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Design and Synthesis of Near-Infrared Emissive Lanthanide Complexes Based on Macrocyclic Ligands

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This review firstly summarizes our recent work on the preparation and photophysical properties of cationic or neutral lanthanide(III) monoporphyrinate complexes, as well as some bridging dinuclear complexes, in which the porphyrinate anion can sensitize the NIR emission of Nd^{III}, Yb^{III} and Er^{III} ions by serving as an antenna that absorbs visible light and transfers the energy to the excited state of the lanthanide(III) ion, followed by relaxation through the NIR emission. Next, several d–f heterobimetallic diporphyrin complexes, in which a transition metal (M = Zn, Pd, and Pt) porphyrinate moiety serves as a donor by transferring its energy to the Yb^{3+} ion and enhances the NIR emission, are described. In addition, the synthesis and photophysical properties of some Gd^{III} porphyrinate complexes and monophthalocyaninato lanthanide complexes are also described in this contribution. Apart from the above compounds, we also discuss the construction of multidecker multimetallic lanthanide Schiff base assemblies, which demonstrate that these varieties of salen-type Schiff base ligands can stabilize Ln^{III} centers and provide the antenna for lanthanide luminescence. By taking advantage of the absorption and emission properties of transition-metal Schiff base complexes, multinuclear and polynuclear Zn^{II}–Ln^{III} Schiff base complexes have also been constructed with improved luminescence properties.

Introduction

Lanthanides or the lanthanoid (IUPAC nomenclature) series from lanthanum to lutetium occupy unique positions in the periodic table. All lanthanides are f-block elements and their trivalent cations possess characteristic electronic structure [Xe]4f^n (n = 0–14); thereafter the chemistry of the lanthanides differs from that of the main group elements and transition metals because of the nature of the 4f orbitals.[1] With the exception of La^{III} and Lu^{III}, all of the lanthanide trivalent ions are luminescent, either fluorescent (Pr^{III}, Nd^{III}, Ho^{III}, Er^{III}, Yb^{III})[2] or phosphorescent (Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Tm^{III}),[3] or both. Their emission covers the entire spectrum (0.3–3 µm), from UV (Gd^{III}) to visible (e.g. blue Tm^{III}, green Tb^{III}, orange Sm^{III}, or red Eu^{III}), and NIR spectral ranges. Because of the core nature of the 4f electrons, which are shielded from the coordination environment by the $5s^25p^6$ electrons, little vibrational coupling with the environment is seen, and the emission band of the Ln^{III} ions based on f–f transitions is narrow and ion-specific, which leads to pure colors and potentially high emission efficiencies.[4] These ions have been the most popular luminescent elements for practical applications such as lasers, sensors, and display devices, and, indeed, complexes of Tb^{III} and Eu^{III} that emit strongly in the visible region of the spectrum are employed for applications such as fluoroimmunoassay and fluorescence microscopy, where the long luminescence lifetimes and sharp, line-like emission make detection particularly easy.[5] Recently, there is considerable interest in the study of the photophysical properties of lanthanide complexes such as Yb^{III}, Nd^{III}, Pr^{III}, and Er^{III}, which are luminescent in the NIR region.[6] There are two particular driving forces for this recent interest in NIR luminescence. Firstly, telecommunication plays an increasingly important role in our society, and optical telecommunication networks based on silica fibers are spanning the earth to send information by NIR radiation (in the range of ca. 1–1.6 µm) because of its high transparency in the NIR part of the electromagnetic spectrum. However, even the slightest losses will eventually lead to significant intensity dissipation over long distances, and occasional amplification of the optical signals will thus be necessary. In particular, the emission lines of Pr^{III} at 1.3 µm ($^1G_4 \rightarrow {}^3H_5$) and Er^{III} at 1.5 µm ($^4I_{13/2} \rightarrow {}^4I_{15/2}$) match well the "transparency window" in silica and are consequently used in optical amplifiers for fiber-optic networks.[7] Secondly, human tissue is relatively transparent at around 0.8–1 µm. In the visible region, the absorbance is high principally because of the porphyrin chromophores; further into the NIR region, the absorbance is high because of the O–H vibrational overtones from water. Metal ions that are luminescent in the intermediate region, e.g. Yb^{III} at 980 nm and Nd^{III} at

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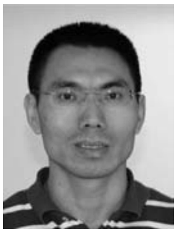
880 nm, are ideal candidates for in vivo luminescence imaging, since their emission can be detected through a considerable thickness of the animal tissue.[8]

As a consequence of electric dipole selection rules, even if many lanthanide-containing compounds display a high quantum yield, direct excitation of the $\mathrm{Ln^{III}}$ ions rarely yields highly luminescent materials. Indirect excitation, termed sensitization or the antenna effect, has to be used. There are three important principles to take into account when designing complexes for the sensitization of NIR emission of lanthanide ions. First of all, effective sensitization of NIR emission requires energy transfer from a strongly absorbing antenna group, usually an organic chromophore, to overcome the difficulty of direct excitation into the parity-forbidden, and hence extremely weak, f–f transitions.[9] For energy transfer from the sensitizer to work requires that its lowest-energy triplet state lies above (by 1000–2000 $\mathrm{cm^{-1}}$) the energy of the emitting state of the lanthanide ion.[10] With NIR emitters, this allows the use of relatively long wavelength light for excitation, which has important practical advantages. For medical imaging, for example, it means that excitation of the probe (as well as the resultant emission) can occur at a long wavelength to which body tissue is relatively transparent. For optical devices, long-wavelength sensitization will allow the use of cheap and widely available semiconductor diode lasers in the red region of the spectrum. To this end, sensitization of NIR lanthanide emission has been demonstrated by using chromophores such as fluoroscein, eosin, and fluorexon, which have absorption maxima at ca. 500 nm.[11] Next, the antenna group must be close to the metal to overcome the strong distance dependence of the energy-transfer process and minimize the competing deactivation of its triplet state by oxygen. Finally, the low-energy excited states responsible for NIR emission are easily quenched by nearby O–H, N–H, and C–H oscillators.[12] It is therefore desirable to minimize the number of these groups close to the metal center by using units such as C–D or C–F bonds instead of C–H.[13]

Many kinds of organic ligands fall into this category and 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.[14] Those complexes have been studied for more than forty years. Carboxylic acids can readily coordinate to lan-



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thanide ions because of the strong affinity between oxygen atoms and lanthanide ions. Usually, lanthanide complexes based on aromatic carboxylic acids exhibit good stability and luminescence properties.[15] Lanthanide macrocyclic chemistry started in the late 1960s when the need for NMR shift reagents prompted the study of lanthanide phthalocyanines and porphyrins.[16] Another most studied class of macrocyclic ligands in lanthanide coordination chemistry is, without any doubt, the molecules derived from 1,4,7,10-tetraazadodecane (cyclen), a 12-membered ring bearing four amino functions.[6w,17] Macrocyclic ligands are often able to provide a coordination cage of suitable size for lanthanide ions. Appended chromophores on the macrocyclic ring can efficiently capture UV light for the sensitization of lanthanide ions.

On the other hand, the use of strongly absorbing d-block chromophores as sensitizers for the NIR emissions from lanthanides has attracted increasing attention since the first report by van Veggel and co-workers on Nd^{III} and Yb^{III} luminescence sensitized by the transition-metal complexes $Ru(bpy)_3^{2+}$ and ferrocene in 2000.[18] Subsequently, many d-block chromophores, based on related transition metals, such as Pt^{II},[19] Ru^{II},[20] Re^{I},[8a,19b] Os^{II},[20b,20d,21] Pd^{II},[22] Zn^{II},[23] Cr^{III},[20b] and Co^{III}[20b,24] that sensitize the NIR emissions of lanthanides (Nd^{III}, Yb^{III}, and Er^{III}) were extensively studied. Specifically, zinc(II) Schiff base complexes, which are known to be effective emitters, could act as effective antenna chromophores for lanthanide-ion sensitization.[23,25] Because most of the energy levels of these d-block chromophores are at around 13000–18000 cm^{-1}, energy transfers from the transition metals to the lanthanide centers are most efficient, and the characteristic emissions from these NIR-emitting lanthanide complexes were successfully obtained.

In this review, we will mainly summarize our efforts on the design and synthesis of NIR-emitting complexes containing Nd^{III}, Er^{III}, or Yb^{III} based on macrocyclic ligands (viz. porphyrins and their derivatives) and half-macrocyclic ligands (i.e. Schiff bases and their transition-metal complexes). We focus on describing the various synthetic strategies proposed for encapsulating these ions into molecular edifices and making use of macrocyclic or acyclic ligands or of d-transition-metal complexes. We also describe the photophysics of the NIR-emitting trivalent lanthanide ions. This contribution will end with a brief conclusion on the chromophores for sensitizing NIR-emitting trivalent lanthanide ions. A literature search up to March 2011 will be covered here.

Lanthanide(III) Porphyrinate Complexes

Porphyrins undoubtedly represent one of the most studied macrocyclic rings with exceedingly delocalized π systems and high stability. Consequently, they exhibit a wide range of intriguing optical, electrical, magnetic, and spectroscopic properties, which render them useful in the fields of materials science,[26] catalysis,[27] biology, and medicine.[26a,28] They absorb strongly in the UV/Vis region, which is not available for many other chromophores. The energy level of its triplet state is at ca. 15000 cm^{-1}, which is aligned above the energy level of excited states of the lanthanide ions and is perfect for effective energy transfer during sensitization.[29] Porphyrins also bind strongly to lanthanide ions through direct coordination of four central pyrrolic nitrogen atoms.[29–30] This direct contact between the porphyrin ring and the lanthanide ion facilitates the sensitization process for NIR emission. The first examples of lanthanide monoporphyrinate complexes were demonstrated in 1976 by Horrocks et al.[31] Since then, there has been an increasing number of papers describing the use of porphyrins to sensitize the NIR emission from lanthanide ions.[6v,6w,30a,30c,30d,30h,30i,30p,30q,32] Energy transfer from the porphyrin chromophore was ascertained by the excitation spectrum of the Yb^{III} luminescence being identical to the absorption spectrum of the complex. Figure 1 shows a simple, widely accepted photophysical model for the description of the sensitization process. In this process, the porphyrin absorbs the light and is excited to its singlet state (S_1). The energy is then transferred to its triplet state (T_1), which is, in part, transferred to the excited state of lanthanide ion (Ln^{III})*, and lastly produces the luminescence.

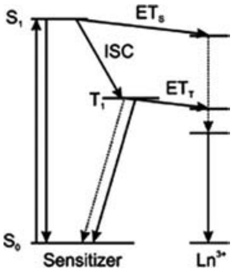
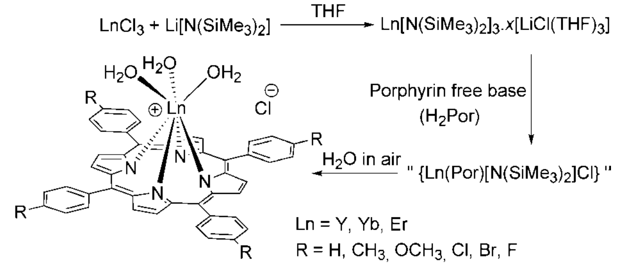


Figure 1. A Jablonski diagram for the sensitization of Ln^{III} by a porphyrin ring.

Cationic and Neutral Lanthanide(III) Monoporphyrinate Complexes

Initially, the synthesis of lanthanide tetraphenylporphyrinates was targeted at utilizing them as dipolar probes for nuclear magnetic resonance, which involved distillation of acetylacetone from a lanthanide acetylacetonate in the presence of the tetraphenylporphyrin dianion (TPP^{2-}) to give [Ln(TPP)(acac)] (acac = acetylacetonate) in low yield (10–30%).[33] However, this method cannot be applied to the preparation of non-β-diketonate-coordinated monoporphyrinate lanthanide complexes because it is quite difficult to displace β-diketonate by other ligands in [Ln(Por)(β-diketonate)] complexes (Por = porphyrinate dianion). Therefore, the luminescence properties and application of these lanthanide ions in porphyrinate dianion coordinated complexes were not fully explored. Synthetic routes for the preparation of lanthanide monoporphyrinate complexes with non-diketonate anionic axial ligands have been developed in recent years. The lanthanide alkyl monoporphyrinate complexes [Ln(OEP)(R)] [H_2OEP = octaethylporphyrin; Ln = Lu, Y; R = $CH(SiMe_3)_2$] was prepared by protonolysis of LnR_3 with H_2OEP in toluene[34] and the lanthanide halide monoporphyrinate complexes [Ln(Por)(X)(S)] [X = Cl or I; S = dimethoxyethane or bis(2-methoxyethyl) ether] either by protonolysis of $LnX[N(SiMe_3)_2]_2$ with H_2Por or interaction of $[LnX_3(THF)_4]$ with porphyrinate dianions $Li_2(Por)$.[35]

A higher yield synthesis was also proposed by our group (Scheme 1), which involves the reaction of $Ln[N(SiMe_2)_3]\cdot x[LiCl(THF)_3]$ with a porphyrin free-base in bis(methoxyethyl) ether; yields of up to 85% have been obtained.[36] However, the above synthetic route did not work for lanthanide ions with large ionic radii. For instance, with lighter lanthanide ions, such as Nd^{III}, which has a larger ionic radius, the $[Nd(Por)(H_2O)_3]Cl$ complex, which was only observed spectroscopically, was found to be rather unstable and decomposed rapidly by demetallation to regenerate the porphyrin free-base upon exposure to air and moisture.[32j]



Scheme 1. Synthesis of the $[Ln(Por)(H_2O)_3]Cl$ (Ln = Y^{III}, Er^{III}, and Yb^{III}) complexes.

The structures of the $[Ln(Por)(H_2O)_3]Cl$ (Ln = Y^{III}, Er^{III}, and Yb^{III}) complexes were ascertained by X-ray crystallography and are isomorphous.[36c] A perspective drawing of $[Yb(TMPP)(H_2O)_3]Cl$ is shown in Figure 2. Crystal structure analyses reveal that the lanthanide(III) ions are eight coordinate, surrounded by four N atoms of the porphyrinate dianion and four aqua ligands of which two are disordered with a site occupancy of 0.5, and have a square-antiprismatic coordination geometry. The average dihedral angle between a pair of N–Yb–N and O–Yb–O planes is 47.6°. The structural data are similar to that of $[Tb(Cl_8TPP)(O_2CMe)(Me_2SO)_2]$,[37] in which the metal also adopts a square-antiprismatic coordination geometry in which the average dihedral angle between a pair of N–Tb–N and O–Tb–O planes is 46.7°. The average Yb–N and Yb–O bond lengths are 2.301 and 2.307 Å, respectively. The displacement of the Yb atom from the mean planes formed by four N atoms and four O atoms are 1.082 and 1.640 Å, respectively. The two mean planes are almost parallel to each other with a separation of 2.716 Å. The porphyrin ring exhibits a saddle-like distortion. As shown by the edge-on view [Figure 2(b)], the independent THF solvate molecules and the anionic Cl atom form acceptor hydrogen bonds with the aqua ligands.

The $[Ln(Por)(H_2O)_3]Cl$ (Ln = Y^{III}, Er^{III}, and Yb^{III}) complexes are stable in air and in most organic solvents and can be purified by column chromatography. Their electronic absorption spectra are characteristic of normal metalloporphyrins[38] and are similar to those of the cationic lanthanide monoporphyrinate complexes $[Ln(TMPyP)(acac)]I_4$ [Ln = Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}; H_2TMPyP = tetrakis(*N*-methylpyridinium-4-yl)porphyrin tetracation].[33] Figure 3 shows the typical UV/Vis spectra for $[Yb(TMPP)(H_2O)_3]Cl$ and tetrakis(*p*-methoxyphenyl)porphyrin (H_2TMPP) in chloroform. The Soret band is observed at ca. 425 nm, which is very close to that of their porphyrin free-base. However, the Q bands for the metal complexes are quite different from those for the free base. The number of absorption bands in the Q region is reduced from four to two, and the bands are centered at 554 and 593 nm. The ab-

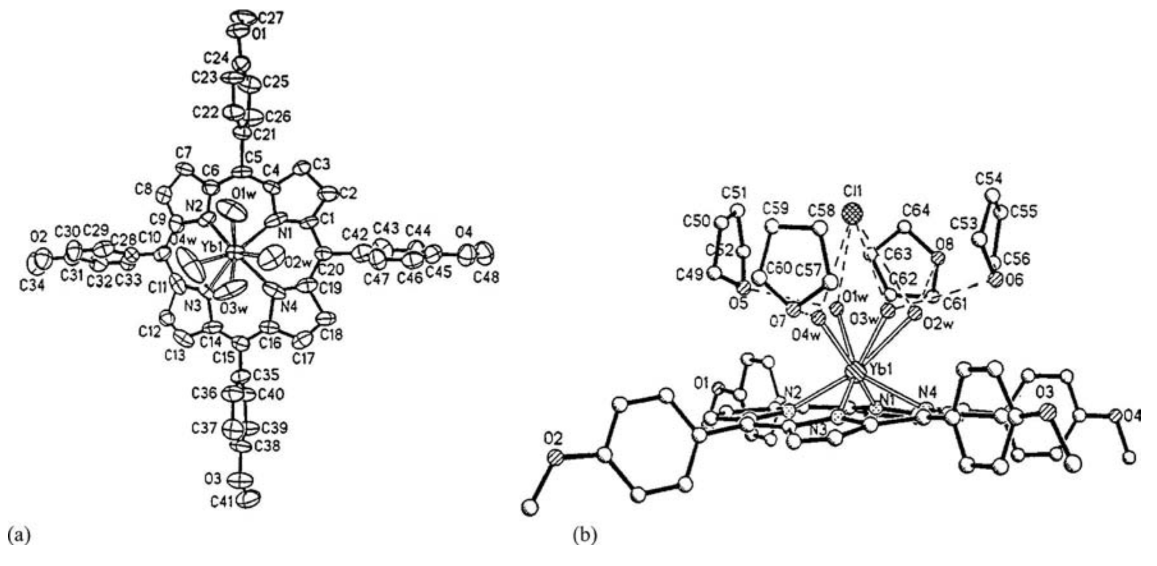


Figure 2. (a) Perspective view of the cation of $[Yb(TMPP)(H_2O)_3]Cl$. (b) A side view of the molecular structure of the complex.[36c] Reproduced by permission of *The Royal Society of Chemistry.*

sorbance at 554 nm is greater than that at 593 nm. This is in good agreement with Gouterman's four-orbital model, which predicts that because of an increase in symmetry, the four Q bands of the porphyrin free-base will be reduced to two upon the formation of a metalloporphyrin.[39]

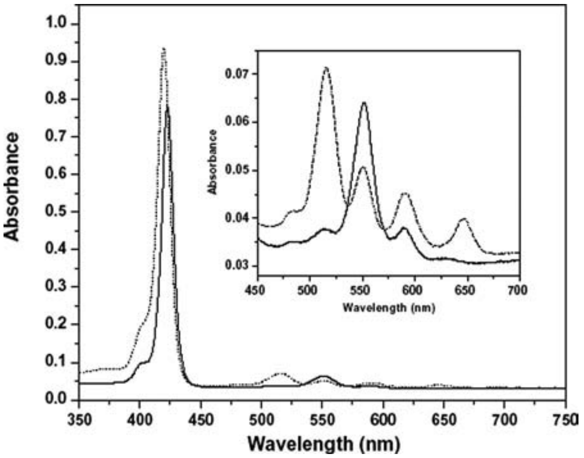


Figure 3. UV/Vis spectra of [Yb(TMPP)(H_2O)$_3$]Cl (solid line) and H_2TMPP (dotted line) in $CHCl_3$ at room temperature (concentration 1.5×10^{-6} mol L^{-1}). Reprinted from ref.[36d] with permission of Elsevier.

