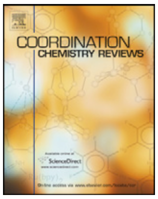
Coordination Chemistry Reviews 252 (2008) 2512–2527

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

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



Review

Recent developments in the field of supramolecular lanthanide luminescent sensors and self-assemblies

Cidália M.G. dos Santos, Andrew J. Harte, Susan J. Quinn, Thorfinnur Gunnlaugsson*

School of Chemistry, Centre for Synthesis and Chemical Biology, Trinity College Dublin, Dublin 2, Ireland

Contents

ARTICLE INFO

Article history:
Received 26 March 2008
Accepted 28 July 2008
Available online 22 August 2008

Keywords:
Lanthanide luminescence
Self-assembly
NIR
Europium
Terbium
Ytterbium
Neodymium
Erbium
Sensors
Chemosensors
Anions
Cations
Self-assemblies
f–f-Assemblies
f–d-Assemblies
Metal directed synthesis

ABSTRACT

The lanthanide ions possess long lived excited states, which can be populated by sensitizing antennae, and emit at long wavelengths in the visible and the near infrared (NIR) regions. These are particularly desirable features for: (a) sensing as it overcomes drawbacks such as light scattering and auto fluorescence associated with short wavelength emitting sensors and (b) for probing metal directed synthesis of large supramolecular systems often formed between f–f or f–d metal ions. This review article focuses on some of the recent work published in the areas of lanthanide luminescent sensing of ions and molecules, and the formation of self-assembly structures. These examples are based on the use of structurally defined organic (or coordination) ligands which complement (either as a single ligands or through metal-directed self-assembly formation between several ligands) the coordination requirements of lanthanide ions. Examples of ligands that can either in a step-wise manner or simultaneously bind lanthanide and transition metal ions will also be discussed.

1. Introduction

The development of luminescent signalling systems is highly topical within the field of supramolecular chemistry [1–3]. Luminescence (output), generated from excited state species can be modulated by external perturbation (or inputs) be it chemical (ions and/or molecules)[4–6] or physical, *e.g.* by using light [7,8], heat [9], etc. Such modulation has been used to develop and study many elegant supramolecular systems such as switches, sensors, etc. The attractiveness of using luminescence to study supramolecular function lies in the fact that emission can be generated through energy transfer or electron transfer processes from

---

* Corresponding author. Tel.: +353 1 896 3459; fax: +353 1 671 2826.
E-mail address: gunnlaut@tcd.ie (T. Gunnlaugsson).

0010-8545/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2008.07.018

either purely organic, *i.e.* aromatic chromophores or conjugated systems, or from inorganic coordination complexes and conjugates [10]. The use of lanthanide f-ions such as Eu(III), Tb(III), Sm(III), Yb(III), Nd(III), etc. in such luminescent supramolecular systems, has become a very active area of research [11–13]. From the view of developing luminescent chemical sensors, changes in various photophysical properties such as wavelength, lifetimes and quantum yield (the outputs) can all be modulated as a result of external perturbation. This phenomenon can also be employed to investigate the formation and physical properties of complexed supramolecular structures and self-assemblies [14]. These properties of the lanthanides have been the scope of many reviews [15] and we would like to draw the readers attention to the work of Tsukube and co-workers [16], Parker and co-workers [17], Bünzli [12,18], de Sá et al. [19], Piguet and co-workers [20], Ward [21] and Faulkner and Matthews [22], to name just a few. The scope of this review is, however, to discuss some of the more recent work in the area of luminescence supramolecular chemistry. This review begins with a short introduction to some of the physical and photophysical properties of the lanthanide. Next, examples of lanthanide based luminescent switches and sensors where the emission is modulated by the presence of cations and anions is considered. Finally, supramolecular systems where changes in the lanthanide emission are used to probe the structural nature of metal directed self-assemblies will be discussed.

2. Some of the physical properties of lanthanides

The 15 elements from lanthanum to lutetium with access to their 4f shell are known as the lanthanides. They are all hard, electropositive metals and the nature of their 4f shells imparts some unique properties to the lanthanides [23]. The electronic shielding of the f electrons is quite weak and hence as one proceeds from La to Lu the increasing atomic number or nuclear charge causes a decrease in the radii of the atoms, which is known as the lanthanide contraction. The lanthanides are easily oxidised and favour the III+ oxidation state with few exceptions. Since the f orbitals are buried within the atom they interact only very weakly with ligand orbitals. As a result the f → f transitions, which occur in the visible region of the spectrum, give rise to very narrow bands and the lifetimes of their excited states are quite long lived (μs–ms) [24].

In this review article, the luminescent properties of the lanthanide ions such as Eu(III), Tb(III), Nd(III) and Yb(III) will be given particular attention. As stated, systems which utilise lanthanide luminescence as reporters, or luminescent signalling moieties, have some significant advantages over analogous fluorescent systems allowing them to overcome the auto-fluorescence and light scattering of body tissue [24,25]. Their long lived excited states (ms for Eu(III) and Tb(III)) allows the short-lived background fluorescence to disperse before the lanthanide emission occurs. Moreover, the long wavelengths at which lanthanides emit (500–750 nm for Eu(III)) occur beyond the absorbance of body tissue, which is important for signal quality. Furthermore, ions such as Yb(III) and Nd(III) emit at even longer wavelengths in the near infrared part of the spectrum, which is particularly attractive for diagnostic applications [26]. The lanthanides line-like emission bands (~10 nm bandwidth) can also give a rise to better signal to noise ratio compared to fluorescent bands (several hundred nm). Furthermore, some of these are considered, as in the case of Eu(III), hypersensitive to changes in either the coordination or the magnetic properties of the lanthanide ‘environment’ (coordination sphere). This gives rise to significant changes in the intensity, or the appearances of the lanthanide emission, all of which can be used to quantify the number or the nature of the ‘input’ [27,28].

In order for lanthanide emission to occur, the lanthanide ion must first be elevated into an excited state. Direct excitation of a lanthanide ion is not easily achieved, as it requires a Laporte forbidden f–f transition (low extinction coefficient $\varepsilon \sim 5\text{–}10\,\mathrm{M^{-1}\,cm^{-1}}$). As a result lanthanides are usually “photophysically silent” and have low molar absorbancies. However, this problem can be circumvented *via* indirect excitation by a sensitizing chromophore or “*antenna*” (Fig. 1A) [29]. Excitation of the antenna(e) can pass this energy onto the lanthanide ion by an energy transfer process. The indirect excitation of a lanthanide ion is best illustrated by a Jablonski diagram (Fig. 1B). The sensitizing antenna, denoted Ar, absorbs a photon of energy $h\nu$, and is excited to its singlet excited state, ^{1}Ar. From here the energy can be passed into the antennas triplet excited state, ^{3}Ar, *via* intersystem crossing (ISC). The lanthanide's excited state, *Ln, can now be populated from the antennas triplet state, by means of an intramolecular energy transfer (ET), provided that this triplet state is higher in energy than the lanthanide excited state [30]. The excited energy now resides within the lanthanide ion, and can be lost by emission of light, resulting in the characteristic lanthanide emission spectra with each transition corresponding to an emission band. Though singlet and triplet excited states share a common geometry where their potential energy curves intersect, intersystem crossing from a S_1 to T_1 state is a spin forbidden process. However, the presence of the lanthanide ions improves the efficiency of this process due to the heavy atom affect of the lanthanide, which gives rise to a significant amount of spin–orbit

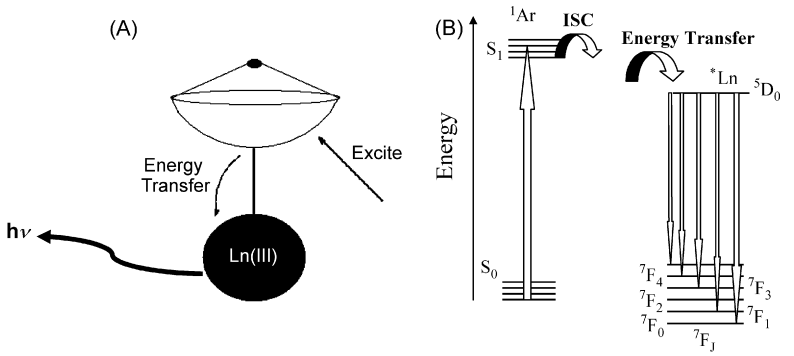
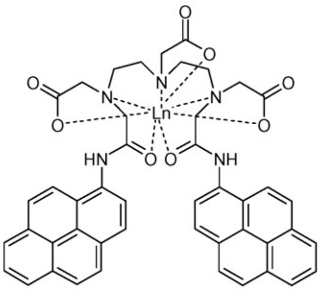


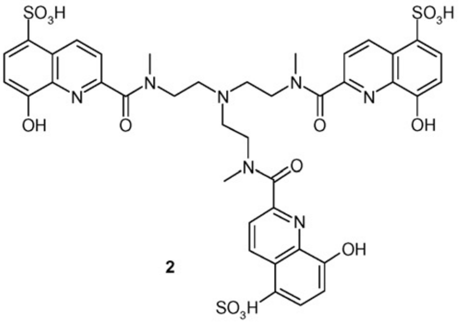
Fig. 1. (A) Indirect lanthanide excitation, or sensitization, involving the excitation of the antenna, followed by energy transfer to the lanthanide ion resulting in a lanthanide emission. (B) Jablonski diagram illustrating sensitization of a lanthanide ion. Other deactivation (energy loss) pathways have been omitted for clarity.

coupling which provides a mechanism for intersystem crossing from the S_1 to T_1 state.

