Linear Polynuclear Helicates as a Link between Discrete Supramolecular Complexes and Programmed Infinite Polymetallic Chains


Abstract: The contribution of the solvation energies to the assembly of polynuclear helicates reduces the free energy of intermetallic repulsion, \( \Delta E_{\text{MM}} \), in condensed phase to such an extent that stable \( D_3 \)-symmetrical tetranuclear lanthanide-containing triple-stranded helicates \( [\text{Ln}_4 (L4)_3]^{12+} \) are quantitatively produced at millimolar concentrations, despite the twelve positive charge borne by these complexes. A detailed modelling of the formation constants using statistical factors, adapted to self-assembly processes involving intra- and intermolecular connections, provides a set of five microscopic parameters, which can be successfully used for rationalizing the stepwise generation of linear bi-, tri- and tetranuclear analogues. Photophysical studies of \( [\text{Eu}_4 (L4)_3]^{12+} \) confirm the existence of two different binding sites producing differentiated metal-centred emission at low temperature, which transforms into single site luminescence at room temperature because of intramolecular energy funnelling processes.

Keywords: helical structures · multicomponent assembly · polynuclear · statistical factors · thermodynamics

Introduction

A challenge in supramolecular chemistry is the development of a rational bottom-up process, which would produce nanoscopic, or even macroscopic objects from the assembly of molecular edifices obeying some simple rules based on molecular recognition processes.\[^{[5]}\] The latter approach is particularly attractive when specific properties and functions can be amplified by the supramolecular interactions operating between the building blocks in the self-assembled edifices. For instance, sophisticated multifunctional photophysical devices based on inter-connected \([\text{Ru}(2,2'\text{-bipyridine})]^{2+}\) derivatives benefit from supramolecular energy funnelling pathways,\[^{[2]}\] while artificial machines and motors,\[^{[3]}\] nano-imprinted devices,\[^{[4]}\] and programmed luminescent liquid crystals\[^{[5]}\] could not be designed without a significant increase in molecular complexity.

However, the rationalization of the underlying multicomponent assemblies is still limited to some semiempirical transcriptions of macroscopic intuition into the microscopic domain, while statistical mechanics, the natural tool for connecting micro- and macroscopic worlds, is usually not considered (we use the word “microscopic” in the usual way, that is, as opposed to “macroscopic”, while it really means “molecular or atomic scale”). Except for some remarkable attempts, which aim at correlating the intriguing stabilities of multicomponent assemblies with preorganization and cooperativity concepts,\[^{[6]}\] we are aware of a single case, in which the transfer matrix formalism, inherited from statistical mechanics, has been used to predict the partition function of simple one-dimensional chains of charged metal ions bound to a single receptor.\[^{[7]}\] Starting from the modelling of
the thermodynamic data relevant to the formation of linear binuclear [Ln2(L1)]3+,[8] [Ln2(L2)]3+ and trinuclear [Ln3(L3)]3+ helicates (Ln is a trivalent lanthanide, Figure 1).[9] Statistical mechanics predicts that the binding isotherm of identical metal ions to a long linear receptor strongly depends on the nearest neighbour free-energy pair interaction $\Delta E_{LnLn}^{1,2}/C_0^2$. When $\Delta E_{LnLn}^{1,2}/C_0^2 = 0$, the binding sites are statistically occupied by the metals, thus leading to a...
random arrangement along the chain (Figure 2a, non-cooperative process). When $\Delta E_{2-1}^{1-2} > 0$, the repulsive interaction between adjacent metals produces a plateau in the binding isotherm corresponding to the half occupancy of the sites, in which alternating empty and occupied sites are expected (Figure 2b, anti-cooperative process). Finally, $\Delta E_{2-1}^{1-2} < 0$ relates to attractive neighbouring intermetallic interactions producing clusters of metals along the chains during the metal loading process (Figure 2c, cooperative process).

