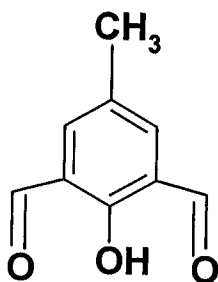
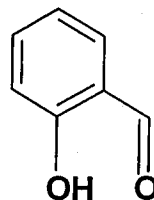


ABSTRACT

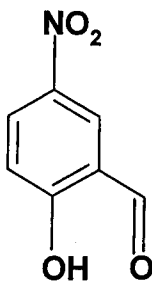
A systematic study of the syntheses, structure and luminescence characteristics of novel polynuclear lanthanide complexes based on **HL**, **HL¹**, **HL²**, **H₆₄L³** and **H₁₂₈L⁴** was undertaken in order to discern the factors affecting formation, stability and the potential for cooperative electronic communication among lanthanide ions in such edifices.



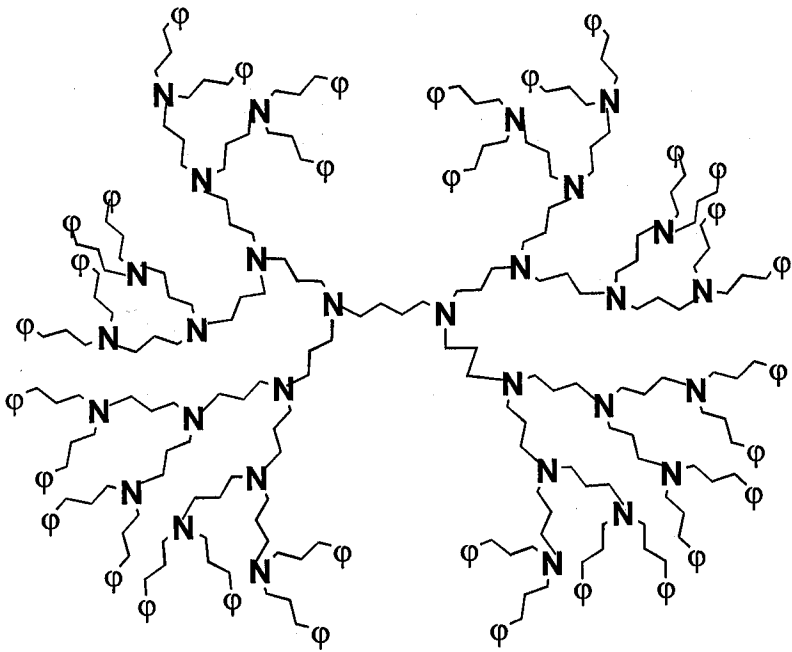
HL



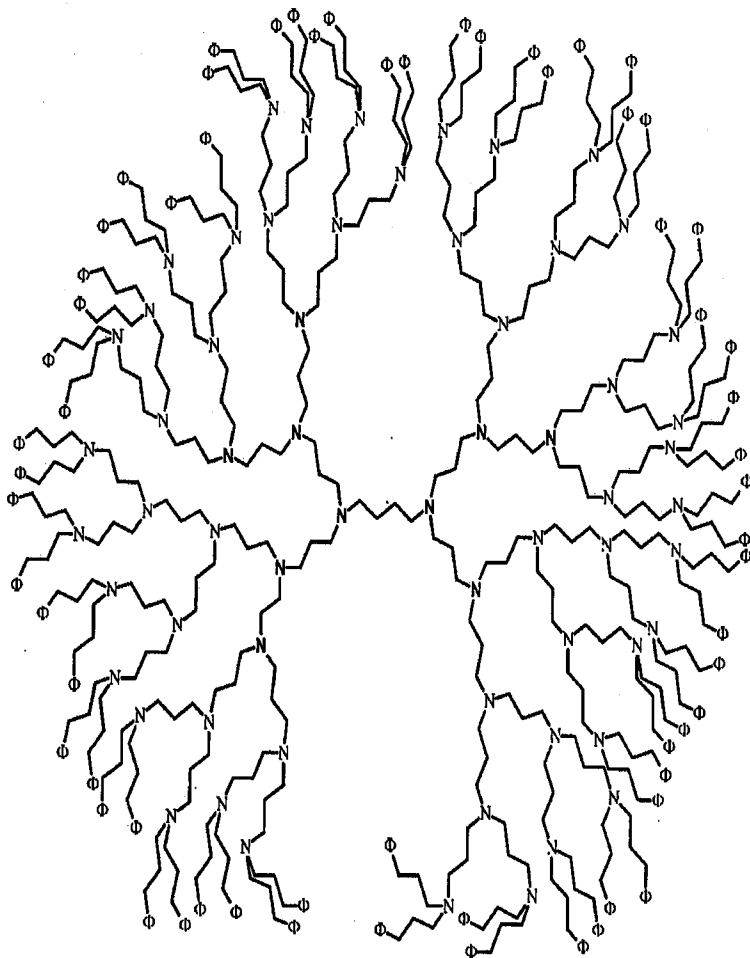
HL¹



HL²



When $\phi = \text{NH}_2$ ligand = H_{64}L^3



When $\varphi = \text{NH}_2$ ligand = H_{128}L^4

Dinuclear ($[\text{Ln}_2(\mu_2\text{-L})_2(\text{L})_2(\text{H}_2\text{O})_4](\text{ClO}_4)_2$ (8), $[\text{Ln}_2(\mu_2\text{-L})_2(\text{L})_4]$ (9)) and tetranuclear ($[\text{Ln}_4(\mu_4\text{-O})(\mu_2\text{-OH})_2((\mu_2\text{-L})_6)(\text{ClO}_4)_2$, $[\text{Ln}_4(\mu_3\text{-OH})_4((\mu_2\text{-L})_4(\text{H}_2\text{O})_8)](\text{ClO}_4)_4$) complexes were synthesized from the reaction between lanthanide(III) perchlorates, sodium hydroxide and HL under various conditions of reaction stoichiometries, pH and solvent medium. The syntheses demonstrate the potential for HL to serve as a useful synthon in the synthesis of a variety of polynuclear complexes in which the Ln^{3+} ions are trapped as pairs. The formation of the tetranuclear complexes also shows the adhesive effect of small anions such as O^{2-} and OH^- , which favour the formation of stable polynuclear complexes.

Luminescence decay studies on $[\text{Eu}_2(\mu_2\text{-L})_2(\text{L})_4].n\text{H}_2\text{O}$ show the occurrence of defect sites that are accessible through indiscriminate excitation of Eu^{3+} ($^5\text{D}_0$) and are responsible for quenching emission from normal Eu^{3+} sites. Competitive complexation studies reveal that the metal coordination sites are selective towards the smaller lanthanides and suggest a significant presence of homodinuclear as well as heterodinuclear species in mixed lanthanide