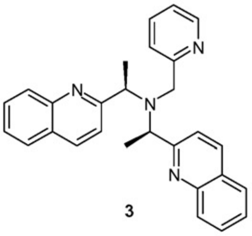
Recent examples of antenna sensitized lanthanide luminescence developed for a range of applications include systems **1**–**4**. Complex **1** was developed by Pope, who used a diethylenetriaminepentaacetic acid (DTPA) core as the lanthanide chelating ligand that was appended with two pyrenyl chromophores by amide bonds [31]. Excitation of these antennae resulted in efficient energy transfer to the excited states of NIR-emitting ions such as Er(III), Nd(III) and Yb(III) in ethanol. A related system is **2**, recently developed by Bünzli and co-workers and involved the use of an 8-hydrozxyquinolinate based tripodal platform [32]. Here the antennae sensitized the Nd(III), Er(III) and Yb(III) ions in HBS buffered aqueous solution at pH 7.4. Such tripodal ligands have recently been explored for the use in the construction of anion sensors using Eu(III) based emission and chiral quinoline ligands. Examples include that of Tsukube and co-workers, who developed **3** for the recognition of Cl^- after the formation of a Eu(III) complex between **3** and $Eu(NO_3)_3$ through coordination of the pyridyl nitrogen atoms [33]. Another recent example is compound **4** that was developed by Parker and co-workers and employed for intracellular imaging upon excitation at 355 nm [34].



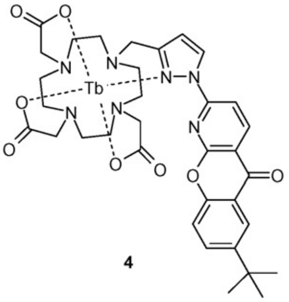
1
Ln = Er(III), Nd(III) and Yb(III)



2



3



4

The mechanism for energy transfer from the $^3Ar \rightarrow {}^*Ln$ state is somewhat debated. One possible mechanism is the Förster energy transfer mechanism, which involves overlap of energy levels [35]. In the Förster mechanism energy transfer occurs through space and has r^{-6} distance dependence, where r is the distance between the metal ion and the antenna(e). The alternative mechanism for the energy transfer is the Dexter mechanism and involves an electron exchange between the excited chromophore and the metal ion in a through bond interaction and should display *a* e^{-r} dependency [36]. For both of these mechanisms the energy transfer process is made more efficient by minimising the distance between the lanthanide ion and the antenna(e) [37].

The pathways discussed above are not the only means by which the excited energy can be lost. This pathway must compete with other mechanisms through which the energy can be discarded. Energy can be lost from the singlet excited state ^1Ar through radiative decay, *i.e.* fluorescence, or non-radiative decay by collisions and vibration interactions with the surrounding molecules. Triplet states may also be quenched by interactions with molecular oxygen. The lanthanide excited state $^*Ln$ can also lose its energy through non-radiative decay by vibrational interactions with other molecules, such as water. In order for the preferred pathway to operate, *i.e.* population of the lanthanide excited state followed by a lanthanide emission, the design must minimise energy loss to other pathways. By maximising the efficiency of the intersystem crossing and energy transfer processes, it is possible to minimise the amount of time that the excited energy spends in the ^1Ar and ^3Ar states and therefore minimise the loss to deactivation pathways from these states. As stated before, ISC is made possible by spin–orbit coupling, which is increased by the presence of a heavy atom, so the very presence of a lanthanide ion itself will elegantly increase the efficiency of this process. Once in the lanthanides orbitals, the energy is somewhat isolated from its environment. However, back energy transfer is possible but can be minimised if the ^3Ar state is of sufficiently higher energy than that of the $^*Ln$ state [38].

Vibrational quenching by metal bound water molecules is one of the main competing deactivation pathways [39]. The use of a tightly binding chelating ligand reduces the number of metal bound water molecules, and thus minimises non-radiative quenching by O–H, but N–H oscillators are often as effective in such quenching. In fact, as demonstrated by Parker and co-workers, such quenching is possible by C–H oscillators, though to a much lesser extend [40]. The number of such deactivating water molecules associated with lanthanide ion structures can be determined spectroscopically as established by Horrocks and Sudnick by measuring the luminescent lifetimes (τ) of the lanthanide-excited states in H_2O and in D_2O, where it is not quenched by O–D vibrations [41]. The method provides a convenient way to monitor the coordination environment of the lanthanide ion. This quantification of the hydration state, is referred to as the “q-value” and for Eu(III) was determined by Horrocks and Sudnick [41]and later modified by Parker [38] by Eq. (1):

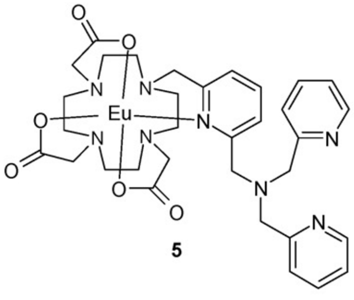
$$q^{\mathrm{Eu(III)}} = 1.2\left[\left(\frac{1}{\tau_{\mathrm{H_2O}}} - \frac{1}{\tau_{\mathrm{D_2O}}}\right) - 0.25 - 0.075x\right] \qquad (1)$$

Other modifications of this equation have also recently been published [42].

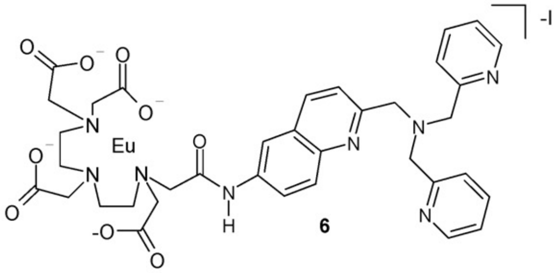
To summarise, in order to produce a lanthanide emission an antenna with triplet energy above that of the lanthanide excited state must be positioned in close proximity to the lanthanide ion. Furthermore, the design requires the lanthanide ion to be tightly bound by a ligand to minimise the number of metal bound water molecules and maximise stability and solubility. The next section shall detail some examples where sensors have utilised lanthanide luminescence as a signalling moiety.

3. Recent examples of cation-induced luminescent changes

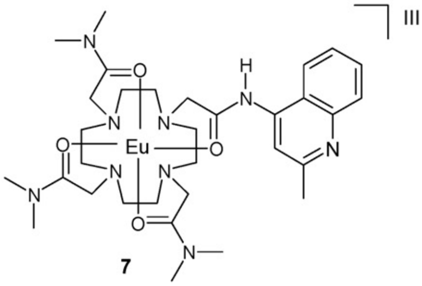
To date several examples of lanthanide luminescent sensors and switches have been developed where the emission is modulated by cations such as H^+, groups I and II as well as transition metal ions. The first examples of such systems were developed by de Silva et al. [43,44] and Parker et al. [27,45], respectively, for protons. These and many other recent examples [28] have been extensively reviewed [11,13,24].



5



6

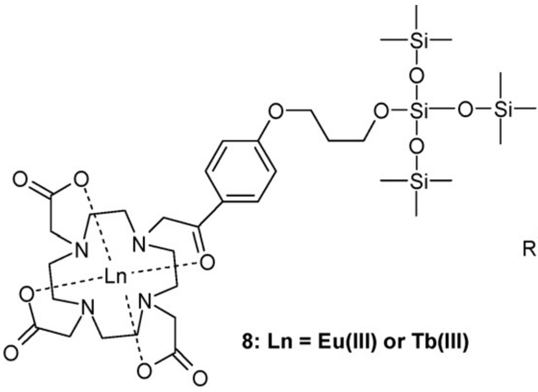


7

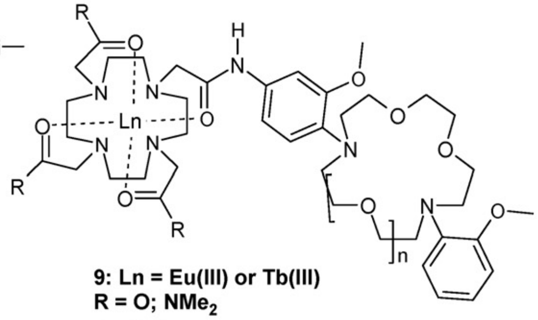
In the last a few years, many new examples have been published. New members of this family of sensors have included the Zn(II) sensors **5** and **6** and the pH sensor **7**, the latter having also been incorporated into soft materials. The charge neutral complex **5** was developed by Pope and Laye [46] who showed that the modulation of Eu(III) emission could be achieved using the picolyl unit as a Zn(II) receptor. This elegant example was designed in such a way that the Eu(III) coordination sphere involved one of the pyridyl nitrogen moieties, which was directly bound to the cyclen based Eu(III) ion. This not only just fulfilled the high coordination requirement of the ion, but also enabled the pyridyl antenna to populate the excited state of the lanthanide ion effectively, due to its close proximity to the ion. This coordination also prevented water molecules binding to the Eu(III) ion. Hence, quenching by O–H oscillators was also removed. However, upon addition of Zn(II) the pyridyl moieties coordinates to the Zn(II), opening up a vacant side a the Eu(III) ions which becomes filled with water and hence, the Eu(III) emission is quenched. In a similar manner, Nagano and co-workers [47] developed a sensor for Zn(II) using a diethylenetriaminepentaacetic acid (DTPA) based chelate conjugated to a quinoline antenna to prepare the Eu(III) and Tb(III) complexes of **6**. This sensor was shown to bind Zn(II) through the tetrakis(2-pyridylmethyl)ethylenediamine (TPEN) part of the structure, which also function as the antenna. A pH dependence study showed the ability of this receptor to bind to group I, II and transition metal ions. The results showed that the sensor was pH independent between pH *ca.* 4–9 and that the emission was significantly modulated in the presences of Zn(II).

