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Review

Dinuclear and polynuclear lanthanide coordination complexes containing polyazine ligands: Synthesis and luminescent properties

Shawn Swavey*, Rochael Swavey

Department of Chemistry, University of Dayton, Dayton, OH 45469-2357, USA

Contents

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ABSTRACT

The role of homodinuclear and heterodinuclear lanthanide complexes as building blocks for polymeric materials is a significant field of study in recent years. Accessing the desired luminescent properties of lanthanides in the most efficient and practical way is an important part of designing such complex structures. This review describes the background of the photophysical properties of a select number of lanthanide ions. The synthesis and photophysical properties of dinuclear lanthanides have been split into two sections: (i) heterdinuclear d–f complexes and (ii) homodinuclear lanthanides bridged by polyazine ligands. A section on polymeric lanthanide arrays is also included highlighting d–f polymeric structures and a section on homodinuclear polymeric arrays formed from polyazine bridging ligands.

1. Background

Lanthanides have a complex electronic configuration due to the existence of 4f, 5d and 6s orbitals. Stabilization of these orbitals favors the $4f^n$ open-shell oxidation states of +3 for most lanthanides. When Sc and Y are included the lanthanides are commonly referred to as rare-earth metals, however, the rare earths are more abundant than many of the commonly used transition metals, for example Rh, Ag, Pd, Ir, Au and W. The diffuse nature of the 4f orbitals leads to complexes that have both coordination and ionic characteristics. As a result ligand field stabilization common to transition metal complexes plays a lesser role in stabilizing lanthanide complexes. Since the large lanthanide(III) cations prefer strong bidentate Lewis bases, β-diketones offer not only a strong coordination sphere but typically act as a conduit for energy or electron transfer enhancing the luminescent properties of the lanthanide complex. The distinctive decrease in ionic radii of the lanthanide ions as their atomic number increases is referred to as the lanthanide contraction. Due to the size and spherical nature of these ions coordination numbers vary from as few as six to as many as twelve, making these complexes extremely unique in the world of coordination chemistry.

Lanthanide complexes have been utilized in the fabrication of materials for diode lasers and optical fibers [1]. Other applications include biomedical assays [2], immunoassays [3], early detection of cancer [4] and in time resolved luminescence measurements [5]. Their unusual spectroscopic properties which include sharp long-lived emissions in the visible region of the spectrum are the primary reason for their utility. Excitation of the 4f electrons and subsequent relaxation generates the spectroscopic properties which have made lanthanide complexes attractive for such a wide variety of applications. The interest in lanthanide complexes due to

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* Corresponding author. Tel.: +1 937 229 3145; fax: +1 937 229 2635.
E-mail address: shawn.swavey@notes.udayton.edu (S. Swavey).

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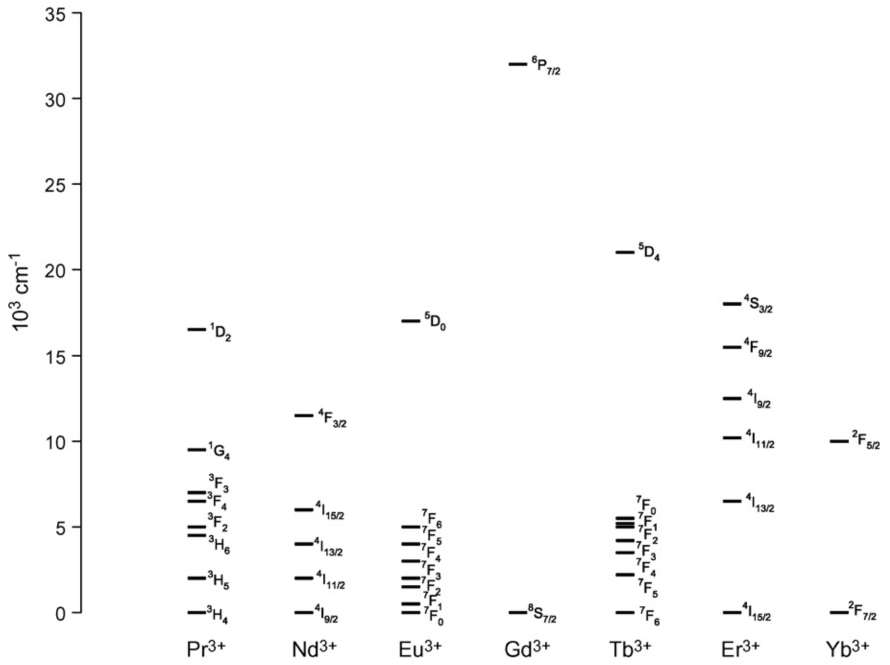


Fig. 1. Partial energy diagram for selected lanthanide(III) ions.

their spectroscopic properties is surprising in light of the parity forbidden 4f–4f transitions associated with the lanthanide ions. In a typical lanthanide complex accessing the excited states of the metal center is achieved by exciting the π–π* transitions of the ligand to stimulate, through energy transfer, the metal centered luminescence [6]. This "antenna" effect has been well documented for β-diketones which form facile coordination complexes with Ln(III) ions [5,7–9]. Absorption of light by the "antenna" ligand in the UV region of the spectrum leads to energy transfer and population of the metal centered excited states. The result is emission of light upon relaxation of the excited metal to its ground state. The emission wavelength associated with the lanthanide complex is related to the energy difference between the emissive level and the ground state of the 4f orbitals which is of course related to the lanthanide metal. This allows the emission wavelength to be tuned by choice of the lanthanide metal. Representative lanthanide 3+ ions and the energy associated with their ground states and the first excited state are presented in Fig. 1.

Ideally the triplet state of the sensitizing ligand, in this case the β-diketonate, will be close to the excited state energy of the lanthanide center. This will lead to more efficient energy transfer and therefore higher emission intensity and quantum efficiency. Pr, Nd, Er, and Yb complexes typically emit in the near infrared region (NIR) of the spectra while Gd complexes do not typically show emission spectra because the excited state is in the UV region of the spectra and therefore there is rarely good overlap between triplet excited states of ligands with this state. Eu complexes emit in the red region of the spectrum while Tb complexes emit in the green region (Fig. 2).

2. Dinuclear bridged complexes

2.1. Introduction to bridging ligands

The past decade has seen an increased interest in dinuclear lanthanide complexes. A variety of complexes have been studied including heterobimetallic lanthanides, dinuclear lanthanide–transition metal complexes and homobimetallic lanthanides. The reasons for combining metal centers through bridging ligands vary. Attempts to enhance the luminescent properties of monometallic complexes through combining metal centers has lead to some interesting complexes, while others have been synthesized to investigate magnetic interactions between metal centers as models for more complex materials [10]. A number of dimeric complexes have been studied as precursors for polymer based light emitting diodes or light-emitting layers in electroluminescent devices [11]. In special cases dinuclear complexes have been designed as catalysts for polymerization of ethylene, isoprene and methyl methacrylate [12]. The focus of this section is a review of lanthanides bridged by polyazine ligands. A number of reviews dealing with bridged lanthanide complexes have been presented [13–17]. The goal of the present review is to complement the current review articles dealing with similar topics.

2.2. Polyazine bridged heterometallic lanthanide–transition metal complexes

Most antenna ligands used to sensitize lanthanide luminescence involve excitation in the UV region of the spectrum. To

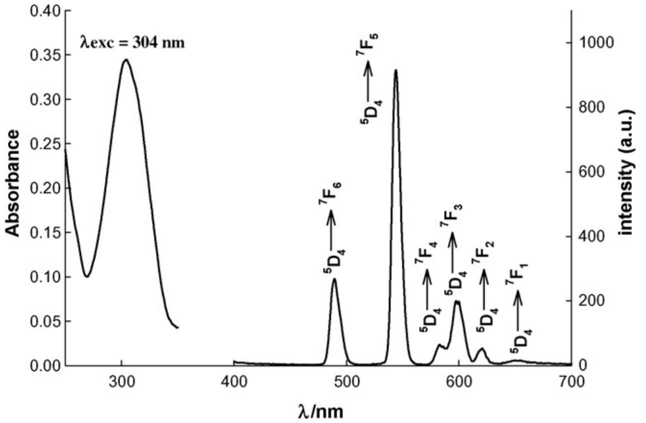


Fig. 2. Excitation and emission spectra for Tb(hfa)$_3$bpm (hfa = 1,1,1,5,5,5-hexafluoroacetylacetone and bpm = 2,2′-bipyrimidine).