It is known that OH oscillators, e.g. bound water molecules and OH-containing solvents, can quench the luminescence.[12e] As a result of the effect of the coordinated aqua molecule on the luminescence efficiency, a solution of [Yb(Por)(H_2O)$_3$]Cl in acetone or methanol exhibits quite a weak NIR emission centered at 976 nm with an emission lifetime of 1.24 µs (Figure 4), which can be assigned to the $^2F_{5/2}\rightarrow{}^2F_{7/2}$ transition of Yb^{III}. The results show that the emission intensity is quite weak in methanol and acetone, and quite strong in DMF. On the other hand, the emission enhancement of the [Ln(Por)(H_2O)$_3$]Cl complexes in DMF can only be attributed to the substitution of coordinated H_2O by DMF. This is further demonstrated by X-ray crystallography as a neutral species [Yb(TPP)(Cl)(DMF)$_2$].[25g]

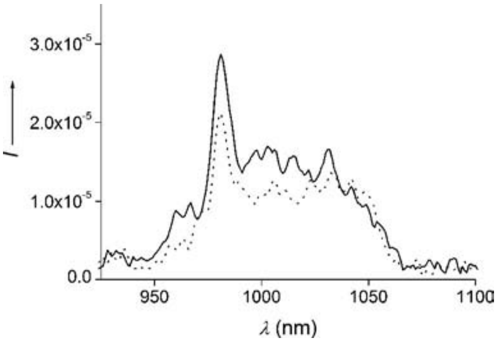
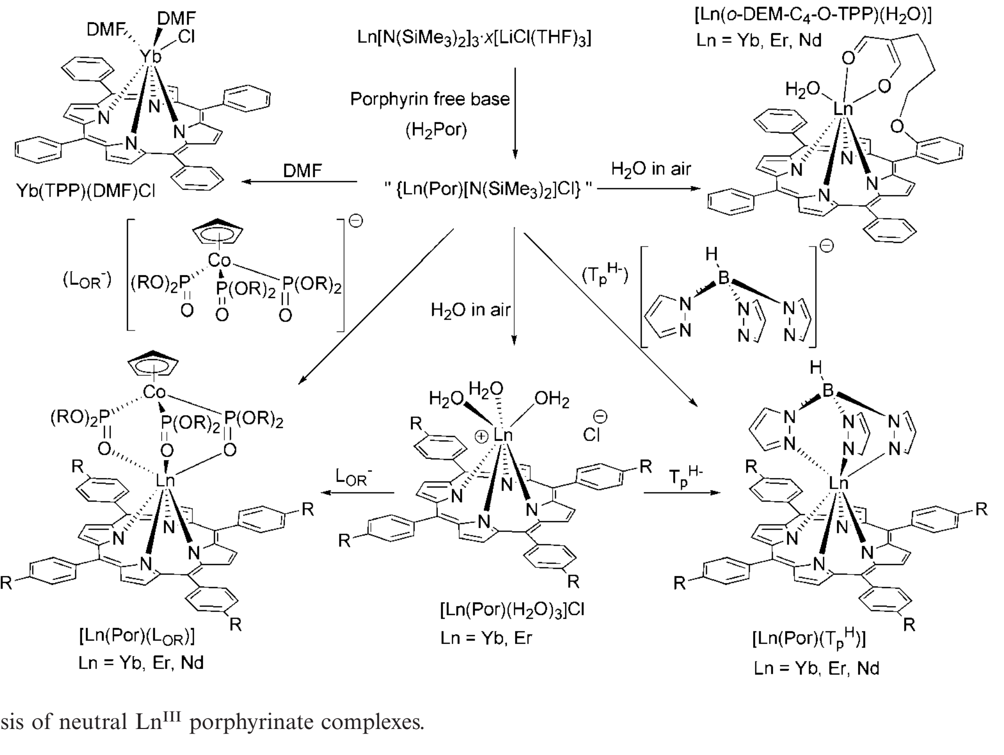


Figure 4. Room-temperature NIR emission (excited at 420 nm) of [Yb(Por)(H_2O)$_3$]Cl (dotted line) and [Yb(TPP)(Cl)(DMF)$_2$] (dashed line).

As pointed out above that the NIR luminescence of lanthanide ions can be quenched by O–H vibrations,[12e] replacement of the aqua molecules of the [Ln(Por)(H_2O)$_3$]Cl complexes (Ln = Nd^{III}, Yb^{III}, and Er^{III}) by ligands that do not contain the OH functional group should be able to enhance the NIR emission of the lanthanide ions. Kläui's O_3-tripodal ligand L_{OR}^- [(cyclopentadienyl)tris(dialkylphosphito)cobaltate][40] and Trofimenko's scorpionate ligands T_p^{R-} [hydridotris(pyrazolyl)borate][41] are mono-anionic 6-electron donors that are isoelectronic to the cyclopentadienyl ligands (η^5-C_5R_5). These tripodal ligands are



Scheme 2. Synthesis of neutral Ln^{III} porphyrinate complexes.

known to stabilize metal ions in high oxidation states and should be able to stabilize oxophilic metal ions such as Ln^{3+} metal ions. These ligands should be ideal ligands to displace the three coordinated aqua molecules of the $[Ln(Por)(H_2O)_3]^+$ complexes, to stabilize the resultant lanthanide porphyrinate complexes, and to enhance their NIR luminescence. At room temperature, the cationic lanthanide porphyrinate complexes $[Ln(Por)(H_2O)_3]^+$ (Ln = Yb^{III} and Er^{III}) reacted readily with the anionic tripodal nucleophile L_{OR}^- or T_p^{H-} to give the neutral complexes $[Ln(Por)(L_{OR})]$ or $[Ln(Por)(T_p^H)]$, respectively, in high yields (Scheme 2).[30q,36b,42] Although we cannot isolate the unstable cationic $[Nd(Por)(H_2O)_3]Cl$ complexes yet, $[Nd(Por)(L_2X)]$ (L_2X^- = L_{OR}^- or T_p^{H-}) complexes can be prepared in high yield by first protonolyzing the lanthanide amide with porphyrins, followed by addition of the tripodal anions before workup in air. The results are depicted in Scheme 5.[30q,36b,42] Presumably, the precursor intermediate $[Nd(Por)(NR_2)Cl]^-$, generated upon protonolysis of the lanthanide amide with the porphyrin, underwent a nucleophilic displacement reaction with the tripodal anion to form the stable product $[Nd(Por)(L_2X)]$ (L_2X^- = L_{OR}^- or T_p^{H-}) before it hydrolyzed to form the unstable cationic complex $[Nd(Por)(H_2O)_3]Cl$. All the neutral $[Ln(Por)(L_2X)]$ (Ln = Nd^{III}, Yb^{III}, and Er^{III}) complexes are air stable and soluble in most organic solvents and can be purified by column chromatography. Their absorption spectra are similar to that of $[Ln(Por)(H_2O)_3]Cl$ and are characteristic of normal metalloporphyrins.[38] Recently, $[Ln(Por)(L_{OEt})]$ and $[Ln(Por)(T_p^H)]$ were also prepared by nucleophilic displacement of the halide ligand from [Ln(Por)(X)(DME)] (Ln = Yb, Tm, Er, Ho, Nd, Pr; X = Cl, I; DME = dimethoxyethane) by the anionic tripodal ligands L_{OEt}^- and T_p^{H-}.[35]

The solid-state structures of $[Ln(Por)(L_{OR})]$ and $[Ln(Por)(T_p^H)]$ (Ln = Nd^{III}, Yb^{III}, and Er^{III}) complexes were ascertained by X-ray crystallography.[32m,36b,42–43] Perspective drawings of $[Yb(TMPP)(L_{OEt})]$[36b] and $[Yb(TPP)(T_p^H)]$[43b] are shown in Figure 5.[36b,43b] The corresponding Nd and Er complexes are isostructural to the Yb complexes. Specifically, the decrease in the Ln–N distance in the series $Nd^{III} > Er^{III} > Yb^{III}$ is in good agreement with lanthanide contraction and reflects a decrease in the ionic radii: 1.12 > 1.03 > 1.01 Å.[44] The data show clearly that because of the larger radius of the Nd^{III} ion, the distances between Nd^{III} and the porphyrin ring are longer than those for the Er^{III} and Yb^{III} complexes. This may be the reason why the $[Nd(Por)(H_2O)_3]Cl$ complexes are so unstable relative to their Er^{III} and Yb^{III} analogues. Since the lanthanide ions are too large to fit into the cavity of the porphyrinate ring, the porphyrinate ring adopts a domed conformation to maximize the Ln–N interactions. The structures further show that the sterically bulky anions provide a congested environment around the metal center. This minimizes the metal–solvent interactions, which may reduce the quantum yield for luminescence.

When $[Yb(porp)(H_2O)_3]Cl$ was treated with sterically bulky nucleophiles such as hydridotris(3,5-dimethylpyrazol-1-yl)borate (T_p^{Me-}), the μ-OH bridged dimer $[Yb(TPP)(\mu\text{-}OH)(H_2O)]_2$[25g] was obtained instead of the expected neutral complex $[Yb(TPP)(T_p^{Me-})]$. This implies that there is competition between the formation of dimers and adducts. When the externally added ligand is sterically hindered, dimerization is preferred even though the N and O atoms in these ligands have a strong coordinating ability to the metal ions.

Figure 6 shows the absorption, emission (excited at 414 nm), and excitation (monitored at 648 nm) spectra of $[Yb(TPP)(T_p^H)]$, which are typical for lanthanide monoporphyrinate complexes. The absorption bands at 421, 550, and 588 nm and the emission peak at 648 nm (τ = 12.9 ns and $\Phi_{em} = 0.11 \times 10^{-3}$) for $[Yb(TPP)(T_p^H)]$ can be assigned to the intraligand $\pi \rightarrow \pi^*$ transitions of the porphyrinate ligand. In addition to the visible emission, all Nd^{III}, Yb^{III}, and Er^{III} monoporphyrinate complexes exhibit Ln^{III} ion emission in the NIR region. For the Nd^{III} monoporphyrinate complexes, the emissions at 875 and 1068 nm can be assigned to the ${}^4F_{3/2} \rightarrow {}^4F_{9/2}$ and ${}^4F_{3/2} \rightarrow {}^4F_{11/2}$ transitions of Nd^{III}, respectively. For the Yb^{III} and Er^{III} monoporphyrin-

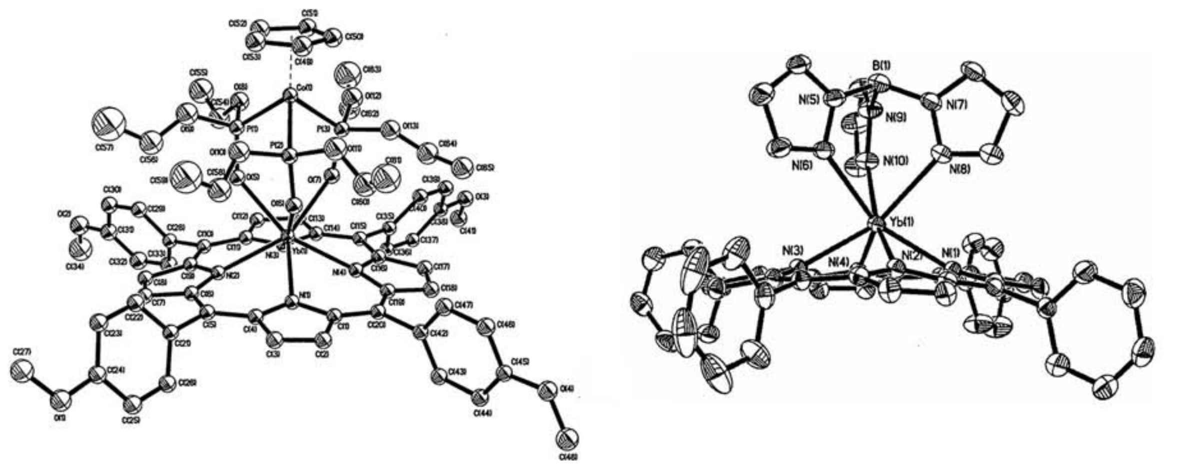


Figure 5. A perspective drawing of $[Yb(TMPP)(L_{OEt})]$ (left)[36b] (reproduced by permission of *The Royal Society of Chemistry*) and $[Yb(TPP)(T_p^H)]$ (right).

ate complexes, the emission peaks at 1515 and 976 nm can be assigned to the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition of Er^{III} and to the $^2F_{5/2}\rightarrow{}^2F_{7/2}$ transition of Yb^{III}, respectively. These NIR emissions are very similar to those reported for Nd^{III}, Er^{III}, and Yb^{III}, and the lifetime values are in good agreement with the literature values.[45] The NIR luminescence lifetime is about 20 µs for the Yb^{III} complexes and 450–825 ns for the Nd^{III} complexes and is much longer than the lifetime of the porphyrinate emission. Because of the limitation of our equipment, we were unable to measure the excitation (monitored at 1540 nm) spectrum and the NIR luminescence lifetime of the Er^{III} complexes. The NIR sensitization process was carefully examined by using [Ln(TPP)(L$_2$X)] (Ln = Nd^{III} and Yb^{III}; L$_2$X = L_{OR}^- and T_p^{H-}) as model complexes.

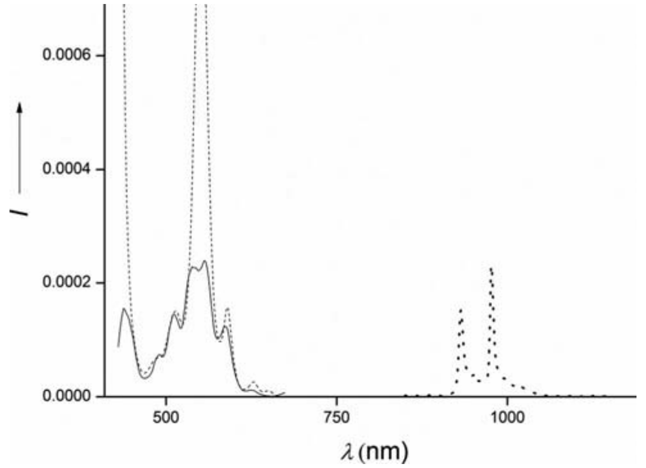
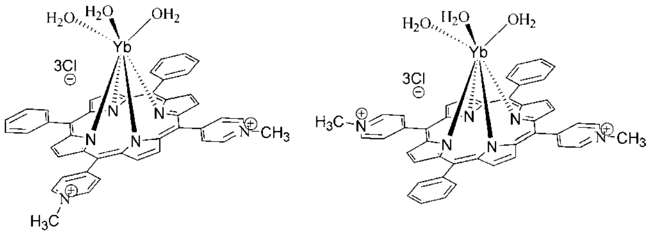


Figure 6. Room-temperature absorption, NIR emission (excited at 414 nm) and excitation (monitored at 648 nm) spectra of [Yb(TPP)(T_p^H)].

Excitation bands of [Yb(TPP)(T_p^H)] in chloroform solution at 298 K (monitored at 980 nm) are observed at 560 and 596 nm, which almost coincide with its visible absorption bands at 550 and 588 nm. This clearly shows that the excitation of the Yb^{III} ion originates from the π→π* transitions of the porphyrinate antenna, and excitation of the porphyrin represents the photophysical pathway leading to the observable NIR luminescence. Photophysical studies show that the porphyrinate antenna transfers its absorbed visible energy of the Q band to the excited state of the metal ion, which then relaxes through emission in the NIR region.

The NIR emission intensity of the lanthanide porphyrinate complexes follows the trend Yb^{III} > Nd^{III} > Er^{III}. The trend is consistent with observations for other luminescent lanthanide complexes and reflects the fact that the efficiency of nonradiative decay increases as the energy of the luminescent state decreases according to the energy gap law. The emission yields of the [Ln(TPP)(L_{OR})] and [Ln(TPP)(T_p^H)] complexes are generally higher than those for other Yb^{III}, Nd^{III} and Er^{III} complexes.[35a,46] The enhanced emission yields for the [Ln(TPP)(L_{OR})] and [Ln(TPP)(T_p^H)] complexes are believed to arise because the coordination environment provided by the porphyrinate in combination with the tripodal anion (L_{OR} or T_p^H) effectively shield the Ln^{III} ion from interacting with the solvent (C–H) vibrational modes, which enhance the rate of nonradiative decay.[13b] This premise is supported by the observation that Φ_{em} of [Yb(TPP)(T_p^H)] only increases from 0.032 in CHCl$_3$ to 0.034 in CDCl$_3$.[35a] The observed emission lifetime of neutral lanthanide porphyrinate capped with a tripodal anion (20 µs) is almost twenty times longer than that of the aqua-coordinated complex [Yb(Por)(H$_2$O)$_3$]Cl (1.24 µs).

Previous studies highlight the potential of developing novel lanthanide hydrophilic porphyrinate complexes as anticancer therapeutics, which can combine the unique features of the lanthanide ions with those of the water-soluble porphyrins, rendering them biocompatible with human tissues. Very recently, several novel water-soluble lanthanide porphyrinate complexes based on the *meso*-pyridyl-substituted porphyrin free-base were prepared and fully characterized (Figure 7).[47] In addition to the photophysical properties of the complexes, particularly the NIR emissions corresponding to the Ln^{III} ion, the interaction of water-soluble lanthanide(III) porphyrinate complexes with DNA was investigated. The complexation of the aqua-coordinated complexes [(*cis*/*trans*-DMPyDPP)Yb(H$_2$O)$_3$]Cl$_3$ with DNA results in a loss of the coordinated water, which therefore leads to the observed enhanced NIR luminescence and increased lifetime. For example, without CT-DNA, the NIR lifetime measured for [(*cis*-DMPyDPP)Yb(H$_2$O)$_3$]Cl$_3$ (monitored at 980 nm) is 388 ns, while in the presence of 1- and 2 equiv. CT-DNA, the NIR lifetimes increase to 645 ns. The primary research result indicates that these novel water-soluble lanthanide porphyrinate complexes are potential candidates as anticancer photodynamic therapeutic agents.