Unlike the above two examples, compound **7** was only found to be sensitive to pH [48]. While the solution behaviour of this molecule, and other related pH sensors, is established, the sensing behaviour within soft materials, such as hydrophilic polymers had not been explored [49]. With this in mind we incorporated this molecule into three different hydrogel matrices comprised of crosslinked poly[methylmethacrylate-co-2-(hydroxy-ethylmethacrylate)]. The control hydrogel matrices were prepared using methylmethacrylate (MMA) and 2-(hydroxyethylmethacrylate) (HEMA) in three different ratios: 1:1 (MMA:HEMA, w/w), 1:3 (MMA: HEMA, w/w) and 100% HEMA. All the hydrogels demonstrated Eu(III) emission upon excitation of the antenna and importantly, the luminescence could be ‘switched on–off’ as a function of pH. Not surprisingly, this process was much slower than that observed in solution.

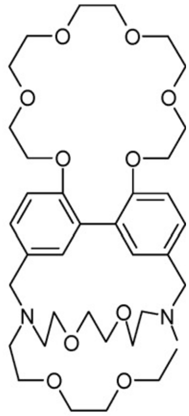
Recently Accorsi and co-workers [50] have incorporated several lanthanide complexes into silica single layers by doping the SiO_2 layers with compounds **8**. Here, the emission was not modulated by external source such as cations but served as an extension of the hydrogel approach and a further example of the versatile role the lanthanides play in current material design.



8: Ln = Eu(III) or Tb(III)



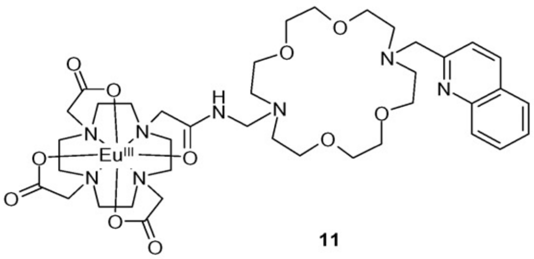
9: Ln = Eu(III) or Tb(III)
R = O; NMe_2
n = 1, 2



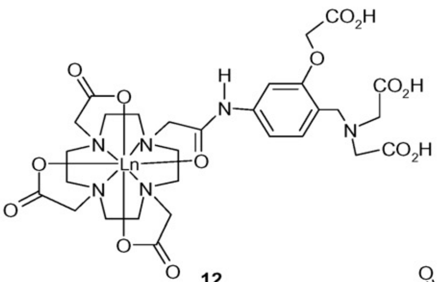
10

Another example of the use of cations to modulate the lanthanide emission is **9**, which was developed to sense Na^+ or K^+ ions, depending of the size of the crown ether ring [51,52]. The resulting Eu(III) or Tb(III) complexes could yield an overall charge neutral or cationic species. Only the Tb(III) complexes gave rise to significant changes in the emission spectra. The Eu(III) systems were found to be only weakly emissive due to effective electron transfer quenching of the Eu(III) excited state by the crown ether antenna. Both the $n = 1$ or 2 Tb-complexes of **9** were investigated in buffered aqueous solutions. The luminescence of both exhibited interesting pH dependence, where the emission was ‘switched on’ in either highly acidic or basic media, while being quenched within the physiological pH range. Consequently, the complexes could be employed as a sensor for Na^+ or K^+ within the physiological pH range.

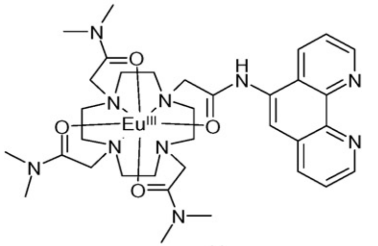
The ditopic macrocyle **10** developed by Pope and Rice is an extension of this idea [53]. It consists of a crown-ether fused pyridyl-cryptane ring, the latter able to complex lanthanide ions such as Nd(III). In CH_3CN complexation of Ba(II) by the crown ether moiety modulated the NIR emission of Nd(III). Here the chelation of the Ba(II) perturbed the sensitization ability of the bipyridine ligand, resulting in significant emission quenching. Significant changes were also observed in the absorption spectra of **10** upon binding to Ba(II). Wong and co-workers developed the Tb(III) complexes of **11** and related analogues, which showed that the emission was modulated in the presence of ions such as Na^+ but, particularly in the presence of K^+ in aqueous solution [54]. This design principle was also used by the same authors to develop sensors for anions [55].



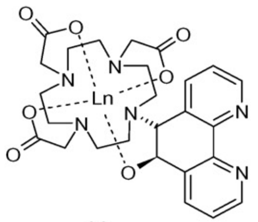
11



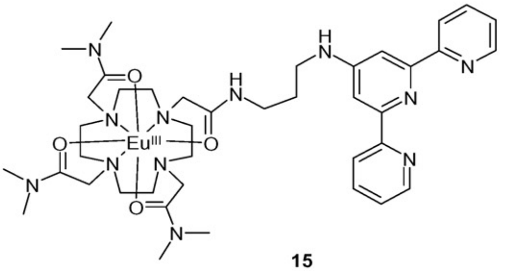
12



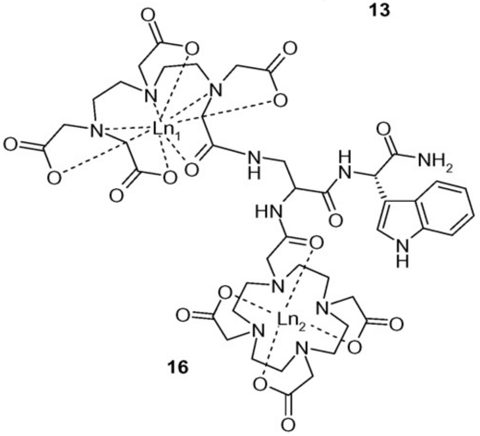
13



14



15



16

Previously, we discussed the Zn(II) sensors **5** and **6**. Related to these systems is compound **12** [56]. This example was originally developed for group II metal ions, in collaboration with Parker and co-workers [57]. However, the sensors gave excellent selectivity for Zn(II) where the Tb(III) emission of **12** was significantly modulated. The corresponding Eu(III) complex suffered however, from poor quantum yield due to quenching of the Eu(III) excited sate by the antenna. Compound **12** was also one of the first examples of f–d metal ion assemblies.

Compound **13**, was developed in our laboratory as a potential sensor for d-metal ions [58]. This compound, based on the phenanthroline antenna, which has also been elegantly employed by Armaroli and co-workers [59] for the formation of lanthanide luminescent complexes, also displayed pH-modulated emission in a similar manner to that seen for **9**. However, here the emission was 'switched on' within the physiological pH range [58]. This system was used for the selective sensing of Cu(II), but cations such as Fe(II) and Co(II) also modulated the Eu(III) emission of **13**, albeit at significantly higher concentration than Cu(II) [58]. We had anticipated that Cu(II) would be capable of coordinating two equivalents of **13** to form a new self-assembled system. Indeed this was found to be the case, but unexpectedly we also observed the formation of 1:3 complex between **13** and Cu(II). This was one of the first examples of the formation of f–d metal ion assembly through the use of structurally defined ligands. Previously, the charge neutral compound **14** had been prepared for the use in MRI and while no luminescent properties were reported the same approach to constructing mixed f–d metal ion frameworks was explored [60].

To overcome the formation of mixed f–d–f and $(f)_3$–d assemblies in solution we undertook the synthesis of **15**, where the terpyridine chromophore acted as both antenna and d-metal coordinating ligand [61]. The Eu(III) emission from **15** was clearly visible at pH 7.4

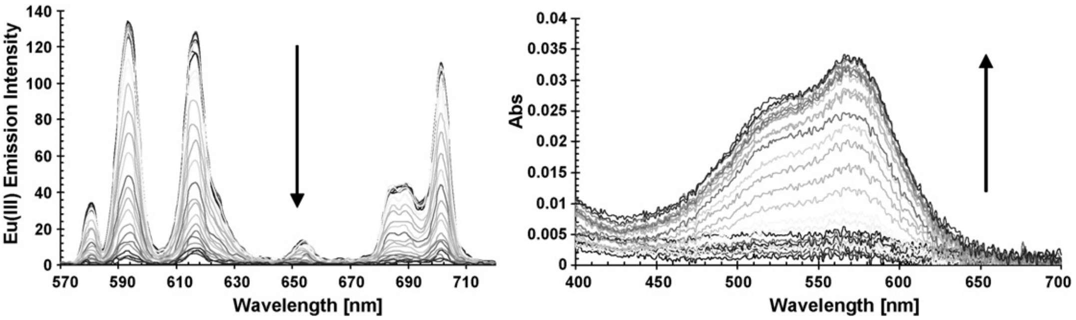
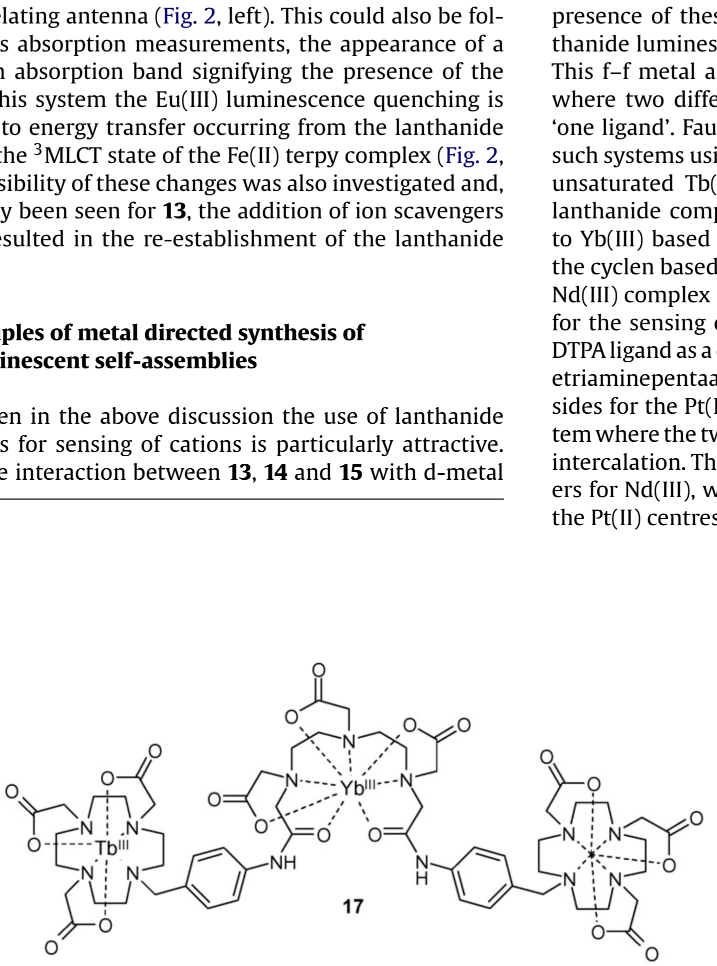


Fig. 2. *Left*: The changes in Eu(III) emission upon coordination of Fe(II) to **14**. *Right*: The formation of the MLCT band in the ground state spectrum of **14** upon addition of Fe(II).