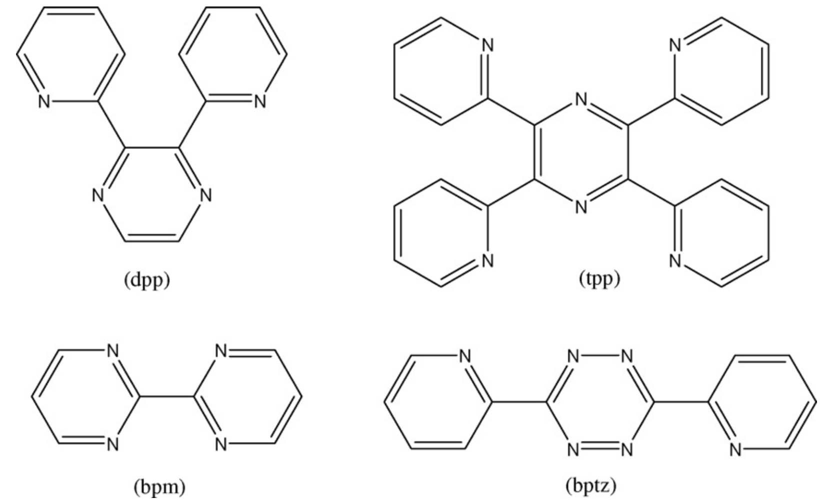


Fig. 3. Example of polyazine bridging ligands.

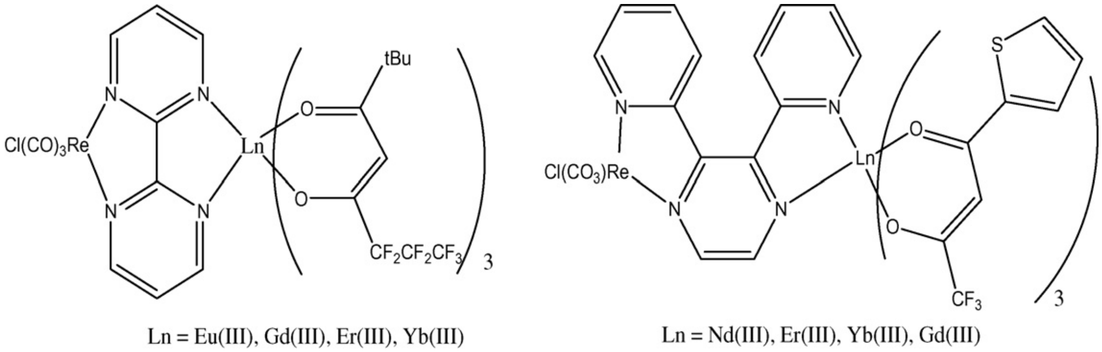


Fig. 4. Heterodinuclear Re/Ln complexes [23].

obtain greater energy transfer efficiency transition metal complexes incorporating low energy (visible light) metal-to-ligand charge transfer (MLTC) transitions have been coupled to lanthanides as antenna complexes. Although a relatively young field of study; reviews of d–f complexes has been presented [18,19]. Several interesting complexes containing polypyridyl bridging ligands relevant to this review are presented. Polyazine bridging ligands have been used with transition metals to create supramolecular assemblies. These ligands bind to metal centers through a coordinate covalent σ-bond using the lone pair of electrons of the nitrogen. Low lying empty π^* orbitals function as acceptors for π-backbonding stabilizing the metal–ligand interaction. The most common polyazine ligands used with lanthanides are 2,3-bis-dipyridylpyrazine (dpp), 2,2′-bipyrimidine (bpm), tetra-2-pyridylpyrazine (tpp), and 3,6-bis(2-pyridyl)tetrazine (bptz) (Fig. 3).

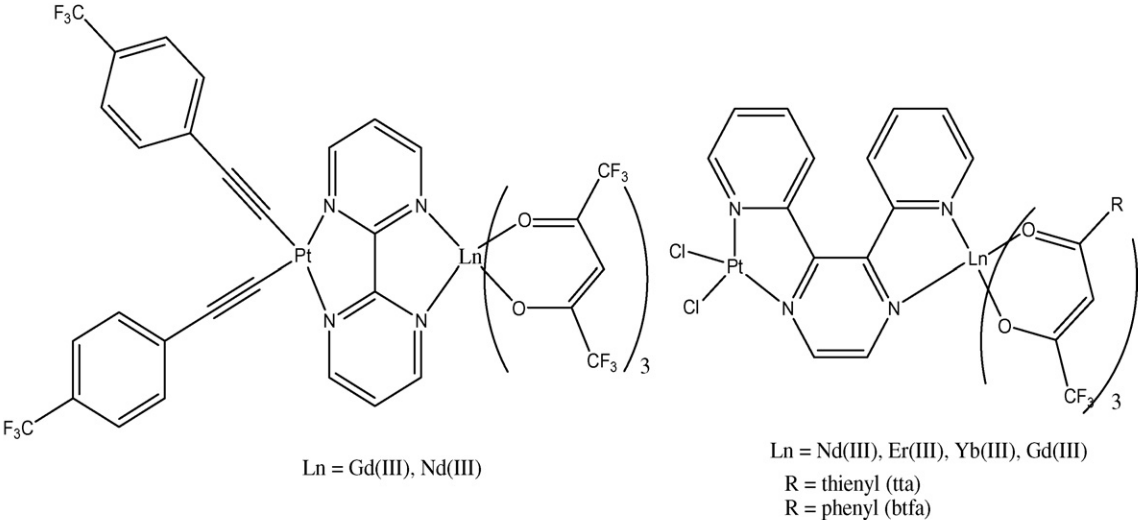


Fig. 5. Heterodinuclear Pt/Ln complexes [24].

The use of polyazine multidentate ligands, such as bpm and dpp, to bridge transition metals is a well-established area of coordination chemistry [20–22]. These bridging ligands have been used to generate mixed d–f complexes [23]. For example, by reacting [Re(CO$_3$)$_3$Cl(bpm)] with Ln(fod)$_3$ or [Re(CO$_3$)$_3$Cl(dpp)] with Ln(tta)$_3$ (where Ln = Yb, Nd, Er) the following heterometallic binuclear complexes, illustrated in Fig. 4, have been isolated. Stabilization of the Re d-orbitals, through π-backbonding of the bpm ligand, upon coordination of the Re complex to the lanthanide results in a red shift of the MLCT transition of Re. In addition the emission spectra of the Re moiety usually observed at 650 nm is quenched by the lanthanide β-diketonate, indicating efficient energy transfer from the d-orbitals to the lanthanide f-orbitals.

In a similar set of experiments using dpp and bpm bridging ligands, lanthanide β-diketonate complexes and PtCF$_3$ or PtCl$_2$ have been assembled into heterobimetallic complexes (Fig. 5) [24].

Spectroscopic titrations of [PtCl$_2$(dpp)] with Gd(btfa)$_3$ in CH$_2$Cl$_2$ give a binding constant of $1.7 \times 10^4\,M^{-1}$ which is considerably smaller than the binding constants determined for Gd(btfa)$_3$ and polypyridyl ligands such as 1,10-phenanthroline or 2,2′-bipyridine. The lower binding affinity can be explained by a reduction in the basicity of the dpp bridging ligand upon coordination to the electron withdrawing Pt(II) moiety. Excitation of the Pt(II) chromophores leads to NIR emissions for each of the lanthanides in the solid state with lifetimes longer than the aquated lanthanide mononuclear precursors. These studies indicate that efficient energy transfer between metal centered complexes is achieved with the polyazine bridging ligands while the increased lifetimes upon coordination are due to the elimination of the O–H vibrational quenching mode associated with coordinated water molecules.

Equilibrium constants of ca. $10^7\,M^{-1}$ have been determined for the formation of [Ln(dik)$_3$NN] complexes however upon coordination of PtCF$_3$ to bpm the basicity of the bpm free nitrogens decreases, similar to dpp, leading to smaller equilibrium constants for the formation of the heterobimetallic complex (ca. $\sim 10^5\,M^{-1}$) [25]. Excitation of the PtCF$_3$ moiety at 460 nm results in observation of the NIR emissions associated with the Nd(III) metal center. These experiments were run in the solid state due to decomplexation of the complex in solution leading to monometallic emissions.