For the $[\text{Ln}_n(\text{L}k)_3]^{3+}$ (k = 1–3) helicates, the experimental $\Delta E_{2-1}^{1-2}$ values systematically correspond to weak repulsive intermetallic interactions and anti-cooperative behaviours. However, some significant improvements of our understanding of the behaviour of discrete chains of metal ions in helicates have emerged during the past three years thanks to i) the explicit consideration of intra- and intermolecular binding events in self-assembly processes, which allows the estimation of physically meaningful intermetallic interactions and anti-cooperative behaviours and ii) the collection of a sufficient amount of thermodynamic formation constants to reliably estimate the intermolecular intermetallic interactions ($\Delta E_{2-1}^{1-2}$), and iii) the design of a simple thermodynamic model for predicting the energetics of multicomponent metallosupramolecular assemblies. The syntheses of the ligand L4 and of its complexes $[\text{Ln}_4(L4)_3]^{-}$ (CF$_3$SO$_3$)$_2$, and the crystal structure of $[\text{Eu}_{4}(L4)]^{12+}$ have been described in a preliminary communication.

Results and Discussion

Quantitative predictions for the self-assembly of the tetranuclear helicate $[\text{Eu}_4(L4)]^{12+}$ in solution: The application of the extended site-binding model, which holds for self-assembly processes involving intra- and intermolecular binding events, requires the consideration of one statistical factor for the description of any microscopic stability constant $f^{\text{eff}}$ associated with the formation of the supramolecular complex $[\text{M}_n\text{L}_n]$ from its separated components [Eq. (1)].

$$f^{\text{eff}} = f^{\text{MM}} \prod_{i<j} f^{\text{MM}}_{i,j} (1)$$

In this equation, $f^{\text{MM}}$ represents the intermolecular microscopic affinity characterizing the connection of a metal M to the binding site $i$ of a ligand L, $c^{\text{eff}}_{i,j} = e^{-(\Delta E_{\text{im}}^{\text{L-M}} - \Delta E_{\text{so}}^{\text{L-M}})}$ is the so-called effective concentration used for correcting the entropy change occurring in intramolecular connections, $u^{\text{MM}} = e^{-(\Delta E_{\text{im}}^{\text{L-M}} - \Delta E_{\text{so}}^{\text{L-M}})}$ are the Boltzmann’s factors accounting for the intermetallic $\Delta E_{\text{im}}^{\text{L-M}}$, respectively interligand $\Delta E_{\text{so}}^{\text{L-M}}$, free energies of interaction operating in the final $[\text{M}_n\text{L}_n]$ complex. Taking into account the two standard assumptions relevant to helicate self-assemblies with semirigid ligands, 1) no hairpin or constrained structures are formed and 2) the principle of maximum site occupancy is obeyed, application of Equation (1) to the complexation.
of the tetratrdente ligand L4 with EuIII to give [EuL4]2+ [Equilibrium (2)] provides a straightforward model for the associated formation constant $\beta_{3,4}^{\text{Eu,L4}}$ [Eq. (3)].

$$3 \text{L4} + 4 \text{Eu}^{3+} = [\text{EuL4}]_2^{2+} + \beta_{3,4}^{\text{Eu,L4}}$$  \hspace{1cm} (2)

The parameters $f_{\text{NO2}}^{\text{Eu}}$ and $f_{\text{N3}}^{\text{Eu}}$ represent the intermolecular microscopic affinities of EuIII for the tridentate NtO (terminal) and N3 (central) binding sites of L4, respectively; $\epsilon_{\text{eff}}$ is the entropic correction operating when the intramolecular cyclization involves two adjacent tridentate sites bound to EuIII in the final metallamacrocyle. The dependence of $\epsilon_{\text{eff}}$ on the distance is not trivial and an analytical formulation only exists for long flexible polymers (see Appendix, Supporting Information).[15] For highly flexible polymers connecting two sites separated by a distance d in a receptor, $\epsilon_{\text{eff}} \propto d^{-3/2}$, while the use of a related polymer of optimized size leads to $\epsilon_{\text{eff}} \propto d^{-2}$.[16] The ligand strands in the triple stranded helicate [EuL4]2+ can be considered neither as long flexible nor as optimized polymeric chains, but are probably in between. The two limiting cases $\epsilon_{\text{eff}} \propto d^{-n}$ ($a = 1.5$ or 3) are thus systematically considered in our model. We therefore calculate that $\epsilon_{\text{eff}} = \epsilon_{\text{eff}}^{2+}$ and $\epsilon_{\text{eff}} = \epsilon_{\text{eff}}^{3+}$ because the four binding sites are regularly spaced along the ligand strand. The parameter $\epsilon_{\text{eff}}^{+}$ represents the intermetallic interaction occurring between two adjacent EuIII separated by 9.054–9.405 Å as determined in the crystal structure of [EuL4]2+ (average 9.26(18) Å).[15] For the rigid assembly in question, a standard Coulombic approach predicts $f_{\text{NO2}}^{\text{Eu}} \propto \text{const}/d$,[14] which leads to $u_{\text{NO2}}^{\text{Eu}} = (\text{EuNO2})^{0.5}$ and $u_{\text{NO2}}^{\text{Eu}} = (\text{EuNO2})^{0.33}$ because the metals are regularly spaced along the strand. Finally, the interligand interaction $u_{\text{L1}}^{\text{L2}}$ is restricted to operate between two sites bound to the same metal.[13] For instance, the complexation of each EuIII ion in a nine-coordinate site in [EuL4]2+ provides three interligand interactions, thus leading to a total of 3·4 = 12 interligand interactions in the complex. Consequently, Equation (3) reduces to Equation (4), and the same approach can be applied for the modelling of the formation constants of the competitive complexes [EuL4]2+ [Eqs. (5–6)], [EuL4]2+ [Eqs. (7–8)] and [EuL4]3+ [Eqs. (9–10)], which are expected to exist for slightly different stoichiometries (the schematic structures of the [EuL4]2+, [EuL4]3+ complexes are shown in Figure 4; t stands for terminal, c for central and s for shifted).

