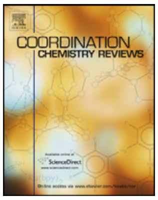
Coordination Chemistry Reviews 254 (2010) 991–1010

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Sensitized luminescence from lanthanides in d–f bimetallic complexes

Fang-Fang Chen, Zhu-Qi Chen, Zu-Qiang Bian, Chun-Hui Huang*

Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Yiheyuan Road 5th, Beijing 100871, China

Contents

ARTICLE INFO

Article history:
Received 26 October 2009
Accepted 18 December 2009
Available online 29 December 2009

Keywords:
Bimetallic complexes
Transition metals
Lanthanides
Red emission
NIR emission

ABSTRACT

This article reviews progress in the research of transition metal–lanthanide (d–f) bimetallic complexes. Through efficient energy transfer, sensitized luminescence of lanthanide ions from the visible range (Eu^{III}) to the near-infrared region (Nd^{III}, Yb^{III}, Er^{III} and Pr^{III}) is obtained in these bimetallic assembles. The d-block in d–f bimetallic complexes mainly contributes to the improvement of lanthanide emission efficiency and the extension of the excitation window for the lanthanide complexes. Examples are catalogued by various transition metals, such as Ru^{II}, Os^{II} (Fe^{II}), Pt^{II} (Au^{I}), Pd^{II}, Re^{I}, Cr^{III}, Co^{III}, Zn^{II} and Ir^{III}. The relevant synthetic procedures, crystal structures and photophysical properties of these d–f complexes are briefly described. Additionally, the molecular properties responsible for the performance of certain d–f systems, such as energy levels, nuclear distances and coordination environments, will be discussed.

1. Introduction

Luminescence from lanthanides has attracted extensive interest because of its wide range of applications, such as analytical sensors, immunoassays or imaging techniques [1–6], and organic light-emitting diodes or optical communication [7,8]. Eu^{III} ($^5D_0 \rightarrow {}^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$, $^7F_4$) provides suitable red luminescence for biological detection and organic electroluminescence. Nd^{III} ($^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$) and Yb^{III} ($^2F_{5/2} \rightarrow {}^2F_{7/2}$), which emit in the range from 900 nm to 1000 nm, are good candidates for biological luminescence imaging, and Nd^{III} has been used in laser systems. Pr^{III} (emits at 1.3 μm, $^1G_4 \rightarrow {}^3H_5$) and Er^{III} (emits at 1.5 μm, $^4I_{13/2} \rightarrow {}^4I_{15/2}$) are used in optical amplifiers for fiber-optic networks because their emission matches well the 'windows of transparency' in silica. The relevant energy levels of these lanthanides are illustrated in Fig. 1.

Though there are a number of energy levels available for the f–f transition of lanthanide ions, these energy levels cannot be populated directly because the lanthanide ions have very low absorption coefficients. The weak absorption originates from the fact that f → f transitions are formally forbidden by the Laporte rule. In addition, a number of transitions are also forbidden by the spin crossover rule. Typically, the extinction coefficients of these transitions are of the order of 1 M^{-1} cm^{-1} [1,9]. Therefore, introduction of organic ligands plays a notable role in the improvement of emission efficiency from lanthanides. The π–π* transitions of organic ligands cause strong absorption in the UV region. The energy absorbed can either be transferred directly to the central lanthanide ions or, more commonly, the absorption is followed by inter-system crossing (ISC) from the singlet state to the triplet state of the ligand. Then, energy transfer takes place from the triplet state to the central lanthanide ion, causing excitation of the lanthanide ion. When the excited lanthanide ions return to the ground state through a radiative process, the corresponding typical emission from the lanthanides are obtained. This mechanism is called the antenna effect,

---

* Corresponding author.
E-mail address: chhuang@pku.edu.cn (C.-H. Huang).

0010-8545/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2009.12.028

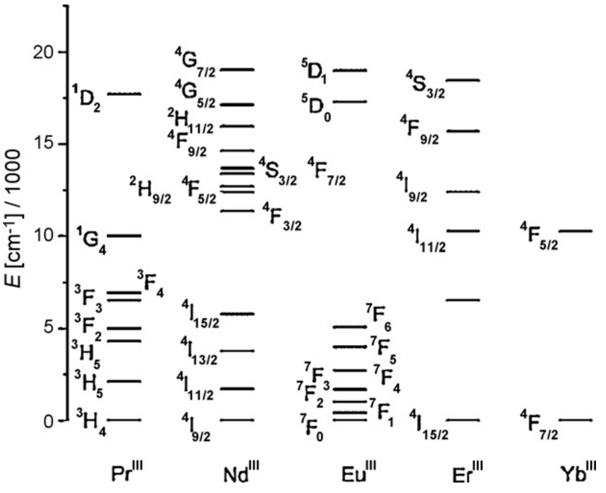


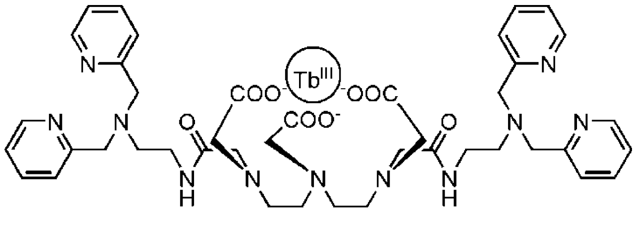
Fig. 1. Low-lying energy levels of lanthanide ions Ln^{III}.

which makes up for the insufficiency of the very low extinction coefficients of lanthanide ions. Thus, seeking appropriate ligands for sensitizing lanthanide ions is a very important topic.

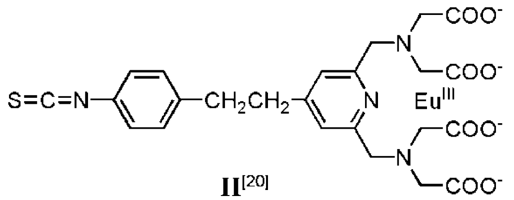
The relative energy gap between the excited state of the ligand and that of the lanthanide ion determines whether or not effective energy transfer takes place [10–14]. The triplet excited state of the ligand should be higher than the lowest excited state of the lanthanide ion, and within an appropriate range. A number of organic ligands suitable for sensitizing lanthanides (mainly Eu^{III} and Tb^{III}) with visible emission have been obtained. In contrast, fewer organic ligands for sensitizing lanthanides (mainly Nd^{III}, Yb^{III} and Er^{III}) in the NIR (near-infrared) region have been reported. Because the excited states of NIR-emitting lanthanides are much lower in energy than those that emit in the visible region, efficient energy transfer might be possible only when the excited state of the ligand is sufficiently low.

Many kinds of organic ligands have been used in lanthanide complexes because lanthanide ions can bond to a variety of elements such as oxygen, nitrogen and carbon. The strong coordination ability and high extinction coefficient in the UV region make β-diketone ligands good antennae for sensitizing lanthanide ions [15]. These complexes have been studied for more than forty years [11]. Carboxylic acids can readily coordinate to lanthanide ions because of the strong affinity between oxygen atoms and lanthanide ions. Usually, lanthanide complexes based on aromatic carboxylic acids exhibit good luminescence and stability. Macrocyclic ligands are often able to provide a coordination cage that is a suitable size for lanthanide ions [16–18]. Appended chromophores on the macrocyclic ring can efficiently capture UV light for the sensitization of lanthanide ions. Moreover, the emission of these complexes is readily quenched by water or solvent molecules in the coordination environment. Strongly coordinating neutral ligands are usually needed to substitute the water or solvent molecules present on the lanthanide precursor to saturate the coordination number of the lanthanide ion. For example, 1,10-phenanthroline (phen) is a very good ligand for Eu^{III}, while triphenylphosphine oxide is widely used in Tb^{III} complexes, because the energy levels of their triplet states are suitable for the corresponding metal ions.

Because Eu^{III} and Tb^{III} ions with strong visible emission are easily detected, they are used extensively as analytical sensors and applied in immunoassays and imaging techniques. For example, Tb^{III} diethylenetriaminepentaacetic acid (DTPA)-bisamide complex **I** can be used as a lanthanide probe for selective detection of Zn^{II}. However, the excitation wavelength used for the measurement is around 260 nm because the absorption edge of this Tb^{III} complex is about 280 nm [19]. When Eu^{III} complex **II** was employed in nucleic acid labeling, central Eu^{III} ions are also excited in the UV region, followed by energy transfer from the lanthanide to the dye-functionalized terminal [20]. Furthermore, lanthanide complexes with specific ligands can be combined with certain proteins in biological tissues. Characteristic emission from lanthanides which have been introduced into cells, upon UV excitation, can be recorded by advanced imaging measurements [21,22]. NIR-emitting lanthanides Nd^{III}, Yb^{III} and Er^{III} are rarely used in analytical detection or as fluorescence probes because of their weak emission as well as a lack of detection methods. However, NIR emission is nearly transparent in biological tissues, so the signal-to-noise ratio can be significantly improved over that of visible emission. The relevant studies are still in progress [23]. Lanthanide complexes are very useful in the biological field, however, most of the systems require UV excitation, which is harmful to organisms. This is the main limitation of the previously described luminescent probes. Because the Tb^{III} ion with a high energy excited state ($^5D_4$, 20,500 cm^{-1}) can be hardly excited under visible light, Eu^{III} which has red emission and Nd^{III}, Yb^{III} and Er^{III} which have NIR emission are more important for the study of the excitation of lanthanide ions in the visible region.



I[19]



II[20]

There are some strategies for achieving excitation of lanthanide complexes with visible light. One is to modify the organic ligands, which can cause a bathochromic shift of the absorption to the visible region. Fused-ring aromatic ligands are considered good candidates for the improvement of the absorption of lanthanide complexes in the visible region. 9-Hydroxyphenal-1-one was used in the formation of Eu^{III} complex **III**, in which the third absorption band was located at 458 nm because of the electron-rich three-ring structure of the ligand (Fig. 2) [24]. This complex allowed Eu^{III} luminescence to be sensitized by visible light (up to 475 nm). However, the relatively low position of the triplet level of the ligand (17,277 cm^{-1}) compared with Eu^{III}, results in possible back energy transfer, which might cause the low quantum efficiency (0.5%) of the complex. NIR lanthanide ions such as Nd^{III}, Yb^{III} and Er^{III} were sensitized more effectively by 9-hydroxyphenal-1-one than Eu^{III} [25]. Therefore, related push–pull sensitizers were introduced into organic ligands as antennae, producing ligands in which an exceptionally small singlet–triplet energy gap might be achieved compared to other organic chromophores. Michler's ketone [26], acridone and its derivatives [27,28] extend the excitation windows of their corresponding Eu^{III} complexes (see complex **IV** as an example) to around 450 nm. On the other hand, visible-light-sensitized red emission from Eu^{III} (complex **V**) was observed *via* the singlet pathway sensitizing the lanthanide ion [29]. Meanwhile, the measured overall quantum efficiency (~52%) of Eu^{III} complex **V**

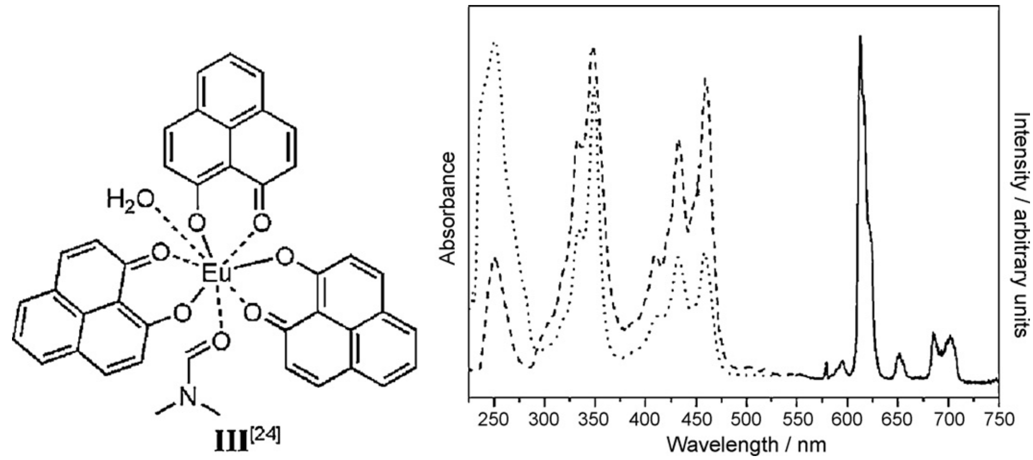
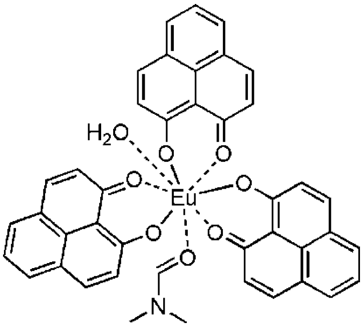


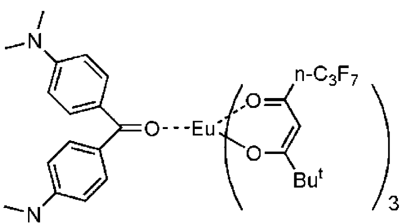
Fig. 2. Absorption spectrum (dotted line), excitation spectrum (dashed line), and emission spectrum (solid line) of complex **III** in THF at the room temperature. (Reprinted with permission from Ref. [24], copyright 2005 the Royal Society of Chemistry.)

showed the two important effects of this ligand in enabling longer wavelength sensitization and improving emission efficiency. Two-photon excitation of Eu^{III} or Tb^{III} can be used for longer wavelength excitation, for example at *ca.* 800 nm [30,31]. However, the quantum efficiency of two-photon excitation is rather low and a laser excitation source is usually needed.

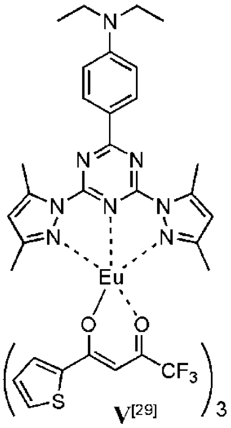
For Nd^{III}, Yb^{III} and Er^{III}, dye-functionalized complexes can be efficiently excited by visible light when organic dyes are introduced into appropriate ligands. For example, Nd^{III}, Yb^{III} and Er^{III} complexes containing fluorescein-bearing calix [4]arene or DTPA, have strong absorption bands at around 500 nm [32,33]. The excitation windows of coumarin or Texas Red functionalized *m*-terphenyl-based Nd^{III} complexes can extend to 590 nm [34]. The dye bora-diazaindacene, which has a high molar extinction coefficient at 529 nm, can be used to sensitize the NIR emission from Nd^{III}, Yb^{III} and Er^{III} [35].



III[24]



IV[26]



V[29]

As mentioned above, different kinds of organic ligands have been synthesized and modified to induce red shifts of the excitation windows of lanthanide complexes. However, the number of lanthanide complexes sensitized by visible light is still limited. On the other hand, the formation of metal to ligand charge transfer (MLCT) excited states between most transition metals and ligands can easily extend the absorption of their complexes to the visible region. Lanthanide complexes can therefore be excited with visible light using d-block chromophores. In this way, one may control the properties of emission from lanthanide complexes by tuning the physicochemical properties of d-block chromophores. Up to now, Ru^{II}, Os^{II} (Fe^{II}), Pt^{II} (Au^{I}), Pd^{II}, Re^{I}, Cr^{III}, Co^{III}, Zn^{II} and Ir^{III} have been involved in multimetallic edifices with lanthanide ions. Most of the Ru^{II}, Os^{II}, Re^{I} and Ir^{III} complexes are reported to sensitize Ln^{III} ions through their ^{3}MLCT donor level, while Pt^{II} chromophores use their broad mixed ^{3}MLCT and ^{3}MMLCT (metal to metal ligand charge transfer) emission levels. Cr (^{2}E) excited state in Cr^{III} complexes can sensitize lanthanide NIR emitters. On the other hand, in Zn^{III}-Ln^{III} complexes the energy used to sensitize the Ln^{III} ion originated from the ^{3}LC or ^{1}LC excited state of the ligands.