2.3. Homodinuclear lanthanides bridged by polyazine ligands

The synthesis of new homodinulcear lanthanide complexes has become an exciting field of study for a number of reasons including their use as potential supramolecular building blocks for molecular electronics. This is due, in part, to delocalization of electron density over the more diffuse and larger lanthanide ions when compared to transition metal ions. In a recent study the reaction of Cp$_2$*Yb(OEt)$_2$ (Cp* = C$_5$Me$_5$) with tpp (tetra-2-pyridynylpyrazine) resulted in a new homodinuclear Yb complex (Fig. 6).

In this unusual complex the ground electronic state contains the Yb(II) 4f^{13} and a ligand radical anion antiferromagnetically coupled [26]. This results in an electronic configuration of $[f^{13}(tpp)^{2}f^{13}]$.

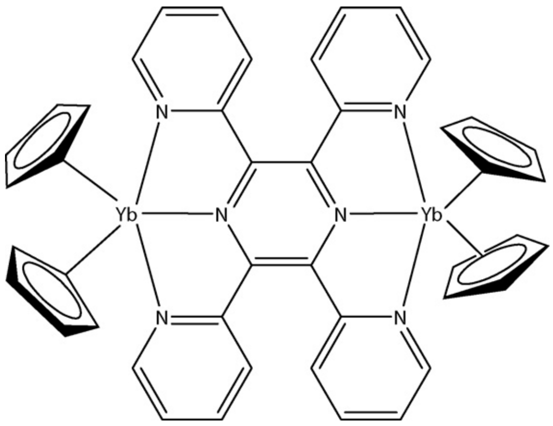


Fig. 6. Homodinuclear [Cp*Yb]$_2$(tpp) complex [26].

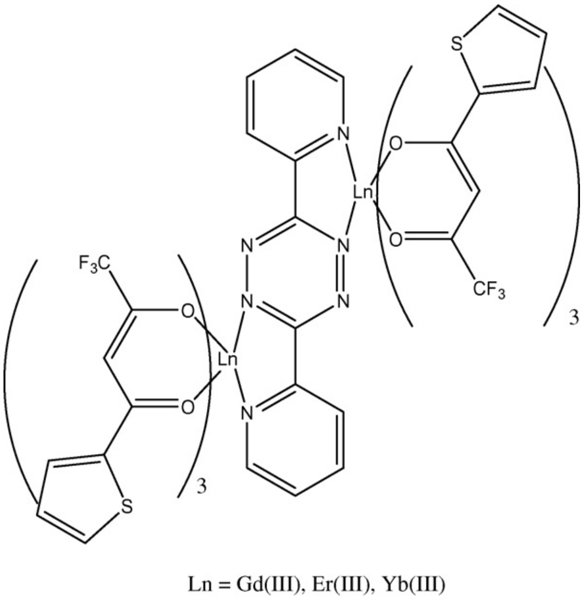


Fig. 7. Homodinuclear lanthanide complexes bridged by BPTZ [28].

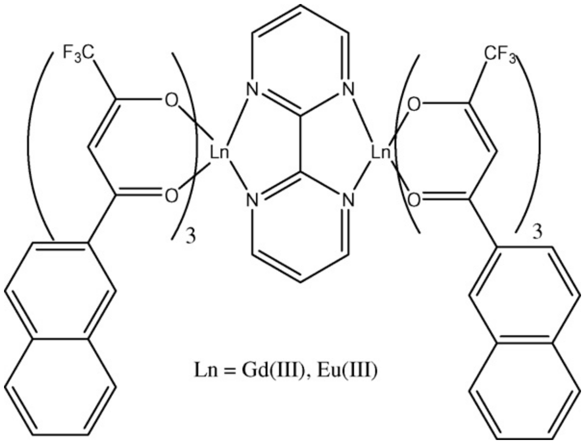


Fig. 8. Homodinuclear Ln(III) complexes [29].

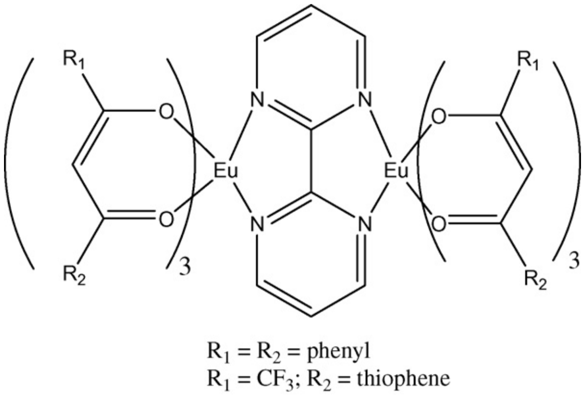


Fig. 9. Homodinuclear Eu(III) complexes [30].

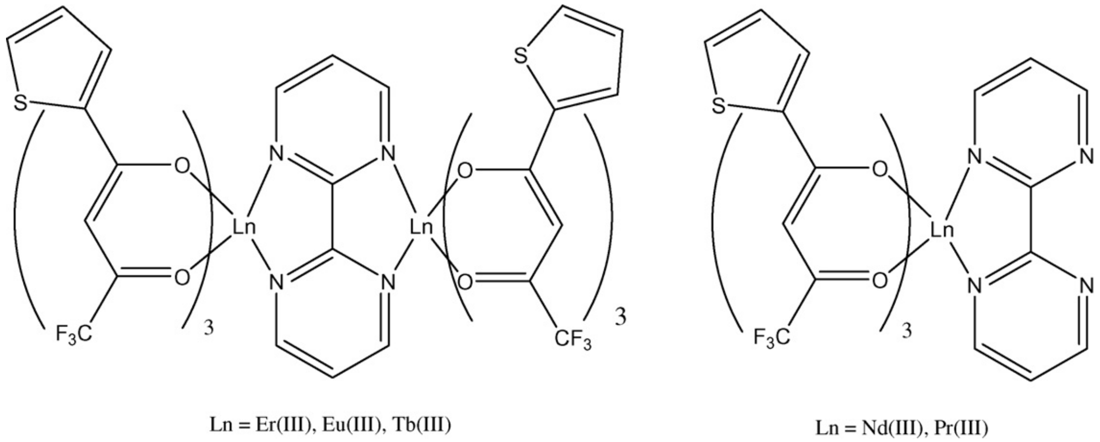


Fig. 10. Monometallic and bimetallic lanthanide complexes [31].

Cyclic voltammetry of the homodinuclear complex shows four reversible redox waves. The first two reductions are assigned as one electron reductions of the tpp ligand based on comparisons of CV's of tpp solutions. The reversible oxidation waves are assigned as one electron oxidation of one Yb center followed by oxidation of the second Yb center. These oxidations would be overlapping if there were no electronic communication between the metal centers. The fact that they are separated by 600 mV indicates electronic communication through the tpp bridging ligand. Separate studies have shown that ytterbocene complexes containing f^{13} metal electronic configurations have shown antiferromagnetic coupling through the bridging ligands bpm and dpp at low temperatures (20 K) [27].

Reaction of 3,6-bis(2-pyridyl)tetrazine (BPTZ) with two equivalents of $[Ln(tta)_3(H_2O)_2]$ (where tta = thenoyl(trifluoro)acetone and Ln = La, Nd, Gd, Er, Yb) afforded bimetallic bridged complexes with Gd(III), Er(III) and Yb(III) (Fig. 7) [28].

With the larger lanthanides, e.g. La(III) and Nd(III), only monometallic complexes were isolated under the same stoichiometric reaction conditions as the bimetallic complexes. Each metal center is eight coordinate in both bimetallic and monometallic complexes. The BPTZ bridging ligand has an absorption maximum at 550 nm allowing for sensitization of the lanthanide metal centers. In the case of Yb(III) the binding constant for coordination of the first metal is $10^6\ M^{-1}$ but decreases to $7.5 \times 10^4\ M^{-1}$ for the second metal due to a decrease in the basicity of the BPTZ ligand. Excitation of the tta ligands (337 nm) and the BPTZ ligand (520 nm) results in emission from the Yb(III) and Er(III) centers with comparable lifetimes indicating that both ligands act as "antenna" ligands.