$$2 \text{L4} + 3 \text{Eu}^{3+} = [\text{EuL4}]_2^{3+} + \beta_{3,2}^{\text{Eu,L4}}$$  \hspace{1cm} (5)
However, the statistical factors $\omega_{\text{chiral}}$, $\omega_{\text{Eu,L4}}$, used for the latter calculation relied on combinatorial analyses based on binomial distributions, an approach limited to multicompartment assemblies involving only intermolecular binding processes.[13] Recently,[13] it has been demonstrated that statistical factors adapted to assemblies mixing intra- and intermolecular connections can be obtained with the symmetry number method,[13] which fully agrees with the direct counting technique.[13] Let us apply these two methods for the calculation of the partial statistical factor $\omega_{k,3}^{\text{Eu,L4}}$ characterizing the formation of the tetranuclear helicate [Eu(L4)]$^{3+}$ [Eq. (2)]. According to the symmetry number method, $\omega_{k,3}^{\text{Eu,L4}}$ is given by the ratio between the products of the symmetries of the reactants and that of the product species, taken to the power of their stoichiometric coefficients $n_i$ [Eq. (11)].

$$\omega_{k,3}^{\text{Eu,L4}} = \prod_i (\sigma_i^{\text{reactant}})^{n_i} / \prod_j (\sigma_j^{\text{product}})^{n_j} = \frac{(\sigma_4^{\text{Eu}})^{3} \cdot (\sigma_2^{\text{L4}})^{3}}{\sigma_{\text{Eu,L4}}} \quad (11)$$

Each factor $\sigma$ is itself the product of external $\sigma^{\text{ext}}$ and internal $\sigma^{\text{int}}$ symmetry numbers; $\sigma^{\text{int}}$ corresponds to the number of different, but indistinguishable atomic arrangements that can be obtained by rotating a molecule with symmetry operations of the first kind; $\sigma^{\text{ext}}$ refers to the same definition relevant to internal rotations about single bonds within a molecule. In order to calculate the symmetry numbers, the solvent molecules in the first coordination spheres of the metals must be explicitly considered, and the notation of Equation (2), which is common in supramolecular chemistry, must be replaced with Equation (12),[20] thus allowing the calculation of the statistical factor $\omega_{k,3}^{\text{Eu,L4}} = 1728$ [Eq. (13), Figure 4 entry 1].

$$3 \, L4 + 4 \, [\text{Eu(CH}_3\text{CN)}]_3^{3+} \quad \Rightarrow \quad [\text{Eu}_4(L4)]^{12+} + 36 \, \text{CH}_3\text{CN} \quad \vec{b}_{\text{Eu,L4}}^{\text{Eu,L4}} \quad (12)$$