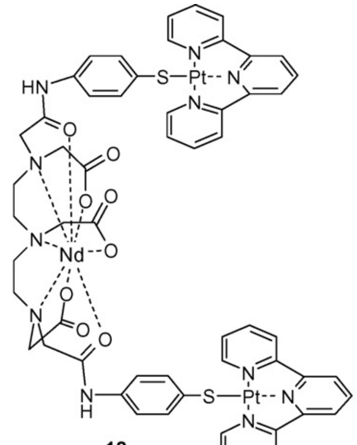
in buffered aqueous solution. The addition of transition metal ions such as Fe(II) resulted in *ca.* 95% quenching of $^5D_0 \rightarrow {}^7F_J$. This clearly demonstrated the sensitivity of the Eu(III) emission to coordination status of the chelating antenna (Fig. 2, left). This could also be followed by UV–vis absorption measurements, the appearance of a long wavelength absorption band signifying the presence of the MLCT state. In this system the Eu(III) luminescence quenching is most likely due to energy transfer occurring from the lanthanide excited state to the ^{3}MLCT state of the Fe(II) terpy complex (Fig. 2, right). The reversibility of these changes was also investigated and, as had previously been seen for **13**, the addition of ion scavengers such as EDTA resulted in the re-establishment of the lanthanide emission.

4. Recent examples of metal directed synthesis of lanthanide luminescent self-assemblies

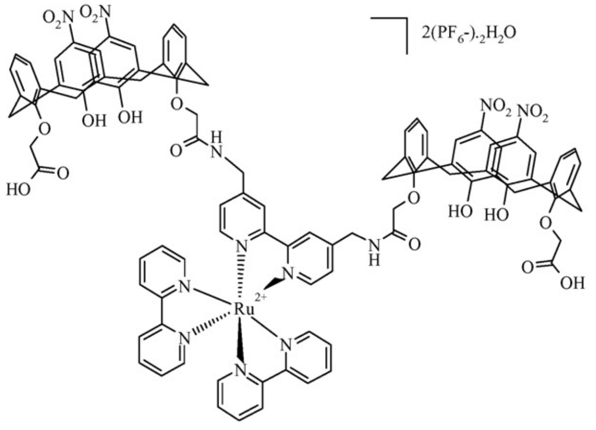
As can be seen in the above discussion the use of lanthanide ions as reporters for sensing of cations is particularly attractive. Furthermore, the interaction between **13**, **14** and **15** with d-metal ions all results in the formation of mixed and ordered f–d metal assemblies. Building from this rationale, several other examples of lanthanide-based metal-directed synthesis of functional assemblies have recently been reported. These lanthanide-based self-assemblies have the potential to yield novel photochemical properties. Compound **16**, capable of binding two lanthanide ions was developed by Tremblay and Sames [62]. This elegant structure is based on two well-known lanthanide coordinating ligands; DOTA and DTPA, both of which featured in the above discussion. In **16** the presence of these two binding domains gives rise to mixed lanthanide luminescence upon excitation of the tryptophan antenna. This f–f metal assembly is one of the first examples of this type where two different lanthanide ions could be incorporated into 'one ligand'. Faulkner and Pope [63] also attempted to developed such systems using DTPA as a central linker and two coordinatively unsaturated Tb(III) based cyclen moieties, the heterotrimetallic lanthanide complex **17** was formed. This f–f–f system, gives rise to Yb(III) based NIR emission at 980 nm upon sensitization from the cyclen based Tb(III) centres. The heterotrimetallic luminescent Nd(III) complex **18** was developed by Pikramenou and co-workers for the sensing of DNA [64]. Again this system was based on the DTPA ligand as a central linker, which is flanked with two diethylenetriaminepentaacetic acid derivatives, which provide two binding sides for the Pt(II). This gives rise to the formation of a d–f–d system where the two planar Pt(II) complexes can bind to DNA through intercalation. The two d-metal moieties were also used as sensitizers for Nd(III), which gave rise to NIR emission upon excitation of the Pt(II) centres.



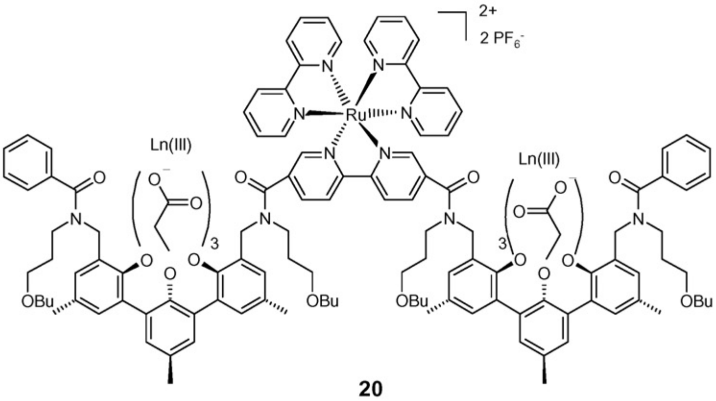
17



18

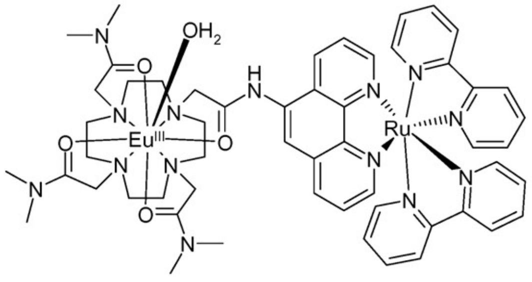


19

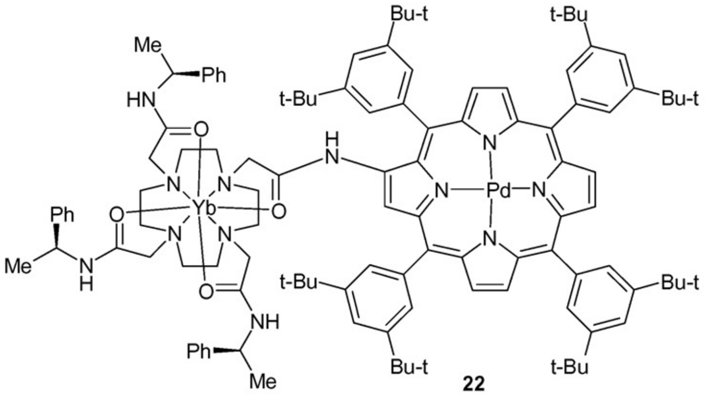


20

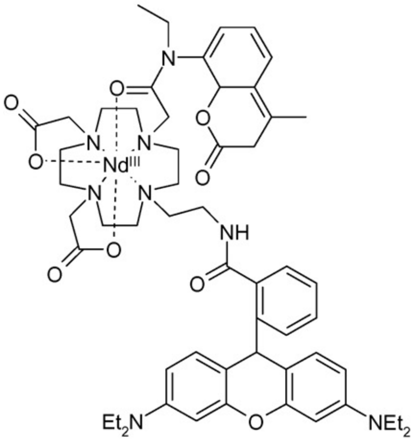
As can be seen in the above discussion, the use of f–f and f–d mixed cations and simple ligands has led to the formation of novel self-assemblies. Other examples of such designs include that of Beer et al. who developed the Ru(II) bipyridyl complexes **19** containing one, two or six lower rim acid-amide modified calix[4]arene macrocycles covalently linked to a bipyridine group [65]. The calix[4]arene moieties were able to coordinate several lanthanide ions such as Nd(III), Eu(III) and Tb(III) in a 2:1 Ln:complex. This coordination gave rise to significant changes in both the absorption and emission spectra of the resulting assemblies. The authors conducted in-depth luminescence studies of these systems upon excitation of the tris(bipyridine)–ruthenium(II) complex at 452 nm. The luminescent nature of the donating state (the ^{3}MLCT state) allowed a detailed study of the energy transfer process to the lanthanide centres. Here, the ruthenium luminescence was quenched by lanthanide ions such as Nd(III), while for ions such as Tb(III) and Eu(III) it was enhanced. A related system is **20** [66]. As in the case of **19**, the Ru(II) bipyridyl complexes sensitized the excited states of both Nd(III) and Yb(III), by energy transfer from the triplet excited state of the ruthenium–tris(bipyridine) complex, upon excitation in the visible region.