Eight coordinate homodinuclear complexes of Eu(III) and Gd(III) bridged by bpm with more conjugated "antenna" ligands have been reported (Fig. 8) [29].

Solutions of bpm in chloroform were added to chloroform solutions of $Ln(NTA)_3$ at a 1:2 ratio respectively (NTA = 1-(2-naphthoyl)-3,3,3,-trifluoroacetone) and stirred at room temperature for 24 h. Slow diffusion of diethyl ether into chloroform solutions of the crude products gave X-ray quality crystals. Emission spectra of ethanolic solutions of $[Eu(NTA)_3]_2$bpm gave four sharp lines representative of the $^5D_0 \rightarrow {}^7F_{0-4}$ transitions. Lifetimes of the monometallic and bimetallic Eu complexes in the solid state were 399 μs and 372 μs respectively with similar quantum efficiencies of ca. 40%.

Reactions of $Eu(tta)_3$ and $Eu(dbm)_3$ (where dbm = dibenzoyl methane) with bpm in a 2:1 stoichiometric ratio respectively led to homodinuclear Eu complexes (Fig. 9) [30]. The homodinuclear complex has two Eu centers each eight coordinate separated by 7.011 Å. Red luminescence was observed when chloroform solutions of these complexes were irradiated at 350 nm, associated with the π–π* transitions of the terminal ligands. The most intense emission at 612 nm is associated with the transition $^5D_0 \rightarrow {}^7F_2$ of the metal center. Films of poly(9-vinylcarbazole) (PVK) and 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) doped with the Eu(III) bimetallic complex at 5 wt% gave stable red emission [30].

Recent attempts to synthesize bpm bridged homodinuclear lanthanides by reaction of $LnCl_3$ (Ln = Nd, Pr, Eu, Tb, Er) with tta and bpm in a ratio of 2:6:1 respectively led to formation of three bimetallic and two monometallic complexes (Fig. 10) [31].

The two monometallic complexes isolated were with the larger lanthanide ions Nd(III) and Pr(III) suggesting that ionic radius plays a role in the formation of the dinuclear complexes. When the more flexible bridging ligand (dpp) was used the only complex isolated contained Er(III), the smallest of the metals used (Fig. 11).

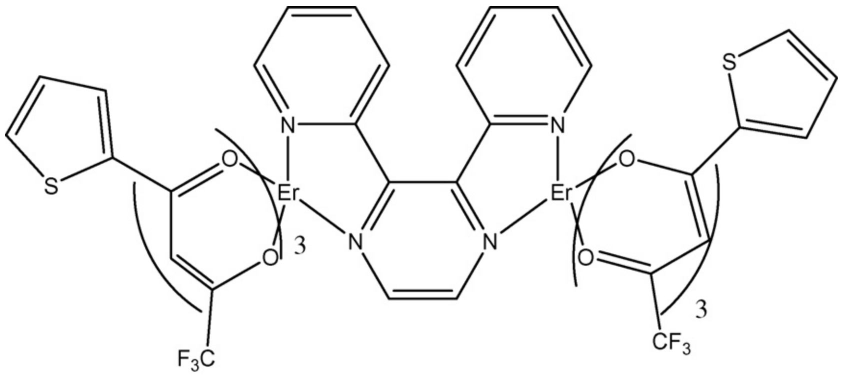


Fig. 11. Homodinuclear Er(III) complex [31].

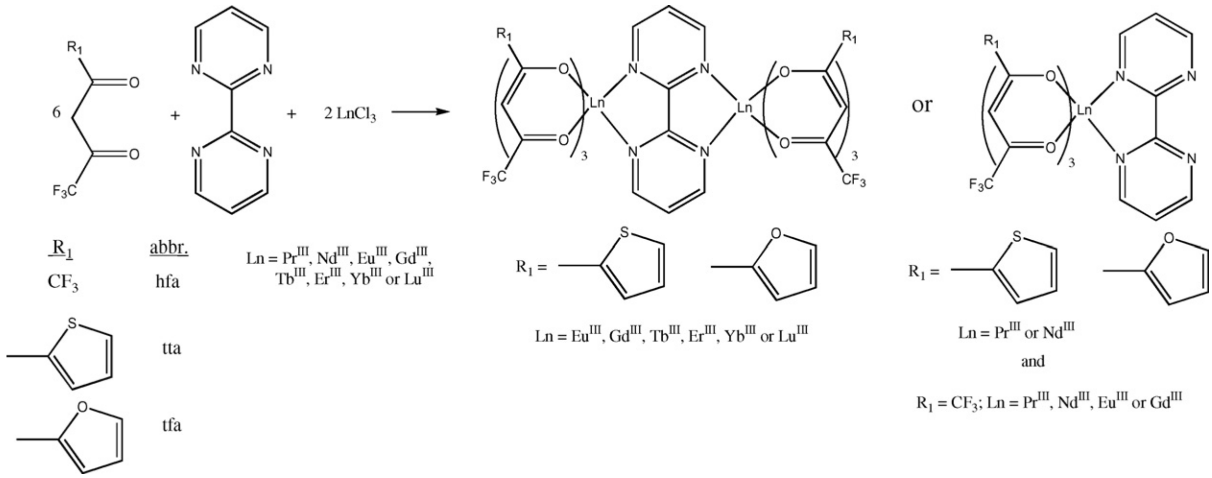


Fig. 12. Synthetic scheme for monometallic and bimetallic lanthanide complexes [32].

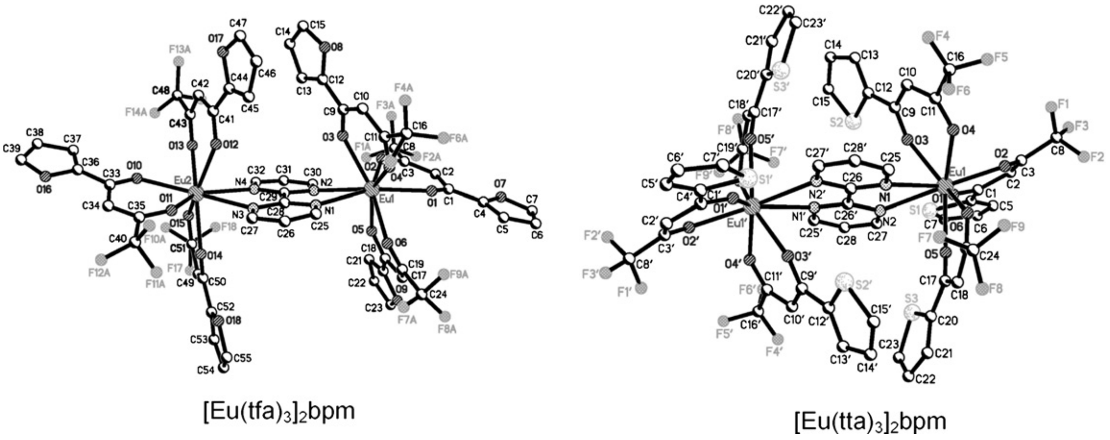


Fig. 13. Structures of $[Eu(tfa)_3]_2bpm$ and $[Eu(tta)_3]_2bpm$ [33].

This led to a systematic study of the role of ionic radius to formation of bridged complexes [32]. Using a variety of β-diketonates and bpm twenty-one new lanthanide complexes were synthesized. Fig. 12 illustrates the synthetic scheme used to make the complexes.

When the lanthanide salt was Eu, Gd, Tb, Er, Yb or Lu and the β-diketonate was tta or tfa bimetallic complexes resulted. In the case of the larger lanthanides, Pr and Nd, only monometallic complexes were isolated based on elemental analysis results. When the β-diketonate hexafluoroacetone (hfa) was used under stoichiometric conditions which favored formation of the bimetallic complexes only monometallic complexes were isolated regardless of the lanthanide used. It can be surmised that formation of the monometallic complexes decreases the basicity of the free nitrogens of the bpm ligand making it less likely to form the bimetallic. Another possible explanation may be that in the stepwise formation of the bimetallic complexes the monometallic is extremely insoluble under the reaction conditions employed resulting in precipitation before the bimetallic can be formed.