Herein we review the research on transition-metal complexes acting as 'ligands' for the sensitization of luminescent lanthanides, which is different from the review by Ward [36], as our review catalogues a more extensive range of transition metals. The sensitized emission from the visible range (Eu^{III}) to the NIR region (Nd^{III}, Yb^{III}, Er^{III} and Pr^{III}) will be discussed. (In the subsequent sections, different structures of d–f complexes will be illustrated. These complexes will be named in numerical order according to the differences in the transition metal complexes. Designations such as **1-Nd** and **1-Yb** will be used when different lanthanide ions need to be distinguished.)

2. Ru^{II}- or Os^{II} (Fe^{II})-based lanthanide complexes

van Veggel and co-workers first introduced the transition metal complexes tris(2,2′-bipyridine)ruthenium(II) ($[Ru(bpy)_3]^{2+}$) and ferrocene as antennae in the *m*-terphenyl-based lanthanide system in 2000 [37]. The corresponding NIR emission from Nd^{III} and Yb^{III} was obtained by excitation with visible light. The antenna $[Ru(bpy)_3]^{2+}$, which has a low triplet state ($E_T = 17{,}400\,cm^{-1}$), exhibited a good ISC quantum yield and strong absorption bands up to 550 nm. This allowed the lanthanide ions to be efficiently excited through the d-block with visible light of up to 500 nm. Time-resolved luminescence measurements showed that the decay of the luminescence from the triplet state of $[Ru(bpy)_3]^{2+}$ and the increase in the emission from Nd^{III} and Yb^{III} possessed the same time-constants, which indicated energy transfer occurred from the antenna to the lanthanide centers (Fig. 3). Moreover, the energy transfer rate (k_{ET}) in **1-Nd** and **1-Yb** can be calculated from the equation $k_{ET} = 1/\tau_q - 1/\tau_u$ (τ_q is the residual lifetime of the transition metal-based emission undergoing quenching by the lanthanide ion, and τ_u is the "unquenched" lifetime of the reference complex; a Gd^{III} complex is usually used as the reference complex). In this study, τ_q represented the luminescence lifetime of the antenna of **1-Nd** and **1-Yb**, and τ_u represented that of **1-Gd**. Thus, the energy transfer process from Ru → Ln occurs with a rate of $1.1 \times 10^6\ s^{-1}$ for **1-Nd** and $\leq 10^5\ s^{-1}$ for **1-Yb**. The electron exchange (Dexter) process as well as the spectroscopic overlap between the antenna and the lanthanide ion appropriately explained the differences in the energy transfer rates of different lanthanide complexes. The photophysical pathway of the sensitization process is summarized in Fig. 4 [38]. These measurement methods and relevant explanations have been used extensively in the study of other d–f bimetallic systems. Similarly, complexes **2-Nd** and **2-Yb**, which are functionalized with ferrocene, exhibited characteristic emission from Nd^{III} and Yb^{III} upon excitation of the ferrocene antenna. By introducing ferrocene moieties into $Ln(TTA)_3(phen)$ (TTA = 4,4,4-trifluoro-1-(thiophen-2-yl)butane-1,3-dionate), the excitation edges of complexes **3** and **4** are shifted from the ultraviolet to the visible region (up to 420 nm) [39]. But the corresponding quantum yields of lanthanides are low, such as (0.09 ± 0.02)% for **3-Yb** and (0.013 ± 0.003)% for **3-Nd**. The results might indicate that the weak absorption of ferrocene in the visible region prevented the achievement of efficient lanthanide luminescence in d–f systems though the low-lying triplet state of ferrocene closely matches receiving luminescent states of lanthanides.

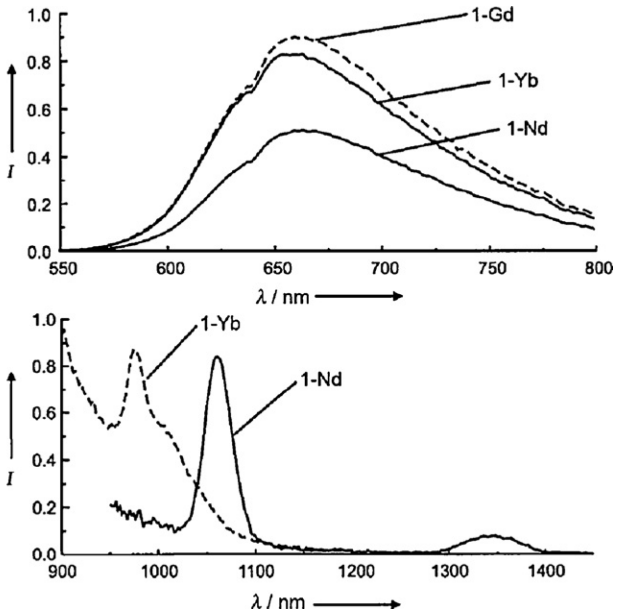
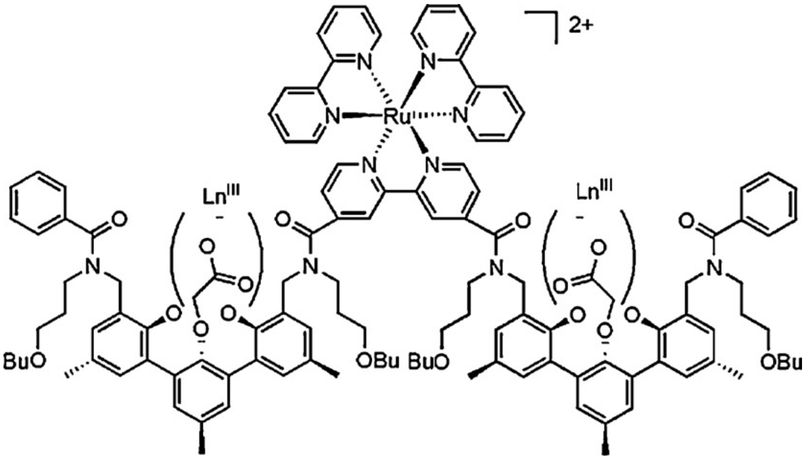
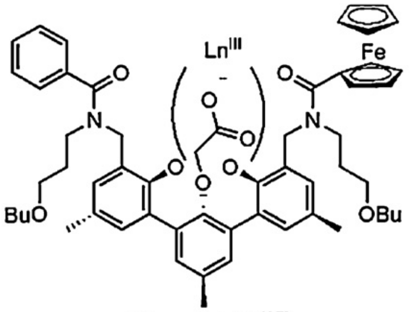


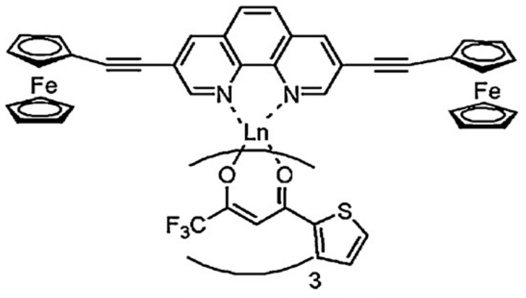
Fig. 3. Visible emission spectra of **1-Gd**, **1-Nd** and **1-Yb** in [D$_6$]DMSO upon excitation at 450 nm (top). The NIR luminescence spectra of **1-Nd** and **1-Yb** in [D$_6$]DMSO upon excitation at 450 nm (bottom). (Reprinted with permission from Ref. [37], copyright 2000 Wiley-VCH Verlag GmbH & Co. KGaA.)



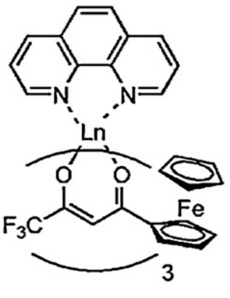
1 Ln = Nd, Yb, Gd[37]



2 Ln = Nd, Yb[37]



3 Ln = Nd, Yb,Eu[39]



4 Ln = Nd, Yb,Eu[39]

Because of its strong absorption in the visible region and the low triplet state of $[Ru(bpy)_3]^{2+}$, much effort has been directed at modifying the ligand 2,2′-bipyridine (bpy) for more efficient coordination with lanthanide ions. Faulkner and co-workers introduced a carboxyl group onto bpy and used the resulting ligand to produce self-assembled d–f hybrid complexes (**5**) that each contained a modified $[Ru(bpy)_3]^{2+}$ cation and a Ln^{III} complex with a 1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid (DO3A) ligand [40]. In these complexes, the luminescence from the MLCT state of the Ru^{III}-based chromophore was attenuated upon binding to the Ln^{III} complex, while the Ln-derived emission appeared in the NIR region. Subsequently, DTPA was covalently linked to one bpy ligand in $[Ru(bpy)_3]^{2+}$ [41]. This design allows the transition metal and lanthanide ion to coordinate stably in the homogeneous system. The corresponding structures (**45** and **46**) will be illustrated in Section 4. The elements Os^{II} and Ru^{II} are in the same group and have similar coordination abilities, so Faulkner and co-workers used $[Os(bpy)_3]^{2+}$ as the antenna in these systems [40,41]. In the Os^{II}–Ln^{III} bimetallic complex **6**, the Os^{II} chromophore was first used to sensitize Ln^{III}, and the results suggested that the short-lived emissive MLCT state from Os^{II}-based complex might be more suitable as donor chromophore than Ru^{II}-based complex [40]. Furthermore, the absorption band from the Os^{II}-based chromophore extended to 700 nm, which made the excitation window for the lanthanide ion reach the NIR region. Meanwhile, the spectroscopic overlap between the ^3MLCT state of $[Os(bpy)_3]^{2+}$ and the lanthanide emissive states was better than that between $[Ru(bpy)_3]^{2+}$ and Ln^{III}, so the energy transfer rate of the Os^{II}-containing complex ($6.2 \times 10^6\ s^{-1}$ for **46-Nd**) is an order of magnitude higher than that of the Ru^{II}-containing complex ($3.8 \times 10^5\ s^{-1}$ for **45-Nd**) [41]. Beer et al. covalently linked rim acid-amide-modified calix [4]arene moieties to the bpy group in $[Ru(bpy)_3]^{2+}$ to coordinate and sensitize luminescent lanthanide ions [42]. When Nd^{III} ions were added, the luminescent intensity of a solution of the Ru^{II} complex decreased, whereas the emission from Nd^{III} obviously increased. Complex **8** is one possible structure of the supramolecular 1:2 (Ru^{II}/Nd^{III}) adduct. The rate constant for the energy transfer process ($^3MLCT(Ru^{II}) \rightarrow {}^4F_{3/2}(Nd^{III})$) was $2.4 \times 10^6\ s^{-1}$. In contrast, the luminescence from Ru^{II} was increased upon addition of Tb^{III} ions. This behavior was ascribed to the electric field created around the Ru calix [4]arene complexes by the Tb^{3+} ions. Ward and co-workers connected two bpy ligands by an alkyl chain (CH_2CH_2) or an aryl chain (phenyl or biphenyl) to produce bridging ligands to link Ru^{II} or Os^{II} with lanthanide ions [43]. The bimetallic complexes **9** and **10** were simply synthesized by coordination of the lanthanide complex $Ln(TTA)_3$ to the uncoordinated bpy segment in the Ru^{II} or Os^{II} complexes. Dexter-type energy transfer over a distance of 20 Å occurred in these dyads.

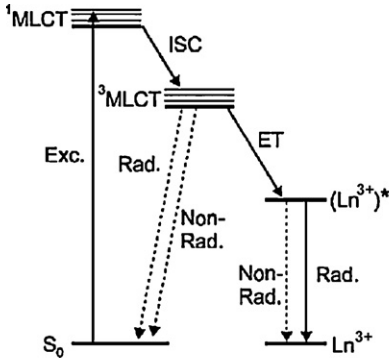


Fig. 4. The photophysical pathway of the sensitization process in transition metal–lanthanide bimetallic complexes. (Reprinted with permission from Ref. [38], copyright 2002 Elsevier Science B.V.)

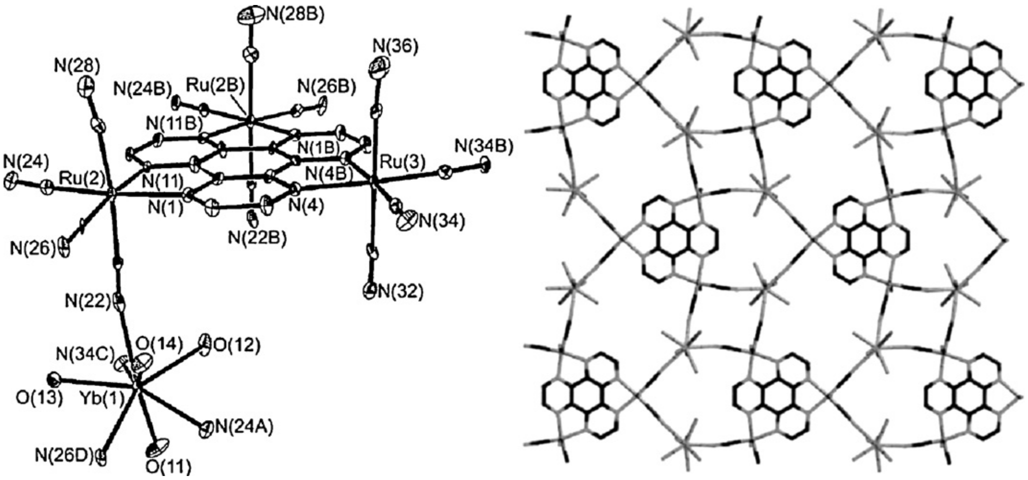
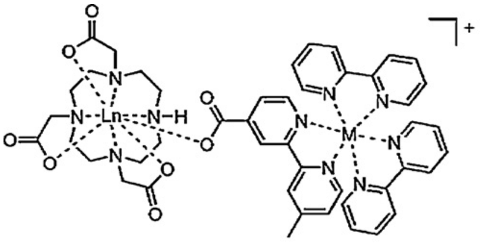
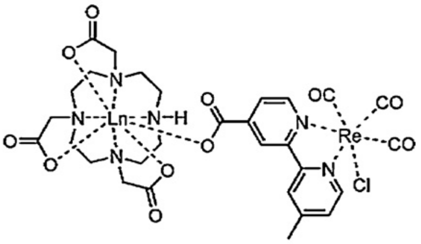


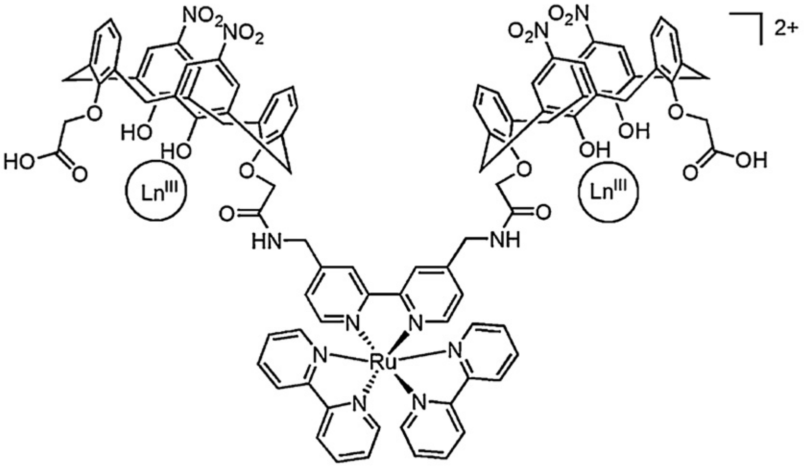
Fig. 5. Asymmetric unit of the structure of $[\{\mathbf{23}\}\{Yb(H_2O)_4\}_2 \cdot 13H_2O]_\infty$ (left) and the corresponding two-dimensional layers in the three-dimensional network structure (right). (Reprinted with permission from Ref. [55], copyright 2007 American Chemical Society.)