<table>
<thead>
<tr>
<th>Microscopic parameters</th>
<th>$k = 1–3$</th>
<th>$k = 1–3$</th>
<th>$k = 1–3$</th>
<th>$k = 1–4$</th>
<th>$k = 1–4$</th>
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<tbody>
<tr>
<td>$\log(\Delta G_{\text{Eu,L4}}^{\text{Eu,L4}} / \Delta G_{\text{Eu,L4}}^{\text{Eu,L4}})$ [kJ mol$^{-1}$]</td>
<td>$5.6(2) / – 32(1)$</td>
<td>$5.1(2) / – 29(1)$</td>
<td>$5.3(2) / – 30(1)$</td>
<td>$5.3(2) / – 30(1)$</td>
<td>$5.4(2) / – 31(1)$</td>
</tr>
<tr>
<td>$\log(\Delta G_{\text{Eu,L4}}^{\text{Eu,L4}} / \Delta G_{\text{Eu,L4}}^{\text{Eu,L4}})$ [kJ mol$^{-1}$]</td>
<td>$5.9(2) / – 34(1)$</td>
<td>$5.4(2) / – 31(1)$</td>
<td>$5.6(2) / – 32(1)$</td>
<td>$5.6(2) / – 32(1)$</td>
<td>$5.7(2) / – 33(1)$</td>
</tr>
<tr>
<td>$\log(\Delta G_{\text{Eu,L4}}^{\text{Eu,L4}} / \Delta G_{\text{Eu,L4}}^{\text{Eu,L4}})$ [kJ mol$^{-1}$]</td>
<td>$–0.9(9)/5(5)$</td>
<td>$–1.9(9)/6(5)$</td>
<td>$–1.5(9)/6(5)$</td>
<td>$–0.8(2)/5(1)$</td>
<td>$–1.0(9)/6(5)$</td>
</tr>
<tr>
<td>$\log(\Delta G_{\text{Eu,L4}}^{\text{Eu,L4}} / \Delta G_{\text{Eu,L4}}^{\text{Eu,L4}})$ [kJ mol$^{-1}$]</td>
<td>$–0.9(9)/5(5)$</td>
<td>$–1.6(3)/5(2)$</td>
<td>$–0.8(3)/5(2)$</td>
<td>$–1.4(3)/9(2)$</td>
<td>$–1.0(3)/6(2)$</td>
</tr>
<tr>
<td>$\log(\Delta G_{\text{Eu,L4}}^{\text{Eu,L4}} / \Delta G_{\text{Eu,L4}}^{\text{Eu,L4}})$ [kJ mol$^{-1}$]</td>
<td>$–2.4(6)/14(5)$</td>
<td>$–1.4(7)/8(4)$</td>
<td>$–1.8(7)/10(4)$</td>
<td>$–1.5(3)/9(2)$</td>
<td>$–1.8(7)/10(4)$</td>
</tr>
</tbody>
</table>

[a] Taken from ref. [13]; [b] Dependence of the effective concentration on the distance $c^{\text{int}}$ and $d^{\text{int}}$ ($\alpha = 1.5$ or 3), see text.
two enantiomers and strands in the final chiral (i.e., helical) complex produces “helicates”[10,21] with now adequate statistical factors, provides the tetrametallic helicate [Eu4(L4)],12+ (Table 2, last line) characterizing the self-assembly of the tetranuclear helicate [Eu4(L4)],12+ [log(β4,3,4,5,6)] = 41.9, Eq. (4)], and of its competitive complexes [Eu(L4)],3+ [log(β3,2,1)] = 25.8, Eq. (6)], [Eu(L4)],1+ [log(β1,2,3)] = 36.2, Eq. (8)] and [Eu(L4)],12+ [log(β12,2)] = 31.3, Eq. (4)]. The calculated predicted speciation at millimolar concentrations of ligand indicates that the target helicate [Eu(L4)],12+ should correspond to more than 90% of the ligand speciation for a stoichiometric ratio Eu:L4 4:3 (Figure S3, Supporting Information); a strong point justifying the synthesis of the ligand L4.[15] We note that the apparent intermetallic repulsion ΔEint affidavit ≈ 8–10 kJ mol−1 (Table 1, columns 3 and 4) is much smaller than that calculated with the Coulomb interaction ΔEint Coulomb = 9.0Nc2ε02εrε0c,C = 1388 kJ mol−1 for two triply charged cations separated by d = 9 Å in a molecule (Nc = 6.022×1023 mol−1, ε0 = 8.859×10−12 CN−1 m2, εr = 1.0).[14] This deviation is mainly due to the contribution of solvation to the intermetallic interactions, which can be estimated with a Born–Haber cycle involving the solvation energies obtained with Born equation for the complexes [Eu(L3)],1+ (Δμ=GO = −607 kJ mol−1), [Eu(L3)],3+ (Δμ=GO = −2208 kJ mol−1), and [Eu(L3)],5+ (Δμ=GO = −4554 kJ mol−1).[14] An exact fit to ΔEint affidavit = 9 kJ mol−1 implies that the successive fixation of the metal ions in going from [Eu(L3)],1+ to [Eu(L3)],3+ + to [Eu(L3)],5+, which is responsible for the increasing total charge of the complexes, is accompanied by a relative 13.8% stepwise increase of their pseudo-spherical sizes, a value comparable to that previously reported for the successive fixation of three Cu2+ cations in famous Lehn’s double-stranded helicates (10%).[14]