complexes. This was corroborated by luminescence decay data, which identified $\text{Eu}^{3+}\text{-Dy}^{3+}$ and $\text{Eu}^{3+}\text{-Yb}^{3+}$ heteropair as well as $\text{Eu}^{3+}\text{-Eu}^{3+}$ homopair interactions. The energy transfer interaction between Eu^{3+} and Dy^{3+} is resonant and the corresponding dipolar coupling constant, $\alpha_{\text{Eu-Dy}}$, is

$5.9 \times 10^{-52} \text{ m}^6 \text{ s}^{-1}$. The quenching of $\text{Eu}^{3+}({}^5\text{D}_0)$ emission by Yb^{3+} is surprising and unusual because of the poor spectral overlap between the two metal ions. However, spectroscopic evidence confirms that the quenching interaction proceeds by a three-body mechanism which involves one Eu^{3+} , one Yb^{3+} and the stretching vibrations of C=O oscillators. The corresponding three-body dipolar-coupling constant, $\alpha_{\text{Eu-Yb}}$, is $2 \times 10^{-52} \text{ m}^6 \text{ s}^{-1}$.

The metal coordination sites in the oxo-centered tetranuclear nanocluster, $[(\text{Ln})_4(\mu_4\text{-O})(\mu_2\text{-OH})_2(\mu_2\text{-L})_6](\text{ClO}_4)_2$ (series **11**) show a preference for the binding of the smaller lanthanides. Efficient energy migration among Eu^{3+} donors results in the trapping of excitation energy by crystal defects. In fact, even in the presence of a large amount of Gd^{3+} scatterers and at low temperatures, the transfer of energy from normal to defect Eu^{3+} sites is detected. In addition to the longer-lived inter-molecular component, intra-cluster Eu-Dy and Eu-Yb interactions in $[(\text{Eu}_x\text{Ln}_{1-x})_4(\mu_4\text{-O})(\mu_2\text{-OH})_2(\mu_2\text{-L})_6](\text{ClO}_4)_2$, where $\text{Ln} = \text{Dy}$ or Yb , are identified. $\text{Eu}^{3+}\text{-Dy}^{3+}$ interaction is a bimolecular process defined by $\alpha_{\text{Eu-Dy}} = 3 \times 10^{-52} \text{ m}^6 \text{ s}^{-1}$. Quenching by Yb^{3+} occurs by the same three-body mechanism found in $[(\text{EuYb}(\mu_2\text{-L})_2(\text{L})_4)]$; the corresponding dipolar coupling constant is $\alpha_{\text{Eu-Yb}} = 6.7 \times 10^{-52} \text{ m}^6 \text{ s}^{-1}$.