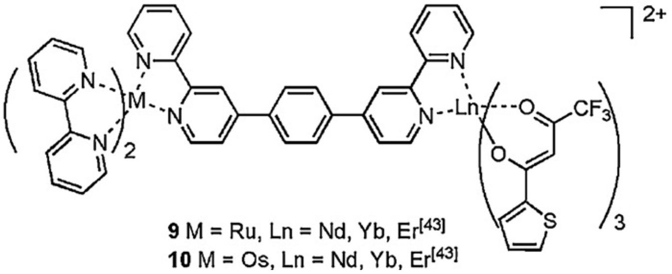
5 M = Ru, Ln = Nd, Er, Yb[40]
6 M = Os, Ln = Nd, Er, Yb[40]



7 Ln = Nd, Er, Yb[40]

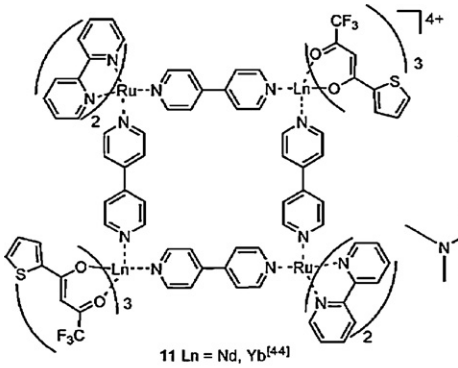


8 Ln = Nd, Eu, Tb[42]

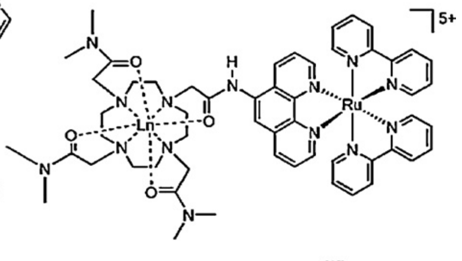


9 M = Ru, Ln = Nd, Yb, Er[43]
10 M = Os, Ln = Nd, Yb, Er[43]

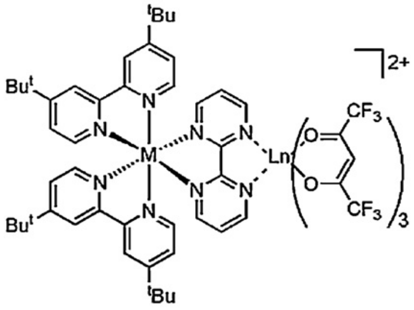
4,4′-Bipyridine has also been substituted for one bpy ligand in $[Ru(bpy)_3]^{2+}$ [44]. New lanthanide heterometallic molecular squares **11-Nd** and **11-Yb** were obtained by mixing $[Ru(bpy)_2(4,4'\text{-bipyridine})]^{2+}$ and $Ln(TTA)_3$ (Ln = Nd and Yb). The bimetallic complexes exhibited sensitized NIR emission upon excitation of the Ru^{II} chromophore at 420 nm. Another bridging ligand, derived from phen, was covalently linked to tetraamide-functionalized cyclen [45,46]. The d–f complexes **12-Yb** and **12-Nd** were synthesized by connecting lanthanide ions and $[Ru(bpy)_2]^{2+}$ with this bridging ligand. Bipyrimidine (bpm) has also been used as a bridging ligand, forming bimetallic complexes **13**–**16** in which the Ru^{II}/Os^{II} centers and Ln^{III} centers are closely separated [47]. Chloride ions or thiocyanate ions were used as auxiliary ligands for the sake of charge balance. X-ray diffraction data showed that the nonbonding distances between the transition metals and lanthanide ions were all around 6.3 Å, which unambiguously showed that efficient energy transfer occurred between the two metal centers.



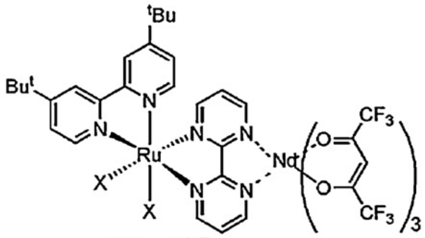
11 Ln = Nd, Yb[44]



12 Ln = Yb, Nd[46]

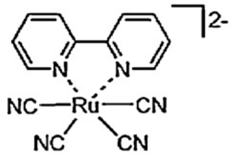


13 M = Ru, Ln = Nd, Yb, Pr[47]
14 M = Os, Ln = Nd, Pr[47]

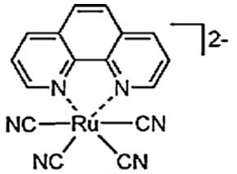


15 X = Cl[47]
16 X = NCS[47]

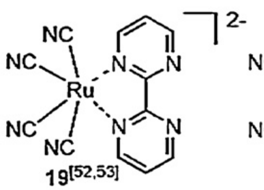
In the Ru^{II}/Os^{II}–Ln^{III} bimetallic complexes shown above, the bridging ligand used for connecting metal centers are derived from 2,2′-bipyridine (bpy) or analogous ligands. Such ligands, especially the cyclen–bpy ligand, often have long conjugation systems so that the distances between the Ru^{II}/Os^{II} center and the lanthanide ion are longer than 7–8 Å. The energy transfer rate from the transition metal to the lanthanide in these bimetallic complexes is usually $10^6\ s^{-1}$ (Ru^{II}–Nd^{III}) or lower (for example, the energy transfer rate from Ru^{II} to Yb^{III} is $<10^5\ s^{-1}$). Ward and co-workers used CN^- and other ancillary ligands, such as bpy (giving complex **17**) [48,49], phen (giving complex **18**) [50,51], bpm (giving complexes **19** and **20**) [52,53], HAT (giving complexes **21**–**23**) [54,55] and other diimine ligands [56], to form a series of $[Ru(diimine)(CN)_4]^{2-}$ complexes, in which the binuclear or trinuclear Ru^{II} complexes were achieved because of the presence of polydentate ligands, bpm and HAT. Then, Ru^{II}–Ln^{III} (Ln = Nd, Er, Yb, Pr and Gd) bimetallic coordination polymers or oligomers with a range of one-, two-, and three-dimensional structures were obtained by co-crystallization of Ru^{II}–CN complexes and lanthanide salts from aqueous solutions. The typical coordination structure in these Ru^{II}–CN–Ln^{III} bimetallic complexes is shown in Fig. 5. The Ru^{II} center is coordinated to the C site of the CN^- ligand, while the vacant N site is free for Ln^{III} ion. The formation of Ru^{II}–CN–Ln^{III} complexes not only extends the dimensions of d–f hybrid systems but also shortens the distance between Ru^{II} and Ln^{III} to ∼5.5 Å due to the short triple bond in CN^-. This strategy significantly improves the energy transfer from Ru^{II} to Ln^{III}. For example, in the coordination networks combining $[Ru(bipy)(CN)_4]^{2-}$ anions and lanthanide(III) cations, the energy transfer rate from Ru^{II} to Nd^{III} was estimated to be $2 \times 10^8\ s^{-1}$, and that of $Ru^{II} \rightarrow Yb^{III}$ was also improved to $3 \times 10^6\ s^{-1}$ [49]. Similarly, CN^- was employed as the bridging ligand in Os^{II}–Ln^{III} systems with bpy [57] or phen [58] as ancillary ligands to saturate the coordination number of the metals. The energy transfer rate of Os^{II}–Yb^{III} had a value of $2.5 \times 10^7\ s^{-1}$, which was an order of magnitude higher than that of the analogous Ru^{II}–Yb^{III} system [58].



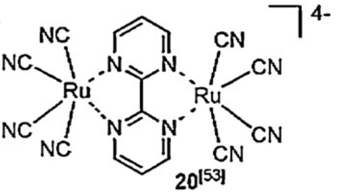
17[48,49]



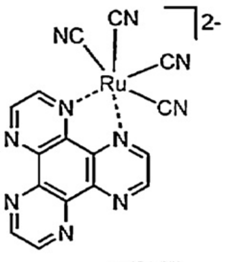
18[50,51]



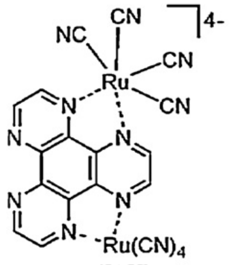
19[52,53]



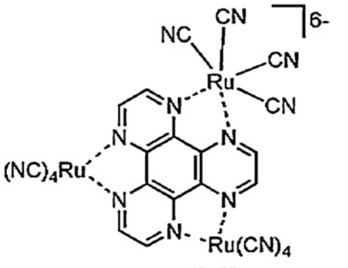
20[53]



21[54,55]



22[54,55]

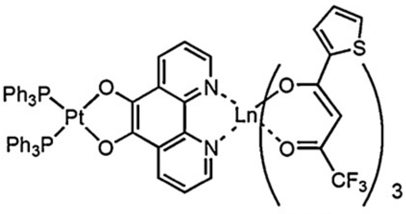


23[54,55]

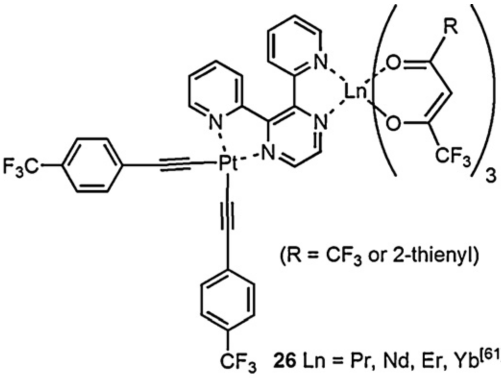
CN^- has an excellent ability to shorten the nonbonding distance between d–f centers. However, there are some water molecules coordinated to the lanthanide ions in the Ru^{II}–CN–Ln^{III} and Os^{II}–CN–Ln^{III} coordination networks. Water causes nonradiative quenching of the energy transfer process, which decreases NIR luminescence. Shortening the distance between the metal centers and decreasing nonradiative vibrational quenching are both important factors in the design of d–f bimetallic systems. To discourage nonradiative quenching, water and other solvent molecules should be avoided to some extent.

3. Pt^{II} (Au^{I})- or Pd^{II}-based lanthanide complexes

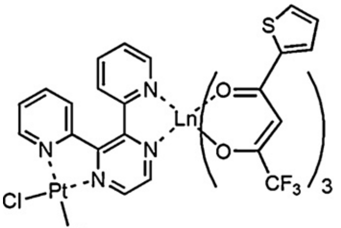
The Ward and Faulkner groups both studied a series of Pt^{II}–Ln^{III} bimetallic complexes. The bridging ligands used were generally tetradentate ligands, such as (O^O)(N^N) style ligands mainly containing pdo (H_2pdo is 5,6-dihydroxy-1,10-phenanthroline) [59,60] and (N^N)(N^N) style ligands mainly containing bppz (2,3-di(2-pyridyl)pyrazine) [60,61] and bpm [62]. In the corresponding Pt^{II} complexes, one of the binding sites of the bridging ligands is occupied by the Pt^{II} fragment and the other site is vacant, so can directly coordinate to lanthanide ions. Furthermore, the Ln(β-diketonate)$_3$·$2H_2O$ complexes are used as starting materials. The coordinating water molecules are substituted by the bridging ligands, which benefit the NIR luminescence of the resulting complexes. The distances between metal centers are determined by the coordination sites of the bridging ligands in the series of Pt^{II}–Ln^{III} bimetallic complexes **24**–**27**. The distance between Pt^{II} and Ln^{III} connected by pdo is about 8.3 Å, which is longer than the metals ions connected by bppz (~7.3 Å) or bpm (~6.3 Å). The differences in the energy transfer rates of the complexes reflect the distances between the metal centers. For example, the $Pt^{II} \rightarrow Ln^{III}$ energy transfer rate in the bppz series is greater than $10^8\,s^{-1}$, and no residual Pt^{II}-based MLCT emission was observed in bpm-related complexes.



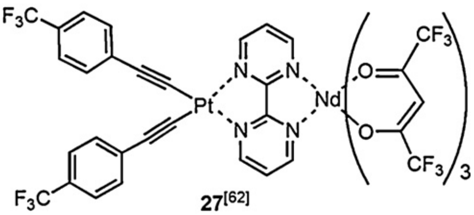
24 Ln = Nd, Yb, Er[59,60]



26 Ln = Pr, Nd, Er, Yb[61]



25 Ln = Nd, Er, Yb[60]



27[62]

Chen and co-workers introduced bifunctional bridging ligands (acetylide-functionalized diimines, mainly bpy/phen/2,2′:6′,2″-terpyridine derivatives) into Pt^{II}–Ln^{III} bimetallic systems. They obtained sensitized lanthanide emission using these Pt^{II}-acetylide chromophores [63,64]. In these systems, two Pt^{II} ions were connected by bis(diphenylphosphino)methane (dppm) to form diplatinum alkynyl complexes, and Pt_2Ln_2 (**28**) and Pt_2Ln_4 arrays were obtained. These arrays were extended to a Pt_6Ln_6 array (**29**) because the vacant N sites in bpy could coordinate to more Pt^{II} centers [65]. Various Pt^{II}–Ln^{III} bimetallic systems with different combinations were synthesized by changing reaction methods or reaction substrates. For example, $PtLn_2$ arrays **30** were achieved, which are similar to the Pt_2Ln_4 array. The only difference in their preparation is that the starting materials were reacted with different ratios [64,66]. The Pt^{II}–Ln^{III} arrays **28**–**30** were mainly obtained from Pt(dppm)Cl_2 or analogous derivatives. More Pt^{II}–Ln^{III} bimetallic systems were designed and synthesized using similar strategies with other Pt^{II} complexes, such as $Pt(PPh_3)_2Cl_2$ (PPh_3 = triphenylphosphine) [67], Pt(bpy)Cl_2 [68] and $Pt(Bu^t{}_2bpy)Cl_2$ ($Bu^t{}_2$bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) [69]. Both of the bimetallic complexes **31** and **32** exhibited $PtLn_2$ arrays. Interestingly, *cis*- and *trans*-Pt^{II} bis-σ-acetylide isomers could be used as prefabricated modules for the preparation of a series of *cis*-$PtLn_2$ (**31**) and *trans*-$PtLn_2$ heterotrinuclear isomeric complexes by using *cis*- and *trans*- $Pt(PPh_3)_2Cl_2$ [67]. Moreover, when the bpy ligand of Pt(bpy)Cl_2 was modified to add more coordination sites, more lanthanides were able to coordinate to the (NN̂) sites and the corresponding $PtLn_3$ array **33** was obtained [68]. When $[Pt(Bu^t{}_3tpy)Cl]^+$ ($Bu^t{}_3$tpy = 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine) was used in further synthesis, the product is a Pt^{II} mono-σ-acetylide because of only one vacant coordination site at the Pt^{II} center. Thus, the Pt^{II} complex and the lanthanide complex reacted with a ratio of 1:1, and the PtLn array **34** was obtained [70]. When two $Pt(Bu^t{}_3tpy)$ moieties were connected by one bpy ligand, the Pt^{II}–Ln^{III} bimetallic complex was synthesized as a Pt_2Ln array [70]. In these Pt^{II}–Ln^{III} systems, when the Pt^{II} center and the Ln^{III} center were directly connected by acetylide-functionalized bpy (or phen), the shortest distance between them in Pt_2Ln_2 arrays was about ~8–9 Å, and the energy transfer from the Pt^{II} center to the Ln^{III} center was nearly complete (Fig. 6) [63]. However, the distances between the Pt^{II} centers and the Ln^{III} centers in the Pt_6Ln_6 array all exceeded 10 Å, and the longest distance was close to 17 Å. Emission from the Pt^{II} centers was clearly observed in the Pt_6Ln_6 array, which indicated incomplete energy transfer from the Pt^{II}-based antennae to the Ln^{III}-based acceptors (Fig. 7) [65].