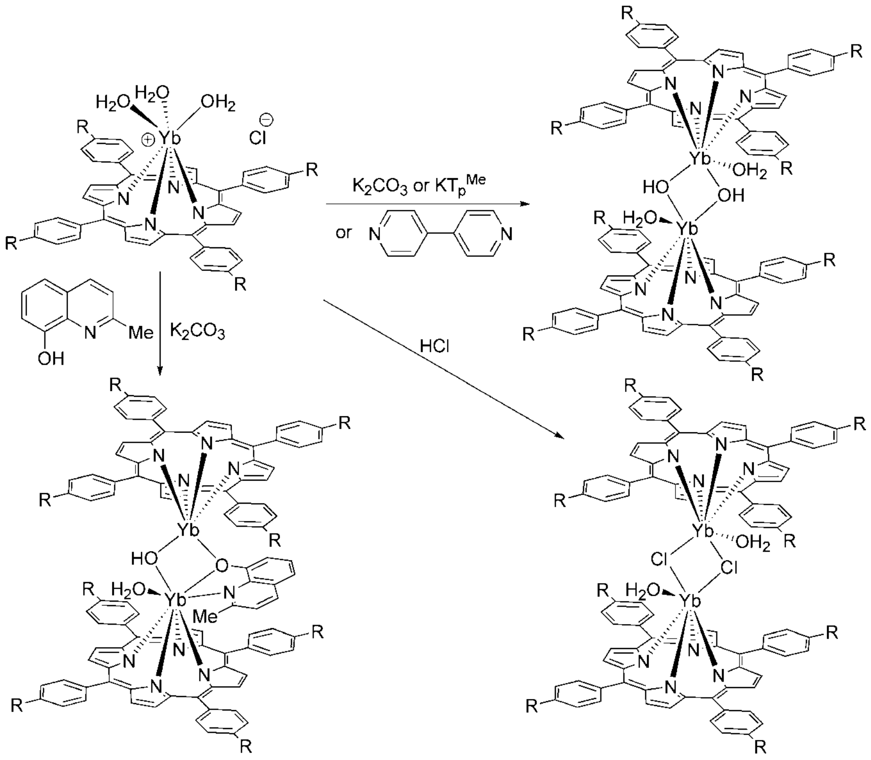


[(*cis*-DMPyDPP)Yb(H$_2$O)$_3$]Cl [(*trans*-DMPyDPP)Yb(H$_2$O)$_3$]Cl

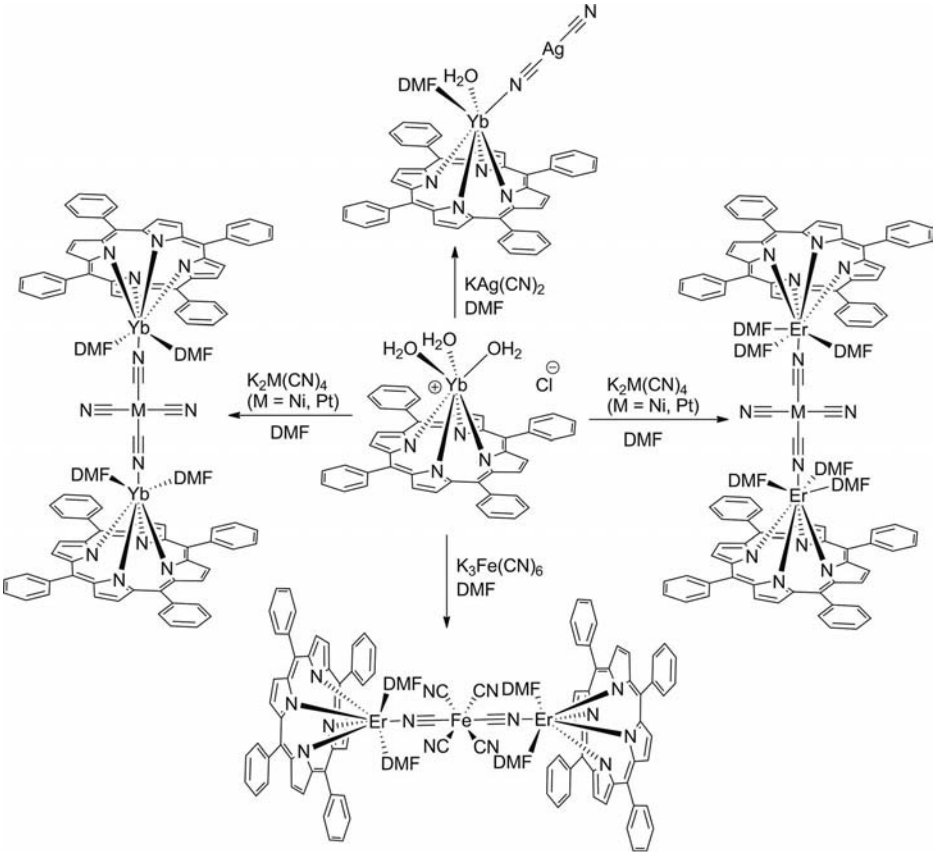
Figure 7. Structure of water-soluble lanthanide(III) porphyrinate complexes.

Reactivity of Cationic Ln^{III} Monoporphyrinate Complexes

The catioinic lanthanide porphyrinate complexes [Ln(Por)(H$_2$O)$_3$]Cl are very versatile precursor complexes for the preparation of other lanthanide monoporphyrinate complexes. Particularly, the [Ln(Por)(H$_2$O)$_3$]Cl complexes have a high tendency to form bridging dinuclear complexes.[25g] During our initial effort of removing H$_2$O for better NIR emission, interaction of the complex [Yb(TPP)(H$_2$O)$_3$]Cl with either 4,4′-bipyridine or K$_2$CO$_3$ in CH$_2$C1$_2$ gave the hydroxy-bridged dimer [Yb(TPP)(µ-OH)(H$_2$O)]$_2$,



Scheme 3. Synthesis of OH-, Cl-, and/or 8-hydroxyquinaldine-bridged dinuclear complexes.



Scheme 4. Synthesis of cyanido-bridged d–f trinuclear lanthanide porphyrinate complexes.

and with 8-hydroxyquinaldine (QH) in the presence of K_2CO_3 gave the bridging dinuclear complex $[Yb(TPP)]_2(\mu\text{-}OH)(\mu\text{-}Q)$ in high yield. Biphasic reaction of $[Yb(TMPP)(H_2O)_3]Cl$ in CH_2C1_2 with aqueous HCl afforded the chloro-bridged dimer $[Yb(TPP)(\mu\text{-}Cl)(H_2O)]_2$, again in good yield (Scheme 3). The structures of these dinuclear complexes were ascertained by X-ray crystallography.[25g] In general, the NIR emission is somewhat more intense for the dimers than for the monomers. This is expected, as there are two emissive centers in the dimers, whereas there is only one in the monomers. Furthermore, both the NIR emission intensity and the observed lifetimes in the range 1.24–3.17 µs decrease as the number of O–H oscillators in the molecule increases.

The metathesis reaction between 2 equiv. $[Ln(TPP)(H_2O)_3]Cl$ (Ln = Yb^{III} and Er^{III}; TPP^{2-} = tetraphenylporphyrinate dianion) and 1 equiv. cyanometallate in DMF at room temperature under nitrogen for 24 h gave the cyanido-bridged d–f trinuclear complexes $\{[Ln(TPP)(DMF)_n]_2[(\mu\text{-}NC)_2M(CN)_2]\}$ (Ln = Yb^{III}, n = 2, M = Ni; Ln = Er^{III}, n = 3, M = Ni; Ln = Yb^{III}, n = 2, M = Pt; Ln = Er^{III}, n = 3, M = Pt), a trinuclear complex $\{[Er(TPP)(DMF)_2][(\mu\text{-}NC)_2Fe(CN)_4][Er(HTPP)(DMF)_2]\}$, and a dinuclear complex $\{[Er(TPP)(DMF)(H_2O)](\mu\text{-}NC)Ag(CN)\}$ when the cyanometallate used is the dianion $[M(CN)_4]^{2-}$ (M = Pt and Ni), trianion $[Fe(CN)_6]^{3-}$, and monoanion $[Ag(CN)_2]$, respectively (Scheme 4). The molecular structures of these complexes were ascertained by X-ray crystallography. Photoluminescence studies of those complexes show that these complexes display photophysical properties characteristic of normal metal porphyrinate complexes. Their absorption bands and emission peaks in the visible region are typical of intraligand transitions of the porphyrinate ligand. Furthermore, these complexes exhibit emissions characteristic of the lanthanide(III) ion in the NIR region, which are quenched by the cyanometallates. Their particularly short luminescence lifetimes (≈1 µs) are approximately one order of magnitude shorter than those of the coordinatively saturated Yb^{III} complexes, typically >10 µs.[43b] We ascribe this to the presence of the relatively high-energy C≡N oscillators at around 2142 cm^{-1}, which are directly coordinated to the lanthanide centers.

Synthesis and Structure of Other Neutral Monoporphyrinate Lanthanide(III) Complexes

N-Confused porphyrins (NCPor) are isomers of porphyrins which contain an inverted pyrrole ring linked to the porphyrin conjugate system through a β-carbon atom (Figure 8). Treatment of *N*-confused porphyrins with $Ln[N(SiMe_3)_2]_3\cdot[LiCl(THF)_3]_x$ in toluene heated to reflux, followed by the addition of $Na(L_{OMe})$ at room temperature, resulted in the crystallization of green complexes with the formula $[Ln(NCPor)(L_{OMe})]$ (Ln = Er^{III}, Yb^{III}) in 75% yield.[43a] According to its X-ray structure (Figure 8), the Yb^{III} compound is eight coordinate, in which the Yb atom is bound to the three O atoms of the capping ligand, to the three N atoms from the confused porphyrin, as well as to the inner C–H edge of $[Yb(NCPor)(L_{OMe})]$ through an agostic η^2 bond. It displays a weak NIR luminescence with a very short lifetime of 0.26 µs upon excitation at 600 nm, the intensity of which is one order of magnitude smaller when compared with $[Yb(por)(L_{OMe})]$. This provides further evidence for the formation of the agostic bond, and the strong quenching of the luminescence is attributed to the presence of a C–H oscillator in the inner coordination sphere.

The aforementioned work demonstrated that the porphyrinate anion can sensitize the NIR emission of the Nd^{III}, Yb^{III} and Er^{III} ions by serving as an antenna that absorbs visible light, transfers the energy to the excited state of the lanthanide(III) ion, which then relaxes through NIR emission. However, the f→f states of gadolinium(III) are located at exceptionally high energies owing to the extreme stability of its half-filled f-shell (f^7). The lowest-energy f→f transition appears as an emission line at 312 nm. Accordingly, Gd^{III} complexes are frequently characterized by emissive in-

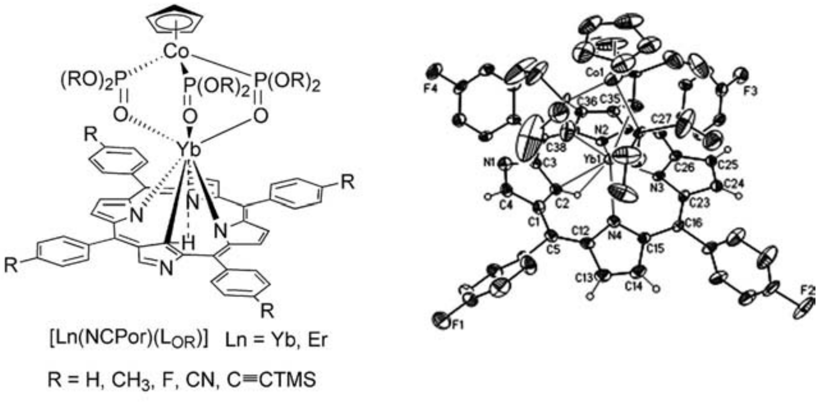


Figure 8. The structures of lanthanide complexes of *N*-confused porphyrins (left) and a perspective drawing of $[Yb(NCPor)(L_{OMe})]$ (R = F) (right).[43a] Reproduced by permission of *The Royal Society of Chemistry.*

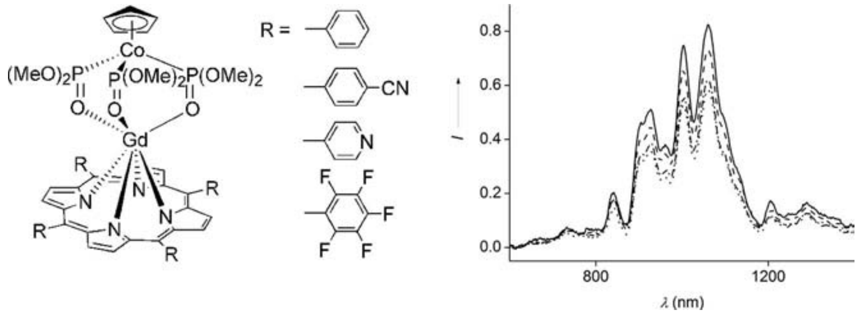


Figure 9. The structures of the Gd^{III} porphyrinate complexes (left) and their NIR phosphorescence spectra excited at 412 nm at 77 K (right). (solid line, R = *p*-C_6H_5CN; dashed line, R = Py; dotted line, R = C_6H_5; dashed-dotted line, R = C_6F_5).

traligand states at lower energies. Owing to its heavy-atom effect and paramagnetism, Gd^{III} induces a strong singlet/triplet mixing in the ligand.[48] It follows that the fluorescence is largely quenched, while the phosphorescence is facilitated.[49] First results on the quite unique luminescence properties of gadolinium porphyrins have recently been reported.[29] We have also extended our study to explore the chemistry of Gd^{III} porphyrinate complexes. A series of Gd^{III} porphrinate complexes supported by the tripodal anion, L_{OMe}^- {L_{OMe}^- = (η^5-C_5H_5)Co[P(=O)(OMe)$_2$]$_3^-$} were prepared (Figure 9 left). The visible emissions, luminescence yields, NIR phosphorescence and lifetimes of these complexes have been examined. The electronic spectra reveal NIR phosphorescence from the triplet state of the porphyrinate ligand and show a very characteristic vibronic-structured emission (Figure 9 right).

Synthesis and Photophysical Properties of d–f Heterobimetallic Bisporphyrin Complexes

Long-lived transition-metal ions, such as Cr^{III}, Ru^{II}, and Pt^{II}, have been explored as sensitizers to extend the emissive lifetime of lanthanide ions in d–f heterobimetallic complexes.[6r,7a,18,20b,32k,50] For example, the lifetime of the lanthanide ions in Cr–Ln (Ln = Nd, Yb) heterobimetallic complexes, through Cr^{III}→Ln^{III} intramolecular energy transfer, can be extended from a microsecond to millisecond timescale at 10 K.[6r] However, for these d–f heterobimetallic complexes, the ligands employ only absorbed light in the high-energy region between 247–334 nm. To extend this strategy to transition-metal complexes that absorb strongly in the UV/Vis region, a series of d–f heterobimetallic diporphyrin complexes, in which a Yb^{III} porphyrinate moiety is linked to a transition-metal (M = Zn, Pd and Pt) porphyrinate moiety through a flexible three-carbon chain, has been reported (Figure 10).[32j] These complexes exhibit both visible and NIR emissions that originate from the π→π* transition of the porphyrinate antenna, and the visible emission corresponds to the fluorescence of the antenna and the NIR emission to the $^2F_{5/2}\rightarrow{}^2F_{7/2}$ transition of Yb^{III}. Fluorescence studies show that for these d–f diporphyrin dyads, in addition to the fact that the porphyrinate unit directly bonded to the Yb^{III} ion acts as an antenna, the [M(TPP)] moiety also serves as a donor by transferring its energy to the Yb^{III} ion, which enhances the NIR emission. Relative to [Yb(TPP)(L_{OMe})], the Yb^{III} luminescence lifetime of the d–f diporphyrin dyad is extended from 30 to 40 and 70 µs for M = Pd and Pt, respectively. A proposed scheme for the energy-transfer process for the d–f diporphyrin dyads is shown in Figure 11.[32j] Optical absorption of the ^{1}M(TPP) unit leads to $S_0\rightarrow S_1$ transition to the singlet excited state ^{1}M(TPP)*, followed by fluorescence emission or intersystem crossing to the triplet excited state ^{3}M(TPP)*, which results in radiative phosphorescence emission and nonradiative deactivation with rate constants, k_r and k_{nr}, respectively. The energy of the ^{3}M(TPP)* excited state can be transferred to (Yb^{III})* with the rate constant k_{ET} so that the Yb^{III} NIR emission is enhanced and lifetime is extended. Furthermore, these d–f diporphyrin dyads, by open-aperture Z-scan studies, were shown to possess two-

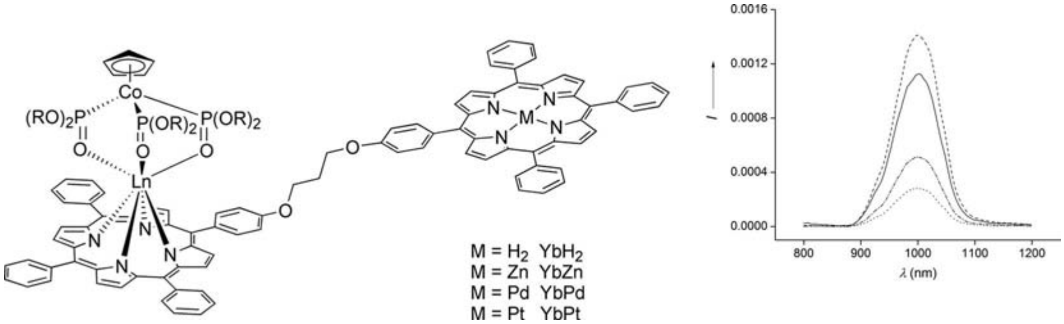


Figure 10. Chemical structure (left) and NIR emissions (right) of d–f heterobimetallic diporphyrin complexes. {solid line, YbPd; dashed line, YbPt; dashed-dotted line, YbZn; dotted line, [Yb(TPP)(L_{OMe})]}.

photon absorption and optical-limiting properties. For instance, the Pt dyad exhibits a two-photon absorption cross-section value of 247 GM at 800 nm, which is about nine times that of H_2TTP (28 GM), and an optical-limiting performance comparable to that of C_{60} at 532 nm.

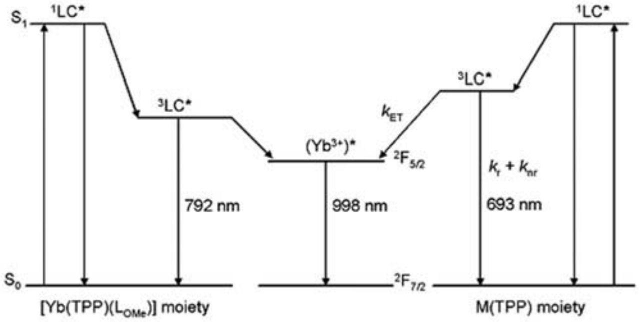
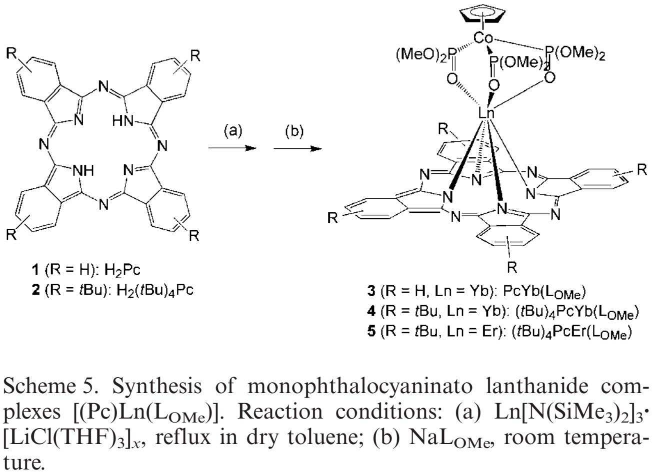


Figure 11. Scheme for the energy transfer from the transition-metal porphyrin unit to the Yb porphyrin unit (LC = ligand center). k_{ET} is the rate constant for energy transfer; k_r is the rate constant for radiative deactivation; k_{nr} is the rate constant for nonradiative deactivation. $k_r + k_{nr} = \tau_0^{-1}$ and $k_r + k_{nr} + k_{ET} = \tau^{-1}$.

Synthesis and Structure of (Monophthalocyaninato) lanthanide(III) Complexes

A macrocyclic ligand that closely resembles a porphyrin is phthalocyanine. Bis(phthalocyaninato)-, heteroleptic bis(phthalocyaninato)-, tris(phthalocyaninato)-, heteroleptic tris(phthalocyaninato)-, and mixed porphyrinato–(na)-phthalocyaninato lanthanide complexes are well studied;[32d,51] however, there are relatively few studies on monophthalocyaninato lanthanide complexes, possibly because of their instability. Recently, we have shown that the anionic capping agent L_{OMe}^- can be used to stabilize the intermediates, and we have synthesized a number of monophthalocyaninato lanthanide complexes [(Pc)Ln(L_{OMe})] (H_2Pc = phthalocyanine free-base; Ln = Yb, Er) (Scheme 5).[32d]



Scheme 5. Synthesis of monophthalocyaninato lanthanide complexes [(Pc)Ln(L_{OMe})]. Reaction conditions: (a) $Ln[N(SiMe_3)_2]_3\cdot[LiCl(THF)_3]_x$, reflux in dry toluene; (b) NaL_{OMe}, room temperature.