Table 2. Experimental stability constants for [Ln3(Ln)],n+ (acetonitrile/ dichloromethane 9:1, 298 K).

<table>
<thead>
<tr>
<th>LnIII</th>
<th>log(β3,2,1)n+</th>
<th>log(β3,1,2)n+</th>
<th>log(β2,3,1)n+</th>
<th>log(β1,2,3)n+</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>39.1(1.5)</td>
<td>25.2(1.5)</td>
<td>30.4(1.5)</td>
<td></td>
</tr>
<tr>
<td>Nd</td>
<td>38.4(1.9)</td>
<td></td>
<td>29.6(1.8)</td>
<td></td>
</tr>
<tr>
<td>Sm</td>
<td>35.7(1.5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eu</td>
<td>43.2(1.6)</td>
<td>28.9(1.4)</td>
<td>32.8(1.4)</td>
<td></td>
</tr>
<tr>
<td>Ho</td>
<td>40.6(1.6)</td>
<td>26.3(1.4)</td>
<td>29.6(1.5)</td>
<td></td>
</tr>
<tr>
<td>Er</td>
<td>38.1(1.5)</td>
<td></td>
<td>28.9(1.3)</td>
<td></td>
</tr>
<tr>
<td>Yb</td>
<td>41.0(1.6)</td>
<td>26.5(1.3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lu</td>
<td>40.8(1.3)</td>
<td>27.5(1.2)</td>
<td>31.1(1.2)</td>
<td></td>
</tr>
<tr>
<td>Eu4+</td>
<td>42.1</td>
<td>24.9</td>
<td>25.8</td>
<td>31.3</td>
</tr>
</tbody>
</table>

[a] Predicted with Equations (4), (6), (8) and (10) and the microscopic parameters of Table 1 (columns 3 and 4).
Experimental characterization of the self-assembly of the 
tetranuclear helicate \([\text{Eu}_4(L_4)_3]^{12+}\) in solution: Electrospray-
Ionization Mass Spectrometric (ESI-MS) titrations of \(L_4\)
\((10^{-3} \text{m})\) with \([\text{Ln(CF}_3\text{SO}_3)_3] \cdot x\text{H}_2\text{O}\) \((x = 3–5)\) in acetonitrile
\((\text{Ln} = \text{La, Eu, Lu})\) is dominated by the signals of the satu-
rated species \([\text{Ln}_4(L_4)_3(CF}_3\text{SO}_3)_3]^{9+}\) \((n = 3–9)\) together with
signals arising from the unsaturated complexes \([\text{Ln}_n(L_4)_3(CF}_3\text{SO}_3)_3]^{9+–n+}\) \((n = 3–9)\) detected in excess of ligand \((\text{Ln}/
L_4 < 1.33), \text{and } [\text{Ln}_n(L_4)_3(CF}_3\text{SO}_3)_3]^{9+–n+}\) and
\([\text{Ln}_n(L_4)_3(CF}_3\text{SO}_3)_3]^{12–n+}\) observed in excess of metal \((\text{Ln}/L_4 > 1.33), \text{Figure } 6).\)