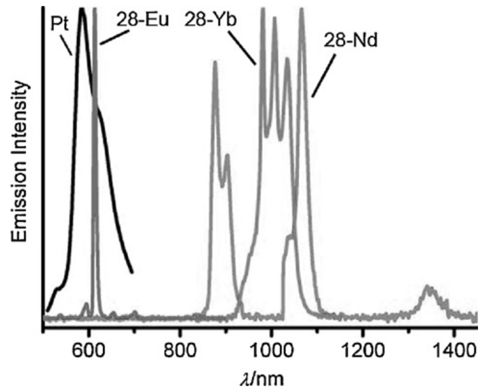


Fig. 6. Emission spectra of the precursor Pt complex and Pt_2Ln_2 arrays **28** in CH_2Cl_2 at 298 K. (Reprinted with permission from Ref. [63], copyright 2006 the Royal Society of Chemistry.)

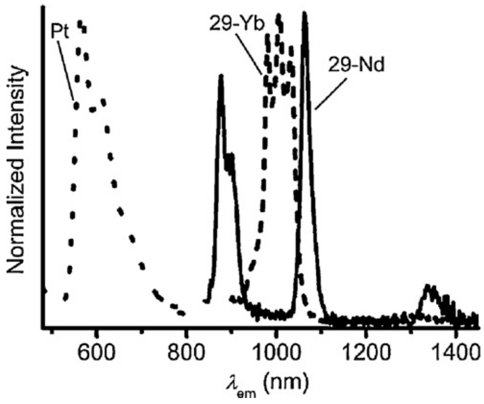


Fig. 7. Emission spectra of the precursor Pt complex and Pt_6Ln_6 arrays **29** in CH_2Cl_2 at 298 K. (Reprinted with permission from Ref. [65], copyright 2007 the Royal Society of Chemistry.)

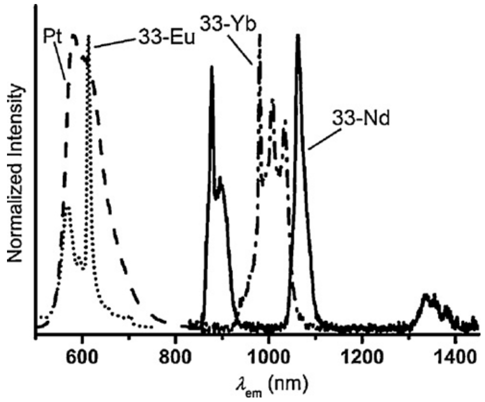
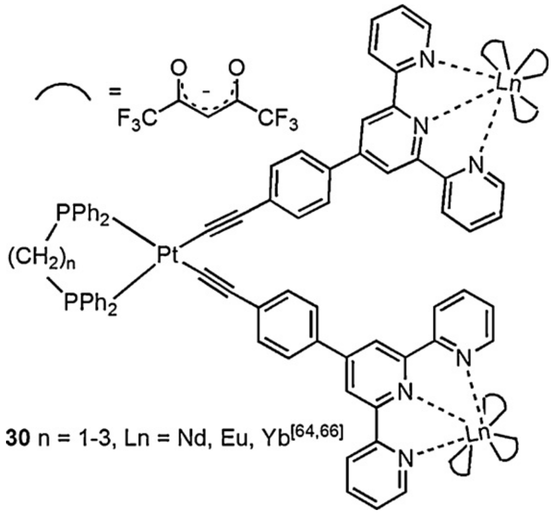
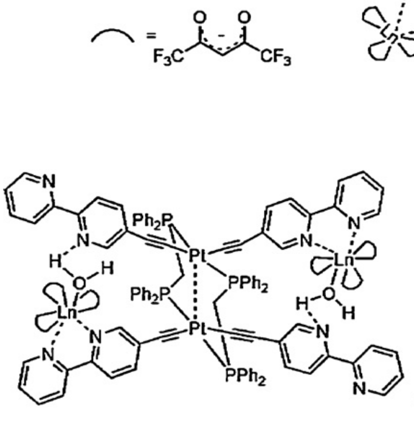


Fig. 8. Emission spectra of the precursor Pt complex and $PtLn_3$ arrays **33** in CH_2Cl_2 at 298 K. (Reprinted with permission from Ref. [68], copyright 2008 the Royal Society of Chemistry.)

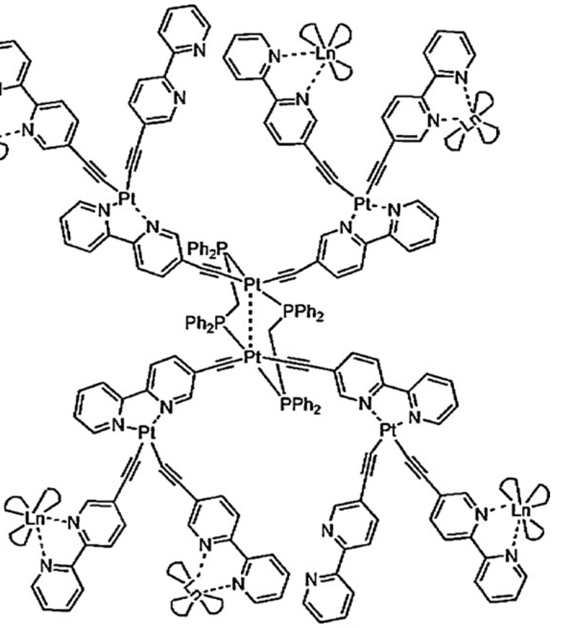


30 n = 1-3, Ln = Nd, Eu, Yb[64,66]

Recently, Chen and co-workers used a similar acetylide-functionalized bpy as the bridging ligand to connect Au^{I} and Ln^{III} ions. Au^{I}–Ln^{III} bimetallic complex **35** was formed in a similar

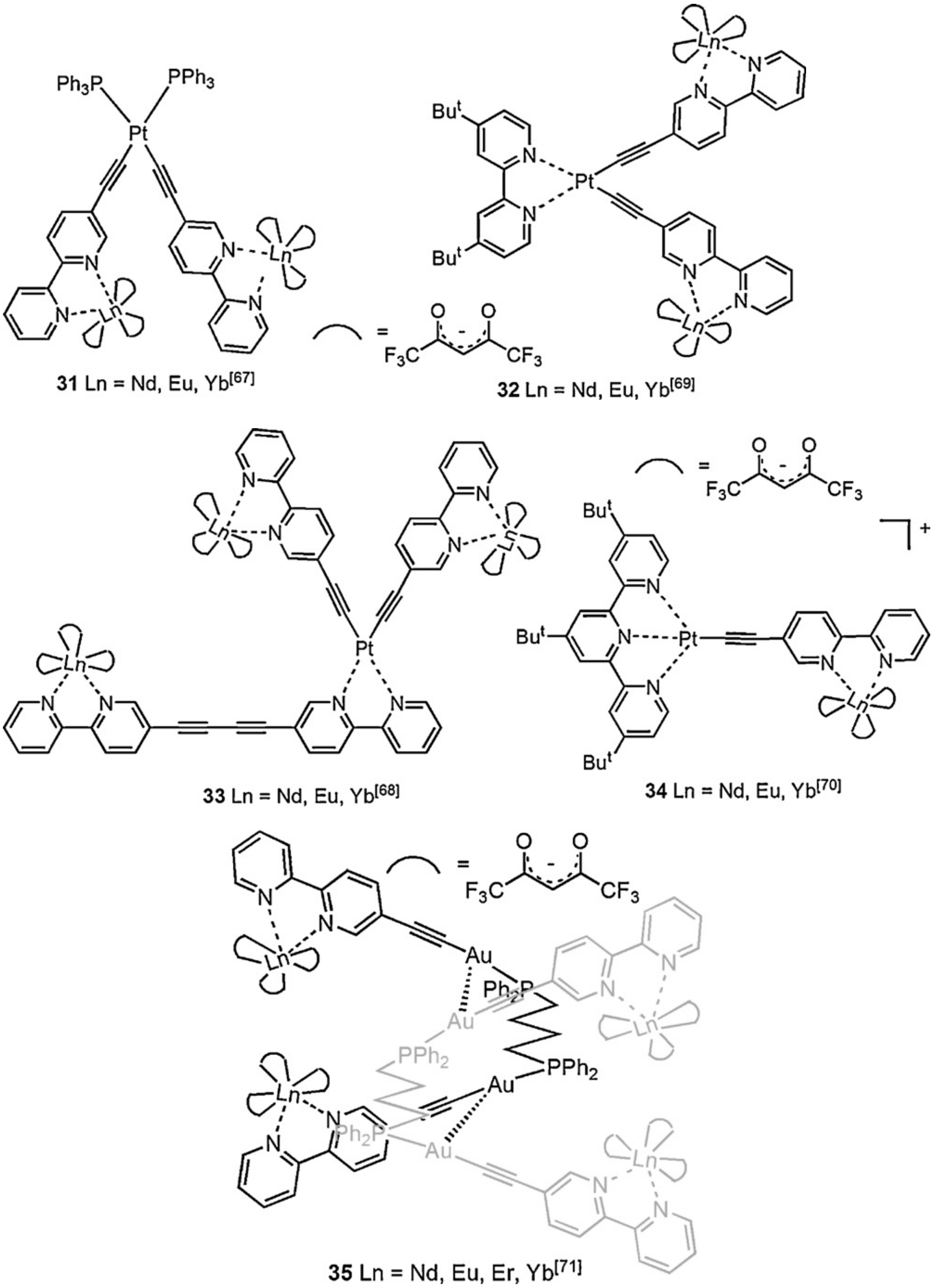


28 Ln = Nd, Eu, Yb[63]



29 Ln = Nd, Yb[65]

manner to the Pt^{II}–Ln^{III} bimetallic systems [71]. Nevertheless, the energy transfer from the Au^{I} alkynyl chromophore to the Ln^{III} centers in these Au^{I}–Ln^{III} arrays was less effective than in the Pt^{II} analogues because of energy mismatching or less spectroscopic overlap between the emission spectra of the Au^{I} alkynyl chromophores and the absorption spectra of the f–f transitions of the Ln^{III} ions.



31 Ln = Nd, Eu, Yb[67]

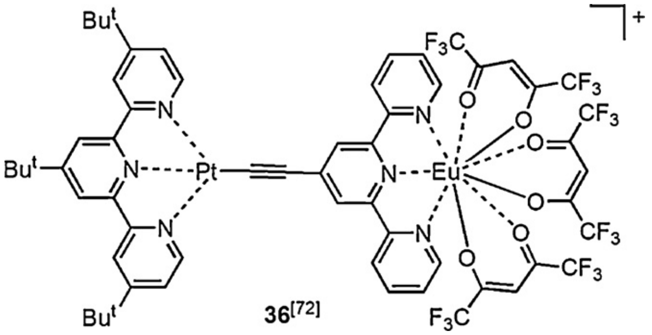
32 Ln = Nd, Eu, Yb[69]

33 Ln = Nd, Eu, Yb[68]

34 Ln = Nd, Eu, Yb[70]

35 Ln = Nd, Eu, Er, Yb[71]

Most of the transition metal complexes were used for the sensitization of NIR lanthanide emission because of their known energy levels. For example, the emission peaks of $[Ru(bpy)_3]^{2+}$ at around 650 nm and its lowest triplet energy level at around 17,400 cm^{-1} are not suitable for sensitization of Eu^{III} (because the excited state of Tb^{III} is even higher, it is not included in this discussion). The Chen group examined some Pt^{II}–Eu^{III} bimetallic systems. They found that Pt^{II}-centered emission was completely quenched and pure red emission from the Eu^{III} center was observed in some cases [63,66,67]. However, when the distance between the Pt^{II} and Eu^{III} ions was increased to about 13.3 Å, emission from Eu^{III} emitter, together with the residual phosphorescence of Pt^{II} donor, was observed (Fig. 8) [68]. Among these Pt^{II}–Eu^{III} bimetallic systems, the best quantum yield of about 15% for pure red emission from Eu^{III} was observed for complex **34** [70]. Ziessel et al. introduced acetylide-functionalized tpy as a bridging ligand to synthesize the Pt^{II}–Eu^{III} bimetallic complex **36**, which exhibited pure red emission from Eu^{III} with a quantum yield of 38% [72]. The ^{3}MLCT emission of the Pt^{II} complex in **36** was centered at 537 nm and the intramolecular Pt^{II}–Eu^{III} separation was around 9 Å. Both of these factors caused near quantitative energy transfer from Pt^{II} to Eu^{III} (Fig. 9). Therefore, the use of a transition metal complex with an appropriate excited state and a short separation between the transition metal center and the lanthanide are both important in photosensitized luminescence of lanthanides, especially for Eu^{III} emission.



36[72]

All of the Pt^{II}–Ln^{III} bimetallic complexes mentioned above formed as discrete molecules. When acetylide-functionalized pyridine was used to connect Pt^{II} and Ln^{III}, the one-dimensional zig-zag chain **37** was formed because of the presence of only one N site in the bridging ligand for the lanthanide to bind to (Fig. 10) [73]. In contrast, Pt^{II}–Ln^{III} bimetallic complex **38** was obtained as discrete molecules when pyridine was changed to phen (Fig. 11) [73].

Pikramenou and co-workers reported the accessibility of hairpin-shaped heterometallic Pt^{II}–Ln^{III} complex **39** by self-assembly of the different components in one pot or in a sequential manner [74]. In these complexes the S atom in the thiophenol ligand coordinated to the Pt^{II} center, in a similar manner to the reaction between an O atom and Pt^{II}. Moreover, a luminescent system with such a structure could be used for DNA intercalative recognition.

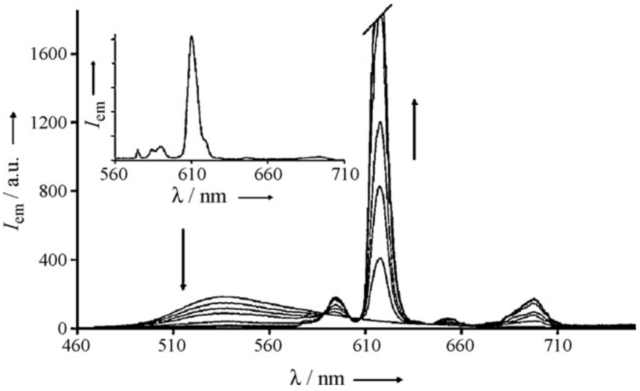
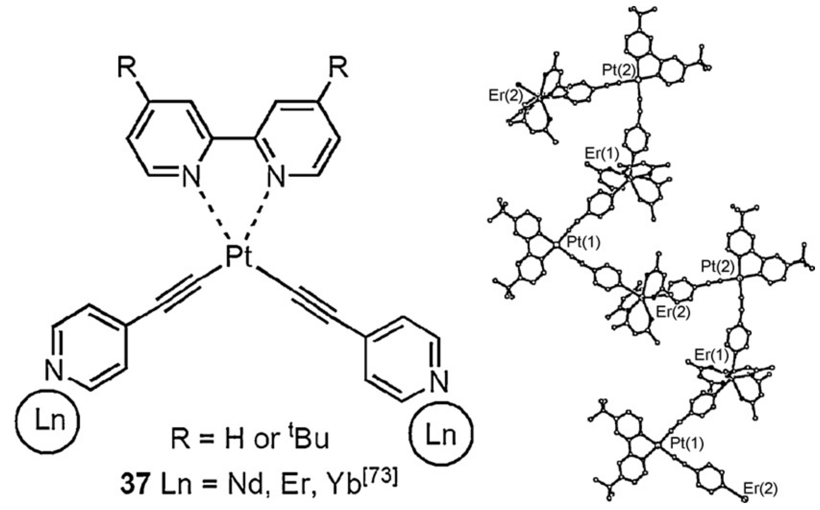
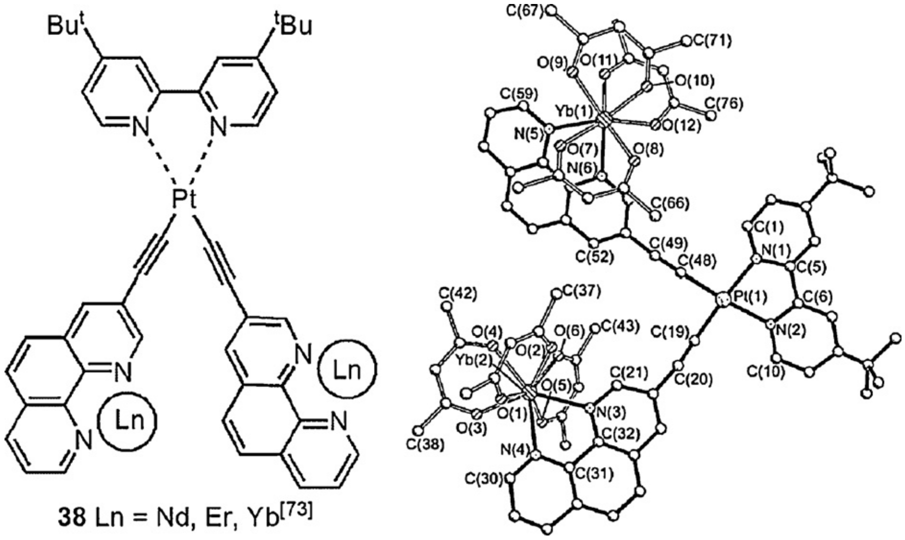


Fig. 9. Luminescence spectra (λ_{ex} = 411 nm) of a solution of the Pt complex in **36** upon addition of different equivalents of a Eu complex. Inset: high-resolution (2.5 Å) phosphorescence spectrum of **36** in CH_2Cl_2. (Reprinted with permission from Ref. [72], copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA.)