The solid-state structure of [(Pc)Yb(L_{OMe})] was ascertained by X-ray crystallography (Figure 12) and is very similar to its porphyrinate analogue [(Por)Yb(L_{OMe})]. The crystal structure analysis reveals that the Yb^{III} ion is sandwiched between the phthalocyaninato ring and the anionic tripodal ligand and is seven coordinate, surrounded by four nitrogen atoms from the phthalocyaninate (Pc) dianion and three oxygen atoms from the L_{OMe}^- anion.

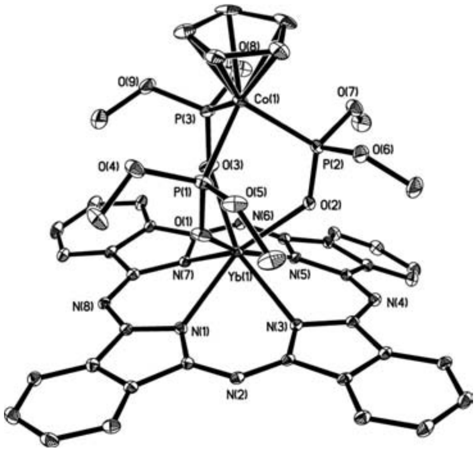


Figure 12. A perspective view of [(Pc)Yb(L_{OMe})]. Hydrogen atoms are omitted for clarity.

Photophysical studies show that the phthalocyaninate dianion is an effective antenna. In addition to the visible fluorescence of the antenna, the complex also displays either singlet oxygen ($^1O_2$) phosphorescence at 1270 nm or lanthanide ion emission at ca. 1530 nm ($^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition of Er^{III}) when the lanthanide metal is Yb^{III} or Er^{III}, respectively.[32d] This metal-ion dependent observation probably arises because of back energy transfer from the metal excited state ($^*Ln^{III}$) to the ligand-centered triplet state (^3LC). It has been shown that efficient back energy transfer takes place in Ln^{III} complexes when $\Delta E(^3LC\text{–}^*Ln^{III}) < 1850\ cm^{-1}$.[51d] The energy level of the ^3LC state of the phthalocyaninate ligand of the complexes can be estimated to be at about 9300 cm^{-1} for metallophthalocyaninate complexes, and is about 2794 cm^{-1} higher than the energy of the $^4I_{13/2}$ Er^{III} luminescence level (6506 cm^{-1}) and lies at almost the same energy of the $^2F_{5/2}$ Yb^{III} luminescence level (10300 cm^{-1}).[52] Thus, efficient ligand-to-metal energy transfer for the Er^{III} complex and significant back energy transfer for the Yb^{III} complex is observed. It is well documented that the ^3LC phosphorescence of the phthalocyaninate ligand can be quenched effectively by molecular oxygen with the production of singlet oxygen ($^1O_2$). The presence of the ^3LC state can be inferred by the photogeneration of $^1O_2$. However, $^1O_2$ phosphorescence was not observed upon photo-irradiation of an aerated solution of the Er^{III} complex. This suggests that the rate of energy transfer from the ^3LC state to the metal excited state ($^*Ln^{III}$) is faster than the rate of reaction between the ^3LC state and molecular oxygen ($^3O_2$). The photophysical and photochemical processes of the Yb^{III} and Er^{III} compounds are shown in Figure 13.[32d] Upon photo-irradiation, the phthalocyaninate ligand is excited to its singlet state (S_1), which then undergoes either fluorescence or energy transfer to its triplet state (T_1). In its triplet state, the phthalocyaninate ligand can either interact with molecular oxygen ($^3O_2$) to generate $^1O_2$ or transfer its energy to the excited state of the lanthanide ion (*Ln^{III}) with a rate constant of $k(O_2)$ or k(et), respectively. In the case of the Er^{III} complex, where the energy of the emissive state $^4I_{13/2}$ of Er^{III} is much lower than that of T_1 and back energy transfer is insignificant, efficient energy transfer takes place [$k(\text{et}) >> k(O_2)$]. This results in the sensitization of the Er^{III} ion without the observation of $^1O_2$ phosphorescence in the NIR region. However, in the case of the Yb^{III} complexes, where the energy of the emissive state $^2F_{5/2}$ of Yb^{III} is about the same as that of T_1 and back energy transfer becomes significant, energy transfer to the emissive state is thus very inefficient, which results in $k(O_2) >> k(\text{et})$. As a consequence, only $^1O_2$ phosphorescence, but not Yb^{III} emission, is observed in the NIR region.

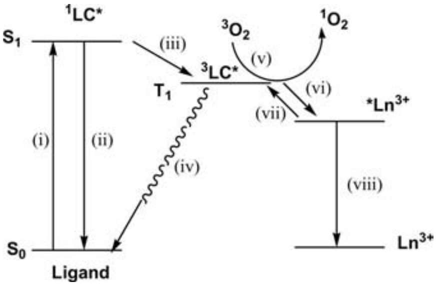


Figure 13. Photophysical and photochemical processes of lanthanide(III) phthalocyaninate complexes. (i) Photoexcitation, (ii) fluorescence, (iii) intersystem crossing, (iv) nonradiative decay, (v) generation of $^1O_2$ with a rate constant of $k(O_2)$, (vi) energy transfer with a rate constant of k(et), (vii) back energy transfer, and (viii) near-infrared emission.

Multimetallic Lanthanide Schiff Base Assemblies

There is currently considerable interest in the rational design and synthesis of coordination framework materials prepared from multifunctional organic ligands and lanthanide ions since they have potential applications related to luminescence, magnetism, gas absorption, and sensing.[7e,53] Schiff base ligands are among the most widely studied chelators for metal ions owing to their relatively easy synthesis and their versatility for the formation of stable complexes. It can act as a flexible linker featuring N and O atom donors in the construction of d block transition metal- or f block lanthanide frameworks. Our recent studies demonstrated that a variety of “salen” style Schiff base ligands can stabilize Ln^{III} centers and provide the antenna for lanthanide luminescence (Figure 14).[54] An interesting emerging feature exhibited by these complexes is the self-assembly of stacked “multidecker” structures in which the Ln^{III} ions are sandwiched between alternating layers of the Schiff base ligands. These studies raised the possibility to construct larger multidecker, multimetallic lanthanide Schiff base assemblies by careful adjustment of the stoichiometry, anion selection, and reaction conditions. Since a multidecker framework could be effective in keeping solvent and water molecules away from Ln^{III} center, it seemed reasonable to assume that enhanced luminescence properties could be achieved with these types of architectures.

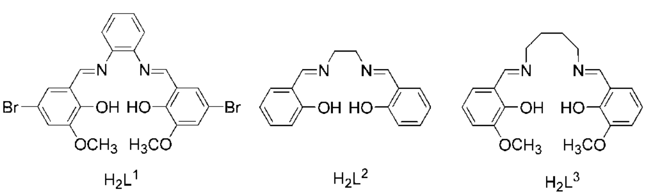


Figure 14. Schiff base ligands H_2L^{1-3}.

The triple-decker complex $[Yb_3(L^1)_3(OAc)_2Cl]$ (**1**) is formed from the reaction of H_2L^1, $YbCl_3·6H_2O$, and $Zn(OAc)_2·2H_2O$ in 25% yield [H_2L^1 = *N,N′*-bis(5-bromo-3-methoxy-salicylidene)phenylene-1,2-diamine].[55] The solid-state structure of this compound reveals the presence of two independent, chiral $Yb_3L^1{}_3$ units of the complex (Figure 15). Intermolecular π–π stacking interactions, C–H···π interactions, and Br···H–C hydrogen bonds between one set of chiral $Yb_3L^1{}_3$ units create a 3D network that encloses 1D strands formed by another set of chiral $Yb_3L^1{}_3$ units. In the chiral $Yb_3L^1{}_3$ unit, each Yb^{III} ion is eight coordinate and is bound by the N_2O_2 donor sets of two L groups; intermetallic distances range between 3.7 and 3.8 Å. A solid-state sample and a solution in acetonitrile exhibit metal-centered NIR luminescence (Figure 16), while solutions in methanol and deuterated methanol are less luminescent, probably because of some dissociation of the complex. When compared to the emission of a solution of $[ZnYb(L^1)(NO_3)_2(OAc)]$[23f] in acetonitrile having the same absorbance, the fluorescence intensity of **1** at 976 nm is higher by a factor 2.7, which supports the idea that the helical ligand framework in the trimetallic complex provides improved shielding of the metal ions.

Interestingly, the reaction conditions and the nature of counter anions used for the synthesis of these types of materials are critical. With the addition of Et_3N, the reaction of H_2L^1 with $Ln(NO_3)_3·6H_2O$ (4:5) (Ln = Nd^{III}) in MeOH heated to reflux gave the pentanuclear tetradecker lanthanide Schiff base complexes, formulated as $[Nd_5(L^1)_4(OH)_2(NO_3)_5MeOH]$ (**2**) (Scheme 6).[56] A view of the structure is shown in Figure 17. The two outer Nd^{III} ions, Nd(1) and Nd(5), have similar coordinate environments and each is bound to the O_2O_2 cavities of the outer Schiff base ligand. Nd(1) is nine coordinate and is surrounded by a total of nine O atoms, four O atoms from the L1 group, three O atoms from two NO_3^- anions, one O atom from the OH^- anion, and one O atom from the MeOH molecule. For Nd(5), an additional bidentate NO_3^- anion results in a coordination number of ten. The two inner Nd^{III} ions, Nd(2)

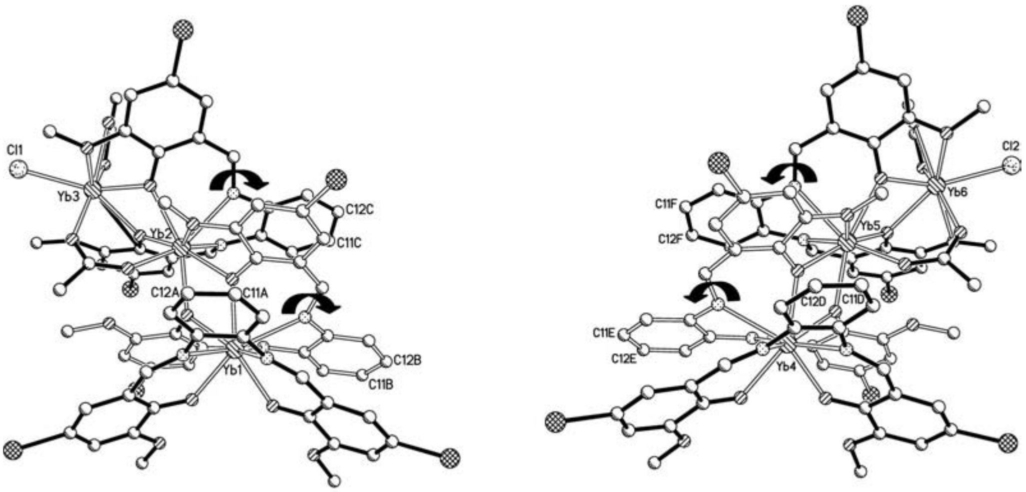


Figure 15. View of the two independent molecules of **1** present in the asymmetric unit. Reprinted with permission from ref.[55] Copyright 2008 American Chemical Society.

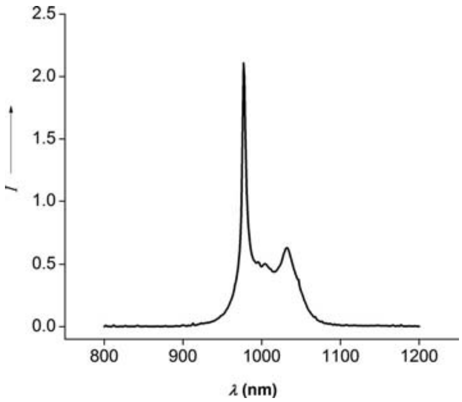
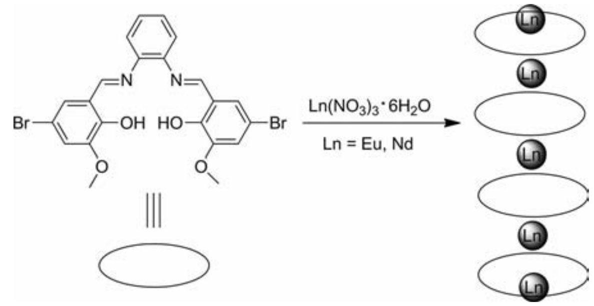


Figure 16. The NIR luminescence of **1** in CH_3CN at room temperature. Reprinted with permission from ref.[55] Copyright 2008 American Chemical Society.

and Nd(4), have similar nine-coordinate environments comprising the N_2O_2 donor set of one outer L^1 group, the O_2O_2 set of one inner L^1 group, and one bridged NO_3^- anion. The central Nd(3) ion has an eight-coordinate pseudo-square-based antiprismatic geometry formed by the two N_2O_2 donor sets of the internal L^1 ligands. The Nd–Nd separations are similar, 3.937 and 3.940 Å for Nd(2)–Nd(3) and Nd(3)–Nd(4), respectively, while they are 3.660 and 3.744 Å for Nd(1)–Nd(2) and Nd(4)–Nd(5), respectively. The inner two L^1 ligands are virtually planar, while the outer two L^1 ligands display a curved bowl-like configuration. Intramolecular π–π stacking interactions between phenylene units are found in the structure, which may further add to the stability of the complex (Figure 17). Upon excitation of the ligand-centered (L^1) absorption band, this complex shows NIR luminescence of the Nd^{III} ion ($^4F_{3/2}\rightarrow{}^4I_{j/2}$ transitions, j = 9, 11, 13) (Figure 18).



Scheme 6. Formation of pentanuclear tetradecker lanthanide complexes.

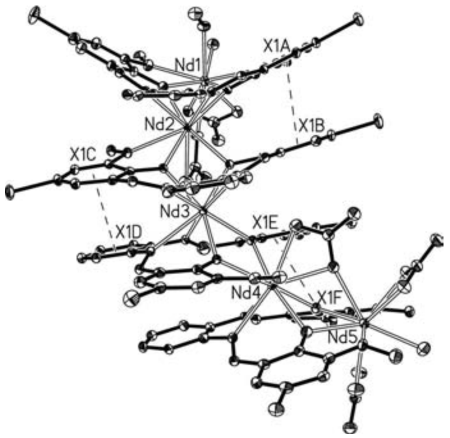


Figure 17. A view of the molecular structure of **2**. Hydrogen atoms are omitted for clarity. Intramolecular π–π stacking interactions: X1A···X1B: 3.705 Å, X1C···X1D: 3.619 Å, X1E···X1F: 3.731 Å.[56] Reproduced by permission of *The Royal Society of Chemistry.*

It should be noted that the skeletal adaptability and coordination flexibility of the ligands enable them to support a myriad of discrete molecular systems and extended net-

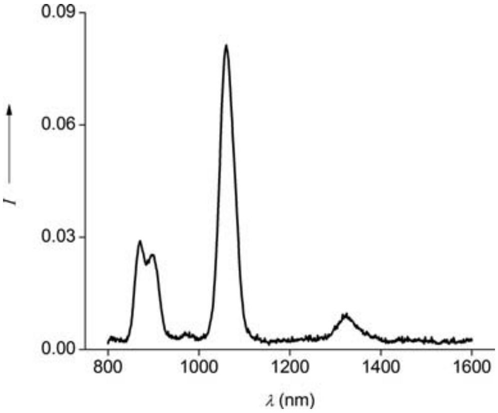


Figure 18. NIR luminescence of **2** in CH_3CN at room temperature.

work materials.[57] By applying more flexible Schiff base ligands H_2L^2 and H_2L^3, four 1D coordination lanthanide polymers $\{[Ln_2(L^2)_2(CF_3SO_3)(H_2L^2)_4(MeOH)]\cdot CF_3SO_3\}_n$ {Ln = Nd (**3**) and Er (**4**)}, $[Yb_2(L^2)_2(OAc)_2(MeOH)_2]_n$ (**5**), and $[Er_2(H_2L^3)(OAc)_6]_n$ (**6**) have been prepared and structurally characterized.[58] The stoichiometry and structures of these compounds are dependent on the Schiff base ligand employed in their syntheses as well as on the nature of the anion present ($CF_3SO_3^-$ vs. OAc^-). Complexes **3** and **4** are isomorphous. As shown in Figure 19, each Nd(1) ion is coordinated to a deprotonated salen group $(L^2)^{2-}$ and two neutral salen ligands H_2L^2, while Nd(2) is coordinated to three salen ligands and one $(L^2)^{2-}$ ligand. Nd(1) and Nd(2) are bridged by a neutral salen ligand with a separation of 10.171 Å to form a 1D polymeric structure. In **5**, each Yb^{III} ion is bound by the N_2O_2 cavity of a deprotonated salen ligand and is eight coordinate (Figure 20). Interestingly, the acetate (OAc^-) group is employed as a linker in the formation of 1D polymeric structures. In **6**, each Er atom is coordinated to one bidentate OAc^- anion (Figure 21). They are bridged by four other OAc^- anions with a separation of 3.985 Å. The 1D polymeric framework is completed by neutral Schiff base ligands (H_2L^3), which link the Er_2 units through the phenol and methoxy O atoms.