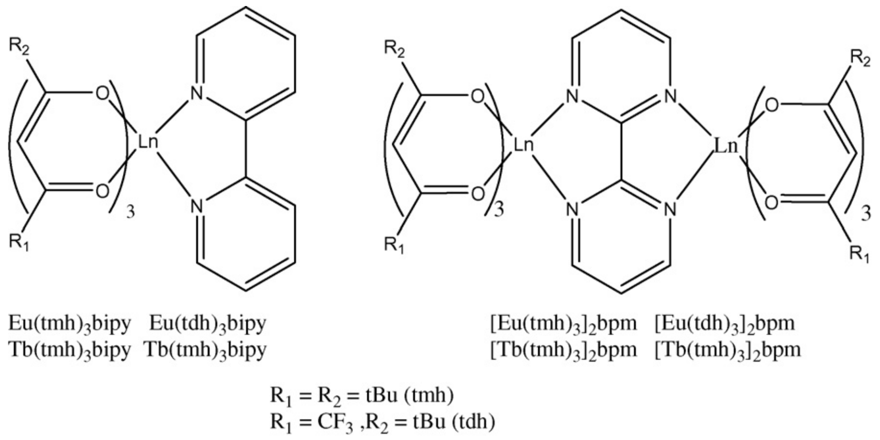


Fig. 14. Monometallic and bimetallic Eu and Tb complexes [37].

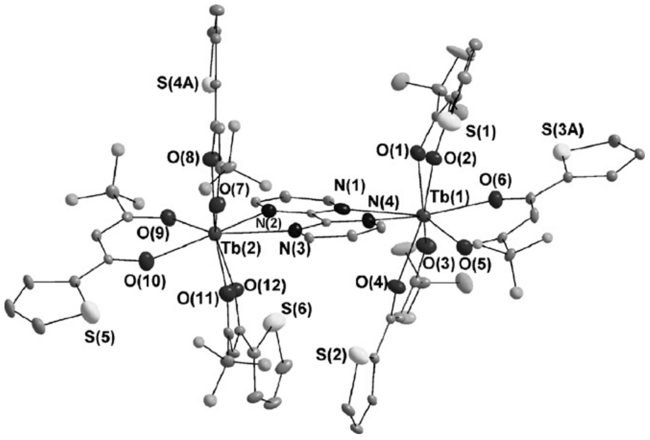
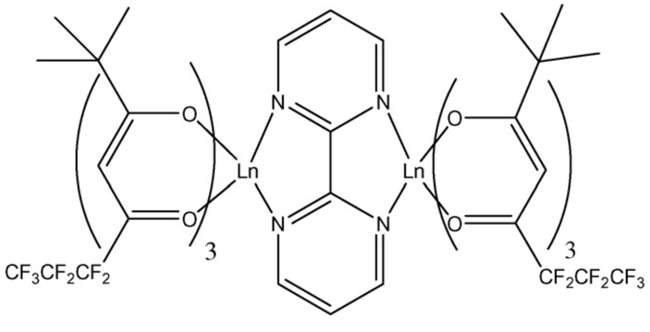


Fig. 15. Structure of $[Tb(tta)_3]_2bpm$ complex [39].



Ln = Nd(III), Eu(III), Tb(III), Lu(III)

Fig. 16. New homodinuclear lanthanide complexes [40].

Structural analysis of two new homodinuclear europium complexes, based on the bonding motif (Fig. 13) has been reported [33]. The metal centers were determined to be eight coordinate with Eu···Eu distance of 6.8035(8) Å. Emission spectra of the bimetallic complexes differ only in intensity revealing sharp lines representative of transitions associated with the $^5D_0$ state of the Eu(III) centers to the ^7F_J manifold. The most intense transition, due to direct coordination of the diketonate to the Eu ion, at ca. 614 nm is associated with the $^5D_0 \rightarrow {}^7F_2$ transition. Deactivation of the $^5D_1$ and $^5D_0$ states through thermal quenching has led to use of europium complexes as temperature probes [34–36]. Luminescent decay curves of the $[Eu(tta)_3]_2bpm$ and $[Eu(tfa)_3]_2bpm$ and their monometallic analogs $Eu(tta)_3bpy$ and $Eu(tfa)_3bpy$ (where bpy = 2,2′-bipyridine) as a function of temperature were fit to an Arrhenius type equation.

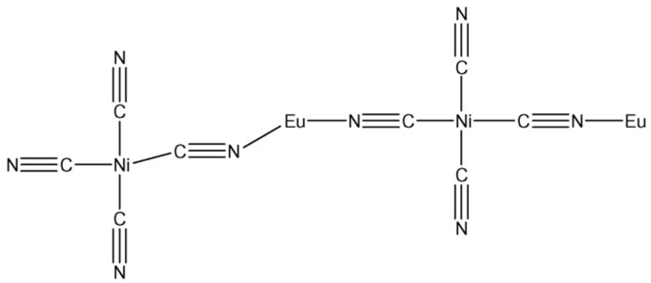


Fig. 17. $\{(DMF)_{10}Eu_2[Ni(CN)_4]_3\}$ repeat unit, DMF is removed for clarity [45].

$$1/\tau = k_0 + k_1\ \exp(-\Delta E/RT)$$

where ΔE represents the energy gap between the emissive $^5D_0$ state and higher energy states of the Eu ion. Values of ca. 50 kJ/mole were determined for the complexes in this study indicating similar thermal quenching mechanisms for mono and bimetallic europium complexes.

Luminescent properties of monometallic and bimetallic Eu(III) and Tb(III) complexes containing the β-diketonates 2,2,6,6-tetramethyl-3,5-heptanedione (tmh) and 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione (tdh) have been compared [37]. The bimetallics were bridged by bpm while their analogous monometallic complexes were capped with 2,2′-bipyridine (Fig. 14). Emission lifetimes of the Tb complexes were monitored at 545 nm corresponding to the $^5D_4 \rightarrow {}^7F_5$ transition while the Eu complexes were monitored at 614 nm corresponding to the

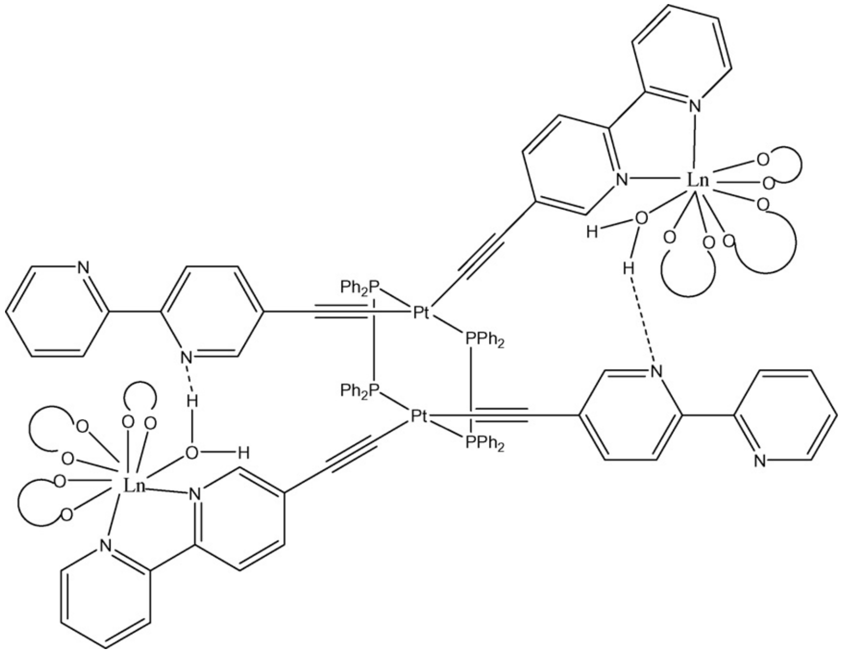


Fig. 18. Pt_2Ln_2 complex [47].