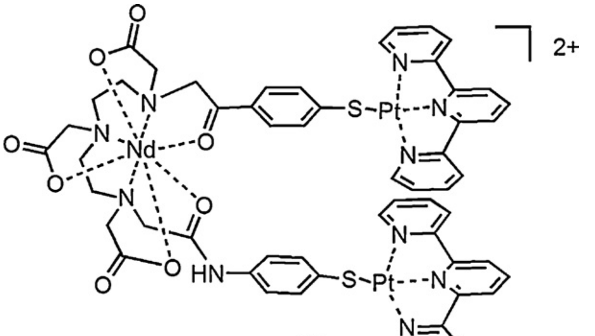
37 Ln = Nd, Er, Yb[73]

Fig. 10. Chemical structure of complex **37-Er**. (Reprinted with permission from Ref. [73], copyright 2006 Wiley-VCH Verlag GmbH & Co. KGaA.)



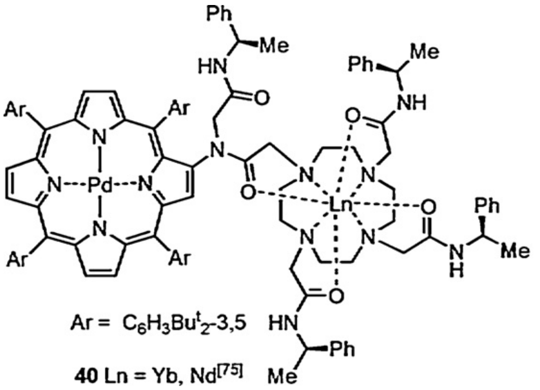
38 Ln = Nd, Er, Yb[73]

Fig. 11. Chemical structure of complex **38-Yb**. (Reprinted with permission from Ref. [73], copyright 2006 Wiley-VCH Verlag GmbH & Co. KGaA.)



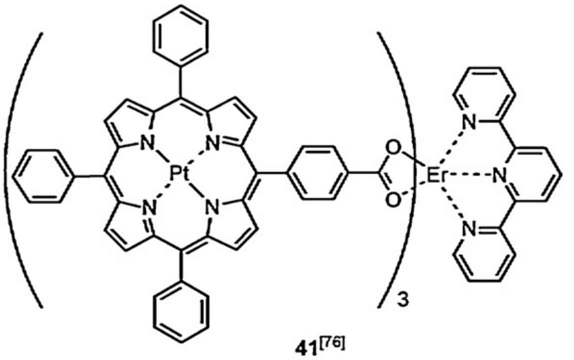
39[74]

Beeby et al. reported the luminescence from Pd^{II}–Ln^{III} systems **40** [75]. A Pd^{II}–porphyrin complex that was used as the antenna, was connected to a cyclen derivative which could coordinate to lanthanide ions. A rapid intramolecular energy transfer process was detected and NIR emission was observed in these systems. Kim and co-workers used an analogous porphyrin ring to coordinate with Pd^{II} and Zn^{II}. The lanthanides were introduced into the systems **41** through coordination to the carboxyl group which was attached to the porphyrin ring [76]. Because no single crystal data was obtained for these systems, the distance between the two metal ions is not known. These complexes were inert, making them useful for optical amplification.



Ar = $C_6H_3Bu^t_2$-3,5

40 Ln = Yb, Nd[75]

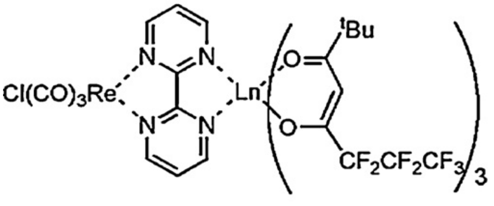


41[76]

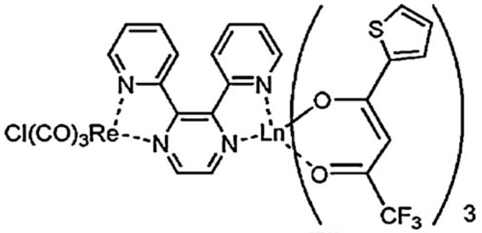
4. Re^I-based lanthanide complexes

The Re^I complexes used in Re^I–Ln^{III} bimetallic systems are usually of the form $[Re(CO)_3Cl(L)]$ (L is a tetradentate bridging ligand). The general preparation of these Re^I complexes involves directly reacting $Re(CO)_5Cl$ with the bridging ligand [77]. Ward and co-workers performed systematic studies on Re^I–Ln^{III} bimetallic complexes. Many bridging ligands that have been used for Ru^{II}–Ln^{III} and Pt^{II}–Ln^{III} systems, such as the derivatives of bpy, bpm and bppz, can also be used for connecting Re^I and Ln^{III}. Other Re^I–Ln^{III} bimetallic complexes analogous to **42** and **43** were obtained with different β-diketone ligands coordinated to the lanthanide ion [61,62,78]. The Faulkner group introduced bpy derivatives into Re^I–Ln^{III} bimetallic complexes as bridging ligands, producing **7** and **44** [40,41,79]. From comparison of them with complexes **45** and **46**, which were mentioned in Section 2, it can be seen that $[Re(CO)_3Cl(L)]$, $[Ru(bpy)_2(L)]^{2+}$ and $[Os(bpy)_2(L)]^{2+}$ exhibit similar behavior in the coordination and sensitization of lanthanides. In these Re^I–Ln^{III} bimetallic complexes, efficient energy transfer occurs from Re^I to Ln^{III} because the lowest electronic excited states around 2.19 eV (17,655 cm^{-1}) of $[Re(CO)_3Cl(L)]$ are close to the excited states of NIR lanthanides (Nd^{III}, Yb^{III} and Er^{III}) [62].

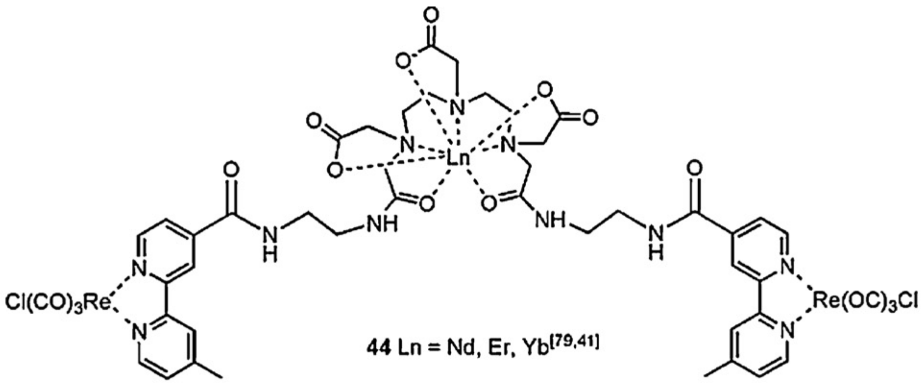
The Beer and Faulkner groups cooperated to design and synthesize supramolecular d–f heterobimetallic Re^I–Ln^{III} complex **47** using an anion-templated assembly approach [80]. Luminescence quenching of the Re^I centered moiety, and NIR emission from the lanthanides were observed upon excitation of the complexes with visible light.



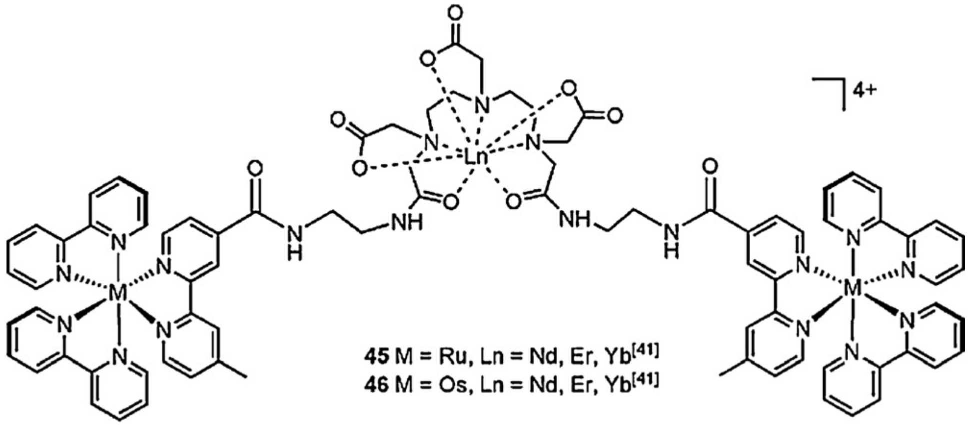
42 Ln = Eu, Er, Yb[78]



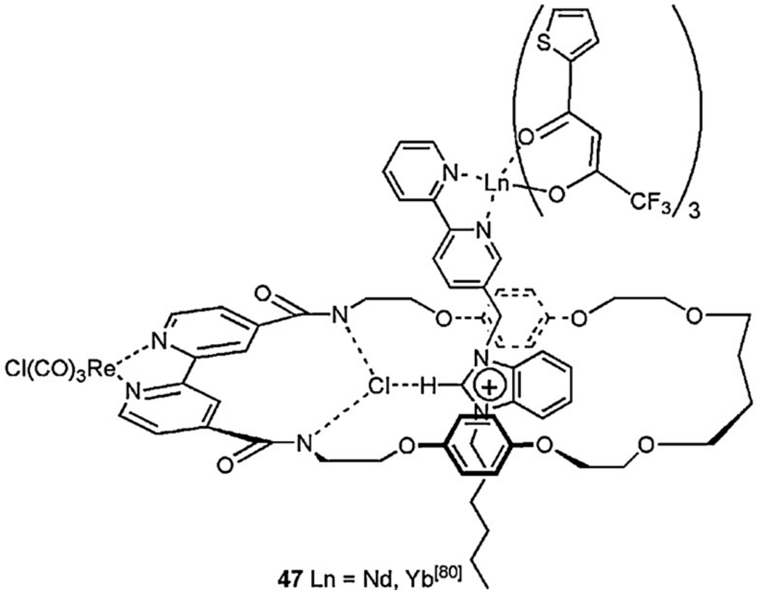
43 Ln = Nd, Er, Yb[78]



44 Ln = Nd, Er, Yb[79,41]



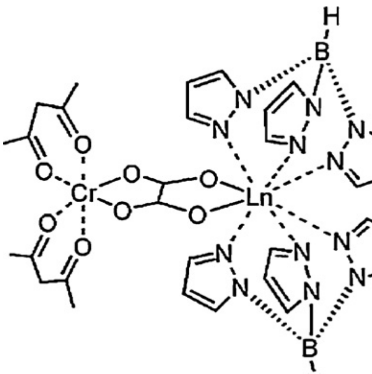
45 M = Ru, Ln = Nd, Er, Yb[41]
46 M = Os, Ln = Nd, Er, Yb[41]



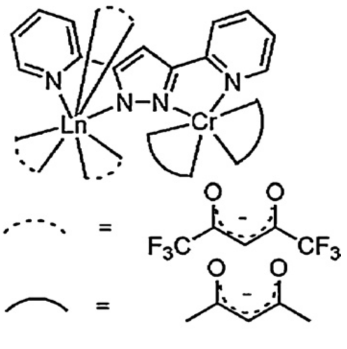
47 Ln = Nd, Yb[80]

5. Cr^{III}- or Co^{III}-based lanthanide complexes

Kaizaki and co-workers used an oxalate ligand to connect Cr^{III} and Ln^{III} and obtained the corresponding Cr^{II}–Ln^{III} bimetallic complex **48** in 1998 [81]. Compared with the Cr^{III}–Eu^{III} and Cr^{III}–Tb^{III} complexes, the Cr^{III}–Yb^{III} complex showed significant quenching of Cr^{III}-based emission, indicating that efficient energy transfer occurred from the ^2E excited state (~13,000 cm^{-1}) of Cr^{III} to the low-lying energy levels of Yb^{III} ($^2F_{5/2}$, 10,300 cm^{-1}). Moreover, the measured lifetime of Yb^{III} emission of 48 μs, was longer than that of most Yb^{III} complexes with small organic ligands [82]. The absolute configurations around the octahedral Cr^{III} and square antiprismatic Ln^{III} moieties were determined by single crystal X-ray structural analysis and circular dichroism (CD) experiments, respectively. When the bridging ligand was changed to 3,5-di(pyridin-2-yl)-1H-pyrazole (bpypz) to give **49**, the Yb^{III}–Cr^{III} distance (4.65 Å) was shortened by almost 1 Å over that in **48-Yb** (5.63 Å), which helps to improve the efficiency of energy transfer. At low temperatures, emission from the Cr^{III} center can be observed in complex **48**, but it is completely quenched in complex **49** [83].

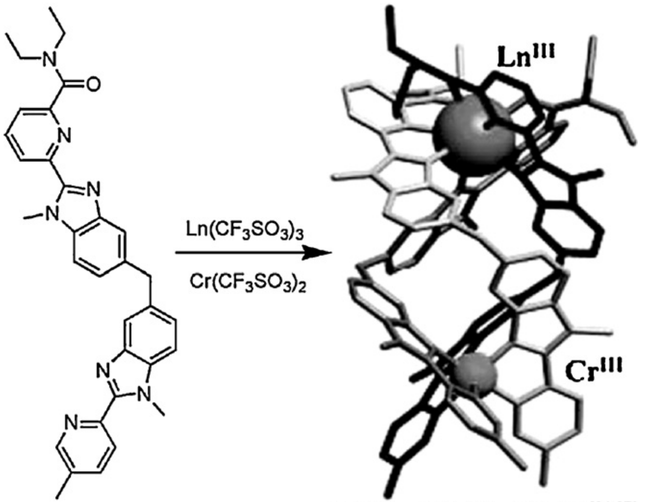


48 Ln = Eu, Tb, Yb[81]



49 Ln = Er, Yb[83]

The Bünzli and Piguet groups reported that Cr^{III} played an important role in extending the excited state lifetimes of Nd^{III} and Yb^{III} [84–86]. The polydentate ligand used in these Cr^{III}–Ln^{III} bimetallic systems is 2-{6-[N,N-diethylcarboxamido]pyridin-2-yl}-1,1′-dimethyl-5,5′-methylene-2′-(5-methylpyridin-2-yl)bis [1H-benzimidazole]. The triple-stranded helicates **50** were achieved through simultaneous coordination of Cr^{III} and Ln^{III} to the ligand [87]. Because Cr^{III} shows a longer excited state lifetime than many other transition metals (~ms), the lifetime of Yb^{III} is 2 ms at 10 K and 240 μs at 295 K in the Cr^{III}-Yb^{III} system, which is also significantly longer than the lifetime of 22 μs in the analogous Ru^{III}–Yb^{III} system (Fig. 12). This approach may be valuable for applications in biomedical analyses and imaging because a longer lifetime improves the sensitivity of time-gated homogeneous fluoroimmunoassays.