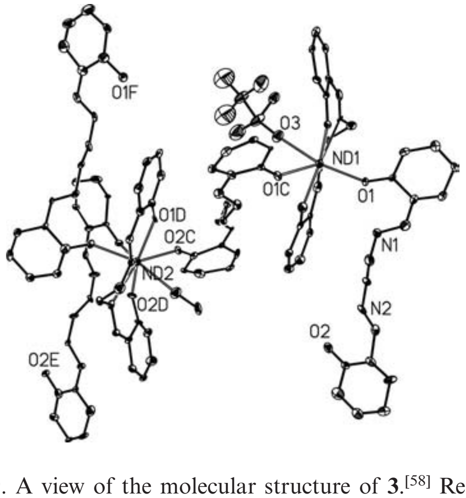


Figure 19. A view of the molecular structure of **3**.[58] Reproduced by permission of *The Royal Society of Chemistry.*

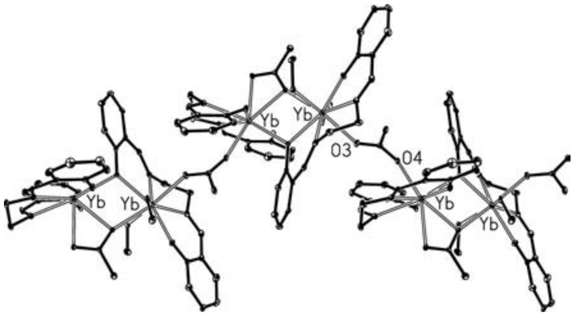


Figure 20. A view of the 1D polymeric chain in **5**.[58] Reproduced by permission of *The Royal Society of Chemistry.*

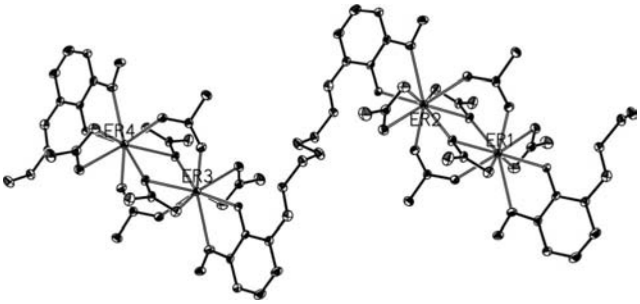
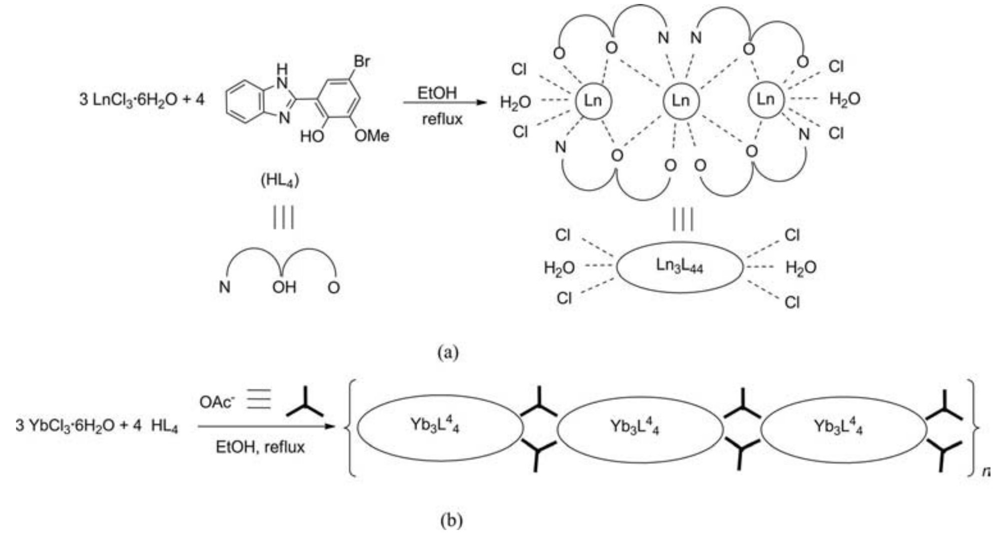


Figure 21. A view of the molecular structure of **6**.[58] Reproduced by permission of *The Royal Society of Chemistry.*

Benzimidazole-based ligands can be used to prepare luminescent lanthanide complexes with supramolecular architectures.[59] Planar benzimidazole-based ligands can engage in π–π stacking interactions and also exhibit ligand-to-metal energy transfer (LMET) properties in lanthanide complexes. Reaction of the benzimidazole-based ligand 2-(1*H*-benzoimidazol-2-yl)-4-bromo-6-methoxyphenol (HL^4) with $LnCl_3\cdot 6H_2O$ gave trinuclear complexes $[Ln_3(L^4)_4Cl_4(H_2O)_2]\cdot Cl$ {Ln = Yb (7) and Er (8)} [see Scheme 7(a)]. Under similar conditions, but in the presence of the OAc^- anion, complex $\{[Yb_3(L^4)_4(OAc)_4]\cdot Cl\}_n$ (9) can be isolated [Scheme 7(b)].[60] Complexes **7** and **8** are isomorphous. The structure of **7** contains three nonlinear Yb^{III} ions (Yb–Yb–Yb angle 141.15°) bound by four deprotonated $(L^4)^-$ ligands (Figure 22). The central Yb ion is eight coordinate and is bonded to six O atoms and two N atoms from the $(L^4)^-$ ligands. The terminal Yb ions are each bound to two Cl^- groups and a water molecule in addition to the $(L^4)^-$ ligands and are seven coordinate. The terminally bound Cl^- and H_2O groups appear to play a key role in the formation of a 3D open network since there are close Cl···H–O interactions that link adjacent molecules. The overall structure of the $Yb_3(L^4)_4$ core of **9** is similar to that of **7**, with the exception that each terminal Yb^{III} ion now bears a chelating OAc^- group (Figure 23). Interestingly, **9** crystallizes in the same space group (*P*4/*ncc*) and exhibits a similar crystal-packing behavior in the solid state as **7** and **8**. These three complexes have similar 3D open network structures. Complex **7** shows the NIR luminescence of the Yb^{3+} ion that is assigned to the $^2F_{5/2}\rightarrow{}^2F_{7/2}$ transition at 978 nm, and



Scheme 7. Formation of two lanthanide complexes: (a) complexes **7** and **8**; (b) complex **9**.

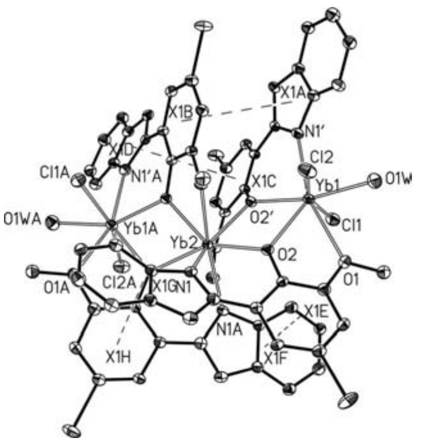


Figure 22. A view of the $Yb_3L^4_4$ core structure of **7**. Reprinted with permission from ref.[60] Copyright 2008 American Chemical Society.

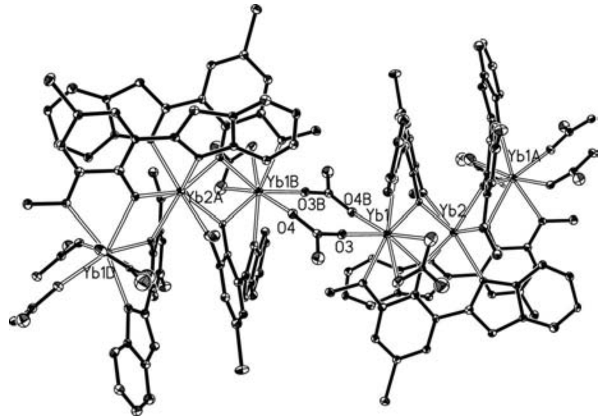


Figure 23. 1D coordination polymer structure of **9**. Reprinted with permission from ref.[60] Copyright 2008 American Chemical Society.

8 shows that of the Er^{III} ion that is attributable to the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition at about 1510 nm (Figure 24). It is noteworthy that **9** shows superior luminescence properties than **7**.

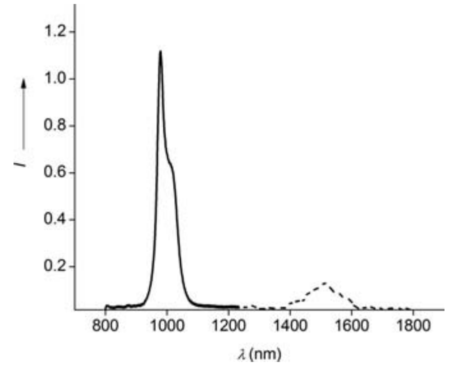


Figure 24. NIR emission spectra of **7** and **8** in CH_3CN at 298 K (solid line, **7**; dashed line, **8**).

Sensitizing the NIR Emission of Lanthanides (Nd^{III}, Yb^{III}, and Er^{III}) by $Zinc^{II}$ Schiff Base Complexes

Acyclic Schiff base derivatives represent a resourceful class of compartmental ligands that are prepared by self-condensation of appropriate formyl and amine precursors. The condensation reaction is simple and generally leads to the desired product in high yield. Metal Schiff base complexes have been shown to be effective emitters.[61] Furthermore, it has been shown that the electronic properties of transition-metal Schiff base complexes could be fine tuned by varying the steric and electronic nature of the spacer between the two imino groups and the substituents on the phenyl rings of the Schiff base ligand.[62] This would enable the tuning of the absorption and emission properties of transition metal Schiff base complexes. Taking advantage of the fact that the triplet state of a metal Schiff base lies at about 18000 cm^{-1}, it can act as antenna chromophores for lanthanide-ion sensitization.

Compartmental salen-type Schiff bases have two dissimilar metal-binding sites, one being specific for the d metal ion and the other for the f metal ion. Our recent studies have focused on the use of a variety of salen-style Schiff base ligands for the synthesis of NIR Zn–Ln complexes (Figure 25). Using the synthetic strategy shown in Scheme 8, we synthesized and structurally characterized a series of 3d–4f bimetallic Schiff base complexes with the general formula $[Zn(L')Ln(NO_3)_3(H_2O)]$ (Ln = La^{III}, Nd^{III}, Gd^{III}, Ho^{III}, Er^{III}, or Yb^{III}).[23f,23g,25e] Structural analyses reveal that the relatively soft transition-metal ion, Zn^{II}, is located in the inner N_2O_2 cavity, and the Ln^{III} ion in the outer O_4 cavity of the compartmental Schiff base ligand (Figures 26 and 27).

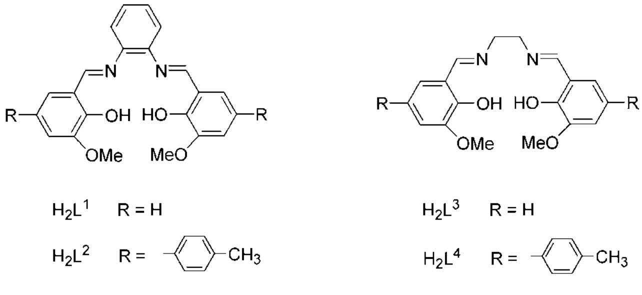


Figure 25. Structure of the Schiff base ligands H_2L^{1-4}.

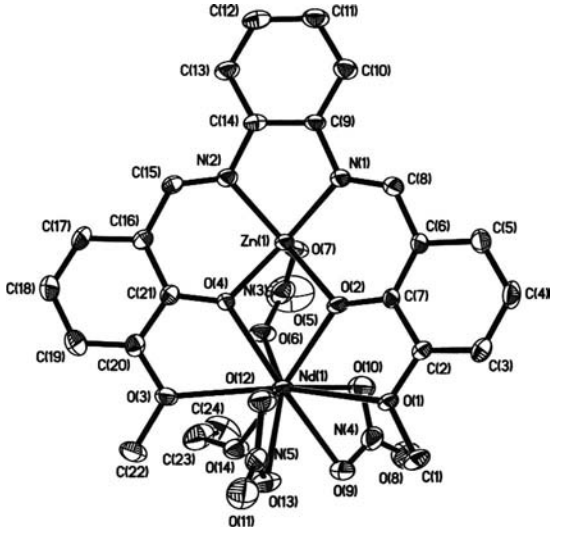


Figure 26. Crystal structure of $[Zn(\mu\text{-}L^1)Ln(NO_3)_3MeOH]$. Reprinted with permission from ref.[23f] Copyright 2008 American Chemical Society.

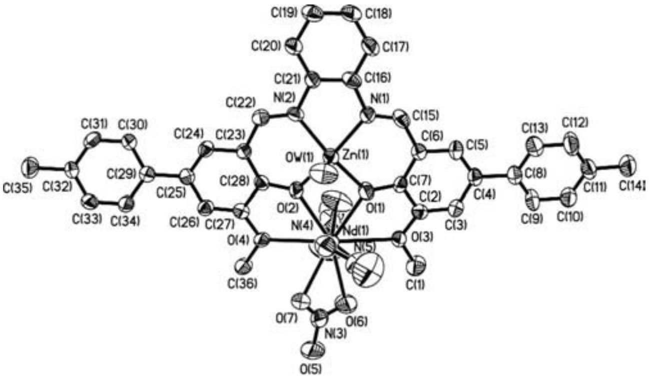
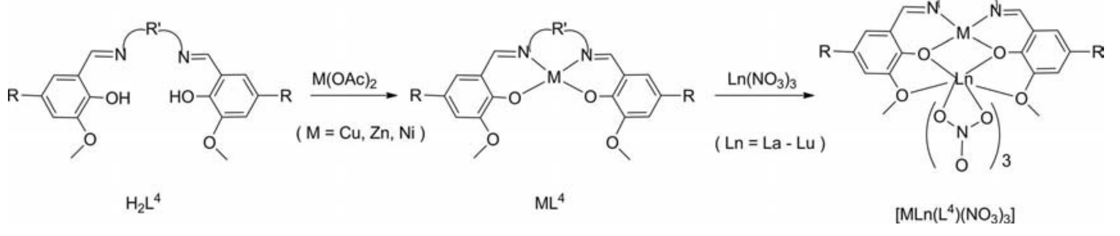


Figure 27. Crystal structure of $[Zn(\mu\text{-}L^2)Ln(NO_3)_3(H_2O)]$. Reprinted with permission from ref.[23f] Copyright 2008 American Chemical Society.

Photoluminescence studies also show that, in methanol solution, the Zn–Ln (Ln = Nd, Yb, or Er) Schiff base complexes exhibit emissions characteristic of the lanthanide(III) ion in the NIR region (Figure 28).[23f,23g,63] For the Zn–Nd complex, the emissions at 875 and 905 nm can be assigned to the $^4F^{3/2}\rightarrow^4I^{9/2}$ transition, 1068 nm to the $^4F^{3/2}\rightarrow^4I^{11/2}$ transition, and 1356 nm to the $^4F^{3/2}\rightarrow^4I^{13/2}$ transition of Nd^{III}. For the Zn–Er and Zn–Yb complexes, the emissions at 1515 and 976 nm can be assigned to the $^4I^{13/2}\rightarrow^4I^{15/2}$ transition of Er^{III} and the $^2F^{5/2}\rightarrow^2F^{7/2}$ transition of Yb^{III}, respectively. The luminescence lifetimes for Zn–Yb (monitored at 976 nm with approximately 10 μs) are similar to those of the coordinatively saturated Yb^{III} porphyrinate complexes (typically > 10 μs).[43b] Photophysical studies reveal that the NIR emissions of the Zn–Ln complexes (Ln = Nd, Er, and Yb) originate from the absorption corresponding to the Zn^{II} Schiff base complex.[23f,23g,63b] We have demonstrated that the Zn^{II} Schiff base complex is capable of generating an antenna effect for lanthanide(III) ions. The effectiveness of this effect depends on the structure of the complex, the nature of the lanthanide(III) ion, and the substituents on the Schiff base. The photophysical properties of the Schiff base complexes can be fine tuned by changing the linkage between the two Schiff base units or the electronic properties of the substituents on the flanking phenyl rings.[23f] By extending the conjugation through the substit-



Scheme 8. Preparation of $[MLn(L^4)(NO_3)_3]$ complexes.

uents, the absorption and emission spectra of the complexes are redshifted by about 20 nm. The effect is even more pronounced with the variation of the spacer. When the spacer is changed from an ethylene to a phenylene bridge, the emission maximum is redshifted by about 60 nm. For the Zn–Nd complexes with Schiff base ligands H_2L^{1-4}, NIR sensitization studies of the $[Zn(\mu\text{-}L')Nd(NO_3)_3(H_2O)_n]$ ($L' = L^1$, L^2, L^3 and L^4) complexes further show that Nd^{III} sensitization takes place via the ^{3}LC and ^{1}LC state when the spacer between the imine groups of the Schiff base ligand is an ethylene and a phenylene unit, respectively.[23f]

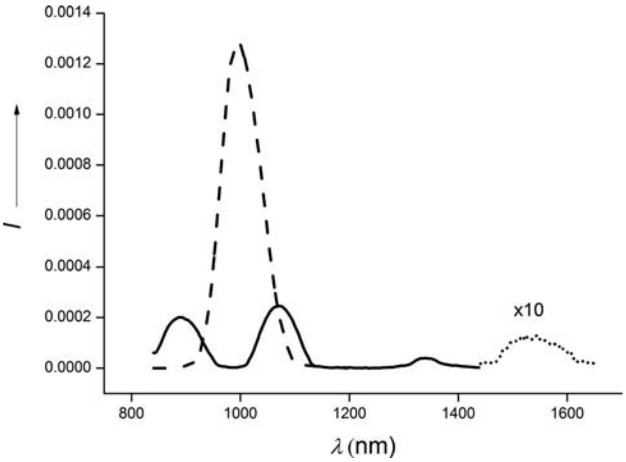
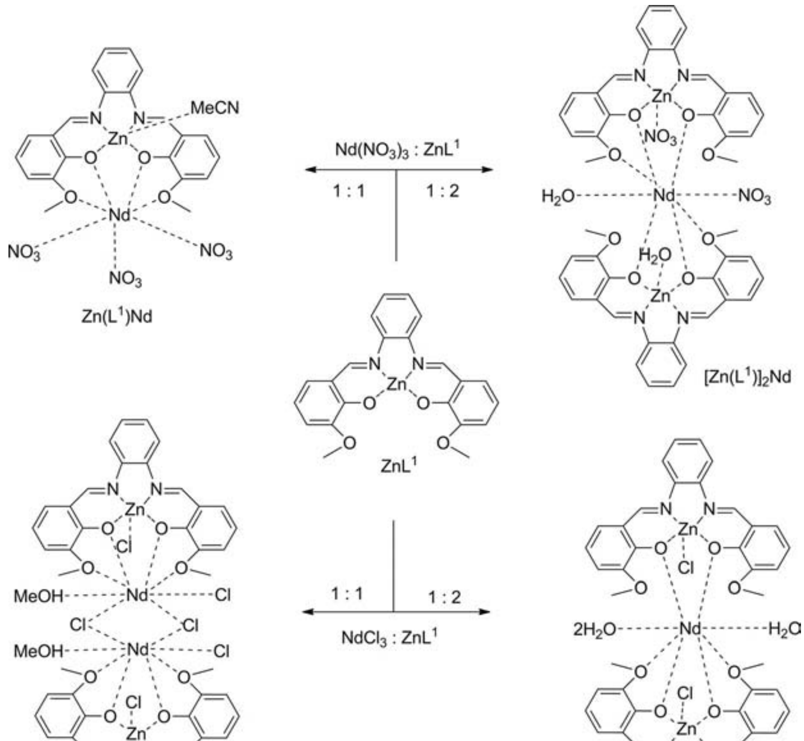


Figure 28. Room-temperature NIR emission of Nd (–), Er (----) and Yb (···) in CH_3OH upon excitation at 350 nm.

We further demonstrated that we could manipulate the nuclearity of the resulting complexes by varying (i) the ratio of the amounts of zinc Schiff base complexes to $LnX_3{\cdot}xH_2O$ and (ii) the nature of the anion X (Scheme 9).[63a] In trinuclear Zn_2Nd complexes $[Nd(ZnL^1)_2(NO_3)_2(H_2O)_2]{\cdot}NO_3$ and $[Nd(ZnL^1)_2Cl_2(H_2O)_3]{\cdot}Cl$, the Nd^{III} ion is sandwiched between the two ZnL^1 units, which are virtually parallel to each other (Figures 29 and 30). Although there is a Nd^{III} ion sandwiched between two ZnL moieties, the planar aromatic groups of each ligand are sufficiently close to each other to form intramolecular π–π stacking interaction in both molecules (the shortest distance between the aryl units is 3.498 Å). The structure of the tetranuclear Zn_2Nd_2 complex $[Nd_2(ZnL^1)_2Cl_6(MeOH)_2]$ comprises two $ZnNdL^1$ units linked together by two bridging Cl atoms bound to both Nd^{3+} ions (Figure 31). The Zn^{II} and Nd^{III} ions in this complex are located in the inner N_2O_2 and O_2O_2 cavities of each Schiff base ligand, respectively. The Nd–Nd separation is 4.477 Å, which effectively rules out the possibility of any π–π stacking between the aromatic groups of the ligands. For all these complexes, excitation of the ligand-centered absorption bands results in Nd^{III} NIR emission bands assigned to the $^4F_{3/2}\rightarrow{}^4I_{j/2}$ (j = 9, 11, 13) transitions. However, their luminescence proper-



Scheme 9. Syntheses of Zn–Nd complexes.

ties are dependent on both the coordination structures and outside solvent environment. In trinuclear Zn_2Nd complexes, the Nd^{III} ion is sandwiched between two ZnL^1 ligands and is fairly well protected from the outside solvent environment; as a result, its photophysical properties are less affected by outside solvent molecules.[63a]

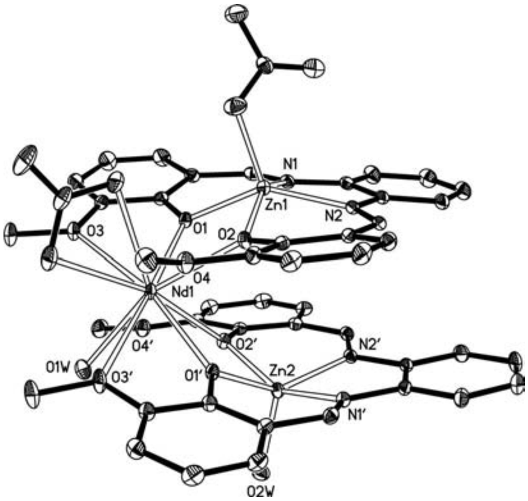


Figure 29. Crystal structure of trinuclear Zn_2Nd $[Nd(ZnL^1)_2(NO_3)_2(H_2O)_2]{\cdot}NO_3$. Reprinted with permission from ref.[63a] Copyright 2008 American Chemical Society.