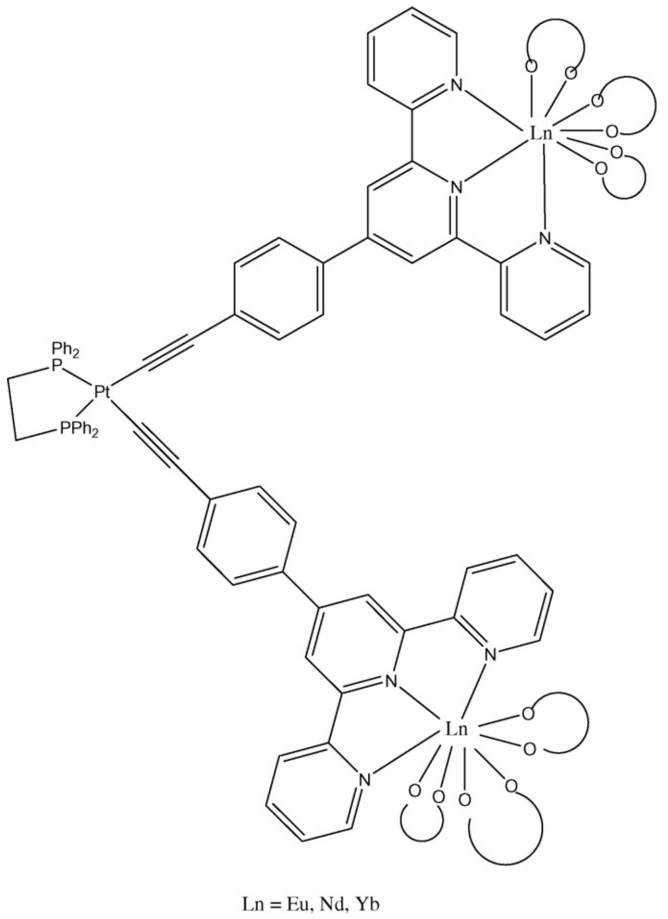


Fig. 19. Heterotrinuclear $PtLn_2$ complex [48,49].

$^5D_0 \rightarrow {}^7F_2$ transition. Lifetimes were longest for the Tb complexes containing the tmh β-diketonate and were independent of the nuclearity of the complex. The opposite was observed for the Eu complexes in which the tdh β-diketonate gave longer excited state lifetimes. A more exhaustive study is needed to draw any conclusions from this unusual result. In a complimentary study the synthesis, structural analysis, electrochemistry and emission spectroscopy of Eu, Sm and Yb complexes using tmh as the antenna ligand and bpm as the bridging ligand were presented [38].

Structural analysis of the bpm bridged bimetallic $[Tb(tta)_3]_2bpm$ complex has been reported [39]. The bpm was not strictly planar in this complex but has a slight torsion angle, while maintaining bonding between the Tb(III) ions and the bpm nitrogens (Fig. 15). The intramolecular distance for $Tb_1 \cdots Tb_2$ across the bpm bridging ligand is 6.7596 Å. Each Tb(III) ion is eight coordinate with six oxygens from the β-diketonates and two nitrogens from the bpm ligand. Luminescence of this complex has been described in a previous report [31].

Recent synthesis of mononuclear $Ln(fod)_3$ (where fod is the anion of 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione and Ln = Nd, Eu, Tb and Lu) bridged by the polyazine ligand bpm have led to new homodinuclear lanthanide complexes (Fig. 16) [40]. Solubility of the dinuclear complexes is less than the mononuclear analogs while the dinuclear complexes have increased thermal stability. Weak absorption bands for $[Nd(fod)_3]_2bpm$ are observed in the visible region of the spectrum and are associated with forbidden transitions from the $^4I_{9/2}$ ground state to higher energy states of the Nd ion. Upon excitation of the fod ligands at 355 nm, emission in the visible region of the spectrum are observed for the $[Eu(fod)_3]_2bpm$ and $[Tb(fod)_3]_2bpm$ complexes. Emission from the $^5D_0$ state to the ^7F_J (J = 0,1,2,3,4) manifold for the europium complex and from the $^5D_4$ state to the ^7F_J (J = 6,5,4,3,2) manifold of the terbium complex are reported.

3. Polynuclear lanthanides

3.1. Introduction

To take advantage of their luminescent properties the instability of lanthanide coordination complexes needed to be addressed. Solving this problem has led to very interesting ligand systems, for example, encapsulating ligands. Polymetallic lanthanide, supramolecular and polymeric assemblies have recently been reviewed [41–44]. This section will review briefly recent advances made in the field of linear polymetallic lanthanide complexes containing the more common bridging ligands like carboxylate and cyano as well as the fledgling area of polyazine bridged linear arrays.

3.2. Mixed lanthanide–transition metal polymers

Linear polymeric heterobimetallic complexes have been synthesized by stirring $EuCl_3$, $NiCl_2$ and KCN at a 2:3:12 stoichiometric ratio in DMF for 7 days (Fig. 17) [45].

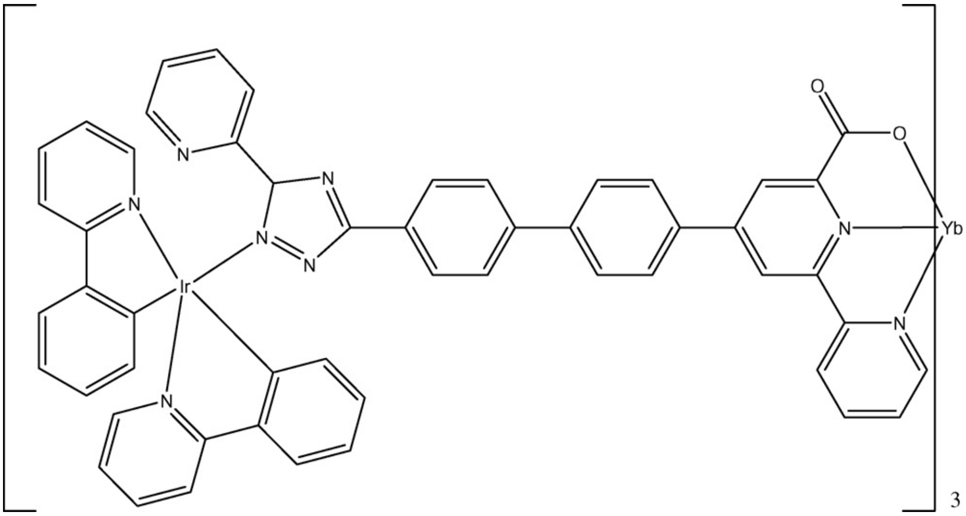


Fig. 20. Ir_3Yb complex [50].

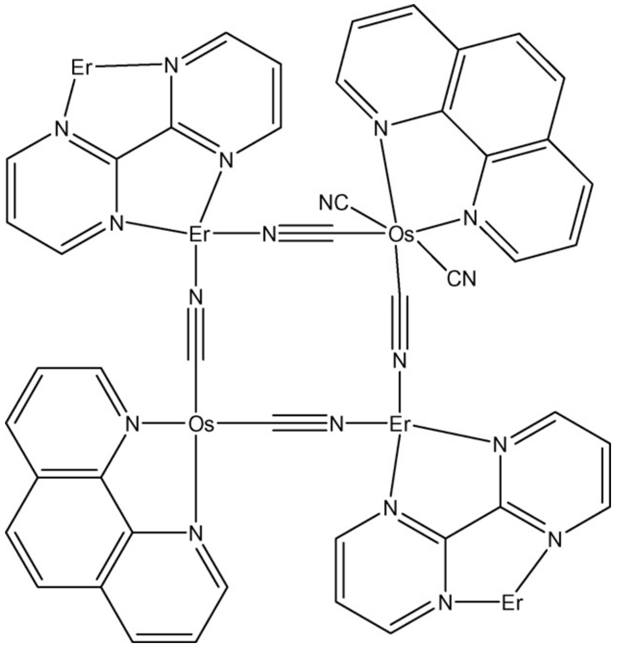


Fig. 21. $\{[Os(phen)(CN)_4]_3[Er(H_2O)_3]_2–[Er(H_2O)_4](bpm)(H_2O)_{13}(MeOH)\}_\infty$ water molecules have been removed for clarity [51].

Depiction of the “type A” one-dimensional array (Fig. 17) is the kinetically more stable form, however, over a period of time in the crystallization solution the complex interconverts to an extended double-strand array (type B). The process is more rapid for the Eu–Ni complex. This type of bonding motif allows for simultaneous loading of lanthanide and transition metals for use in fluorescent or chemical sensor materials. In a similar study two-dimensional coordination polymers with alternating Fe(II) and Nd(III) metals have been linked together using cyano and bpm bridging units [46]. The Nd(III) ions are nine coordinate. Magnetic studies indicate ferromagnetic interactions between the Fe(II) and Nd(III) ions.