50 Ln = Eu, Tb, Nd, Yb[84-87]

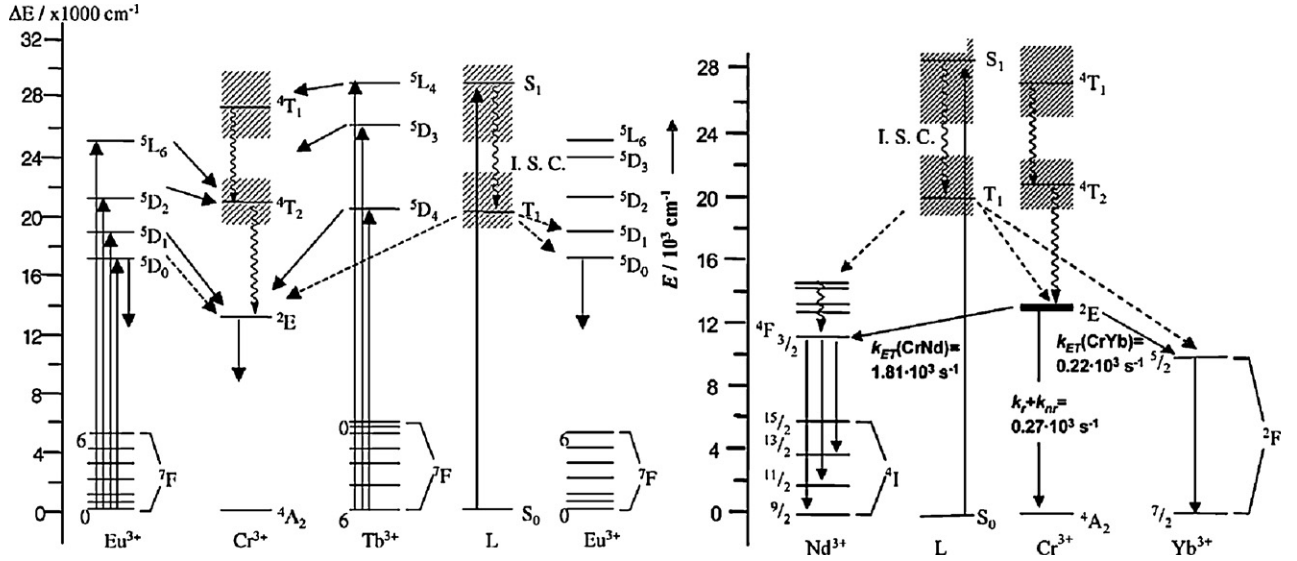
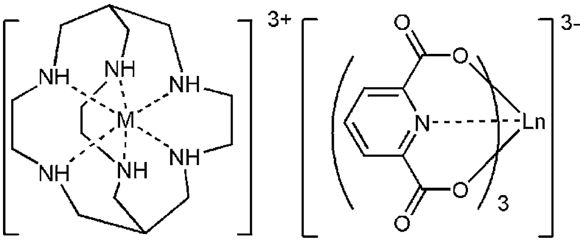


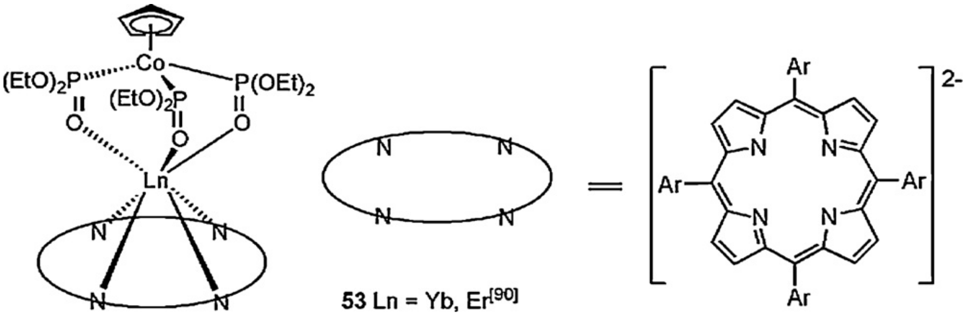
Fig. 12. Energy level diagrams showing (i) the ground and excited state energy levels centered on the metal ions and ligand and (ii) a summary of the excitation, energy transfer and radiative processes occurring in **50**. (Reprinted with permission from Ref. [87], copyright 2002 the Royal Society of Chemistry and with permission from Ref. [84], copyright 2003 American Chemical Society.)

Harrowfield and co-workers reported the ionic systems **51** and **52**, in which the anion is a lanthanide complex and the cation is the Cr^{III} or Co^{III} complex [88]. It is also apparent that the spin forbidden d–d transitions of both Cr^{III} and Co^{III} lie at suitable energy levels. Thus, they provide an efficient pathway for the quenching of luminescence from Eu^{III} and Tb^{III} complexes.



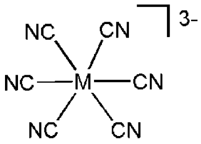
51 M = Cr, Ln = Eu, Tb[88]
52 M = Co, Ln = Eu, Tb[88]

Wong et al. synthesized the series of Co^{III}–Ln^{III} bimetallic complex **53** [89,90]. Kläui's tripodal ligands [91] coordinated to the lanthanide ion with three oxygen atoms and a series of stable Co^{III}–Ln^{III} bimetallic complexes were formed.



53 Ln = Yb, Er[90]

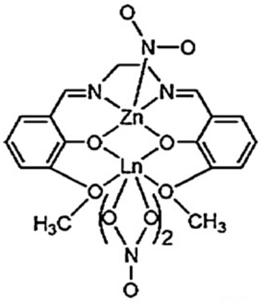
Ward and co-workers studied both Cr^{III}–CN–Ln^{III} and Co^{III}–CN–Ln^{III} systems, based on the extensively studied Ru^{II}–CN–Ln^{III} systems, because of the strong coordination ability of CN^- to Cr^{III} and Co^{III}. The Cr^{III} and Co^{III} precursors **54** and **55** are shown below [92]. The energy transfer rate from to Ln^{III} in both complexes exceeded $10^8\ s^{-1}$ because of the good overlap between the emission spectrum of the Cr^{III}- or Co^{III}-centered moiety and the excitation spectrum of the lanthanide ion.



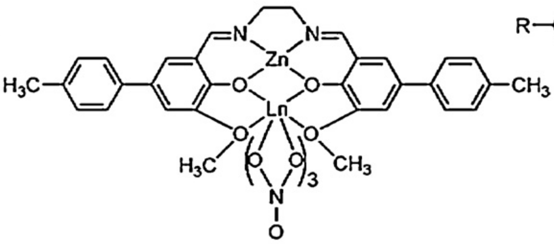
54 M = Cr[92]
55 M = Co[92]

6. Zn^{II}-based lanthanide complexes

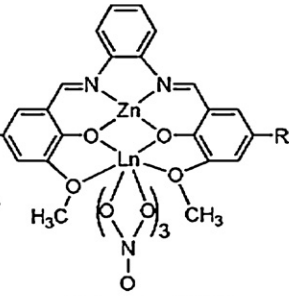
Wong et al. studied various binuclear or polynuclear Zn^{II}–Ln^{III} bimetallic complexes by changing the functional groups to Schiff base ligands. Complexes with a 1:1 ratio of Zn^{II} to Ln^{III} could be readily obtained as long as the stoichiometric ratio was controlled at 1:1 [93–99]. N,N′-bis(3-methoxysalicylidene)ethylene-1,2-diamine was the simplest Schiff base ligand used in these Zn^{II}–Ln^{III} complexes. X-ray crystallography of all of the Zn^{II}–Ln^{III} bimetallic complexes revealed that the Zn^{II} ion is located in the N_2O_2 cavity of the Schiff base ligand. According to the different ionic radii of different lanthanide centers, the Zn^{II}–Ln^{III} complexes exhibited a range of structures and coordination modes. In complexes **56**, **57** and **58**, the Zn^{II} ion is 5-coordinate through coordination with the four sites in N_2O_2 and the additional coordination of a monodentate nitrate ion if the lanthanide center is Ho^{III}, Er^{III} or Yb^{III} [93–95]. However, when the lanthanides are changed to Nd^{III} or La^{III}, three nitrate ions coordinate to the lanthanide ion (one monodentate and two bidentate nitrate ions for Nd^{III} and three bidentate nitrate ions for La^{III}). The other coordination sites of the lanthanide ions are saturated by bridging phenolate groups, methoxy oxygen atoms and appropriate solvent molecules.



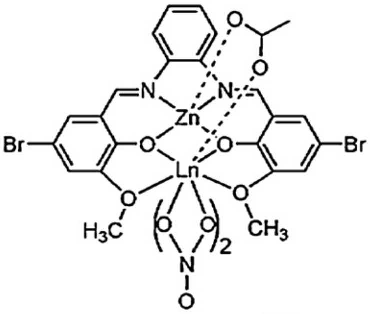
56 Ln = Ho, Er, Yb[93]



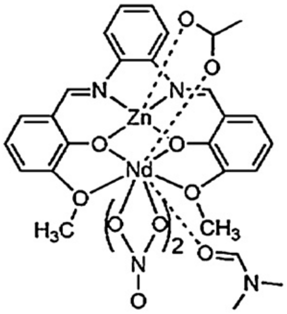
57 Ln = La, Nd[94]



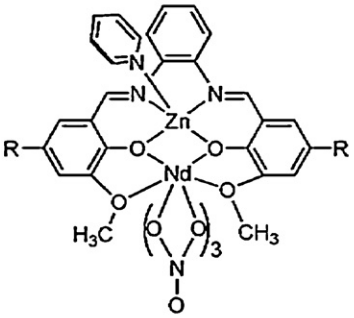
58 Ln = La, Nd[95]



59 Ln = Eu, Nd[96]



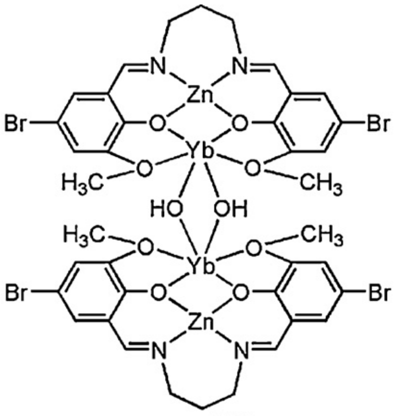
60[97]



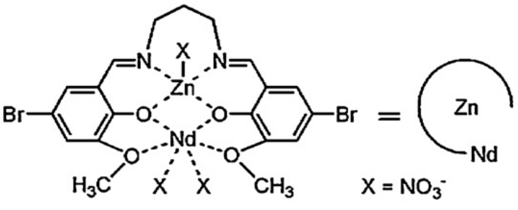
61[99]

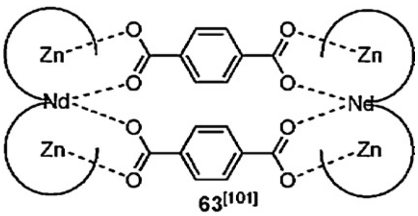
These Zn^{II}–Ln^{III} bimetallic complexes were prepared through the reaction of ZnL (L represents a Schiff base ligand) with $Ln(NO_3)_3{\cdot}6H_2O$. When the reaction of $Zn(OAc)_2{\cdot}2H_2O$ and H_2L was followed by direct addition of $Ln(NO_3)_3{\cdot}6H_2O$, heterodinuclear complexes of the form $[ZnLLn(OAc)(NO_3)_2]$, such as complexes **59** and **60**, were obtained [96–98]. Interestingly, all of the metal centers are bridged by a single bidentate acetate (OAc) ligand in addition to the phenolic oxygen atoms of the Schiff base ligand. Furthermore, when the solvents used in the reaction were altered, the coordinating solvent molecules changed. For example, a DMF molecule coordinated to the lanthanide ion in **60** when DMF was mixed with ethanol, methanol or CH_3CN [97]. When pyridine was used as the solvent in the preparation of **61**, it coordinated to Zn^{II} because of the affinity between transition metals and N atoms [99].

Based on similar Schiff bases with phenolate groups and methoxy groups, the reaction between N,N-bis(5-bromo-3-methoxysalicylidene)propylene-1,3-diamine (L) and $Zn(NO_3)_2{\cdot}6H_2O$ resulted in the formation of $[Zn_3L_2(NO_3)_2]{\cdot}MeOH$ [100]. Addition of $YbCl_3{\cdot}6H_2O$ allowed the isolation of the tetrametallic species **62**. Zn^{II} and Yb^{III} were connected *via* two hydroxide ions, forming a product with the structure Zn_2Yb_2. If tetradentate bridging ligands, such as 1,4-benzene-dicarboxylate (1,4-BDC), were added to the reagents, the remarkable hexanuclear Zn_4Nd_2 assembly **63** was achieved [101]. Similarly, if bidentate ligands, such as 4,4′-bpy or trans-bis(4-pyridyl)ethylene (4,4′-bpe), were used for connecting two ZnNd fragments, the resulting products **64** and **65** were of the Zn_2Nd_2 style [102]. Furthermore, when the counter anions NO_3^- or Cl^- were used, different styles of Zn^{II}–Nd^{III} sandwich complexes could be obtained even if the starting materials had the same stoichiometric ratio [103].

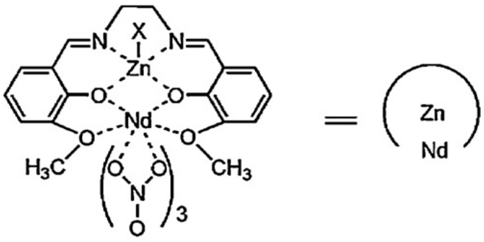


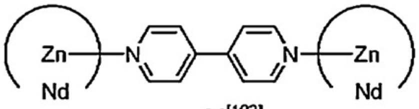
62[100]



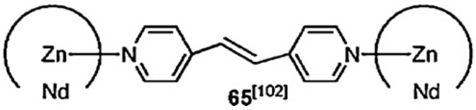


63[101]





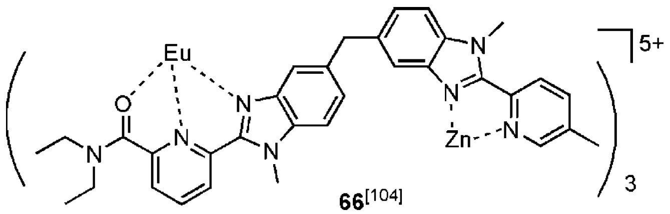
64[102]



65[102]

Early in 1996, the Bünzli and Piguet groups synthesized Zn^{II}–Eu^{III} bimetallic complex **66** using a self-assembly approach. Strong red emission from Eu^{III} was observed [104]. However, photophysical data indicated that the terminal N,N-diethylcarbamoyl group in the bridging ligand favored efficient intramolecular L → Eu^{III} energy transfer, leading to strong Eu^{III}-centered red luminescence. It also implied that Zn^{II} did not contribute to sensitization of lanthanide centers in Zn^{II}–Ln^{III} bimetallic systems.