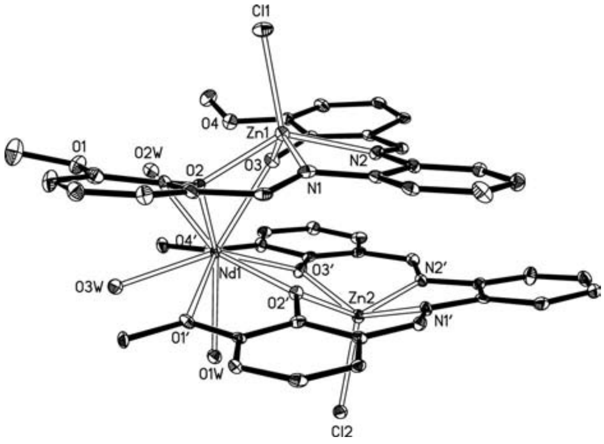


Figure 30. Crystal structure of trinuclear $[Nd(ZnL^1)_2Cl_2(H_2O)_3]{\cdot}Cl$. Reprinted with permission from ref.[63a] Copyright 2008 American Chemical Society.

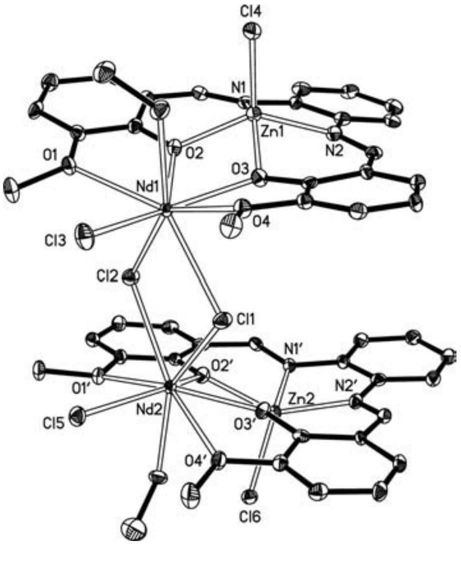
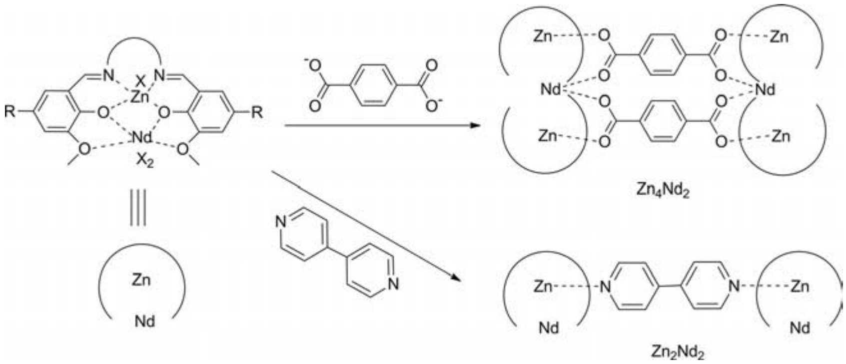


Figure 31. Crystal structure of tetranuclear Zn_2Nd_2 complex $[Nd_2(ZnL^1)_2Cl_6(MeOH)_2]$. Reprinted with permission from ref.[63a] Copyright 2008 American Chemical Society.

The nuclearity of 3d–4f Schiff base complexes can be manipulated by using different linkers to interact with the 3d–4f building blocks.[64] Recently, we have also shown that the di- and trinuclear 3d–4f complexes can be used as building blocks for making molecules of higher nuclearity by employing different linkers (Scheme 10).[65] The structures of these tetra- and hexanuclear 3d–4f complexes have been ascertained by X-ray crystallography. In the hexanuclear Zn–Nd complex $[Zn_4Nd_2L_4(1,4\text{-}BDC)_2]{\cdot}[Nd(NO_3)_5(H_2O)]$ (1,4-BDC = 1,4-benzenedicarboxylate), the use of the 1,4-BDC ligand results in the stabilization of two trimetallic Zn_2NdL_2 fragments instead of simple bimetallic 3d–4f units (Figure 32). The Zn ions are bound inside the O_2N_2 cavities of each L group, while the Nd ion is bound by the outer O_2O_2 sets of both L groups. Two BDC groups bridge the Zn_2Nd moieties such that each carboxylate group spans a Zn–Nd set. The ^1H NMR spectrum of this complex shows that the complex keeps the same bridged structure in solution as that in the solid state (Figure 33). This complex shows typical NIR emission bands of Nd^{III} assigned to the $^4F_{3/2}{\rightarrow}^4I_{j/2}$ (j = 9, 11, 13) transition upon excitation of the ligand-centered absorption band (Figure 34). Interestingly, this complex, in which the central metal ion is encapsulated by four chromophoric ligands and is shielded from solvent interactions, has superior luminescence properties than those of the related simple dinuclear Zn–Nd complex $[ZnNdL(OAc)(NO_3)_2]$.[23f,23g] With the same absorbance value at 275 nm, the relative emission intensity at 1068 nm is estimated to be 5 times higher than for the simple dinuclear Zn–Nd complex. The structure of the tetranuclear Zn–Nd complex $[Zn_2Nd_2(L^3)_2(4,4'\text{-}bpy)(NO_3)_6]$ (4,4′-bpy = 4,4′-bipyridine) is shown in Figure 35. In this complex, two independent Zn–Nd dimers are linked by one 4,4′-bipyridyl group. NIR luminescence studies show that the use of 4,4′-bipyridyl linkers does not only construct higher nuclearity Zn–Nd complexes but also improves their luminescence properties.

Following the same motivation of improving the NIR luminescence, two of the simplest ligands, with potentially dual binding sites, the linear ions cyanate (OCN^-) and thiocyanate (SCN^-) were selected to construct higher polynuclear species or multidimensional network structures. Reaction of the heterobimetallic 3d–4f precursor compounds $[ZnLn(L^3)(H_2O)(NO_3)_3]$ with potassium cyanate (KOCN) or ammonium thiocyanate (NH_4SCN) in acetonitrile heated to reflux, followed by filtration and slow evaporation of solution, produced analytically pure X-ray quality crystals of the new complexes after several weeks (Scheme 11).[66] Single-crystal X-ray diffraction studies con-



Scheme 10. Controlled design of multinuclear heterometallic 3d–4f complex.

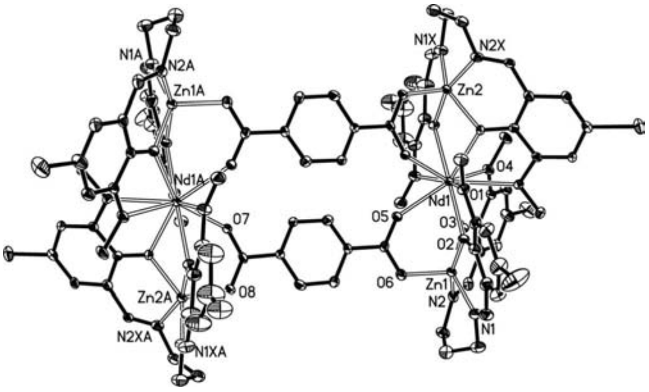


Figure 32. A view of the Zn_4Nd_6 core structure.[65a] Reproduced by permission of *The Royal Society of Chemistry.*

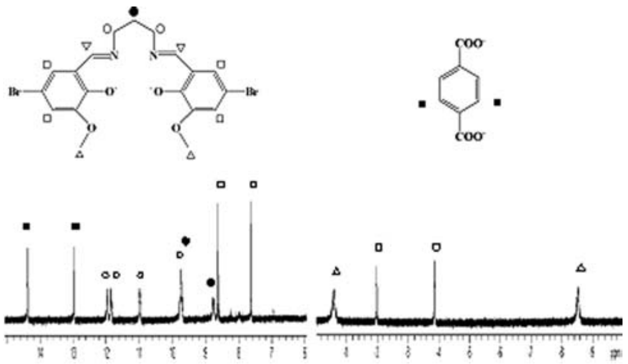


Figure 33. ^1H NMR spectrum of the Zn_4Nd_6 complex in CD_3OD.[65a] Reproduced by permission of *The Royal Society of Chemistry.*

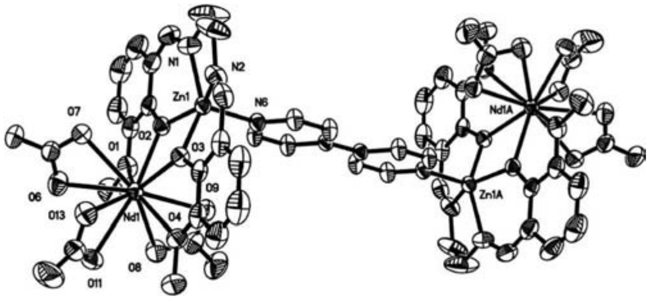


Figure 35. Crystal structure of $[Zn_2Nd_2(L^3)_2(4,4'\text{-bpy})(NO_3)_6]$. Reprinted from ref.[65b] with permission from Elsevier.

firm that a 1D framework species bridged by cyanate (OCN^-) in a zigzag chain and a trinuclear complex based on SCN^- were formed, formulated as $[ZnLn(L^3)(NO_3)_2(H_2O)(\mu\text{-}OCN)]_\infty$ and $[Zn_2Ln(L^3)_2(NO_3)(SCN)_2]$, respectively. The 1D polymeric structure of $[ZnLa(L^3)(NO_3)_2(H_2O)(\mu\text{-}OCN)]_\infty$ is shown in Figure 36. The OCN^-groups bridge the (L^3ZnLa) moieties through coordination of the N atom to Zn and the O atom to La, as expected from the hard/soft donor–acceptor properties of the ligand and the 3d and 4f metals. The structure of the trinuclear complex $[Zn_2Nd(L^3)_2(NO_3)(SCN)_2]$ is shown in Figure 37. Interestingly, since the S atom in SCN^- is much softer than the O atom in OCN^-, it does not coordinate with the hard Ln^{3+} ions in this complex. As a result, it does not show the 1D framework structure found in the complex with cyanate li-

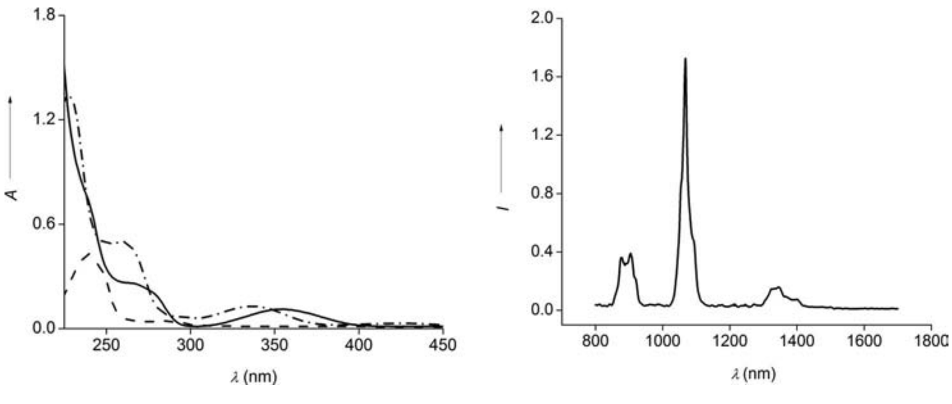
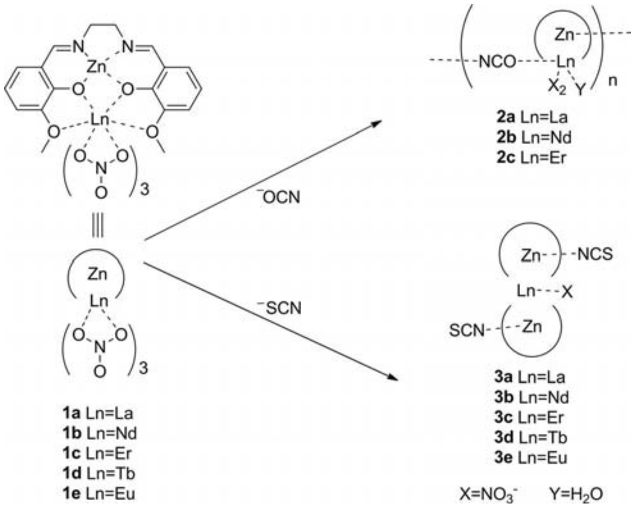


Figure 34. (left) Absorption spectra of the free ligands: BDC (dashed line), H_2L (dashed-dotted line), and Zn_4Nd_6 complex (solid line) in CH_3OH; (right) NIR luminescence of the Zn_4Nd_6 complex in CH_3OH.

gand. The photophysical properties of these complexes in solution are also reported. This work demonstrates that cyanato-bridged 1D 3d–4f polymeric or trinuclear 3d–4f–3d Schiff base complexes with enhanced luminescence properties can be formed from the corresponding bimetallic precursors by self-assembly.



Scheme 11. Synthesis of heterometallic 1D polymeric and trimetallic 3d–4f complexes.

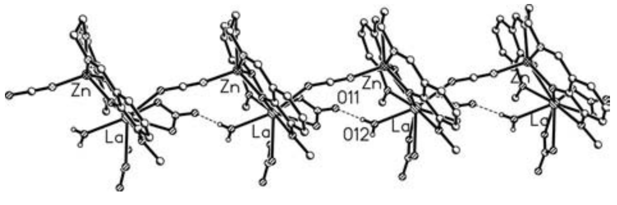


Figure 36. A view of the 1D polymeric chain in $[ZnLa(L^3)(NO_3)_2(H_2O)(\mu\text{-}OCN)]_\infty$.[66] Reproduced by permission of *The Royal Society of Chemistry.*

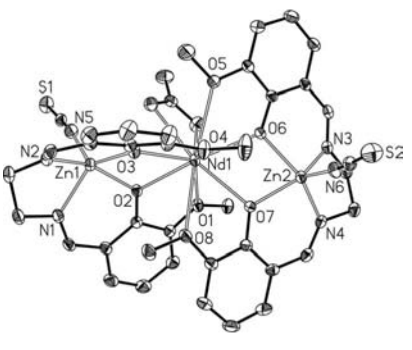


Figure 37. Crystal structure of the trinuclear complex $[Zn_2Nd(L^3)_2(NO_3)(SCN)_2]$.[66] Reproduced by permission of *The Royal Society of Chemistry.*

Conclusions

This review describes the synthetic route for the preparation of cationic or neutral lanthanide(III) monoporphyrinate complexes, as well as some bridging dinuclear complexes. Photoluminescence studies of lanthanide(III) porphyrinate complexes show that the porphyrinate anion can sensitize NIR emission of the Nd^{III}, Yb^{III}, and Er^{III} ions by serving as an antenna that absorbs visible light and transfers the energy to the excited state of the lanthanide(III) ion, which then relaxes through NIR emission. The NIR emission intensity increases as the number of O–H, N–H, and C–H oscillators within the molecules decreases. Several d–f heterobimetallic diporphyrin complexes, in which a Yb^{III} porphyrinate moiety is linked to a transition-metal (M = Zn, Pd, and Pt) porphyrinate moiety by a flexible three-carbon chain, are also presented. Fluorescence studies show that for these d–f diporphyrin dyads, in addition to the fact that the porphyrinate unit directly bonded to the Yb^{III} ion acts as an antenna, the [M(TPP)] moiety also serves as a donor by transferring its energy to the Yb^{III} ion, which enhances the NIR emission. As for the monophthalocyaninato lanthanide complexes capped by a tripodal anion, in addition to the visible fluorescence of the antenna, the complexes display either lanthanide-ion emission at ca. 1530 nm ($^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition of Er^{III}), which results from efficient ligand-to-metal energy transfer, or singlet oxygen ($^1O_2$) phosphorescence at 1270 nm without Yb^{III} ion emission when back energy transfer becomes significant and energy transfer to the emissive state is thus very inefficient. Further, a series of Gd^{III} porphyrinate complexes capped by the tripodal anion $L_{OMe}{}^-$ $\{L_{OMe}{}^- = (\eta^5\text{-}C_5H_5)Co[P(=O)(OMe)_2]_3{}^-\}$ were prepared. The electronic spectra reveal the NIR phosphorescence from the triplet state of the porphyrinate ligand and show a very characteristic vibronic structured emission. The Schiff base ligands, which are the most widely studied chelators, can also act as flexible linkers that feature N and O atom donors in f-block lanthanide frameworks. We constructed a series of larger multidecker, multimetallic lanthanide Schiff base assemblies by careful adjustment of the stoichiometry, anion selected and reaction conditions, which demonstrates that these varieties of "salen"-type Schiff base ligands can stabilize the Ln^{III} centers and provide the antenna for lanthanide luminescence. It should be noted that the multidecker framework can be effective in keeping solvent and water molecules away from the Ln^{III} centers, and enhanced NIR luminescence can be achieved because of the decreasing energy of the vibrational oscillators located in the surroundings of the emitting ion. Given the characteristic absorption and emission properties of transition-metal Schiff base complexes, multinuclear and polynuclear Zn^{II}–Ln^{III} Schiff base complexes have also been constructed with improved luminescence properties.

However, exploration of organic ligands or transition-metal chromophores to sensitize NIR luminescence remains a real challenge because of the intrinsically weak f–f transitions. On the other hand, almost every field of our present technological society needs the help of lanthanide luminescence. In order to obtain effective and useful materials based on lanthanide ions, we must further focus on the design and synthesis of ligands or d block chromophores, which are easily obtained and thermally stable with the lanthanide metal complexes and have better energy transfer to the lanthanide ions.

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[1] a) E. G. Moore, A. P. S. Samuel, K. N. Raymond, *Acc. Chem. Res.* **2009**, *42*, 542–552; b) V. Alexander, *Chem. Rev.* **1995**, *95*, 273–342.

[2] a) F. Zapata, A. Caballero, A. Espinosa, A. Tarraga, P. Molina, *Eur. J. Inorg. Chem.* **2010**, 697–703; b) B. M. van der Ende, L. Aarts, A. Meijerink, *Phys. Chem. Chem. Phys.* **2009**, *11*, 11081–11095; c) M. R. Ganjali, B. Veismohammadi, M. Hosseini, P. Norouzi, *Spectrochim. Acta Part A* **2009**, *74*, 575–578; d) Y. Lu, Y. Xu, Y. G. Li, E. B. Wang, X. X. Xu, Y. Ma, *Inorg. Chem.* **2006**, *45*, 2055–2060; e) H. C. Yang, C. Y. Li, H. He, Y. Tao, J. H. Xu, Q. Su, *J. Lumin.* **2006**, *118*, 61–69; f) E. Rukmini, C. K. Jayasankar, *Opt. Mater.* **1995**, *4*, 529–546.