Electronic coupling interactions in mixed lanthanide tetra-hydroxo nanoclusters, $[(\text{Eu}_x\text{Ln}_{1-x})_4(\mu_3\text{-OH})_4((\mu_2\text{-L})_4(\text{H}_2\text{O})_8)](\text{ClO}_4)_4$, are stronger than those seen in either $[(\text{Eu}_x\text{Ln}_{1-x})_2(\mu_2\text{-L})_2(\text{L})_4]$ or the oxo-centered cluster, $[(\text{Eu}_x\text{Ln}_{1-x})_4(\mu_4\text{-O})(\mu_2\text{-OH})_2(\mu_2\text{-L})_6](\text{ClO}_4)_2$. A three body mechanism involving two Dy^{3+} and one Eu^{3+} ion, defined by a dipolar coupling constant of $1.5 \times 10^{-51} \text{ m}^6 \text{ s}^{-1}$ accounts for the unusually strong interaction between Eu^{3+} ($^5\text{D}_0$) and Dy^{3+} . The unexpected discrepancy between the strength of Eu^{3+} - Dy^{3+} interactions in $[(\text{Eu}_x\text{Dy}_{1-x})_4(\mu_3\text{-OH})_4(\mu_2\text{-L})_4(\text{H}_2\text{O})_8](\text{ClO}_4)_4$ and $[(\text{Eu}_x\text{Dy}_{1-x})_4(\mu_4\text{-O})(\mu_2\text{-OH})_2(\mu_2\text{-L})_6](\text{ClO}_4)_2$ is enigmatic and the only satisfactory explanation is that the orientation of the interacting dipoles in the $[\text{Ln}_4(\mu_3\text{-OH})_4]^{8+}$ core featured in $[(\text{Eu}_x\text{Dy}_{1-x})_4(\mu_3\text{-OH})_4(\mu_2\text{-L})_4(\text{H}_2\text{O})_8](\text{ClO}_4)_4$ favours stronger interaction among metal ions.

The hexanuclear cluster, $[\text{Nd}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\text{H}_2\text{O})_{24}](\text{ClO}_4)_8$, previously synthesized by Zheng et al in tetragonal space group, was synthesized via a modified procedure and in cubic space group. In addition to sharp intra-configurational $4f^n$ transitions, luminescence excitation and emission spectra of $[\text{Eu}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\text{H}_2\text{O})_{24}](\text{ClO}_4)_8$ show broad band features which are thought to be due to structural defects in crystals of $[\text{Eu}_6(\mu_6\text{-O})(\mu_3\text{-OH})_8(\text{H}_2\text{O})_{24}](\text{ClO}_4)_8$.

One dimensional coordination polymers $[\{\text{Na}\}\{\text{Ln}(\text{L}^1)_4\}]_n$ (series 15), and dinuclear complexes $[\{\text{Na}\}\{\text{Ln}_2(\text{L}^2)_7(\text{CH}_3\text{OH})_2\}]$ (series 17), have been synthesized from lanthanide perchlorates and HL^1 and HL^2 respectively. The syntheses demonstrate the potential for cationic species such as Na^+ to direct the aggregation of metal complexes through exo-coordination of metal ions. Luminescence studies on both complexes reveal the presence of defect Eu^{3+} sites, some arising from swapping of regular Eu^{3+} and Na^+ positions and some arising from the termination of the infinite chains in 15a or the occurrence of polymeric chains in 17b. Extremely strong Eu^{3+} - Eu^{3+} interactions in $[\{\text{Na}\}\{\text{Ln}(\text{L}^1)_4\}]_n$ result in multidimensional energy migration across distances as large as 10.49 Å. The Eu^{3+} - Dy^{3+} dipolar coupling constant is $\alpha_{\text{Eu-Dy}} = 3.7 \times 10^{-52} \text{ m}^6 \text{ s}^{-1}$.

A common feature of the emission spectra of Eu^{3+} complexes derived from HL , HL^1 and HL^2 is the dominance of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition which is forbidden under the site symmetries of D_{4d} and D_{3h} present in these systems. This feature is discussed under the inhomogeneous dielectric ligand polarization model, which predicts an enhanced intensity of quadrupolar allowed electronic transitions ($\Delta J = \pm 2$) such as $\text{Eu}^{3+}({}^5\text{D}_0 \rightarrow {}^7\text{F}_2)$.

Crystals of $[\{\text{Na}\}\{\text{Ln}(\text{L}^1)_4\}]_n$ are used as precursors in the synthesis of dendritic Schiff base complexes of the amines H_{64}L^3 and H_{128}L^4 . Preliminary luminescence studies reveal the binding and interaction of the ligands L^3 and L^4 with multiple lanthanide ions.

This is the first systematic study of synthesis, structure and electronic coupling interactions among Ln^{3+} ions in a variety of polynuclear complexes within the same ligand framework. The details of formation, structure and luminescence give valuable insights into specific factors which need to be considered in the design and development of synthetic protocols for the assembly of stable polynuclear lanthanide complexes which feature strongly coupled Ln^{3+} ions.