All of the Zn^{II}–Ln^{III} bimetallic complexes exhibited similar luminescence properties in the NIR region upon excitation of a ligand-centered absorption band. Meanwhile, the energy which was sensitizing Nd^{III}, Yb^{III} and Er^{III} originated from the ^{3}LC or ^{1}LC excited state of the ligands in the Zn^{III} complexes through the combination of experiment results and theoretical calculations of these systems [95]. Therefore, the Zn^{II} ion plays a more important role in the Zn^{II}–Ln^{III} bimetallic complexes as a structural stabilizer than as an energy transfer agent.



66[104]

7. Ir^{III}-based lanthanide complexes

In 2005, De Cola and co-workers reported the formation of the first Ir^{III}–Eu^{III} bimetallic assembly **67** [105]. A carboxylic acid derivative of 2-(5-phenyl-4H-[1,2,4]triazol-3-yl)-pyridine was used as the bridging ligand. (N^N) sites coordinated to Ir^{III} while the carboxyl group coordinated to Eu^{III}. In this system, partial transfer of excited state energy from the Ir^{III} center to the Eu^{III} center leads to white light emission (Fig. 13). Recently, a Ir^{III}–Yb^{III} bimetallic complex **68** containing an analogous bridging ligand was produced [106]. The energy could be transferred to the Yb^{III} ions by selective excitation of the iridium moiety at 400 nm.

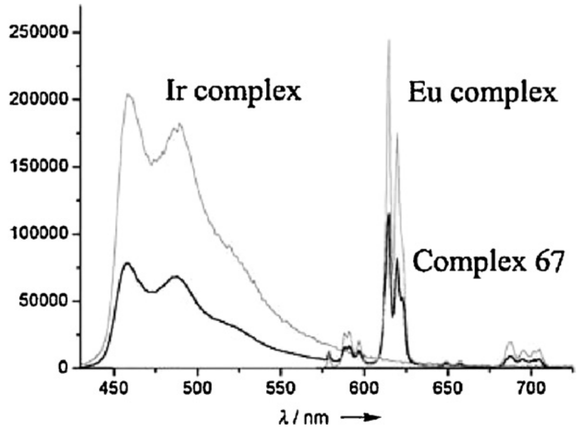
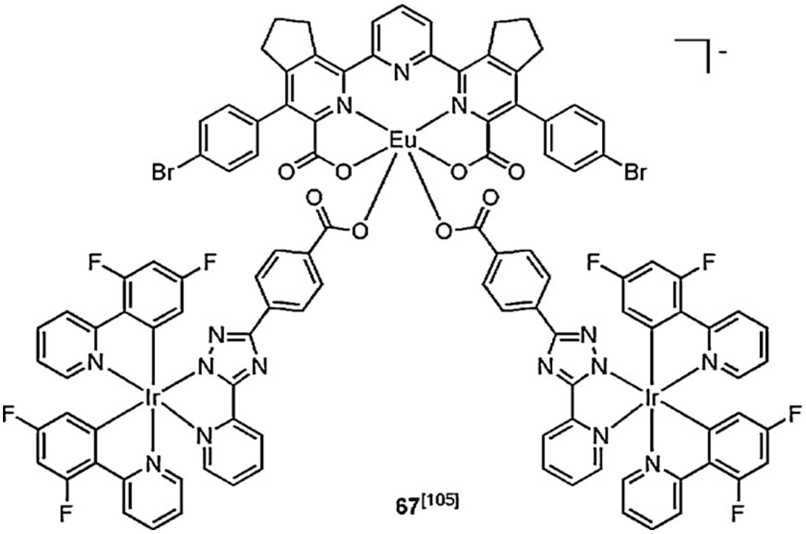
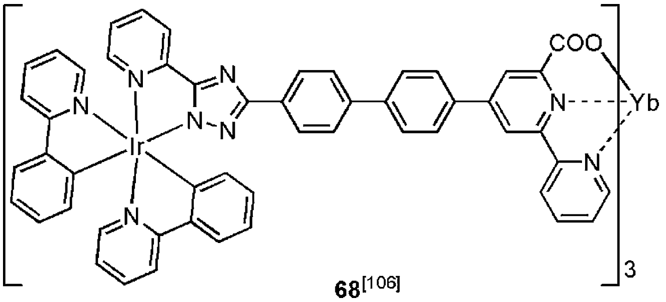


Fig. 13. Relative steady-state emission spectra of solutions of Ir complex, Eu complex (I/6), and **67** in CD_3OD upon excitation at λ = 400 nm. (Reprinted with permission from Ref. [105], copyright 2005 Wiley-VCH Verlag GmbH & Co. KGaA.)



67[105]



68[106]

Our group synthesized new Ir^{III}–Eu^{III} bimetallic complexes and studied their structural and photophysical properties. Complexes **69** and **70** were synthesized with a well-designed bridging ligand [107]. The X-ray diffraction data showed that the nonbonding distances between Eu^{III} and Ir^{III} are 6.028, 5.907, and 6.100 Å in **69** (Fig. 14). Photophysical studies implied that the highly efficient red luminescence observed from Eu^{III} ions was sensitized by the ^{3}MLCT energy of the Ir^{III} moiety. The excitation window of **69** extended to 530 nm (at a concentration of 1×10^{-3} M in EtOH), indicating that this bimetallic complex can emit red light upon irradiation with sunlight (Fig. 15). The quantum yield of complex **70** reached 17.7% ($[Ru(bpy)_3]Cl_2$ was used as the reference), whereas the quantum yield of the Eu^{III} complex without the Ir^{III} moiety was less than 3%. This implied that highly efficient d–f energy transfer occurred in these systems.

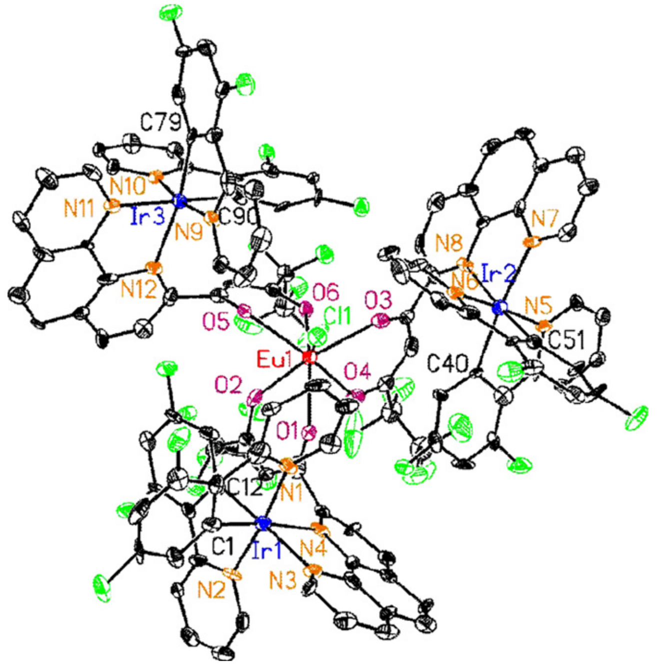
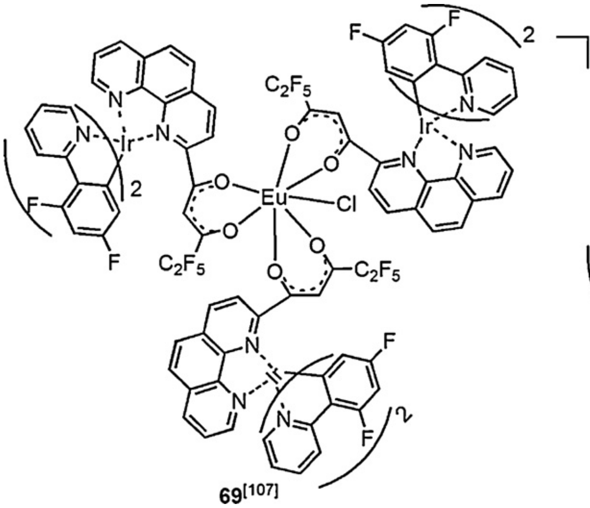
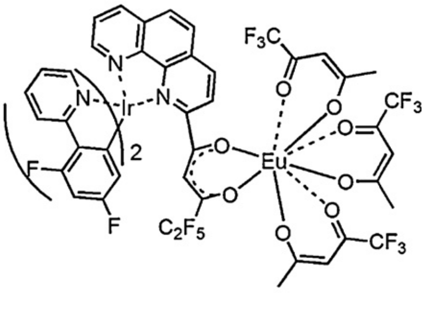


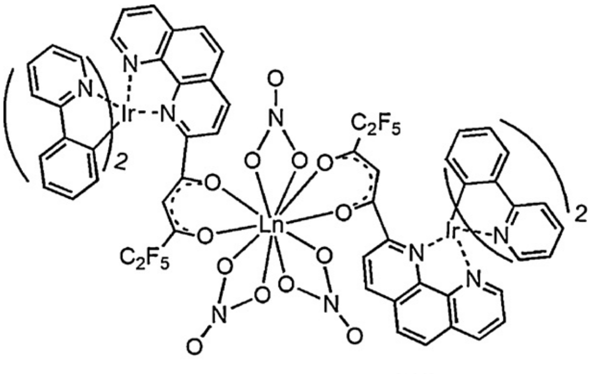
Fig. 14. Crystal structure of complex **69**. (Reprinted with permission from Ref. [107], copyright 2008 American Chemical Society.)



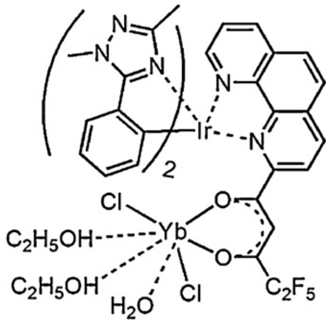
69[107]



70[107]



71 Ln = Nd, Er, Yb, Eu[108]



72[109]

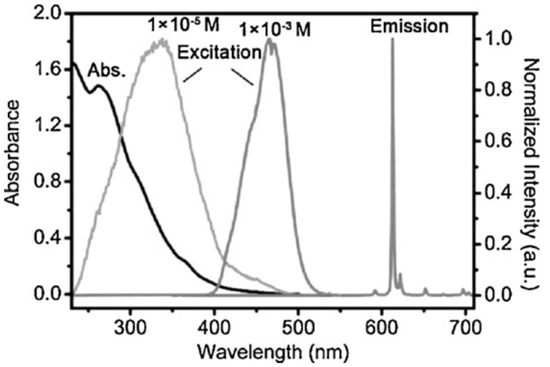


Fig. 15. UV–vis absorption, and normalized excitation (λ_{em} = 613 nm) and photoluminescence (λ_{ex} = 326 nm) spectra of complex **69** in EtOH at room temperature. (Reprinted with permission from Ref. [107], copyright 2008 American Chemical Society.)

Subsequently, we changed the cyclometalated ligand to decrease the triplet energy level of the transition metal fragment, making it more suitable for the sensitization of NIR-emitting Ln^{III} (Ln = Nd, Yb, and Er) ions [108]. The Ir^{III} → Ln^{III} energy transfer rates for the Nd^{III}, Yb^{III}, and Er^{III} complexes **71** were all estimated to be higher than $4 \times 10^8\,s^{-1}$, implying that efficient energy transfer occurs in all three Ir^{III}–Ln^{III} complexes. Upon irradiation of the MLCT absorption of the Ir^{III} complex at excitation wavelengths from 380 nm to 490 nm, the characteristic NIR emission of the three different lanthanide ions was obtained both in the solid state and in solution. Similarly, other Ir^{III} complexes can be designed for lanthanide NIR emission by the proper combination of a cyclometalated ligand with a tetradentate ancillary ligand. For instance, another cyclometalated ligand was used to form Ir^{III}–Yb^{III} complex **72** [109]. In these Ir^{III}–Ln^{III} systems, the emission from the Ir^{III} moiety in the solid state is quenched because of the presence of NIR-emitting lanthanides. Furthermore, the π–π interaction between the aromatic molecules played an important role in luminescence.

8. Conclusions

Up to now mixed transition metal–lanthanide assemblies have been broadly explored. Different transition metal complexes with appropriate bridging ligands exhibit a variety of styles in their coordination to lanthanide ions. Most d-blocks can efficiently sensitize NIR-emitting lanthanides because of their suitable energy levels. In particular, Cr^{III} increases the excited state lifetimes of Nd^{III}, Yb^{III} and Er^{III}. Some transition metal complexes, such as those containing Pt^{II} and Ir^{III}, possess tunable excited states energy levels that can be adjusted over a large range. Thus, they are good candidates to act as antennae for achieving visible-light-sensitized Eu^{III} emission. This approach presents a broad range of opportunities in luminescent science both for theoretical and practical usage.

Acknowledgements

The authors are grateful to the National Basic Research Program (2006CB601103) and the NNSFC (90922004, 20971006, 20821091, and 20671006) for financial support.

References

[1] G.R. Motson, J.S. Fleming, S. Brooker, Adv. Inorg. Chem. 55 (2004) 361.
[2] J.-C.G. Bünzli, C. Piguet, Chem. Soc. Rev. 34 (2005) 1048.
[3] S. Faulkner, S.J.A. Pope, B.P. Burton-Pye, Appl. Spectrosc. Rev. 40 (2005) 1.
[4] J.L. Yuan, G.L. Wang, TRAC-Trends Anal. Chem. 25 (2006) 490.
[5] J.-C.G. Bünzli, Acc. Chem. Res. 39 (2006) 53.
[6] C.M.G. dos Santos, A.J. Harte, S.J. Quinn, T. Gunnlaugsson, Coord. Chem. Rev. 252 (2008) 2512.
[7] J. Kido, Y. Okamoto, Chem. Rev. 102 (2002) 2357.
[8] A. de Bettencourt-Dias, Dalton Trans. (2007) 2229.
[9] W.T. Carnall, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 4, North-Holland Publishing Company, Amsterdam, 1979, p. 171.
[10] G.A. Crosby, R.E. Whan, R.M. Alire, J. Chem. Phys. 34 (1961) 743.
[11] W.F. Sager, N. Filipescu, F.A. Serafin, J. Phys. Chem. 69 (1965) 1092.
[12] N. Filipescu, W.F. Sager, F.A. Serafin, J. Phys. Chem. 68 (1964) 3324.
[13] F.J. Steemers, W. Verboom, D.N. Reinhoudt, E.B. van der Tol, J.W. Verhoeven, J. Am. Chem. Soc. 117 (1995) 9408.
[14] M. Latva, H. Takalo, V.-M. Mukkala, C. Matachescu, J.C. Rodríguez-Ubis, J. Kankare, J. Lumin. 75 (1997) 149.
[15] G.F. de Sá, O.L. Malta, C. de Mello Donegá, A.M. Simas, R.L. Longo, P.A. Santa-Cruz, E.F. da Silva Jr, Coord. Chem. Rev. 196 (2000) 165.
[16] R.C. Holz, C.A. Chang, W.D. Horrocks Jr., Inorg. Chem. 30 (1991) 3270.
[17] S. Quici, G. Marzanni, M. Cavazzini, P.L. Anelli, M. Botta, E. Gianolio, G. Accorsi, N. Armaroli, F. Barigelletti, Inorg. Chem. 41 (2002) 2777.
[18] I. Nasso, C. Galaup, F. Havas, P. Tisnès, C. Picard, S. Laurent, L.V. Elst, R.N. Muller, Inorg. Chem. 44 (2005) 8293.
[19] K. Hanaoka, K. Kikuchi, H. Kojima, Y. Urano, T. Nagano, Angew. Chem. Int. Ed. 42 (2003) 2996.
[20] P. Hurskainen, J. Alloys Compd. 225 (1995) 489.
[21] G. Vereb, E. Jares-Erijman, P.R. Selvin, T.M. Jovin, Biophys. J. 74 (1998) 2210.
[22] N. Weibel, L.J. Charbonnière, M. Guardigli, A. Roda, R. Ziessel, J. Am. Chem. Soc. 126 (2004) 4888.
[23] M.H.V. Werts, R.H. Woudenberg, P.G. Emmerink, R. van Gassel, J.W. Hofstraat, J.W. Verhoeven, Angew. Chem. Int. Ed. 39 (2000) 4542.
[24] R. Van Deun, P. Nockemann, P. Fias, K. Van Hecke, L. Van Meervelt, K. Binnemans, Chem. Commun. (2005) 590.
[25] R. Van Deun, P. Fias, P. Nockemann, K. Van Hecke, L. Van Meervelt, K. Binnemans, Inorg. Chem. 45 (2006) 10416.
[26] M.H.V. Werts, M.A. Duin, J.W. Hofstraat, J.W. Verhoeven, Chem. Commun. (1999) 799.
[27] A. Dadabhoy, S. Faulkner, P.G. Sammes, J. Chem. Soc., Perkin Trans. 2 (2000) 2359.
[28] A. Dadabhoy, S. Faulkner, P.G. Sammes, J. Chem. Soc., Perkin Trans. 2 (2002) 348.
[29] C. Yang, L.-M. Fu, Y. Wang, J.-P. Zhang, W.-T. Wong, X.-C. Ai, Y.-F. Qiao, B.-S. Zou, L.-L. Gui, Angew. Chem. Int. Ed. 43 (2004) 5010.
[30] L.-M. Fu, X.-F. Wen, X.-C. Ai, Y. Sun, Y.-S. Wu, J.-P. Zhang, Y. Wang, Angew. Chem. Int. Ed. 44 (2005) 747.
[31] M.H.V. Werts, N. Nerambourg, D. Pélégry, Y. Le Grand, M. Blanchard-Desce, Photochem. Photobiol. Sci. 4 (2005) 531.