[3] a) J. Wu, G. L. Wang, D. Y. Jin, J. L. Yuan, Y. F. Guan, J. Piper, *Chem. Commun.* **2008**, 365–367; b) Q. Xin, W. L. Li, W. M. Su, T. L. Li, Z. S. Su, B. Chu, B. Li, *J. Appl. Phys.* **2007**, *101*, 044512; c) J. S. Zhang, Z. D. Hao, X. Zhang, Y. S. Luo, X. G. Ren, X. J. Wang, J. H. Zhang, *J. Appl. Phys.* **2009**, *106*, 113918; d) C. S. Stan, D. Sibiescu, M. S. Secula, I. Rosca, I. Cretescu, *Mater. Plast.* **2010**, *47*, 324–327.

[4] Y. Hasegawa, T. Nakagawa, T. Kawai, *Coord. Chem. Rev.* **2010**, *254*, 2643–2651.

[5] a) G. L. Law, C. Man, D. Parker, J. W. Walton, *Chem. Commun.* **2010**, *46*, 2391–2393; b) R. Pal, D. Parker, *Org. Biomol. Chem.* **2008**, *6*, 1020–1033; c) R. A. Poole, C. P. Montgomery, E. J. New, A. Congreve, D. Parker, M. Bottab, *Org. Biomol. Chem.* **2007**, *5*, 2055–2062; d) A. Beeby, S. W. Botchway, I. M. Clarkson, S. Faulkner, A. W. Parker, D. Parker, J. A. G. Williams, *J. Photochem. Photobiol. B: Biology* **2000**, *57*, 83–89.

[6] a) B. F. Moore, G. A. Kumar, M. C. Tan, J. Kohl, R. E. Riman, M. G. Brik, T. J. Emge, J. G. Brennan, *J. Am. Chem. Soc.* **2011**, *133*, 373–378; b) W. S. Perry, S. J. A. Pope, C. Allain, B. J. Coe, A. M. Kenwright, S. Faulkner, *Dalton Trans.* **2010**, *39*, 10974–10983; c) S. Dang, J. B. Yu, X. F. Wang, Z. Y. Guo, L. N. Sun, R. P. Deng, J. Feng, W. Q. Fan, H. J. Zhang, *J. Photochem. Photobiol. A: Chem.* **2010**, *214*, 152–160; d) B. Branchi, P. Ceroni, V. Balzani, F. G. Klarner, F. Vogtle, *Chem. Eur. J.* **2010**, *16*, 6048–6055; e) M. Correa-Ascencio, E. K. Galvan-Miranda, F. Rascon-Cruz, O. Jimenez-Sandoval, S. J. Jimenez-Sandoval, R. Cea-Olivares, V. Jancik, R. A. Toscana, V. Garcia-Montalvo, *Inorg. Chem.* **2010**, *49*, 4109–4116; f) F. F. Chen, Z. Q. Chen, Z. Q. Bian, C. H. Huang, *Coord. Chem. Rev.* **2010**, *254*, 991–1010; g) O. M. G. Zucchi, P. Thuery, F. Gumy, J. C. G. Bünzli, M. Ephritikhine, *Chem. Eur. J.* **2009**, *15*, 9686–9696; h) G. Accorsi, G. Verri, M. Bolognesi, N. Armaroli, C. Clementi, C. Miliani, A. Romani, *Chem. Commun.* **2009**, 3392–3394; i) J. Zhang, C. M. Shade, D. A. Chengelis, S. Petoud, *J. Am. Chem. Soc.* **2007**, *129*, 14834–14835; j) M. Albrecht, O. Osetska, R. Frohlich, J. C. G. Bünzli, A. Aebischer, F. Gumy, J. Hamacek, *J. Am. Chem. Soc.* **2007**, *129*, 14178–14179; k) 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.* **2007**, *129*, 11491–11504; l) T. Lazarides, T. L. Easun, C. Veyne-Marti, W. Z. Alsindi, M. W. George, N. Deppermann, C. A. Hunter, H. Adams, M. D. Ward, *J. Am. Chem. Soc.* **2007**, *129*, 4014–4027; m) R. F. Ziessel, G. Ulrich, L. Charbonniere, D. Imbert, R. Scopelliti, J. C. G. Bünzli, *Chem. Eur. J.* **2006**, *12*, 5060–5067; n) J. C. G. Bünzli, *Acc. Chem. Res.* **2006**, *39*, 53–61; o) P. Coppo, M. Duati, V. N. Kozhevnikov, J. W. Hofstraat, L. De Cola, *Angew. Chem.* **2005**, *117*, 1840; *Angew. Chem. Int. Ed.* **2005**, *44*, 1806–1810; p) S. Arenz, A. Babai, K. Binnemans, K. Driesen, R. Giernoth, A. V. Mudring, P. Nockemann, *Chem. Phys. Lett.* **2005**, *402*, 75–79; q) D. Guo, C. Y. Duan, F. Lu, Y. Hasegawa, Q. J. Meng, S. Yanagida, *Chem. Commun.* **2004**, 1486–1487; r) D. Imbert, M. Cantuel, J. C. G. Bünzli, G. Bernardinelli, C. Piguet, *J. Am. Chem. Soc.* **2003**, *125*, 15698–15699; s) T. S. Kang, B. S. Harrison, T. J. Foley, A. S. Knefely, J. M. Boncella, J. R. Reynolds, K. S. Schanze, *Adv. Mater.* **2003**, *15*, 1093–1097; t) V. Vicinelli, P. Ceroni, M. Maestri, V. Balzani, M. Gorka, F. Vogtle, *J. Am. Chem. Soc.* **2002**, *124*, 6461–6468; u) F. R. G. E. Silva, O. L. Malta, C. Reinhard, H. U. Gudel, C. Piguet, J. E. Moser, J. C. G. Bünzli, *J. Phys. Chem. A* **2002**, *106*, 1670–1677; v) B. S. Harrison, T. J. Foley, M. Bouguettaya, J. M. Boncella, J. R. Reynolds, K. S. Schanze, J. Shim, P. H. Holloway, G. Padmanaban, S. Ramakrishnan, *Appl. Phys. Lett.* **2001**, *79*, 3770–3772; w) Y. Korovin, N. Rusakova, *Rev. Inorg. Chem.* **2001**, *21*, 299–329; x) M. H. V. Werts, R. H. Woudenberg, P. G. Emmerink, R. van Gassel, J. W. Hofstraat, J. W. Verhoeven, *Angew. Chem.* **2000**, *112*, 4716; *Angew. Chem. Int. Ed.* **2000**, *39*, 4542–4544; y) H. A. Alvarez, J. R. Matos, P. C. Isolani, G. Vicentini, E. E. Castellano, J. Zukerman-Schpector, *J. Coord. Chem.* **1998**, *43*, 349–360.

[7] a) J. C. G. Bünzli, S. V. Eliseeva, *J. Rare Earth* **2010**, *28*, 824–842; b) J. Feng, S. Y. Song, R. P. Deng, W. Q. Fan, H. J. Zhang, *Langmuir* **2010**, *26*, 3596–3600; c) X. Y. Li, Z. J. Si, C. L. Pan, L. Zhou, Z. F. Li, X. N. Li, J. K. Tang, H. J. Zhang, *Inorg. Chem. Commun.* **2009**, *12*, 675–677; d) J. C. G. Bünzli, S. Comby, A. S. Chauvin, C. D. B. Vandevyver, *J. Rare Earth* **2007**, *25*, 257–274; e) J. C. G. Bunzli, C. Piguet, *Chem. Soc. Rev.* **2005**, *34*, 1048–1077; f) L. N. Sun, H. J. Zhang, L. S. Fu, F. Y. Liu, Q. G. Meng, C. Y. Peng, J. B. Yu, *Adv. Funct. Mater.* **2005**, *15*, 1041–1048; g) F. X. Zang, Z. R. Hong, W. L. Li, M. T. Li, X. Y. Sun, *Appl. Phys. Lett.* **2004**, *84*, 2679–2681; h) D. Ananias, A. Ferreira, L. D. Carlos, J. Rocha, *Adv. Mater.* **2003**, *15*, 980–985; i) J. K. R. Weber, J. J. Felten, B. Cho, P. C. Nordine, *Nature* **1998**, *393*, 769–771.

[8] a) T. Koullourou, L. S. Natrajan, H. Bhavsar, S. J. A. Pope, J. H. Feng, J. Narvainen, R. Shaw, E. Scales, R. Kauppinen, A. M. Kenwright, S. Faulkner, *J. Am. Chem. Soc.* **2008**, *130*, 2178–2179; b) J. Zhang, S. Petoud, *Chem. Eur. J.* **2008**, *14*, 1264–1272; c) K. Aita, T. Temma, Y. Kuge, H. Saji, *Luminescence* **2007**, *22*, 455–461; d) S. Faulkner, S. J. A. Pope, B. P. Burton-Pye, *Appl. Spectrosc. Rev.* **2005**, *40*, 1–31; e) A. Nonat, D. Imbert, J. Pecaut, M. Giraud, M. Mazzanti, *Inorg. Chem.* **2009**, *48*, 4207–4218; f) A. Fratini, G. Richards, E. Larder, S. Swavey, *Inorg. Chem.* **2008**, *47*, 1030–1036.

[9] a) N. Sabbatini, M. Guardigli, I. Manet, R. Ungaro, A. Casnati, R. Ziessel, G. Ulrich, Z. Asfari, J. M. Lehn, *Pure Appl. Chem.* **1995**, *67*, 135–140; b) Z. Q. Chen, F. Ding, Z. Q. Bian, C. H. Huang, *Org. Electron.* **2010**, *11*, 369–376; c) D. Li, F. F. Chen, Z. Q. Bian, Z. W. Liu, Y. L. Zhao, C. H. Huang, *Polyhedron* **2009**, *28*, 897–902; d) A. S. Chauvin, S. Comby, B. Song, C. D. B. Vandevyver, J. C. G. Bünzli, *Chem. Eur. J.* **2008**, *14*, 1726–1739; e) S. Comby, D. Imbert, A. S. Chauvin, J. C. G. Bünzli, *Inorg. Chem.* **2006**, *45*, 732–743; f) M. P. Oude Wolbers, F. C. J. M. van Veggel, B. H. M. Snellink-Ruël, J. W. Hofstraat, F. A. J. Geurts, D. N. Reinhoudt, *J. Chem. Soc. Perkin Trans. 2* **1998**, 2141–2150; g) M. H. V. Werts, J. W. Hofstraat, F. A. J. Geurts, J. W. Verhoeven, *Chem. Phys. Lett.* **1997**, *276*, 196–201.

[10] 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**, 5577–5583.

[11] a) M. H. V. Werts, J. W. Verhoeven, J. W. Hofstraat, *J. Chem. Soc. Perkin Trans. 2* **2000**, 433–439; b) M. Halim, M. S. Tremblay, S. Jockusch, N. J. Turro, D. Sames, *J. Am. Chem. Soc.* **2007**, *129*, 7704–7705; c) G. A. Hebbink, L. Grave, L. A. Wold-

ering, D. N. Reinhoudt, F. C. J. M. van Veggel, *J. Phys. Chem. A* **2003**, *107*, 2483–2491.

[12] a) L. Ning, M. I. Trioni, G. P. Brivio, *J. Mater. Chem.* **2007**, *17*, 4464–4470; b) I. Oueslati, R. A. S. Ferreira, L. D. Carlos, C. Baleizao, M. N. Berberan-Santos, B. de Castro, J. Vicens, U. Pischel, *Inorg. Chem.* **2006**, *45*, 2652–2660; c) G. M. Davies, R. J. Aarons, G. R. Motson, J. C. Jeffery, H. Adams, S. Faulkner, M. D. Ward, *Dalton Trans.* **2004**, 1136–1144; d) S. I. Klink, G. A. Hebbink, L. Grave, F. G. A. Peters, F. C. J. M. Van Veggel, D. N. Reinhoudt, J. W. Hofstraat, *Eur. J. Org. Chem.* **2000**, 1923–1931; e) A. Beeby, I. M. Clarkson, R. S. Dickins, S. Faulkner, D. Parker, L. Royle, A. S. de Sousa, J. A. G. Williams, M. Woods, *J. Chem. Soc. Perkin Trans. 2* **1999**, 493–503.

[13] a) S. Yanagida, Y. Hasegawa, K. Murakoshi, Y. Wada, N. Nakashima, T. Yamanaka, *Coord. Chem. Rev.* **1998**, *171*, 461–480; b) G. A. Hebbink, D. N. Reinhoudt, F. C. J. M. van Veggel, *Eur. J. Org. Chem.* **2001**, 4101–4106; c) Y. Hasegawa, Y. Kimura, K. Murakoshi, Y. Wada, J.-H. Kim, N. Nakashima, T. Yamanaka, S. Yanagida, *J. Phys. Chem.* **1996**, *100*, 10201–10205; d) Y. Hasegawa, T. Ohkubo, K. Sogabe, Y. Kawamura, Y. Wada, N. Nakashima, S. Yanagida, *Angew. Chem.* **2000**, *112*, 365; *Angew. Chem. Int. Ed.* **2000**, *39*, 357–360.

[14] G. F. de Sa, O. L. Malta, C. D. Donega, A. M. Simas, R. L. Longo, P. A. Santa-Cruz, E. F. da Silva, *Coord. Chem. Rev.* **2000**, *196*, 165–195.

[15] a) W. X. Li, W. J. Chai, X. J. Sun, T. Ren, X. Y. Shi, *J. Lumin.* **2010**, *130*, 873–880; b) A. Balamurugan, M. L. P. Reddy, M. Jayakannan, *J. Phys. Chem. B* **2009**, *113*, 14128–14138; c) X. F. Qiao, B. Yan, *J. Organomet. Chem.* **2009**, *694*, 3232–3241; d) L. Guo, W. X. Li, X. Y. Shi, X. J. Sun, X. L. Sun, *J. Lumin.* **2009**, *129*, 639–644; e) B. Yan, X. F. Qiao, *Photochem. Photobiol.* **2007**, *83*, 971–978; f) B. Yan, D. H. Ma, *J. Solid State Chem.* **2006**, *179*, 2059–2066.

[16] a) N. Viola-Villegas, R. P. Doyle, *Coord. Chem. Rev.* **2009**, *253*, 1906–1925; b) A. Chaudhary, R. V. Singh, *Rev. Inorg. Chem.* **2008**, *28*, 35–75; c) R. D. Hancock, D. L. Melton, J. M. Harrington, F. C. McDonald, R. T. Gephart, L. L. Boone, S. B. Jones, N. E. Dean, J. R. Whitehead, G. M. Cockrell, *Coord. Chem. Rev.* **2007**, *251*, 1678–1689; d) N. E. Borisova, M. D. Reshetova, Y. A. Ustynyuk, *Chem. Rev.* **2007**, *107*, 46–79; e) L. Di Bari, P. Salvadori, *Coord. Chem. Rev.* **2005**, *249*, 2854–2879; f) W. Radecka-Paryzek, V. Patroniak, J. Lisowski, *Coord. Chem. Rev.* **2005**, *249*, 2156–2175; g) E. L. Hegg, J. N. Burstyn, *Coord. Chem. Rev.* **1998**, *173*, 133–165; h) J. W. Steed, C. P. Johnson, C. L. Barnes, R. K. Juneja, J. L. Atwood, S. Reilly, R. L. Hollis, P. H. Smith, D. L. Clark, *J. Am. Chem. Soc.* **1995**, *117*, 11426–11433; i) F. Arnaudneu, *Chem. Soc. Rev.* **1994**, *23*, 235–241.

[17] a) A. Bodi, K. E. Borbas, J. I. Bruce, *Dalton Trans.* **2007**, 4352–4358; b) K. E. Borbas, J. I. Bruce, *Org. Biomol. Chem.* **2007**, *5*, 2274–2282; c) K. Senechal-David, S. J. A. Pope, S. Quinn, S. Faulkner, T. Gunnlaugsson, *Inorg. Chem.* **2006**, *45*, 10040–10042; d) T. Gunnlaugsson, J. P. Leonard, *Chem. Commun.* **2005**, 3114–3131; e) R. S. Dickins, D. Parker, J. I. Bruce, D. J. Tozer, *Dalton Trans.* **2003**, 1264–1271.

[18] S. I. Klink, H. Keizer, F. C. J. M. van Veggel, *Angew. Chem.* **2000**, *112*, 4489; *Angew. Chem. Int. Ed.* **2000**, *39*, 4319–4321.

[19] a) X. L. Li, L. X. Shi, L. Y. Zhang, H. M. Wen, Z. N. Chen, *Inorg. Chem.* **2007**, *46*, 10892–10900; b) F. Kennedy, N. M. Shavaleev, T. Koullourou, Z. R. Bell, J. C. Jeffery, S. Faulkner, M. D. Ward, *Dalton Trans.* **2007**, 1492–1499; c) 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.* **2006**, *12*, 9299–9313; d) H. B. Xu, L. X. Shi, E. Ma, L. Y. Zhang, Q. H. Wei, Z. N. Chen, *Chem. Commun.* **2006**, 1601–1603; e) N. M. Shavaleev, G. Accorsi, D. Virgili, D. R. Bell, T. Lazarides, G. Calogero, N. Armaroli, M. D. Ward, *Inorg. Chem.* **2005**, *44*, 61–72; f) N. M. Shavaleev, L. P. Moorcraft, S. J. A. Pope, Z. R. Bell, S. Faulkner, M. D. Ward, *Chem. Eur. J.* **2003**, *9*, 5283–5291.

[20] a) M. V. Lopez, S. V. Eliseeva, J. M. Blanco, G. Rama, M. R. Bermejo, M. E. Vazquez, J. C. G. Bunzli, *Eur. J. Inorg. Chem.* **2010**, 4532–4545; b) M. D. Ward, *Coord. Chem. Rev.* **2010**, *254*, 2634–2642; c) R. A. Vigato, V. Peruzzo, S. Tamburini, *Coord. Chem. Rev.* **2009**, *253*, 1099–1201; d) S. G. Baca, H. Adams, C. S. Grange, A. P. Smith, I. Sazanovich, M. D. Ward, *Inorg. Chem.* **2007**, *46*, 9779–9789.

[21] P. Khandagale, R. Chikate, S. B. Joshi, B. A. Kulkarni, *J. Alloys Compd.* **2005**, *392*, 112–119.

[22] A. Beeby, R. S. Dickins, S. FitzGerald, L. J. Govenlock, C. L. Maupin, D. Parker, J. P. Riehl, G. Siligardi, J. A. G. Williams, *Chem. Commun.* **2000**, 1183–1184.

[23] a) S. Akine, F. Utsuno, T. Taniguchi, T. Nabeshima, *Eur. J. Inorg. Chem.* **2010**, 3143–3152; b) X. Q. Lu, W. X. Feng, Y. N. Hui, T. Wei, J. R. Song, S. S. Zhao, W. Y. Wong, W. K. Wong, R. A. Jones, *Eur. J. Inorg. Chem.* **2010**, 2714–2722; c) W. Y. Bi, T. Wei, X. Q. Lu, Y. I. Hui, J. R. Song, S. S. Zhao, W. K. Wong, R. A. Jones, *New J. Chem.* **2009**, *33*, 2326–2334; d) M. Albrecht, O. Osetska, J. C. G. Bunzli, F. Gumy, R. Frohlich, *Chem. Eur. J.* **2009**, *15*, 8791–8799; e) K. Binnemans, *J. Mater. Chem.* **2009**, *19*, 448–453; f) 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.* **2006**, *45*, 9315–9325; g) W. K. Lo, W. K. Wong, J. P. Guo, W. Y. Wong, K. F. Li, K. W. Cheah, *Inorg. Chim. Acta* **2004**, *357*, 4510–4521; h) W. E. Silva, S. Alves, R. F. De Farias, *J. Coord. Chem.* **2004**, *57*, 967–971; i) C. Saudan, V. Balzani, M. Gorka, S. K. Lee, J. Van Heyst, M. Maestri, P. Ceroni, V. Vicinelli, F. Vogtle, *Chem. Eur. J.* **2004**, *10*, 899–905; j) J. C. Boyer, F. Vetrone, J. A. Capobianco, A. Speghini, M. Bettinelli, *J. Appl. Phys.* **2003**, *93*, 9460–9465.