Reactions of acetylide functionalized phenanthroline and bipyridyl ligands with $Pt(dppm)Cl_2$ followed by reactions with $Ln(hfa)_3(H_2O)_2$ (where Ln = Nd, Eu, Yb and hfa = hexafluoroacetone) yield multi-component complexes (Fig. 18) [47].

Each Ln(III) center is nine coordinate with six oxygens from the β-diketonates, one oxygen from a coordinated water molecule (hydrogen bonded to an adjacent bipyridyl nitrogen) and two nitrogens from a bipyridyl ligand. Excitation between 350 nm and 450 nm associated with the MLCT of the Pt(II) moiety leads to emission associated with the Ln(III) ion. Ligand centered and Pt metal centered emissions are quenched by energy transfer to the f-block metal. When the lanthanide is Nd(III) three emission lines are observed in the NIR at 865, 1060 and 1330 nm respectively, associated with transitions from the $^4F_{3/2}$ state to the ^4I_J (J = 9/2, 11/2, 13/2) manifold. Lifetimes of the 1060 nm emission is 0.49 μs. The Eu(III) complex gives emissions associated with the $^5D_0$ state to the ^7F_J manifold in the visible region with lifetimes of 25 μs at the 615 nm line. An emission line at 980 nm associated with the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ states of Yb(III) gives a lifetime of 12.7 μs.

Using terpyridyl functionalized acetylide ligands and the more structurally rigid $Pt(dppe)Cl_2$ (where dppe = 1,2-bis(diphenylphosphino)ethane) precursor yields very interesting heterometallic Pt/Ln_2 (Ln = Eu, Nd, Yb) complexes (Fig. 19) [48,49]. Each Ln(III) is nine coordinate with six oxygens from the β-diketonates and three nitrogens from terpyridyl.

The binding constant for the $PtEu_2$ complex was determined by titration experiments to be 4.80×10^8 while the binding constants for the Nd and Yb complexes were 9.33×10^{10} and 2.52×10^{11}, respectively. The role of the Pt(II) moiety was observed for these complexes when emission spectra typical of the lanthanide centers was achieved by excitation of the Pt-based groups in the 350–450 nm region.

The NIR emission spectra of Yb(III) was detected upon excitation of Ir(III) groups at 400 nm in multimetallic complexes synthesized by reacting three equivalents of the Ir(III) complex with one equivalent of the hexaaquo salt of $YbCl_3$ in water (Fig. 20) [50]. The Yb(III) center is nine coordinate from a carboxylate oxygen and two nitrogens from the ligand.

Iridium emission is quenched by Yb(III) indicating electronic communication between the metal centers. When irradiated at 300 nm associated with the MLCT state of the Ir(III) moiety an emission line at 976 nm is observed for the $^2F_{3/2} \rightarrow {}^2F_{7/2}$ transition of the Yb(III). The quantum yield for the Yb(III) emission is 0.7% which is high for NIR emitters and is due to prevention of O–H quenching from water molecules that do not have access to the Yb(III) centers that are nine coordinate from the carboxylate–bipyridine ligand.

Crystallization of $Na_2[Os(phen)(CN)_4]$, $Ln(NO_3)_3$ (Ln = Pr, Nd, Er, Yb) and bpm yield a one-dimensional “chain of squares” (Fig. 21) [51]. Both Er ions are eight coordinate with one Er coordinated to two bridging cyanides, two nitrogens from bpm and four oxygens from four water molecules. The second Er is coordinated to three oxygens from three water molecules and an additional cyanide from

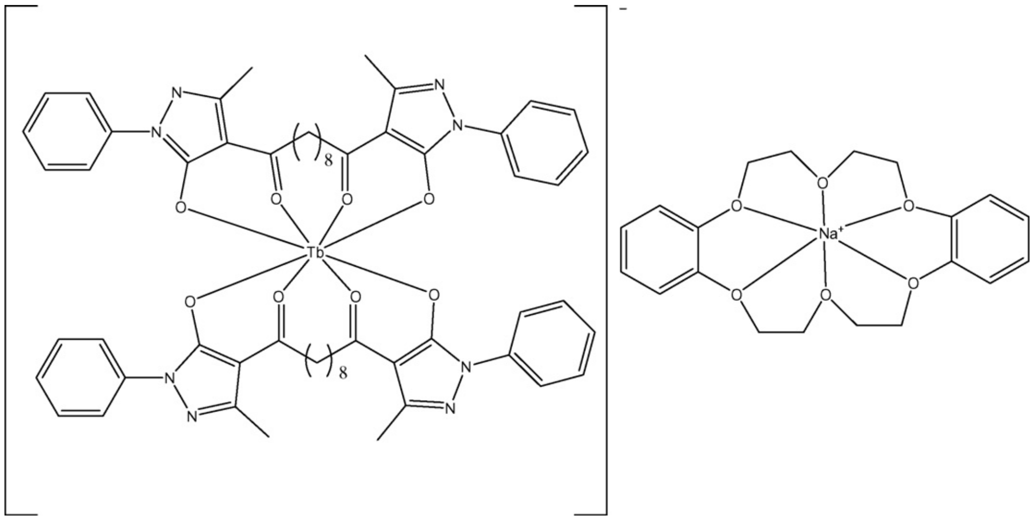


Fig. 22. Tb(III) repeat unit for one-dimensional molecular ladder [52].

another $[Os(phen)(CN)_4]^{2-}$ group. Excitation of the MLCT of the Os center at ca. 430 nm results in a broad emission at 680 nm for the Os–Gd complex with a lifetime of 67 ns. Because the excited state of the Gd(III) center lies in the UV region the emission observed must be due to the Os moiety indicating that Gd(III) does not quench the Os emission. Quenching greater than 90% of the Os emission is achieved when the lanthanide is Pr, Nd, Er or Yb. The most efficient energy transfer from Os → Ln is observed for the Nd(III) complex with emission lines associated with the $^4F_{3/2}$ to ^4I_J (J = 9/2, 11/2, 13/2, 15/2) manifold. The Os/Pr complex does not display emission lines due presumably to population of nonemissive states. Energy transfer from Os → Ln (Ln = Nd, Yb, Er) is faster than the Ru(II)/Ln analogs due to better orbital overlap of the lower energy Os(II) excited state orbitals.

Anionic Tb(III) complexes based on reactions of 1-phenyl-3-methyl-4-sebacoyl-5-pyrazolone (H_2SbBP), $Tb(NO_3)_3$ and dibenzo-18-crown-6 (Fig. 22) in a 3:2:1 ratio respectively resulted in one-dimensional molecular ladders [52]. The Tb(III) ion is eight coordinate. Excitation of the H_2SbBP ligand at 338 nm results in four well-defined emission lines in the visible region associated with transitions from the $^5D_4$ excited state of Tb(III) to the ^7F_J (J = 6,5,4,3) manifold.

3.3. One-dimensional arrays of homodinuclear lanthanides bridged by polyazines

Although only a limited number of polyazine bridged complexes has been reported the potential of this type of bonding motif is only now being realized. The only polyazine ligand which has been utilized for one-dimensional arrays is bpm. In a recent study the reaction of $EuCl_3$, hfa (hexafluoroacetylacetone) and bpm in the ratio 2:6:1 respectively resulted in the monometallic complex $Eu(hfa)_3bpm$ as determined by elemental analysis [53]. The monometallic complex in methanol showed decreased luminescent temperature sensitivity compared with similar europium complexes. Slow diffusion of hexanes into a saturated ethyl acetate solution of $Eu(hfa)_3bpm$ led to colorless crystals of X-ray quality. The structure indicates self-assembly of a linear one-dimensional array (Fig. 23). Each Eu(III) center is ten coordinate with repeating Eu-bpm units. In a similar study monometallic complexes; made under conditions favoring formation of bimetallic complexes, involved reactions of $LnCl_3$ (Ln = Nd, Gd, Tb) hfa and bpm in a stoichiometric ratio of 2:6:1 respectively, determined by elemental analysis [53]. Excitation of the hfa ligands at 304 nm led to emission spectra associated with the $^5D_4$ state to the ^7F_J manifold for the Tb(III) complex. Emission spectra were not observed for the Gd(III) complex because the triplet state of the hfa ligand is lower in energy than the $^6P_{7/2}$ state of the Gd(III). Vibrational deactivation through solvent interactions resulted in no emission spectra in the range of 305 nm to 1100 nm for the Nd(III) complex. Concentrated solutions of the monometallic Gd(III) and Nd(III) complexes in ethyl acetate were slowly evaporated over a two month period. Self-assembly of one-dimensional linear arrays resulted for Gd(III) (Fig. 24) and Nd(III) (Fig. 25) with coordination numbers of 10 for each metal. In the case of the Tb(III) complex a coordinated water molecule hydrogen bonded to a free bpm ligand prevented self-assembly of the polymeric structure (Fig. 26).