The parallel spectrophotometric batch titrations of \(L_4\)
\((2 \cdot 10^{-3} \text{m})\) with \([\text{Ln(CF}_3\text{SO}_3)_3] \cdot x\text{H}_2\text{O}\) \((x = 3–5); \text{Ln} = \text{La, Nd, Sm, Eu, Ho, Er, Yb, Lu})\) in acetonitrile/dichloromethane
\((9:1)\) show complicated variations of the absorption spectra
\((\text{Ln}/L_4 0.1 \text{ to } 4.0, \text{Figure } 7).\) Factor analysis\([23]^{(2)}\) indicates the existence of at least five absorbing species corresponding to the free ligand \(L_4\) and four complexes. Evolving factor analysis\([23]^{(2)}\) suggests end points for \(\text{Ln}/L_4 1.0, 1.3, 1.5 \text{ and } 2.0,\)
which match the stoichiometries of the various complexes
detected in the gas phase during ESI-MS titrations. The
spectrophotometric data can be satisfyingly fitted by using
non-linear least-square techniques\([23]^{(2)}\) with the four absorbing
complexes \([\text{Ln}_n(L_4)_3]^{12+}\) \((\text{end point } \text{Ln}/L_4 1.0, \text{Eq. } (7)), [\text{Ln}_n(L_4)_3]^{12+}\) \((\text{end point } \text{Ln}/L_4 1.33, \text{Eq. } (2)), [\text{Ln}_n(L_4)_3]^{12+}\) \((\text{end point } \text{Ln}/L_4 1.5, \text{Eq. } (5))\) \text{and } [\text{Ln}_n(L_4)_3]^{12+}\) \((\text{end point } \text{Ln}/L_4 2.0, \text{Eq. } (9)).\) Because of the strong correlation
between the calculated absorption spectra of these complexes,
we were able to obtain a set of four independent macro-
scopic stability constants \(p_{\text{m,n}}^{\text{ML}}\) only for \(\text{Ln} = \text{La, Eu, Ho}\) and Lu, while partial data are available for the other lantha-
nides (Table 2).

Despite the uncertainties affecting the stability constants
resulting from \(i)\) the use of a batch method required by the
slow helicate formation \((> 24 \text{ h})\) and \(ii)\) the strong correlation
between the absorption spectra of the four complexes,
stants (Table 3, columns 1 and 8) are slightly less satisfying with this model (AF = 0.03), but its simplicity remains a very strong argument for its use as a first approximation of the energetics governing multi-component self-assembly processes.

The 1H NMR spectra of the tetranuclear complexes [Ln₄(L₄)₃]^{12+} (Figure 8a) and [Lu₄(L₄)]^{12+} (Figure 8b).

**Structural and photophysical properties of the self-assembled tetranuclear helicate [Eu₄(L₄)]^{12+} in the solid state:** Isolation of the target tetranuclear helicate from concentrated methanol solutions with Ln/L₄ = 1.33 gives 70–85% yield of [Eu₄(L₄)]^{12+}·(CF₃SO₃)ₓ·xH₂O·yCH₃OH (Ln = La: x = 8.1, y = 1.6; Ln = Eu: x = 5.0, y = 2.3; Ln = Gd: x = 1.4, y = 0; Ln = Tb: x = 4.4, y = 5.2; Ln = Lu: x = 9.6, y = 4.7, Table S1, Supporting Information). The crystal structure of [Eu₄(L₄)]^{12+} unambiguously confirms the formation of the tetranuclear triple-stranded helicate (Figure 3), characterized by an almost linear arrangement of the metals (Eu₁···Eu₂···Eu₃ 170.71(1)°; Eu₂···Eu₃···Eu₄ 172.03(1)°) combined with their regular spacing along the helical axis (Eu₁···Eu₂ 9.312(1)Å, Eu₂···Eu₃ 9.054(1)Å, Eu₃···Eu₄ 9.405(1)Å, average Eu···Eu 9.26(18)Å). The resulting palindromic helix is 31.6Å long for 2.22 turns, which translates into an average 14.0Å helical pitch, comparable with 13.6Å previously reported for the trinuclear analogous complex [Eu₃(L₃)]^{9+}. The two terminal metals (Eu₁ and Eu₄) are nine-coordinated in pseudo-tricapped trigonal prismatic N₆O₃ sites, while the two central metals (Eu₂ and Eu₃) lie in pseudo-tricapped trigonal prismatic N₉ sites.