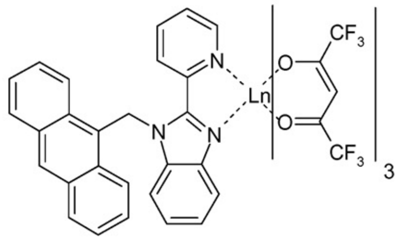
21



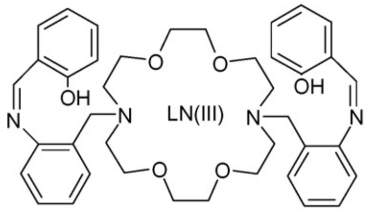
22



23



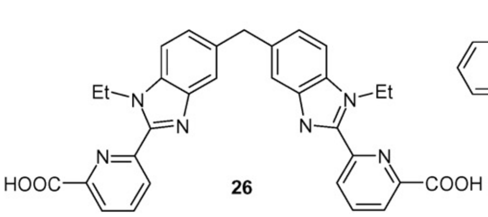
24



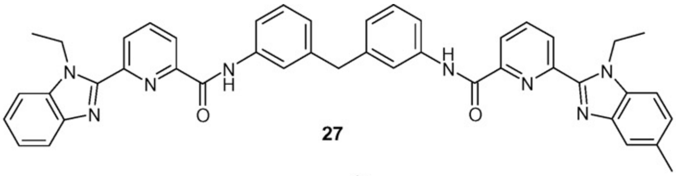
25

Other examples of NIR emitting self-assemblies based on **13** and developed in our group is compound **21**. In collaboration with Faulkner, we demonstrated that the ruthenium–bis(bipyridine) capped complex of **13**, gave **21**, which emitted in the NIR for ions such as Nd(III) and Yb(III) upon excitation of the MLCT band of the complex in water [67]. While the Yb(III) emission was significantly quenched due to back energy transfer; the Nd(III) emission was found to be particularly strong for this system. The Ru(II) centred emission being significantly less intense for the latter system, indicating efficient sensitization of the Nd(III) excited state. The interaction of this complex with calf-thymus DNA was also investigated under buffered conditions. However, only about 20% changes were seen in the NIR emission for these systems, while the Ru(II) based MLCT and the Ru(II) centred emission at *ca.* 900 nm was reduced in intensity upon binding of **21** to DNA. The porphyrin based cyclen complex **22** is another example of the use of mixed f–d complexes [68]. This system, developed by Parker et al. has a Pd(II) conjugated porphyrin moiety that was covalently linked to a chiral cyclen Yb(III) complex. In this mixed metal ion system the excited triplet state of the porphyrinate was quenched by O_2 upon binding of the complex to DNA. This resulted in an enhancement of the NIR lanthanide luminescence.

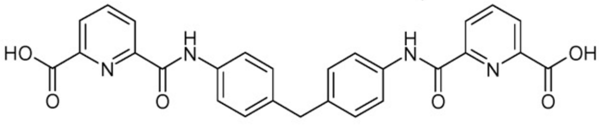
Another example of such mixed f–d systems for DNA targeting is that of Pikramenou and co-workers discussed above [64]. While all of these systems employ excitation of the d-metal complex, Bruce and co-workers has recently extended such DNA targeting toward the use of organic chromophores, *e.g.* **23** [69]. This compound was found to bind to DNA with concomitant changes in the lanthanide emission upon excitation in the visible region. The use of organic chromophores as antennae in such NIR emitting systems has become quite popular in the last a few years, as examples **1**–**3** demonstrate. Additionally, Faulkner and co-workers [70] have demonstrated that simple classical chromophores such as the anthracene based system **24** can also be used as sensitizers for NIR lanthanide ions. This NIR emitting work has been further developed by Faulkner, an example is that developed in collaboration with Rodríguez-Blas, based on the use of simple aryl imine based azacrown ethers, *e.g.* **25** [71]. It is clear that the examples discussed above highlight the scope afforded by mixed f–f or f–d metal systems and in particular of current developments in NIR emitting 'organic' supramolecular lanthanides as well as being is a highly attractive area of research.



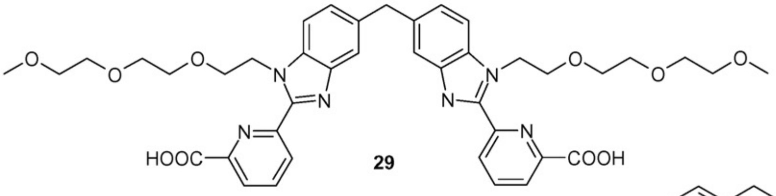
26



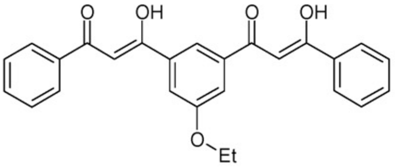
27



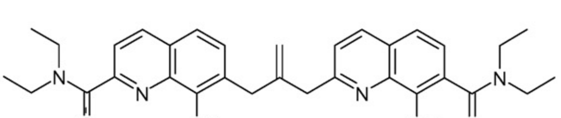
28



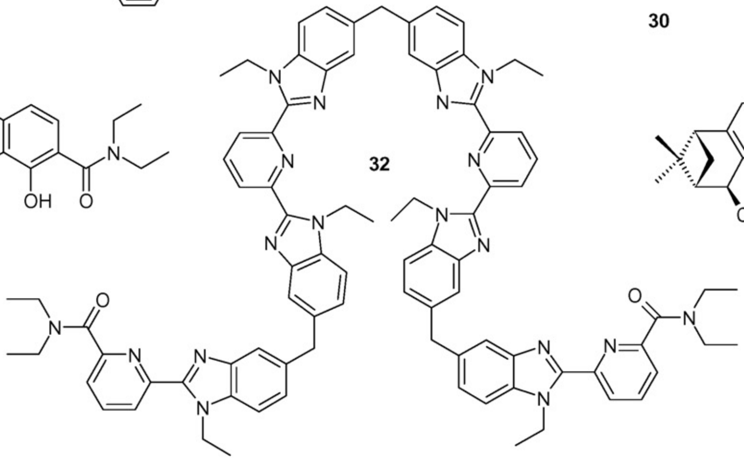
29



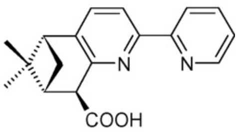
30



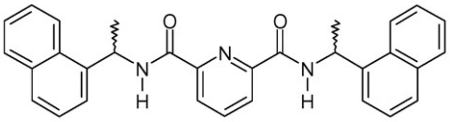
31



32



33



34a ***RR***
34b ***SS***

Furthermore, mixed f–f metal systems also offer the ability to develop novel supramolecular scaffolds and architectures. In a similar manner to the transition metal based helicates developed by many others. A recent elegant example is that of Faulkner and Ward, which involved the use of polynuclear lanthanide complexes that were bridged by two tridentate N,O-donors [72]. This gave rise to the formation of helical structures that were analysed using both solution and solid states methods. A number of other such lanthanide directed structures have been achieved using acyclic ligands such as **26**–**32**. Compound **26**, developed by Bünzli and co-workers, was designed to facilitate the assembly of a new class of luminescent lanthanide helicates in water [73]. This compound was used in the formation of the neutral triple-stranded dimetallic helicates, where all the lanthanide ions were investigated where the three equivalents of **26**, wrapped around the two nine-coordinate Ln^{III} ions in pseudo-D_3 symmetry $[Ln_2(\mathbf{26})_3]$. The formation of this helicate was monitored by changes in the ground and the excited states of the ligand and by monitoring the appearance of the lanthanide emission at long wavelengths. Compound **27** is another example of such a self-assembly that gives rise to the formation of triple-stranded helicate $[Ln_2(\mathbf{27})_3]^{6+}$ for a 2:3 Ln:**27** ratio [74]. Many other examples were developed in collaboration between the Swiss based groups of Bünzli and Piguet in this area [12]. Compound **28** is another example of a ligand able to form a lanthanide directed helical system [75]. Developed by Horrocks et al. ligand **28** consists of the use of tridentate chelating units dpa (2,6-pyridinedicarboxylic acid) linked by an organic diamine. In these, each ligand can coordinate to two different metal ions. Hence, the resulting assembly gives rise to the formation of dinuclear trigonal prismatic, D_3 geometry. However, the authors reported that these assemblies were formed as mixtures in solution.

A number of related systems have been developed by the Bünzli group for application in lanthanide luminescence-based intracellular imaging, which has only recently been achieved successfully. The addition of two polyethoxy chains onto the structure of **26** afforded **29** [76]. Again lanthanide emission changes yield information on both the stability and the ion-to-ligand stoichiometry of the resulting assembled complex. Importantly, the ethoxy chain conferred water solubility to the complexes allowing their incorporation into cells such as HeLa, Jurkat and 5D10, facilitated, most likely through edocytosis. The complexes were imaged by excitation of the ligand based antenna and observing the Eu(III) emission. This design is very attractive as it also opens the door to the use of mixed luminescent and magnetic detection (MRI) of tissues and cells and possibly larger organs. Other recent example of lanthanide complexes for cellular imaging is **4**, previously discussed above and developed by Parker and co-workers [34]. This area of research has recently brought new dimension to the field of lanthanide chemistry [14,17a].

Other helical structures developed for lanthanide directed synthesis include examples such as **30** [77a]. The structure obtained from **30** was analysed by various spectroscopic techniques, but the authors were unable to obtain X-ray crystallographic structure of their resulting helicates. Several other examples of the use of both homopolymetallic and heteropolymetallic self-assemblies, which results in the formation of self-assemblies containing large number of metal ions, and detailed analyses of their optical properties, including studies of their visible and NIR emissions, have also been developed by several researchers such as Bünzli and co-workers [77b], Bünzli and co-workers [77c], Mazzanti co-workers [77d] and Hou et al. [77e]. While some of these examples are outside the scope of this review, we direct interesting readers to these publications and the references therein.

