of compound 8 (15.00 g, 60.17 mmol) and SeO₂ (8.34 g, 75.16 mmol) were suspended in dioxane (120 mL). The white solid quickly dissolved and the color of the suspension turned red in a few minutes. The reaction mixture was then heated at 80°C under an inert atmosphere. After 2 h, the suspension turned brown and no more starting material could be detected (TLC: CH₂Cl₂/MeOH 98:2). Selenium was filtered through Celite, and washed with dichloromethane. The yellow filtrate was evaporated, dried, and filtered under vacuum. The colorless solution was quickly turned red and a precipitate was formed. The reaction mixture was heated at reflux until complete consumption of the start material (1 h). The resulting solids varied from yellow [La₂(L12b-2H)₃] to dark red [Lu₂(L12b-2H)₃]. The reaction mixture was evaporated and dried under vacuum. The red solid was suspended in H₂O (100 mL) and sonicated for 5 min to obtain a homogeneous suspension. Aqueous saturated NaHCO₃ was slowly added (over about 1 h) to adjust the pH to 7.5. The colorless precipitate was filtered and washed with water to completely remove benzyl bromide. The solid was dried for 2 h under vacuum at 120°C and yielded 6 (1.08 g, 1.83 mmol, 94%) as a beige solid. 1H NMR (400 MHz, CDCl₃): δ = 1.17 (t, J = 7.2 Hz, 4H), 7.37–7.65 (m, 7H), 8.32 (d, J = 8.4 Hz, 1H), 8.40 ppm (d, J = 8.4 Hz, 1H).

Preparation of 5: A solution of the complex in CH₃CN. The resulting solids were separated and washed with MeOH (5 mL) and heptane (10 mL). A BBr₃ solution in CH₂Cl₂ (1.50 g, 1.95 mmol) was slowly added (over about 1 h) to adjust the pH to 7.5. The colorless precipitate was filtered and washed with water to completely remove benzyl bromide. The solid was dried for 2 h under vacuum at 120°C and yielded 5 (1.19 g, 1.33 mmol, 99%) as a beige solid. 1H NMR (400 MHz, CDCl₃): δ = 1.40 (t, J = 7.1 Hz, 4H), 4.25 (s, 2H), 5.07 (q, J = 7.1 Hz, 4H), 7.20 (dd, J = 7.1 Hz, J = 1.6 Hz, 2H), 7.31 (dd, J = 8.5 Hz, J = 1.6 Hz, 2H), 1.44–1.53 (m, 4H), 7.64 (d, J = 8.5 Hz, 2H), 7.70 (s, 2H), 8.41 (d, J = 8.7 Hz, 2H), 8.45 (d, J = 8.7 Hz, 2H), 9.83 ppm (s, 2H). ESIMS (DMSO): m/z: 591.5 [M+H]+, 1182.3 [2M+H]+; elemental analysis calcd (%) for C₁₄₈₁₀₂₀₈₅₅₄₆₅₁₄: C 72.63, H 5.33, N 13.74; found: C 72.67, H 5.04, N 13.41.

Preparation of the [Ln₂(L12b-2H)₃] (Ln = La, Nd, Eu, and Y) complexes: Ligand L12b with 2 equiv per phenol function was added and the suspension was stirred at 60°C for 5 min before filtering and washing with water to completely remove benzyl bromide. The solid was dried for 2 h under vacuum at 120°C and yielded 5 (1.19 g, 1.33 mmol, 99%) as a beige solid. 1H NMR (400 MHz, CHDCl₃/CDCl₃): δ = 1.40 (t, J = 7.1 Hz, 4H), 4.25 (s, 2H), 5.07 (q, J = 7.1 Hz, 4H), 7.20 (dd, J = 7.1 Hz, J = 1.6 Hz, 2H), 7.31 (dd, J = 8.5 Hz, J = 1.6 Hz, 2H), 1.44–1.53 (m, 4H), 7.64 (d, J = 8.5 Hz, 2H), 7.70 (s, 2H), 8.41 (d, J = 8.7 Hz, 2H), 8.45 (d, J = 8.7 Hz, 2H), 9.83 ppm (s, 2H). ESIMS (DMSO): m/z: 591.5 [M+H]+, 1182.3 [2M+H]+; elemental analysis calcd (%) for C₁₄₈₁₀₂₀₈₅₅₄₆₅₁₄: C 72.63, H 5.33, N 13.74; found: C 72.67, H 5.04, N 13.41.