A detailed photophysical analysis has been performed by using Eu³⁺ as a structural and electronic probe in [Eu₄(L₄)]^{12+}. The high-resolution excitation profile of the Eu(5D₀ → 7F₀) transition in [Eu₄(L₄)]^{12+} at 10 K indeed confirms the existence of two main Eu³⁺ sites, labeled I and II (Figure 9a). The most intense transition displays two main components, labeled Ia (ν = 17323 cm⁻¹) and Ib (17322 cm⁻¹). Selectively excited emission spectra are, however, extremely similar, so that these two components are ascribed to a single metal ion environment I, the small differences evidenced probably arising from slight con-
formational changes, a fact corroborated by the almost equal values of $\tilde{\nu}$ for Ia and Ib at room temperature. In agreement with the detailed assignment previously established for the analogous complex [Eu(bipy)2]3+ (site EuN2O3: 17219 cm⁻¹ at 10 K), this chemical environment is ascribed to the terminal NeO3 coordination sites. The associated emission spectrum recorded upon selective excitation of site I in [Eu(bipy)2]3+ shows a crystal-field splitting compatible with a pseudo-D3 symmetry around Eu3+ (Figure 9b and Table S2, Supporting Information). The three observed transitions to the F1 level can be labeled A1 → A2 (F1(A2) located at 312 cm⁻¹ with respect to F1(A1)) and A1 → split E (barycenter: 409 cm⁻¹, Figure S5, Supporting Information). The splitting of the E sublevel is related to the distortion from idealized D3 symmetry and amounts to ΔEee = 38 cm⁻¹. These characteristics closely match those reported for the terminal EuN2O3 sites in [Eu(bipy)2]3+ (F1(A1) = 327 cm⁻¹, F1(E) = 402 cm⁻¹, ΔEee = 42 cm⁻¹), in agreement with very similar structural organizations of the EuN2O3 terminal sites in both triple-stranded helices.

The Eu(5D0 → F1) transition in [Eu(bipy)2]3+ shows roughly two groups of two emission bands assigned to the allowed electric dipole transitions A1 → E in D3 symmetry, the latter being further split into two components separated by ca. 20 cm⁻¹ (Figure S6, Table S2, Supporting Information). Because of low-lying ligand-to-metal charge transfer (LMCT) states, which quench the L4(\(\pi\)π* → Eu3+) energy transfer responsible for metal-centred luminescence of EuN9 sites,[10,25] the associated emission intensity of the central sites in [Eu(bipy)2]3+ is very weak and cannot be observed upon broad band irradiation (Figure 9b). However, selective excitation of site II at 17235 cm⁻¹ (10 K) produces a weak, but detectable emission spectrum reflecting trigonal symmetry, which is compatible with its attribution to EuN9 (found at 17238 cm⁻¹ in [Eu(bipy)2]3+ under the same conditions).[10]

Due to thermally-activated EuN9 → EuN0O3 energy migrations, the photophysical signature of site II disappears at 295 K, but we can estimate $\tilde{\nu}$(Eu(5D0 → F0)) = 17250 cm⁻¹ at 295 K by taking into account the 1 cm⁻¹/24 K dependence of this transition.[24] Application of eq 16, which empirically models the nephelauxetic effect produced by the donor atoms in this first coordination sphere:[26] predicts that $\tilde{\nu}_{\text{N6O3}}$ = 17235 cm⁻¹ for a Eu3+ atom coordinated by six heterocyclic nitrogen atoms (δN-heterocycle = -15.3 cm⁻¹)[27] and three amide oxygen atoms (δO-amide = -15.7 cm⁻¹).[28] The EuN9 is 17236 cm⁻¹ when Eu3+ is coordinated by nine heterocyclic nitrogen atoms at 295 K (δ = 17.374 cm⁻¹) is the energy of the Eu(5D0 → F0) transition in the free ion, C_{CN} is an empirical coefficient depending on the coordination number of the metal, C_{CN} = 1.06, C_{CN} = 1.0, C_{CN} = 0.95 and δ represents the nephelauxetic effect produced by an atom i bound to Eu3+.[26]