Compound **31** recently yielded another example of an NIR emitting helicate constructed using either two Yb(III) or a mixture of Yb(III) and Al(III) ions [78]. Interestingly, for these structures K(I) was also found to coordinate the center of the helicate, possibly functioning in the self-assembly process as a template, as it coordinates both the hydroxy groups on each 'wing' of **31**, giving rise to a six coordinate K(I) species. Compound **32** was designed and synthesised by Piguet and co-workers and is the first example of a triple stranded helicate with more than three metal ions [74]. This elegant structure was designed by employing a novel strategy developed by the Geneva group. While this example is a major step in the development of 'predictable' supramolecular self-assemblies using lanthanide directed synthesis, it does suffer from lengthy ligand synthesis. In the case of **33**, developed by Mamula et al. [79] a large chiral complex was formed, which gave rise to both intense lanthanide luminescence that could be resolved by circularly polarised luminescence (CPL).

The use of metal directed synthesis has become a very popular area of research, and ligand **34a** and **34b** consisting of a simple pyridyl-2,6,-diamide unit flanked by two chiral naphthalene moieties was developed in our laboratory with the aim of using lanthanide ions to direct the formation of novel self-assemblies [80]. In our case, the reaction of the *RR* or *SS* ligands with a series of either visible or NIR emitting lanthanide ions, resulted in the formation of a single product for each ligand, per lanthanide ion. In all cases a 1:3 Ln:ligand stoichiometry was obtained. The presence of the chiral moieties in **34** aided in the formation of highly ordered chiral self-assembly.

The chirality of these self-assemblies was resolved using X-ray crystallography. These result showed that this rather simple ligand gave rise to helical structure and that the *S*,*S* ligand induces Δ chirality about the metal ions whereas the *R*,*R* ligand induces Λ chirality, as demonstrated in Fig. 3A. These chiral systems also showed each of the three-pyridyl moieties intercalated between two naphthalene moieties, one from each of the remaining three ligands. This gave rise to an extended π–π network that was also observed in the packing diagram of these structures, which consisted of honeycomb networks of interpenetrating Ln-complexes of **34**. This was characterized by a variety of spectroscopic techniques, including Circular Dichroism and CPL. The complexes gave rise to CPL upon excitation of the antennae, with enantiomers giving rise to equal and opposite signs in the CPL spectra, as shown in Fig. 3B, for the Sm(III) complexes. The steady-state Sm(III) luminescence is also demonstrated in Fig. 3B. These examples demonstrate the use of lanthanide directed synthesis in the formation of chiral self-assemblies from structurally simple, but defined ligands. Here, both the steady-state as well as the CPL can be employed to elucidate the structural features of the self-assembly of such systems. These ligands are similar to those developed by Piguet and co-workers that gave only a mixture of products [81] and more recently of that of Muller and co-workers, who also elegantly demonstrate the use of CPL in the analysis of his systems [82a]. Similarly, the use of CPL has recently been demonstrated by Muller and co-workers and Raymond and co-workers, for probing the luminescence of Eu(III) complexes derived from octadentate ligands based on 1-hydroxy-2-pyridinones [82b] and chiral, 2-hydroxyisophthalamide ligands [82c].

This section has dealt with the modulation of lanthanide luminescence, either through the use of external perturbation; *i.e.* where group I, II and d- or even f-metal ions modulated the lanthanide luminescence within a coordination complex. This was followed by the discussion of some of the more recent examples of other supramolecular architectures, which are formed by the use of lanthanide ions and the way their luminescence can be employed to elucidate their structural features. The next section details some of the recent examples of lanthanide complexes that have been developed, where the lanthanide emission is modulated through the coordination of anions.

5. Recent examples of anion-induced lanthanide luminescent changes

Monitoring the concentration of ions and molecules *in vivo* is of critical importance as many of these ions and molecules are involved in crucial biological and chemical processes [4,5]. Anions, in particular [5], are essential to life, as many biological processes depend on the presence or transport of these negatively charged species, or use them to carry out chemical transformations. They

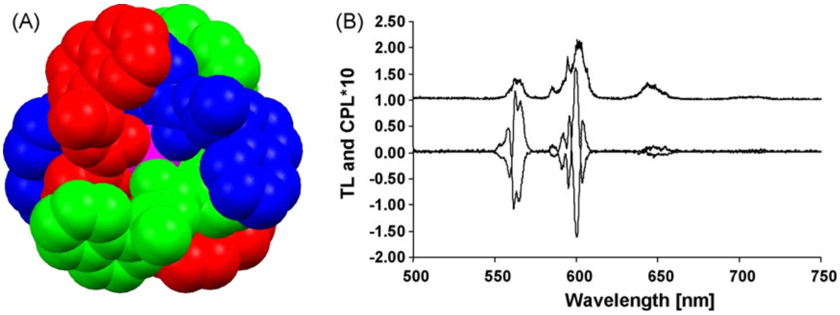
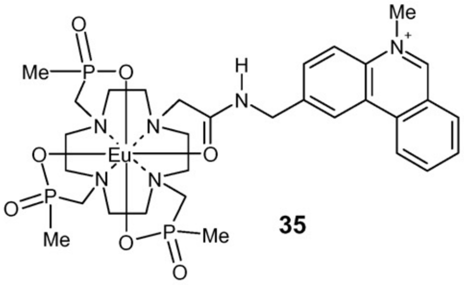


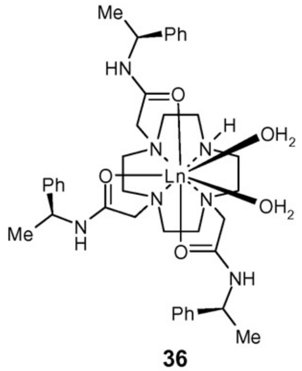
Fig. 3. (A) The X-ray crystal structure of the self-assembly of **34a** (*RR*) with Nd(III). (B) The lanthanide emission from Sm(III) and the corresponding emission from the Δ and the Λ chiralities of **34** as measured using CPL. Published with permission from Journal of the American Chemical Society.

have also become progressively more used in industrial processes as well as in agriculture, which consequently puts them in the class of pollutants. It has thus become evident that there is a significant need for the development of synthetic receptors able to report the presence of anions. This has been the driving force for the formation of anion sensors in recent time.

The high coordination numbers of the lanthanides is often difficult to achieve. Hence, coordinative unsaturated complexes often fulfil this requirement by coordinating additional solvent molecules, or ligands such as anions. Such binding interactions may perturb the excited state properties of the complex directly, due to the direct binding to the lanthanide ion, or through interactions with other coordinating ligands such as antennae. Relatively, hard anions such as carboxylates or phosphates, can displace metal bound water molecules, with subsequent modulation in the luminescence properties of the lanthanide ions. Examples of such architectures that exploit this are compounds **35**–**38**.

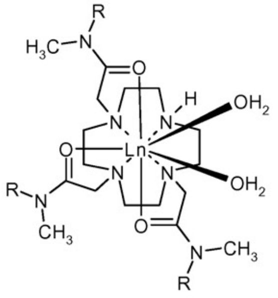


35

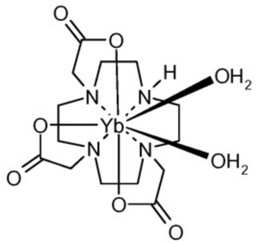


36

Ln = Tb(III), Eu(III)



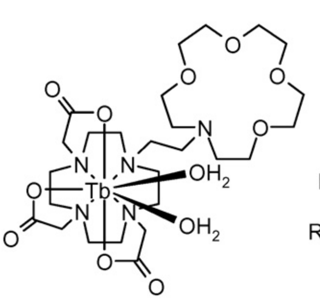
37a Ln = Tb(III), R = CH_3
37b Ln = Tb(III), R = H



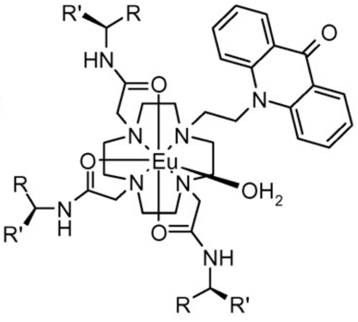
38

Compound **35** was developed by Parker and Williams, as a sensor for Cl^- [83]. The system is based on the use of *N*-alkylated phenanthridinium antenna, which is known to be quenched by halide anions in aqueous media. Indeed, the addition of halide ions to **35** leads to a decrease in the intensity of the phenanthridinium fluorescence (405 nm) and an associated decrease in the Eu(III) luminescence intensity, by a factor of four. The halide quenching effect was independent of added acetate, $H_2PO_4^-$, citrate, and HCO_3^-, and followed the quenching order $I^- > Br^- > Cl^-$, the mechanism of which was proposed to involve charge transfer from the halide ion to the excited singlet of the chromophore. This phenomenon has been further employed by the Parker group in the development of assays for Cl^- ion in biological media [84]. Developed by Parker and co-workers [85], complex **36** is coordinatively unsaturated as the cylen ligand only satisfies seven of the coordination sites for lanthanide ions such as Eu(III) and Tb(III). This complex possesses three chiral phenyl antennae which populated the excited state of these ions through sensitization. The luminescence of **36** is quenched by effective O–H harmonics in the presence of two metal bound water molecules **36** (*i.e.* $q = 2$ as determined by excited state measurements in H_2O and D_2O). However, it was observed that in aqueous solution both water molecules could be displaced from **36** by anions such as $H_2PO_4^-$, acetate, HCO_3^- and CO_3^{2-}, to yield a 1:1 adduct. The formation of the resulting ternary complex was signalled by large changes in the lifetime of the Eu(III) and Tb(III) excited states. In contrast, the lifetimes remained unchanged for ions such as Br^- and Cl^-, while in the case of CH_3COO^-, F^-, and $H_2PO_4^-$, q was determined to be *ca.* 1, implying the loss of a single bound water molecule upon coordination of these anions to the lanthanide ions.