Preparation of [Ln₂(L12b-2H)₃] (Ln = La, Nd, Eu, and Y) samples for 1H NMR spectroscopy in CD₃CN: Ligand L12b (20 mg, 3.38 × 10⁻¹⁰ mol, 1 equiv) was suspended in CH₃CN (20 mL), shortly sonicated, and Lantit(OTf)₃·H₂O (2.27 × 10⁻¹⁰ mol) was added. The solid rapidly disappeared and the color of the solution changed from colorless to yellow or pale orange after 5 min heating at 65°C. An excess of solid K₂CO₃ (2 equiv per phenol function) was added and the solution was stirred at 65°C for 2 h. During this time the solutions turned orange. The reaction mixture was dried for 24 h at 65°C for 24 h to give binuclear complexes [Ln₂(L12b-2H)₃]·H₂O (Table S4 in the Supporting Information). The resulting solids varied from yellow [La₂(L12b-2H)₃] to dark red [Lu₂(L12b-2H)₃]. Suitable X-ray quality crystals of [Nd₂(L12b-2H)₃] were obtained by slow diffusion of Et₂O into a diluted solution of the complex in CH₃CN.

Preparation of [Ln₂(L12b-2H)₃] (Ln = La, Nd, Eu, and Y) samples for 1H NMR spectroscopy in CD₃CN: Ligand L12b (5.0 mg, 8.46 × 10⁻¹⁰ mol, 1 equiv) was suspended in CD₃CN (0.5 mL) and shortly sonicated. Lantit(OTf)₃·H₂O (2.27 × 10⁻¹⁰ mol) was added and the suspension was stirred at 65°C for 2 h to get a yellow or pale orange solution. An excess of solid K₂CO₃ (about 2 equiv per phenol function) was added and the suspension was stirred at 65°C for 2 h, then washed with water, and dried for 24 h under vacuum. The resulting solids were separated and washed with MeOH (5 mL) and heptane (10 mL). A BBr₃ solution in CH₂Cl₂ (1.50 g, 1.95 mmol) was slowly added (over about 1 h) to adjust the pH to 7.5. The colorless precipitate was filtered and washed with water to completely remove benzyl bromide. The solid was dried for 2 h under vacuum at 120°C and yielded 6 (1.08 g, 1.83 mmol, 94%) as a beige solid. 1H NMR (400 MHz, CDCl₃): δ = 1.17 (t, J = 7.2 Hz, 4H), 7.37–7.65 (m, 7H), 8.32 (d, J = 8.4 Hz, 1H), 8.40 ppm (d, J = 8.4 Hz, 1H).
were performed using Microsoft Excel. Elemental analyses were performed using an ICP-OES ICAP7600 system equipped with a Turbo Ionspray source. Least-square fits were performed using factor analysis and with the SPECTFIT program. H and 13C NMR spectra were recorded at 200 MHz using a Bruker Avance DRX 500 MHz spectrometer. Chemical shifts are given in ppm with respect to TMS. Pneumatically assisted electrospray mass spectra (ESIMS) were recorded on an Agilent 1200 series LC/MS system equipped with an Electro-spray source. The solvent in the sample vials was exchanged for 

Preparation of the samples for 1H NMR spectroscopy and ESIMS titrations. The samples were prepared in a similar fashion as described in the literature. 

Concentration measurements in 

Acknowledgements

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[57] R. D. Shannon, *Acta Crystallogr. Sect. A* **1976**, *32*, 751–767. The ionic radii are calculated by using $r(N)=1.16$ Å and $r(O)=1.35$ Å and amount to $R_{\text{e}}(\text{Na})=1.19$ Å and $R_{\text{e}}(\text{Ca})=1.16$ Å in 10 and $R_{\text{e}}(\text{Na})=1.17$ Å in HTPf[Li(L10)]121h.


[66] The diastereotopic methylene protons of the ethyl residues (H10 in Figure 5) provide two pseudo-sextets (ABX3 spin system with $F^\neq2$) without implying any blocked rotations as suggested in ref. [12].


[70] A. Mulder, J. Huskins, D. N. Reinholdt, *Org. Biomol. Chem.* **2004**, *2*, 3409–3424. The effective concentration ($c_{\text{eff}}$) is often referred to as the effective molarity (EM) when focusing on its experimental value. For the sake of clarity, we will only use this work in the effective concentration for both the concept and its experimental value.


[75] Microsoft Excel 2003, Microsoft Corporation, USA.