As previously noticed for [Eu(bipy)2]3+,[10] predictions for both central and terminal Eu3+ sites significantly deviate from the experimental values recorded for the Eu(5D0 → F0) transitions at 295 K (Eqs. (17, 18)). This observation suggests that pyridine and benzimidazole rings in ligand L3 and L4 possess different nephelauxetic parameters, in agreement with the substantially larger π-donating properties of benzimidazole rings, compared with pyridines.[28] The straightforward mathematical solution of Equations (17–18) gives δN-pyridine = -25.3 cm⁻¹ and δN-benzimidazole = -8.0 cm⁻¹, a result in line with the expected larger capacity of pyridine rings to expand the metallic electronic cloud.[28]

\[
\tilde{\nu}_{\text{EuN0O3}} = \tilde{\nu}_0 + 3 \cdot \delta_{\text{O-carboxamide}} + 3 \cdot \delta_{\text{N-pyridine}} + 3 \cdot \delta_{\text{N-benzimidazole}} = 17227 \text{ cm}^{-1}
\]

\[
\tilde{\nu}_{\text{EuN9}} = \tilde{\nu}_0 + 3 \cdot \delta_{\text{N-pyridine}} + 6 \cdot \delta_{\text{N-benzimidazole}} = 17250 \text{ cm}^{-1}
\]

The Eu(5D0) lifetimes in [Eu(bipy)2]3+ at 10 K (2.00–2.24 ms, Table S3, Supporting Information) and at 295 K (1.63–1.74 ms, Table S3, Supporting Information) point to the absence of high-frequency oscillators (νO-H, νNH) in direct contact with Eu3+ in both types of coordination sites. Moreover, these spectroscopic and photophysical characteristics still hold for millimolar acetonitrile solutions of [Eu(bipy)2]3+. [www.chemeurj.org]
which demonstrates that the tetranuclear triple-stranded helical structure is maintained in solution. Finally, Table 4 summarizes the main photophysical characteristics of the ligand-centred $1^\pi\pi^*$ and $3^\pi\pi^*$ excited states in $L_4$, which closely resemble those reported previously for $L_3$ ($E(1^\pi\pi^*) = 23000$ cm$^{-1}$, $E(3^\pi\pi^*) = 19800–20000$ cm$^{-1}$). [10] This phenomenon may explain the self-assembly of linear helicates based on CuI [39] or of trivalent lanthanides ([Ln$_2(L_k)_3$]$^{6+}$ ($k = 1, 2$), [Ln$_3(L_3)_3$]$^{9+}$, and [Ln$_4(L_4)_3$]$^{12+}$ in this contribution). The alternative recurrent argument invoking strong ion-pairing for stabilizing highly charged objects in solution does not agree with a simple calculation of the charge density on the Connolly surface around the cation, [46] which amounts to $9/1682.6 = 5.35 \times 10^{-3}$ e/Å$^2$ for [Eu$_3(L_3)_3$]$^{9+}$ and $12/2044 = 5.83 \times 10^{-3}$ e/Å$^2$ for [Eu$_4(L_4)_3$]$^{12+}$, while that obtained for Na$^+$ (4.35 $\times 10^{-2}$ e/Å$^2$), Ca$^{2+}$ (7.22 $\times 10^{-2}$ e/Å$^2$) and La$^{3+}$ (8.85 $\times 10^{-2}$ e/Å$^2$) are one order of magnitude larger. [31] With this observation in mind, the use of statistical factors adapted to self-assembly processes mixing intra- and intermolecular connections combined with simple additive thermodynamic site-binding models [11, 13] provides an efficient tool for predicting stabilities of target supramolecular complexes within a family, for which basic microscopic parameters can be estimated. In this context, the priori prediction (and experimental confirmation) of the quantitative formation of [Eu$_4(L_4)_3$]$^{12+}$ at millimolar concentration is unprecedented in coordination and metallo-supramolecular chemistry. Moreover, the deeper understanding of the thermodynamic driving forces controlling multi-component self-assembly processes, among which tuneable intermetallic interactions play a crucial role, opens

**Conclusion**

The formation of stable tetranuclear helicates [Ln$_4(L_4)_3$]$^{12+}$ in condensed phase demonstrates that highly charged molecular systems ($Q = \Sigma q$, $q$ is the charge borne per metal) do not drastically suffer from the large internal electrostatic repulsion $\Delta_{e,\text{el}}G^{\text{MM}} \propto \Sigma (q^2/r)$, as long as the total size of the microscopic objects (approximate spherical radius $R$) is adapted for providing solvation energies $\Delta_{solv}G^{\text{a}} Q^2/R$, which are able to balance the latter repulsion in polar solvents. [14]
null
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