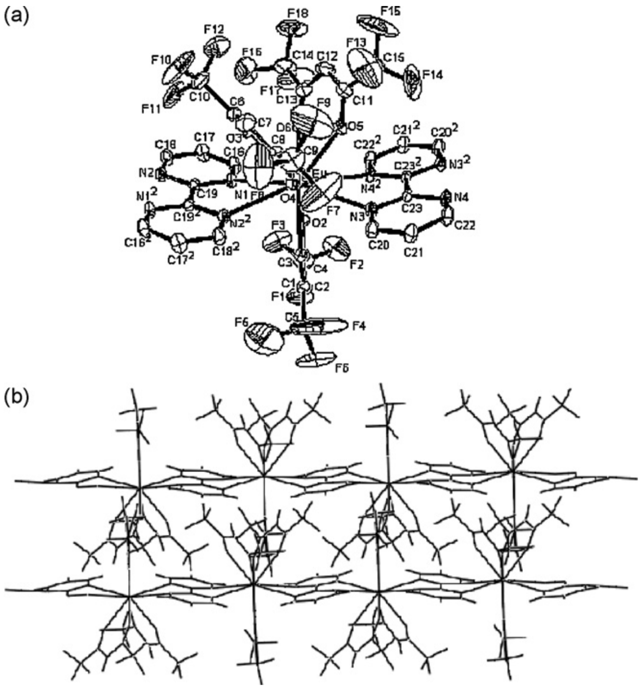


Fig. 23. Crystal structure of $[Eu(hfa)_3bpm]_n$. (a) An ORTEP view showing the asymmetric unit (with additional symmetry related atoms labeled with superscript 2 added to complete the bipyrimidine ligand). (b) A view showing the one-dimensional array structure [53].

A similar one-dimensional polymeric array has been obtained by reaction of $NdCl_3$ with tta and bpm in a 1:3:1 ratio respectively with repeating Nd-bpm units [55]. Excitation of the β-diketonate (tta) at 350 nm resulted in NIR emission associated with transitions from the $^4F_{3/2}$ excited state to the ^4I_J manifold of the Nd(III) ion. In

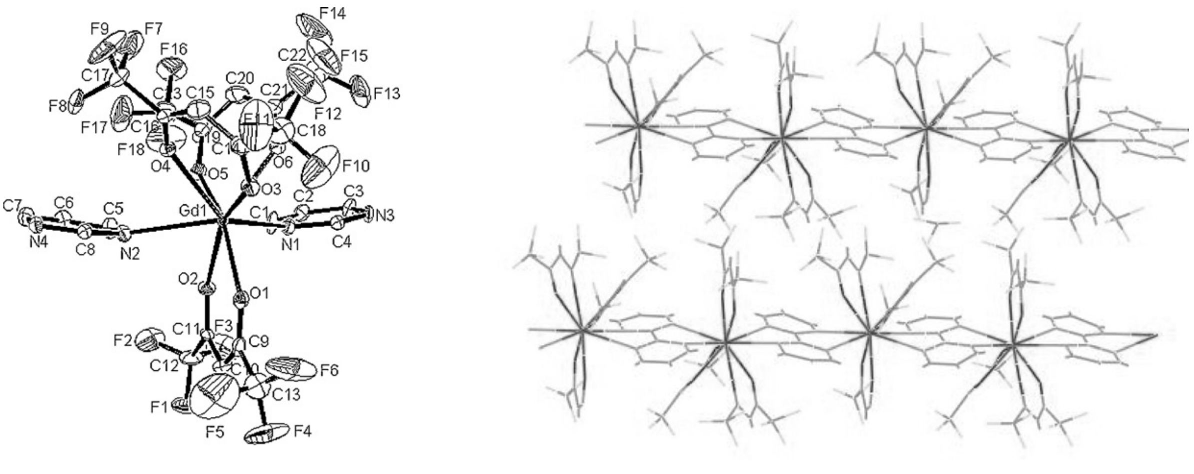


Fig. 24. ORTEP of the repeat unit for $Gd(hfa)_3bpm$ and the one-dimensional array formed by addition of symmetry related atoms [54].

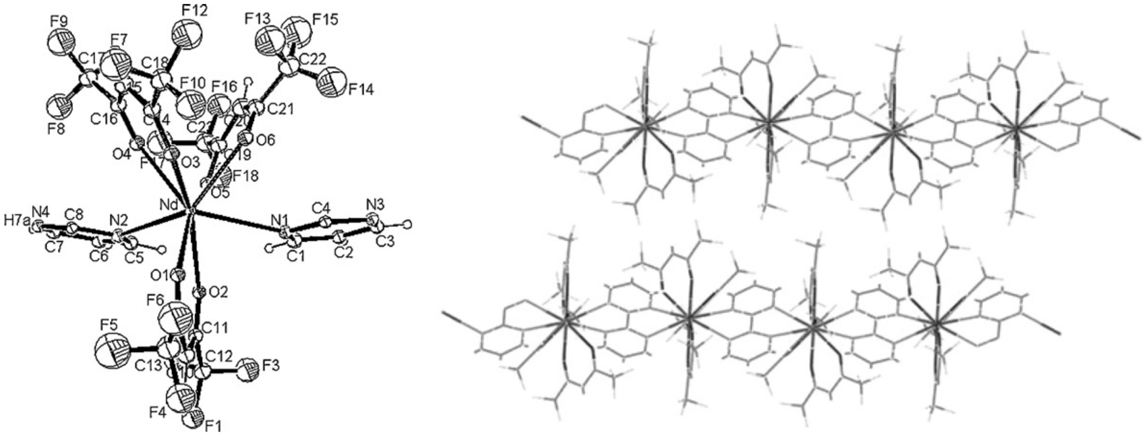


Fig. 25. ORTEP of the repeat unit Nd(hfa)$_3$bpm and the one-dimensional array formed by addition of symmetry related atoms [54].

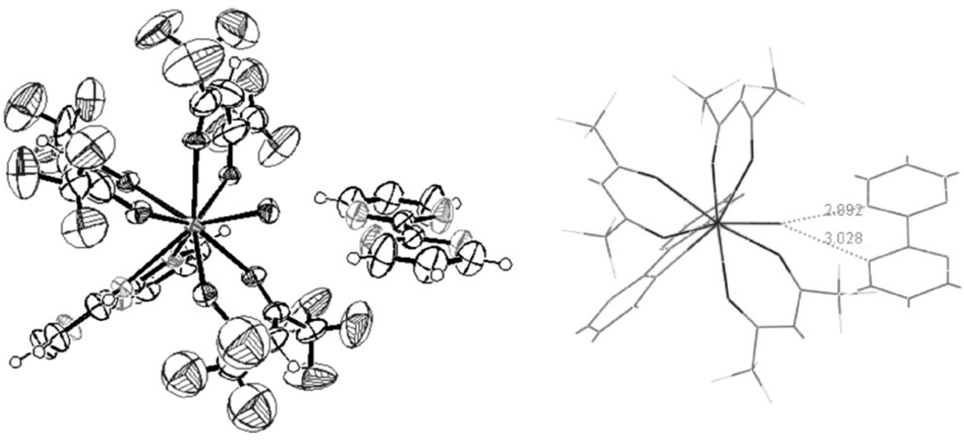


Fig. 26. ORTEP of Tb(hfa)$_3$bpmH$_2$O and the hydrogen bonded bpm ligand [54].

addition excitation of the higher energy bpm ligand at 260–270 nm also resulted in NIR emissions associated with the Nd(III) ion.

4. Conclusions

This review has attempted to illustrate the diverse nature of dinuclear and polynuclear lanthanide complexes. Gaining access to the important photophysical properties associated with lanthanides while maintaining their structural integrity is the goal of many research groups. In this review we have presented how these groups are achieving this goal through unique and interesting synthetic routes. The future of this field is wide open and promises to yield new materials of numerous uses for decades to come.

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