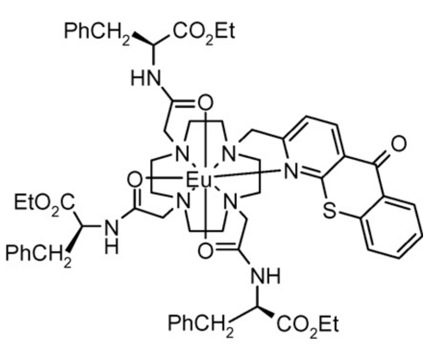
Compounds **37** and **38** also exploit coordinatively unsaturated lanthanide complexes, all of which have $q = 2$ for sensing. Compounds **37a** and **37b** were developed in our laboratory [86] and lack the antennae shown for **36**. In these systems displacement of the metal bound water molecules by coordinating aromatic carboxylates, such as *N*,*N*-dimethylaminobenzoic acid and salicylic acid, results in the population of the Tb(III) excited states [87]. A similar design was reported by Faulkner et al. who used the charge neutral IR-emitting Yb(III) complex **38**, for the sensing of tetrathiafulvalene carboxylate [88]. In methanolic solution, the carboxylate coordinate **38** through displacement of the two bound water molecules in a similar manner to that of **36** and **37**, upon which the tetrathiafulvalene antenna is then able to transfer energy to Yb(III), with concomitant emission from the lanthanide ion in the NIR. More recently, this research group demonstrated the sensitization of the Nd(III) analogue of **38**, using pyrene carboxylate as the sensitizing antenna [89]. Upon coordination of the pyrene carboxylate in water, intense characteristic Nd(III) emission bands at 1055 and 1350 nm were observed. These results are of significant importance for the development of lanthanide based sensors and probes for biological applications in the NIR as well as it demonstrated the use of organic chromophores with longer absorption wavelengths (>400 nm) as antennae for such systems.



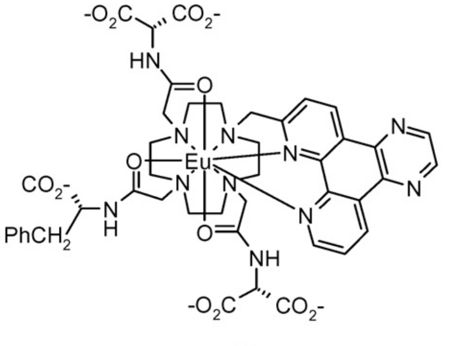
39



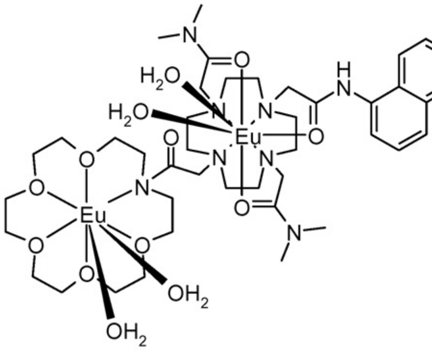
40 R = CO_2Et, R' = Me
41 R = CO_2^-, R' = Me
42 R = CO_2^-, R' = $(CH_2)_2CO_2^-$



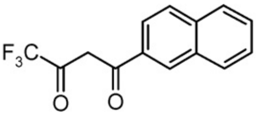
43



44



45



46

In a similar manner, to that shown above, Li and Wong have reported that a cyclen based Tb(III) complex **39**, capable of signalling the presence of anions such as acetate and salicylate under physiological conditions [90]. As in the case for the previous examples, **39** lacks the presence of a sensitizing chromophore and hence is non-luminescent. However, the luminescence lifetime and intensity are observed to vary greatly upon addition of lactate and salicylate. Other derivatives of this design have also been reported by this research group [54,55]. A series of cationic, zwitterionic, and anionic Eu(III) complexes, such as **40**–**42**, have recently been developed by Parker and co-workers for the detection of HCO_3^- [91,92]. Here, the acridone chromophore served as an antenna, the advantages of using such an antenna as a sensitizer had been previously noted by Faulkner et al., which allowed sensitization of the Eu(III) emission following excitation at 390–410 nm. Both **40** and **41** were found to selectively bind bicarbonate at physiological pH [91]. The binding process was signalled by changes of the luminescence lifetimes and emission intensities of the Eu(III), where q changed from $1 \rightarrow 0$. This supported the displacement of the metal bound inner sphere water molecule. By monitoring the ratio of the emission intensity of Eu(III) of the 618/588 nm or 618/702 nm emission bands, the solution concentration of HCO_3^- could be assessed in a background of competing anions such as acetate, citrate, and $H_2PO_4^-$.

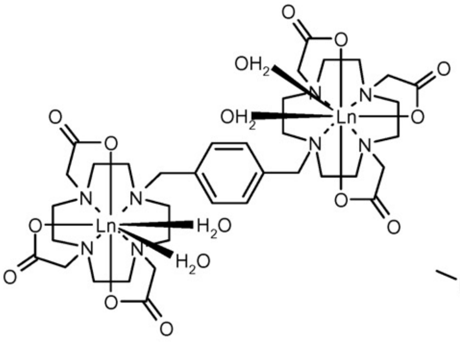
Compound **42** is a particularly interesting extension to this design idea, as it could be employed for the sensing of phosphates [92]. The binding of selected phosphates, as well as phosphorylated amino acids such as Ser-OP and Tyr-OP was investigated by observing the emission spectra of the complexes. Job plot analysis revealed the formation of 1:1 adducts, which displayed subtly different emission spectra with Tyr-OP showing the lowest $\Delta J = 2/\Delta J = 1$ intensity ratio. In each case, the data obtained was consistent with formation of mono-aqua species with phosphate anion acting as a monodentate ligand. The Parker group has recently further extended this design principle, by employing coordinatively unsaturated lanthanide complexes for sensing larger poly-anions, such as DNA as well as developing novel lanthanide based markers for imaging of living cells, an example of the latter is compound, **43** [93]. This was found to selectively stain nucleoli of NIH 3T3, HeLa and HDF cells, and could be used in fixed cell imaging [17a]. Compound **44** was, developed for targeting DNA, where the antenna was able to intercalate into DNA, with concomitant modulation in the lanthanide emission [94]. The Parker group has more recently further extended this design to target uric acid in serum [95], as well as other biological species [96].

Compound **45** was developed in our laboratory [97]. This dinuclear-Eu(III)-bismacrocyclic conjugate was designed as a delayed luminescent lanthanide sensor for dicarboxylates. The sensor was shown to bind small dicarboxylic acids such as aspartic, malonic, succinic, and glutaric acid in pH 6.5 solutions. Nevertheless, only malonic acid gave rise to selective Eu(III) luminescence enhancements, as the emission intensity was reduced for the other acids. Compound **45** gave rise to ternary complex formation with anions, which was formed upon displacement of metal bound water molecules. In a similar manner we have also developed complexes of the Eu(III) complex of **36** using the antenna **46**, which can bind to the metal ion by displacing the aforementioned metal bound water molecules [98]. This gave rise to a very strongly luminescent assembly where the red emission from the Eu(III) ion was visible to the naked eye. However, upon titrating this complex with anions such carboxylates and phosphates, the antenna was displaced and the emission was switched off due to the displacement of the antenna. This work has recently been extended, by incorporating these complexes onto gold nanoparticles via an alkylthiol linkage. This gave rise to the formation of highly saturated lanthanide complexes that were employed for the sensing of large biological relevant anions through the use of displacement assays [99].

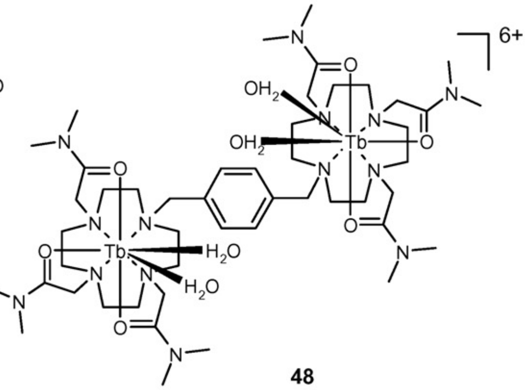
This part of this review has discussed some of the recent development of lanthanide complexes that can interact with anions, which results in modulation of the lanthanide luminescence. While the focus has been mostly on anion sensing, then the idea of being able to replace either metal bound water molecules or coordinating antennae, can also be employed to give rise to the formation of higher order self-assembly structures. This will be the topic of next section, where a few recent examples will be discussed.