[24] C. E. Plecnik, S. M. Liu, X. N. Chen, E. A. Meyers, S. G. Shore, *J. Am. Chem. Soc.* **2004**, *126*, 204–213.

[25] a) B. Raju, B. N. Sivasankar, *J. Therm. Anal. Calorim.* **2008**, *94*, 289–296; b) M. Ferhi, K. Horchani-Naifer, M. Ferid, *J. Lumin.* **2008**, *128*, 1777–1782; c) R. B. Fu, S. M. Hu, X. T. Wu, *Cryst. Growth Des.* **2007**, *7*, 1134–1144; d) L. Vikram, B. N. Sivasankar, *Indian J. Chem. Sect. A* **2006**, *45*, 864–871; e) X. P. Yang, R. A. Jones, Q. Y. Wu, M. M. Oye, W. K. Lo, W. K. Wong, A. L. Holmes, *Polyhedron* **2006**, *25*, 271–278; f) J. R. Sharmila, B. N. Sivasankar, *J. Therm. Anal. Calorim.* **2004**, *78*, 933–940; g) H. S. He, X. J. Zhu, A. X. Hou, J. P. Guo, W. K. Wong, W. Y. Wong, K. F. Li, K. W. Cheah, *Dalton Trans.* **2004**, 4064–4073; h) D. M. L. Goodgame, A. M. Menzer, S. Menzer, A. J. P. White, D. J. Williams, *Inorg. Chim. Acta* **2003**, *355*, 314–321; i) R. Rolli, K. Gatterer, M. Wachtler, M. Bettinelli, A. Speghini, D. Ajo, *Spectrochim. Acta Part A* **2001**, *57*, 2009–2017; j) J. C. Liu, Z. G. Song, L. F. Wang, J. H. Zhuang, X. Y. Huang, *Acta Chem. Scand.* **1999**, *53*, 90–94.

[26] a) J. S. Lindsey, *Acc. Chem. Res.* **2010**, *43*, 300–311; b) G. M. A. Rahman, A. Troeger, V. Sgobba, D. M. Guldi, N. Jux, M. N. Tchoul, W. T. Ford, A. Mateo-Alonso, M. Prato, *Chem. Eur. J.* **2008**, *14*, 8837–8846; c) J. P. Bearinger, G. Stone, A. T. Christian, L. Dugan, A. L. Hiddessen, K. J. J. Wu, L. Wu, J. Hamilton, C. Stockton, J. A. Hubbell, *Langmuir* **2008**, *24*, 5179–5184; d) V. Sgobba, G. Giancane, S. Conoci, S. Casilli, G. Ricciardi, D. M. Guldi, M. Prato, L. Valli, *J. Am. Chem. Soc.* **2007**, *129*, 3148–3156; e) T. Mizutani, S. Yagi, *J. Porphyrins Phthalocyanines* **2004**, *8*, 226–237; f) D. Dini, M. Hanack, *J. Porphyrins Phthalocyanines* **2004**, *8*, 915–933; g) A. de la Escosura, M. V. Martinez-Diaz, P. Thordarson, A. E. Rowan, R. J. M. Nolte, T. Torres, *J. Am. Chem. Soc.* **2003**, *125*, 12300–12308; h) W. T. Huang, H. Xiang, Q. H. Gong, Y. Y. Huang, C. H. Huang, J. Z. Jiang, *Chem. Phys. Lett.* **2003**, *374*, 639–644; i) A. Tsuda, A. Osuka, *Adv. Mater.* **2002**, *14*, 75–79; j) M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature* **1998**, *395*, 151–154.

[27] a) C. Jahier, M. F. Coustou, M. Cantuel, N. D. McClenaghan, T. Buffeteau, D. Cavagnat, M. Carraro, S. Nlate, *Eur. J. Inorg. Chem.* **2011**, 727–738; b) F. Jaouen, E. Proietti, M. Lefevre, R. Chenitz, J. P. Dodelet, G. Wu, H. T. Chung, C. M. Johnston, P.

Zelenay, *Energy Environ. Sci.* **2011**, *4*, 114–130; c) M. O. Senge, *Chem. Commun.* **2011**, *47*, 1943–1960; d) C. Monnereau, J. N. Rebilly, O. Reinaud, *Eur. J. Org. Chem.* **2011**, 166–175; e) A. B. Sorokin, E. V. Kudrik, *Catal. Today* **2011**, *159*, 37–46; f) L. Carlucci, G. Ciani, S. Maggini, D. M. Proserpio, F. Ragaini, E. Gallo, M. Ranocchiari, A. Caselli, *J. Porphyrins Phthalocyanines* **2010**, *14*, 804–814.

[28] a) R. M. Wang, Y. F. Zhu, Y. F. He, Y. Li, C. W. Mao, N. P. He, *Prog. Chem.* **2010**, *22*, 1952–1963; b) M. Voicescu, R. Ion, A. Meghea, *J. Serb. Chem. Soc.* **2010**, *75*, 333–341; c) W. Zhao, B. Tong, J. G. Zhi, Y. X. Pan, J. B. Shen, Y. P. Dong, *Prog. Chem.* **2009**, *21*, 2625–2634.

[29] G. E. Khalil, E. K. Thompson, M. Gouterman, J. B. Callis, L. R. Dalton, N. J. Turro, S. Jockusch, *Chem. Phys. Lett.* **2007**, *435*, 45–49.

[30] a) H. S. He, M. Dubey, A. G. Sykes, P. S. May, *Dalton Trans.* **2010**, *39*, 6466–6474; b) K. P. Birin, Y. G. Gorbunova, A. Y. Tsivadze, *Magn. Reson. Chem.* **2010**, *48*, 505–515; c) H. S. He, A. G. Sykes, P. S. May, G. S. He, *Dalton Trans.* **2009**, 7454–7461; d) X. J. Zhu, F. L. Jiang, C. T. Poon, W. K. Wong, W. Y. Wong, *Eur. J. Inorg. Chem.* **2008**, 3151–3162; e) S. Lipstman, S. Muniappan, S. George, I. Goldberg, *Dalton Trans.* **2007**, 3273–3281; f) S. Muniappan, S. Lipstman, S. George, I. Goldberg, *Inorg. Chem.* **2007**, *46*, 5544–5554; g) S. T. Fu, X. J. Zhu, G. J. Zhou, W. Y. Wong, C. Ye, W. K. Wong, Z. Y. Li, *Eur. J. Inorg. Chem.* **2007**, 2004–2013; h) J. B. Oh, M. K. Nah, Y. H. Kim, M. S. Kang, J. W. Ka, H. K. Kim, *Adv. Funct. Mater.* **2007**, *17*, 413–424; i) R. Pizzoferrato, T. Ziller, R. Paolesse, F. Mandoj, A. Micozzi, A. Ricci, C. Lo Sterzo, *Chem. Phys. Lett.* **2006**, *426*, 124–128; j) K. Padmaja, W. J. Youngblood, L. Y. Wei, D. F. Bocian, J. S. Lindsey, *Inorg. Chem.* **2006**, *45*, 5479–5492; k) X. Y. Cao, Q. S. Li, A. Moritz, Z. Z. Xie, M. Dolg, X. B. Chen, W. H. Fang, *Inorg. Chem.* **2006**, *45*, 3444–3451; l) J. B. Oh, Y. H. Kim, M. K. Nah, H. K. Kim, *J. Lumin.* **2005**, *111*, 255–264; m) G. Bergamini, C. Saudan, P. Ceroni, M. Maestri, V. Balzani, M. Gorka, S. K. Lee, J. van Heyst, F. Vogtle, *J. Am. Chem. Soc.* **2004**, *126*, 16466–16471; n) J. Sokolnicki, R. Wiglusz, S. Radzki, A. Graczyk, J. Legendziewicz, *Opt. Mater.* **2004**, *26*, 199–206; o) D. L. Andrews, D. S. Bradshaw, *J. Chem. Phys.* **2004**, *121*, 2445–2454; p) H. S. He, W. K. Wong, K. F. Li, K. W. Cheah, *Synth. Met.* **2004**, *143*, 81–87; q) H. S. He, Z. X. Zhao, W. K. Wong, K. F. Li, J. X. Meng, K. W. Cheah, *Dalton Trans.* **2003**, 980–986; r) J. Z. Jiang, Y. Z. Bian, F. Furuya, W. Liu, M. T. M. Choi, N. Kobayashi, H. W. Li, Q. C. Yang, T. C. W. Mak, D. K. P. Ng, *Chem. Eur. J.* **2001**, *7*, 5059–5069; s) J. P. Collman, J. L. Kendall, J. L. Chen, K. A. Collins, J. C. Marchon, *Inorg. Chem.* **2000**, *39*, 1661–1667; t) R. Koerner, M. M. Olmstead, A. Ozarowski, S. L. Phillips, P. M. Van Calcar, K. Winkler, A. L. Balch, *J. Am. Chem. Soc.* **1998**, *120*, 1274–1284; u) S. F. Lincoln, *Coord. Chem. Rev.* **1997**, *166*, 255–289; v) J. Lisowski, J. L. Sessler, V. Lynch, T. D. Mody, *J. Am. Chem. Soc.* **1995**, *117*, 2273–2285.

[31] J. W. D. Horrocks, C. P. Wong, R. F. Venteicher, E. G. Hove, *Proc. Rare Earth Res. Conf. 12th*, **1976**, *1*, 241.

[32] a) R. Pizzoferrato, R. Francini, S. Pietrantoni, R. Paolesse, F. Mandoj, A. Monguzzi, F. Meinardi, *J. Phys. Chem. A* **2010**, *114*, 4163–4168; b) N. M. Shavaleev, R. Scopelliti, F. Gumy, J. C. G. Bunzli, *Inorg. Chem.* **2009**, *48*, 7937–7946; c) H. S. He, P. S. May, D. Galipeau, *Dalton Trans.* **2009**, 4766–4771; d) H. Ke, W. K. Wong, W. Y. Wong, H. L. Tam, C. T. Poon, F. Jiang, *Eur. J. Inorg. Chem.* **2009**, 1243–1247; e) H. S. He, A. G. Sykes, *Inorg. Chem. Commun.* **2008**, *11*, 1304–1307; f) H. S. He, A. G. Sykes, D. Galipeau, S. W. Ng, M. Ropp, *Inorg. Chem. Commun.* **2008**, *11*, 1051–1053; g) H. B. Xu, L. Y. Zhang, Z. H. Chen, L. X. Shi, Z. N. Chen, *Dalton Trans.* **2008**, 4664–4670; h) A. X. Hou, Z. Xue, Y. Liu, S. S. Qu, W. K. Wong, *Chem. Biodiversity* **2007**, *4*, 2889–2899; i) W. K. Wong, X. Zhu, W. Y. Wong, *Coord. Chem. Rev.* **2007**, *251*, 2386–2399; j) F. L. Jiang, W. K. Wong, X. J. Zhu, G. J. Zhou, W. Y. Wong, P. L. Wu, H. L. Tam, K. W. Cheah, C. Ye, Y. Liu, *Eur. J. Inorg. Chem.* **2007**, 3365–3374; k) C. Pitois, A. Hult, M. Lindgren, *J. Lumin.* **2005**, *111*, 265–283; l) H. S. He, W. K. Wong, J. P. Guo, K. F. Li, W. Y. Wong, W. K. Lo, K. W. Cheah, *Inorg. Chim. Acta* **2004**, *357*, 4379–4388; m) R. Pizzoferrato, L. Lagonigro, T. Ziller, A. Di Carlo, R. Paolesse, F. Mandoj, A. Ricci, C. Lo Sterzo, *Chem. Phys.* **2004**, *300*, 217–225; n) T. J. Foley, B. S. Harrison, A. S. Knefely, K. A. Abboud, J. R. Reynolds, K. S. Schanze, J. M. Boncella, *Inorg. Chem.* **2003**, *42*, 5023–5032.

[33] C.-P. Wong, R. F. Venteicher, W. DeW. Horrocks Jr., *J. Am. Chem. Soc.* **1974**, *96*, 7149–7150.

[34] a) C. O. Schaverien, A. G. Orpen, *Inorg. Chem.* **1991**, *30*, 4968–4978; b) C. J. Schaverien, *J. Chem. Soc., Chem. Commun.* **1991**, 458.

[35] a) B. S. H. T. J. Foley, A. S. Knefely, K. A. Abboud, J. R. Reynolds, K. S. Schanze, J. M. Boncella, *Inorg. Chem.* **2003**, *42*, 5023–5032; b) T. J. Foley, K. A. Abboud, J. M. Boncella, *Inorg. Chem.* **2002**, *41*, 1704–1706.

[36] a) W. K. Wong, L. Zhang, F. Xue, T. C. W. Mak, *J. Chem. Soc., Dalton Trans.* **1999**, 3053–3062; b) 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**, 3092–3098; c) W. K. Wong, L.-L. Zhang, W. T. Wong, F. Xue, T. C. W. Mak, *J. Chem. Soc., Dalton Trans.* **1999**, 615–622; d) H. S. He, W. K. Wong, K. F. Li, K. W. Cheah, *Synth. Met.* **2004**, *143*, 81–87.

[37] G. A. Spyroulias, A. Despotopoulos, C. P. Raptopoulou, A. Terzis, A. G. Coutsolelos, *Chem. Commun.* **1997**, 783–784.

[38] W. D. Horrocks Jr., C.-P. Wong, *J. Am. Chem. Soc.* **1976**, *98*, 7157–7162.

[39] D. D. E. M. Gouterman, *The Porphyrins*, Vol. III, Academic Press, New York, **1978**, ch. 1.

[40] Q. F. Zhang, T. C. H. Lam, X. Y. Yi, E. Y. Y. Chan, W. Y. Wong, H. H. Y. Sung, I. D. Williams, W. H. Leung, *Chem. Eur. J.* **2004**, *10*, 101–111.

[41] I. Lopes, R. Dias, A. Domingos, N. Marques, *J. Alloys Compd.* **2002**, *344*, 60–64.

[42] H. S. He, W. K. Wong, J. P. Guo, K. F. Li, W. Y. Wong, W. K. Lo, K. W. Cheah, *Aust. J. Chem.* **2004**, *57*, 803–810.

[43] a) X. J. Zhu, W. K. Wong, W. K. Lo, W. Y. Wong, *Chem. Commun.* **2005**, 1022–1024; b) H. S. He, J. P. Guo, Z. X. Zhao, W. K. Wong, W. Y. Wong, W. K. Lo, K. F. Li, L. Luo, K. W. Cheah, *Eur. J. Inorg. Chem.* **2004**, 837–845.

[44] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, Wiley, New York, **1999**, p. 1109.

[45] M. H. V. Werts, J. W. Hofstraat, F. A. J. Geurts, J. W. Verhoeven, *Chem. Phys. Lett.* **1997**, *276*, 196–201.

[46] J. X. Meng, T. K. Li, W. K. Wong, K. W. Cheah, *Appl. Phys. Lett.* **2000**, *77*, 2795–2797.

[47] X. J. Zhu, P. Wang, H. W. C. Leung, W.-K. Wong, W.-Y. Wong, D. W. J. Kwong, *Chem. Eur. J.* **2011**, *17*, 7041–7052.

[48] T. Ishii, K. Ogasawara, H. Adachi, I. Tanaka, *J. Chem. Phys.* **2001**, *115*, 492–508.

[49] a) A. Strasser, A. Vogler, *Chem. Phys. Lett.* **2003**, *379*, 287–290; b) A. Strasser, A. Vogler, *Inorg. Chim. Acta* **2004**, *357*, 2345–2348.

[50] N. M. Shavaleev, L. P. Moorcraft, S. J. A. Pope, Z. R. Bell, S. Faulkner, M. D. Ward, *Chem. Commun.* **2003**, 1134–1135.

[51] a) N. Ishikawa, Y. Kaizu, *Coord. Chem. Rev.* **2002**, *226*, 93–101; b) P. H. Zhu, N. Pan, R. I. J. Li, J. M. Dou, Y. Zhang, D. Y. Y. Cheng, D. Q. Wang, D. K. P. Ng, J. Z. Jiang, *Chem. Eur. J.* **2005**, *11*, 1425–1432; c) N. Ishikawa, T. Iino, Y. Kaizu, *J. Phys. Chem. A* **2003**, *107*, 7879–7884; d) M. Latva, H. Takalo, V. M. Mukkala, C. Matachescu, J. C. RodriguezUbis, J. Kankare, *J. Lumin.* **1997**, *75*, 149–169.

[52] G. Knör, *Inorg. Chem.* **1996**, *35*, 7916–7918.

[53] a) R. J. Hill, D. L. Long, P. Hubberstey, M. Schroder, N. R. Champness, *J. Solid State Chem.* **2005**, *178*, 2414–2419; b) K. Kuriki, Y. Koike, Y. Okamoto, *Chem. Rev.* **2002**, *102*, 2347–2356.

[54] X. P. Yang, R. A. Jones, *J. Am. Chem. Soc.* **2005**, *127*, 7686–7687.

[55] X. P. Yang, R. A. Jones, M. M. Oye, A. L. Holmes, W. K. Wong, *Cryst. Growth Des.* **2006**, *6*, 2122–2125.

[56] X. P. Yang, R. A. Jones, W. K. Wong, *Dalton Trans.* **2008**, 1676–1678.

[57] P. Teo, T. S. A. Hor, *Coord. Chem. Rev.* **2011**, *255*, 273–289.

[58] X. P. Yang, R. A. Jones, J. H. Rivers, W. K. Wong, *Dalton Trans.* **2009**, 10505–10510.

[59] A. Liao, X. P. Yang, J. M. Stanley, R. A. Jones, B. J. Holliday, *J. Chem. Crystallogr.* **2010**, *40*, 1060–1064.

[60] X. P. Yang, R. A. Jones, M. J. Wiester, M. M. Oye, W. K. Wong, *Cryst. Growth Des.* **2010**, *10*, 970–976.

[61] Y. Hamada, T. Sano, M. Fujita, T. Fujii, Y. Nishio, K. Shibata, *Jpn. J. Appl. Phys.* **1993**, *32*, L511–L513.

[62] S. DiBella, I. Fragala, I. Ledoux, M. A. DiazGarcia, T. J. Marks, *J. Am. Chem. Soc.* **1997**, *119*, 9550–9557.

[63] a) 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.* **2006**, *45*, 4340–4345; b) W. K. Wong, H. Z. Liang, W. Y. Wong, Z. W. Cai, K. F. Li, K. W. Cheah, *New J. Chem.* **2002**, *26*, 275–278.

[64] a) M. Andruh, *Chem. Commun.* **2007**, 2565–2577; b) J. Long, L. M. Chamoreau, V. Marvaud, *Dalton Trans.* **2010**, *39*, 2188–2190.

[65] a) X. P. Yang, R. A. Jones, W. K. Wong, V. Lynch, M. M. Oye, A. L. Holmes, *Chem. Commun.* **2006**, 1836–1838; b) X. Q. Lu, W. Y. Bi, W. L. Chai, J. R. Song, J. X. Meng, W. Y. Wong, W. K. Wong, X. P. Yang, R. A. Jones, *Polyhedron* **2009**, *28*, 27–32.

[66] S. S. Zhao, X. Q. Lu, A. X. Hou, W. Y. Wong, W. K. Wong, X. P. Yang, R. A. Jones, *Dalton Trans.* **2009**, 9595–9602.

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