[32] M.P.O. Wolbers, F.C.J.M. van Veggel, F.G.A. Peters, E.S.E. van Beelen, J.W. Hofstraat, F.A.J. Geurts, D.N. Reinhoudt, Chem. Eur. J. 4 (1998) 772.
[33] M.H.V. Werts, J.W. Verhoeven, J.W. Hofstraat, J. Chem. Soc., Perkin Trans. 2 (2000) 433.
[34] S.I. Klink, P.O. Alink, L. Grave, F.G.A. Peters, J.W. Hofstraat, F. Geurts, F.C.J.M. van Veggel, J. Chem. Soc., Perkin Trans. 2 (2001) 363.
[35] R.F. Ziessel, G. Ulrich, L. Charbonnière, D. Imbert, R. Scopelliti, J.-C.G. Bünzli, Chem. Eur. J. 12 (2006) 5060.
[36] M.D. Ward, Coord. Chem. Rev. 251 (2007) 1663.
[37] S.I. Klink, H. Keizer, F.C.J.M. van Veggel, Angew. Chem. Int. Ed. 39 (2000) 4319.
[38] S.I. Klink, H. Keizer, H.W. Hofstraat, F.C.J.M. van Veggel, Synth. Met. 127 (2002) 213.
[39] Y.F. Yuan, T. Cardinaels, K. Lunstroot, K. Van Hecke, L. Van Meervelt, C. Görller-Walrand, K. Binnemans, P. Nockemann, Inorg. Chem. 46 (2007) 5302.
[40] S.J.A. Pope, B.J. Coe, S. Faulkner, E.V. Bichenkova, X. Yu, K.T. Douglas, J. Am. Chem. Soc. 126 (2004) 9490.
[41] S.J.A. Pope, B.J. Coe, S. Faulkner, R.H. Laye, Dalton Trans. (2005) 1482.
[42] P.D. Beer, F. Szemes, P. Passaniti, M. Maestri, Inorg. Chem. 43 (2004) 3965.
[43] T. Lazarides, D. Sykes, S. Faulkner, A. Barbieri, M.D. Ward, Chem. Eur. J. 14 (2008) 9389.
[44] D. Guo, C.-Y. Duan, F. Lu, Y. Hasegawa, Q.-J. Meng, S. Yanagida, Chem. Commun. (2004) 1486.
[45] T. Gunnlaugsson, J.P. Leonard, Chem. Commun. (2005) 3114.
[46] K. Sénéchal-David, S.J.A. Pope, S. Quinn, S. Faulkner, T. Gunnlaugsson, Inorg. Chem. 45 (2006) 10040.
[47] T. Lazarides, H. Adams, D. Sykes, S. Faulkner, G. Calogero, M.D. Ward, Dalton Trans. (2008) 691.
[48] T.A. Miller, J.C. Jeffery, M.D. Ward, H. Adams, S.J.A. Pope, S. Faulkner, Dalton Trans. (2004) 1524.
[49] G.M. Davies, S.J.A. Pope, H. Adams, S. Faulkner, M.D. Ward, Inorg. Chem. 44 (2005) 4656.
[50] S.G. Baca, H. Adams, M.D. Ward, CrystEngComm 8 (2006) 635.
[51] S.G. Baca, H. Adams, D. Sykes, S. Faulkner, M.D. Ward, Dalton Trans. (2007) 2419.
[52] J.-M. Herrera, S.G. Baca, H. Adams, M.D. Ward, Polyhedron 25 (2006) 869.
[53] J.-M. Herrera, S.J.A. Pope, H. Adams, S. Faulkner, M.D. Ward, Inorg. Chem. 45 (2006) 3895.
[54] J.-M. Herrera, M.D. Ward, H. Adams, S.J.A. Pope, S. Faulkner, Chem. Commun. (2006) 1851.
[55] J.-M. Herrera, S.J.A. Pope, A.J.H.M. Meijer, T.L. Easun, H. Adams, W.Z. Alsindi, X.-Z. Sun, M.W. George, S. Faulkner, M.D. Ward, J. Am. Chem. Soc. 129 (2007) 11491.
[56] H. Adams, W.Z. Alsindi, G.M. Davies, M.B. Duriska, T.L. Easun, H.E. Fenton, J.-M. Herrera, M.W. George, K.L. Ronayne, X.-Z. Sun, M. Towrie, M.D. Ward, Dalton Trans. (2006) 39.
[57] S.G. Baca, H. Adams, C.S. Grange, A.P. Smith, I. Sazanovich, M.D. Ward, Inorg. Chem. 46 (2007) 9779.
[58] S.G. Baca, S.J.A. Pope, H. Adams, M.D. Ward, Inorg. Chem. 47 (2008) 3736.
[59] N.M. Shavaleev, L.P. Moorcraft, S.J.A. Pope, Z.R. Bell, S. Faulkner, M.D. Ward, Chem. Commun. (2003) 1134.
[60] N.M. Shavaleev, L.P. Moorcraft, S.J.A. Pope, Z.R. Bell, S. Faulkner, M.D. Ward, Chem. Eur. J. 9 (2003) 5283.
[61] F. Kennedy, N.M. Shavaleev, T. Koullourou, Z.R. Bell, J.C. Jeffery, S. Faulkner, M.D. Ward, Dalton Trans. (2007) 1492.
[62] N.M. Shavaleev, G. Accorsi, D. Virgili, Z.R. Bell, T. Lazarides, G. Calogero, N. Armaroli, M.D. Ward, Inorg. Chem. 44 (2005) 61.
[63] H.-B. Xu, L.-X. Shi, E. Ma, L.-Y. Zhang, Q.-H. Wei, Z.-N. Chen, Chem. Commun. (2006) 1601.
[64] X.-L. Li, L.-X. Shi, L.-Y. Zhang, H.-M. Wen, Z.-N. Chen, Inorg. Chem. 46 (2007) 10892.
[65] H.-B. Xu, L.-Y. Zhang, Z.-L. Xie, E. Ma, Z.-N. Chen, Chem. Commun. (2007) 2744.
[66] X.-L. Li, F.-R. Dai, L.-Y. Zhang, Y.-M. Zhu, Q. Peng, Z.-N. Chen, Organometallics 26 (2007) 4483.
[67] H.-B. Xu, J. Ni, K.-J. Chen, L.-Y. Zhang, Z.-N. Chen, Organometallics 27 (2008) 5665.
[68] H.-B. Xu, L.-Y. Zhang, Z.-H. Chen, L.-X. Shi, Z.-N. Chen, Dalton Trans. (2008) 4664.
[69] H.-B. Xu, L.-Y. Zhang, X.-M. Chen, X.-L. Li, Z.-N. Chen, Cryst. Growth Des. 9 (2009) 569.
[70] J. Ni, L.-Y. Zhang, Z.-N. Chen, J. Organomet. Chem. 694 (2009) 339.
[71] H.-B. Xu, L.-Y. Zhang, J. Ni, H.-Y. Chao, Z.-N. Chen, Inorg. Chem. 47 (2008) 10744.
[72] R. Ziessel, S. Diring, P. Kadjane, L. Charbonnière, P. Retailleau, C. Philouze, Chem. Asian J. 2 (2007) 975.
[73] T.K. Ronson, T. Lazarides, H. Adams, S.J.A. Pope, D. Sykes, S. Faulkner, S.J. Coles, M.B. Hursthouse, W. Clegg, R.W. Harrington, M.D. Ward, Chem. Eur. J. 12 (2006) 9299.
[74] P.B. Glover, P.R. Ashton, L.J. Childs, A. Rodger, M. Kercher, R.M. Williams, L. De Cola, Z. Pikramenou, J. Am. Chem. Soc. 125 (2003) 9918.
[75] A. Beeby, R.S. Dickins, S. FitzGerald, L.J. Govenlock, C.L. Maupin, D. Parker, J.P. Riehl, G. Siligardi, J.A. Gareth Williams, Chem. Commun. (2000) 1183.
[76] J.B. Oh, Y.H. Kim, M.K. Nah, H.K. Kim, J. Lumin. 111 (2005) 255.
[77] R. Ruminski, R.T. Cambron, Inorg. Chem. 29 (1990) 1575.
[78] N.M. Shavaleev, Z.R. Bell, M.D. Ward, J. Chem. Soc. Dalton Trans. (2002) 3925.
[79] S.J.A. Pope, B.J. Coe, S. Faulkner, Chem. Commun. (2004) 1550.
[80] M.R. Sambrook, D. Curiel, E.J. Hayes, P.D. Beer, S.J.A. Pope, S. Faulkner, New J. Chem. 30 (2006) 1133.
[81] T. Sanada, T. Suzuki, T. Yoshida, S. Kaizaki, Inorg. Chem. 37 (1998) 4712.
[82] M.A. Subhan, H. Nakata, T. Suzuki, J.H. Choi, S. Kaizaki, J. Lumin. 101 (2003) 307.
[83] R. Kawahata, T. Tsukuda, T. Yagi, M.A. Subhan, H. Nakata, A. Fuyuhiro, S. Kaizaki, Chem. Lett. 32 (2003) 1084.
[84] D. Imbert, M. Cantuel, J.-C.G. Bünzli, G. Bernardinelli, C. Piguet, J. Am. Chem. Soc. 125 (2003) 15698.
[85] S. Torelli, D. Imbert, M. Cantuel, G. Bernardinelli, S. Delahaye, A. Hauser, J.-C.G. Bünzli, C. Piguet, Chem. Eur. J. 11 (2005) 3228.
[86] M. Cantuel, F. Gumy, J.-C.G. Bünzli, C. Piguet, Dalton Trans. (2006) 2647.
[87] M. Cantuel, G. Bernardinelli, D. Imbert, J.-C.G. Bünzli, G. Hopfgartner, C. Piguet, J. Chem. Soc. Dalton Trans. (2002) 1929.
[88] P.A. Brayshaw, J.-C.G. Bünzli, P. Froidevaux, J.M. Harrowfield, Y. Kim, A.N. Sobolev, Inorg. Chem. 34 (1995) 2068.
[89] J.X. Meng, K.F. Li, J. Yuan, L.L. Zhang, W.K. Wong, K.W. Cheah, Chem. Phys. Lett. 332 (2000) 313.
[90] W.-K. Wong, A.-X. Hou, J.-P. Guo, H.-S. He, L.-L. Zhang, W.-Y. Wong, K.-F. Li, K.-W. Cheah, F. Xue, T.C.W. Mak, J. Chem. Soc. Dalton Trans. (2001) 3092.
[91] W. Kläui, Angew. Chem. Int. Ed. 29 (1990) 627.
[92] T. Lazarides, G.M. Davies, H. Adams, C. Sabatini, F. Barigelletti, A. Barbieri, S.J.A. Pope, S. Faulkner, M.D. Ward, Photochem. Photobiol. Sci. 6 (2007) 1152.
[93] W.-K. Wong, H.-Z. Liang, W.-Y. Wong, Z.-W. Cai, K.-F. Li, K.-W. Cheah, New J. Chem. 26 (2002) 275.
[94] W.-K. Lo, W.-K. Wong, J.-P. Guo, W.-Y. Wong, K.-F. Li, K.-W. Cheah, Inorg. Chim. Acta 357 (2004) 4510.
[95] W.-K. Lo, W.-K. Wong, W.-Y. Wong, J.-P. Guo, K.-T. Yeung, Y.-K. Cheng, X.-P. Yang, R.A. Jones, Inorg. Chem. 45 (2006) 9315.
[96] X.-P. Yang, R.A. Jones, Q.-Y. Wu, M.M. Oye, W.-K. Lo, W.-K. Wong, A.L. Holmes, Polyhedron 25 (2006) 271.
[97] W.-Y. Bi, X.-Q. Lu, W.-L. Chai, W.-J. Jin, J.-R. Song, W.-K. Wong, Inorg. Chem. Commun. 11 (2008) 1316.
[98] W.-Y. Bi, X.-Q. Lu, W.-L. Chai, J.-R. Song, W.-Y. Wong, W.-K. Wong, R.A. Jones, J. Mol. Struct. 891 (2008) 450.
[99] W.-Y. Bi, X.-Q. Lu, W.-L. Chai, J.-R. Song, W.-K. Wong, X.-P. Yang, R.A. Jones, Z. Anorg. Allg. Chem. 634 (2008) 1795.
[100] X.-P. Yang, R.A. Jones, V. Lynch, M.M. Oye, A.L. Holmes, Dalton Trans. (2005) 849.
[101] X.-P. Yang, R.A. Jones, W.-K. Wong, V. Lynch, M.M. Oye, A.L. Holmes, Chem. Commun. (2006) 1836.
[102] X.-Q. Lü, W.-Y. Bi, W.-L. Chai, J.-R. Song, M.-X. Meng, W.-Y. Wong, W.-K. Wong, R.A. Jones, New J. Chem. 32 (2008) 127.
[103] W.-K. Wong, X.-P. Yang, R.A. Jones, J.H. Rivers, V. Lynch, W.-K. Lo, D. Xiao, M.M. Oye, A.L. Holmes, Inorg. Chem. 45 (2006) 4340.
[104] C. Piguet, J.-C.G. Bünzli, G. Bernardinelli, G. Hopfgartner, S. Petoud, O. Schaad, J. Am. Chem. Soc. 118 (1996) 6681.
[105] P. Coppo, M. Duati, V.N. Kozhevnikov, J.W. Hofstraat, L. De Cola, Angew. Chem. Int. Ed. 44 (2005) 1806.
[106] M. Mehlstäubl, G.S. Kottas, S. Colella, L. De Cola, Dalton Trans. (2008) 2385.
[107] F.-F. Chen, Z.-Q. Bian, Z.-W. Liu, D.-B. Nie, Z.-Q. Chen, C.-H. Huang, Inorg. Chem. 47 (2008) 2507.
[108] F.-F. Chen, Z.-Q. Bian, B. Lou, E. Ma, Z.-W. Liu, D.-B. Nie, Z.-Q. Chen, J. Bian, Z.-N. Chen, C.-H. Huang, Dalton Trans. (2008) 5577.
[109] D. Li, F.-F. Chen, Z.-Q. Bian, Z.-W. Liu, Y.-L. Zhao, C.-H. Huang, Polyhedron 28 (2009) 897.