6. Recent examples of anion directed lanthanide luminescent self-assemblies

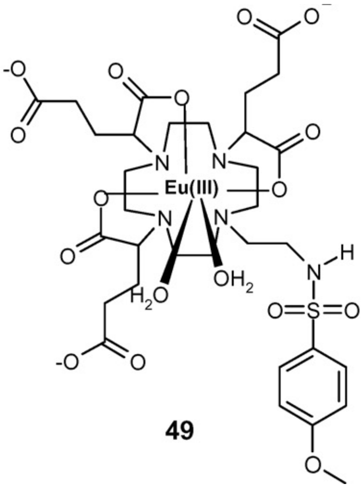
In many of the examples discussed in previous section, anion recognition and sensing was achieved by the coordination of the anion directly to the lanthanide centre, yielding the formation of self-assembly ternary complexes. Thus anions offer the potential to direct higher order assemblies. Next the use of multidendate anions offers the ability to extend this rationale to the assembly of multi lanthanide centred systems is considered. The di-nuclear complexes **47** [100] and **48** [101] are examples of lanthanide complexes capable of this. Faulkner et al. reported the bridged bis-cyclen system **47**, which was able to accommodate two lanthanide ions with each of the cyclen moieties, giving rise to the formation of overall charge neutral complex. Excitation of the bridging antenna of the various lanthanide complexes gave rise to the typical lanthanide emission. In contrast, the cationic xylyl based complex **48**, was prepared in our laboratory with the aim of (a) developing luminescent sensors for di-carboxylates, where the anion would bridge the two metal ion centres, or (b) forming novel self-assemblies where intermolecular manner binding of a suitable anion would give rise to 2 + 2 stoichiometry. This complex was able to detect the presence of mono- or bis-aromatic carboxylates, such as terephthalic acid, in buffered aqueous solution at physiological pH, which was found to occur through the binding of the carboxylates to the metal centre, *via* the displacement of the metal bound water molecules. This gave rise to significant enhancements in the Tb(III) emission. However, in the presence of tartaric acid, the recognition process gave rise to quenching of the Tb(III) emission intensity. Compound **49** is an example of an pH dependent off–on switch, where the Eu(III) emission of **49** was greatly enhanced upon deprotonation of the sulphonamide, which lead to displacement of one of the metal bound water molecules of **49** [102].



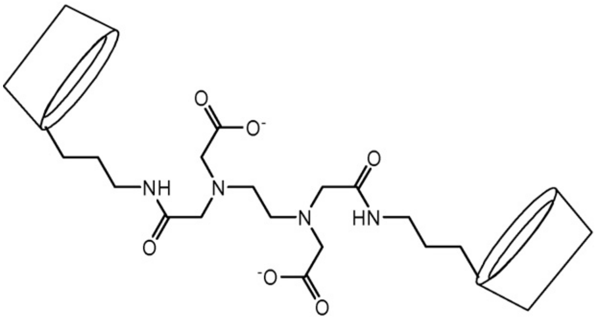
47



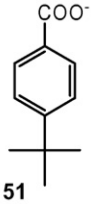
48



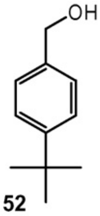
49



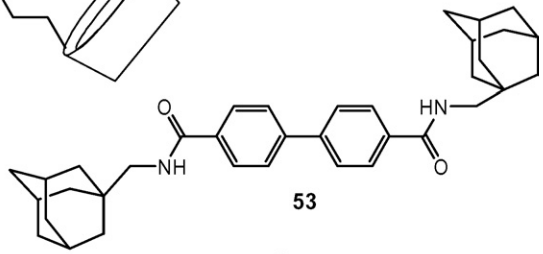
50



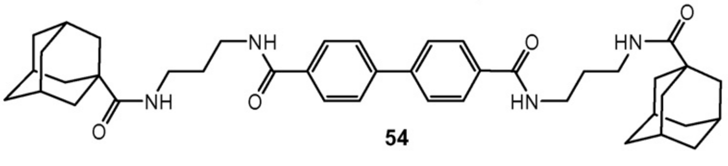
51



52

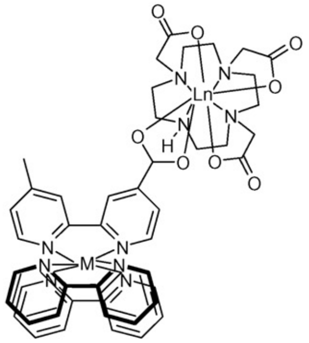


53

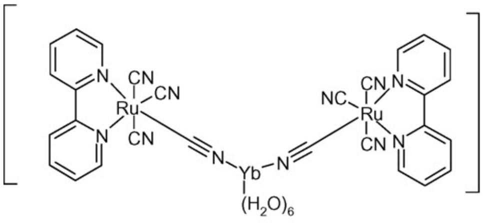


54

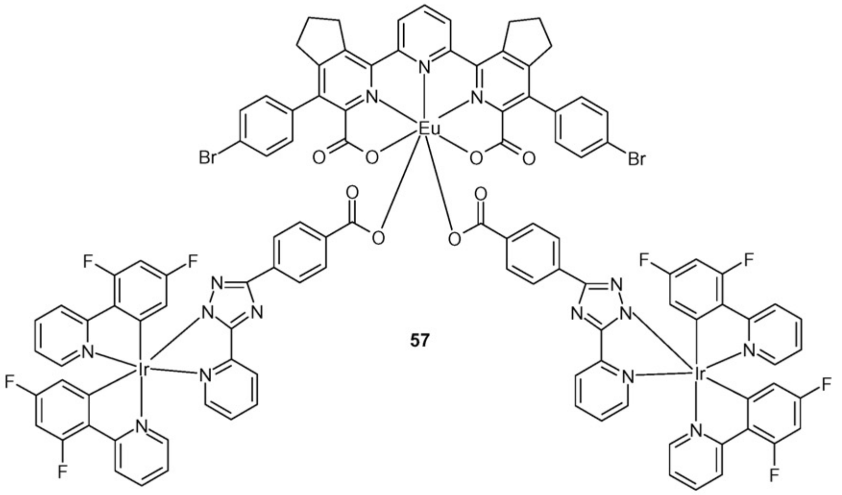
Reinhoudt and co-workers, have recently described the Eu(III) and Tb(III) complexes of the EDTA-based β-cyclodextrin dimer **50**, which operate in H_2O at pH 7.0 as luminescent sensors for aromatic carboxylates [103]. As the ligand does not provide any sensitizing antenna, no luminescence was observed. Nevertheless, upon the addition of **51**, the luminescence intensities of both the Eu(III) and Tb(III) complexes increased by a factor of 350 and 310, respectively, upon excitation of the aromatic antenna at 250 nm. These large enhancements were ascribed to the hydrophobic binding contribution of the β-cyclodextrin units which can bind the aromatic unit thereby positioning the Ln(III) coordinating carboxyl group correctly to function as a sensitizing antenna and allow efficient energy transfer to the lanthanide ion. The stoichiometry was reported to be 1:2 with a stability constant of $K = 5.0 \times 10^4\,M^{-1}$. As expected, the addition of the benzyl alcohol **52**, led to much smaller enhancements of *ca.* twofold. The authors explained this lower enhancement as owing to the lack of a carboxylate functionality through which the chromophore can bind to the lanthanide ion. The interaction between the Eu(III) complex of **50** and bisadamantyl biphenyl sensitizers **53** and **54**, was also investigated. Once again, upon excitation of the sensitizers at 285 nm, large increases in the Eu(III) luminescence was observed, *ca.* 300- and 360-fold for **53** and **54**, respectively, in D_2O. A 1:1 binding stoichiometry was observed for both self-assemblies with very high association constants, which suggest that both of the β-cyclodextrin cavities of **50** were involved in the binding of the bisadamantyl biphenyl sensitizers **53** and **54**.



55



56



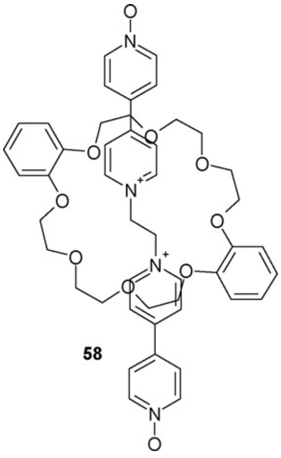
57

Compound **55**, developed by Faulkner and Burton-Pye is an extension to the displacement of the metal bound water displacement discussed above [104]. This mixed f–d self-assembly was formed by the direct coordination of carboxylate functionalised Ru(II) or the Os(II) (M in structure **55**) coordination complexes directly to the lanthanide ion Ln = Yb(III), Nd(III) or Er(III), via the displacement of water molecules form the cyclen–lanthanide complex. This enabled the population of the lanthanide ions by the MLCT band of the transition metal complexes in a similar manner to that discussed above for **22**–**25**. This idea has been further extended by the Faulkner group in collaboration with Ward et al., who has used varieties of such coordination complexes as antennae for the population of NIR emitting lanthanide ions within the visible region. An example of one of these designs is **56** [105], but this work has recently been reviewed in depth by Ward [21], and in other publications by Faulkner and co-workers [106], and consequently will not be discussed further herein.

Compound **57**, is an example of a self-assembly developed by DeCola and co-workers consisting of a heterotrimetallic d–f–d in which the sensitization of the Eu(III) excited state occurred by energy transfer from the two Ir(III)-based moieties [107]. Importantly, the complex is achieved though anion-directed coordination. Unlike many of the above examples, here the emission from the self-assembly was almost-white light, originating from the combination of the red Eu(III) emission combined with residual blue emission occurring from the iridium complexes. Such white emitting molecules are of great current interests and the present example demonstrates the role that lanthanide ions have in the construction of such systems.

7. Miscellaneous

Unlike that of d-metal ions, the use of lanthanide ions in the metal directed synthesis of more traditional supramolecular structures comprising either rotaxanes and catenanes has not been much explored. Loeb and co-workers have recently addressed this deficit by developing three-dimensional polyrotaxane from ‘lanthanide-ion nodes’ based on pyridinum *N*-oxides axles and crown ethers, *i.e.* **58** [108]. The use of **58** in conjunction with various lanthanide ions gave rise to the formation of coordination networks where each of the lanthanide ions was coordinated to six equivalents of the ligand, as shown in Fig. 4A. This gave rise to a three dimensional network of interpenetrating polyrotaxane self-assemblies (Fig. 4B). This is, to the best of our knowledge, the only existing example of such systems and demonstrates quite elegantly the potential that the f-metal ions can play in the construction of such higher order self-assemblies. However, the luminescent properties of this self-assembly were not reported.



58

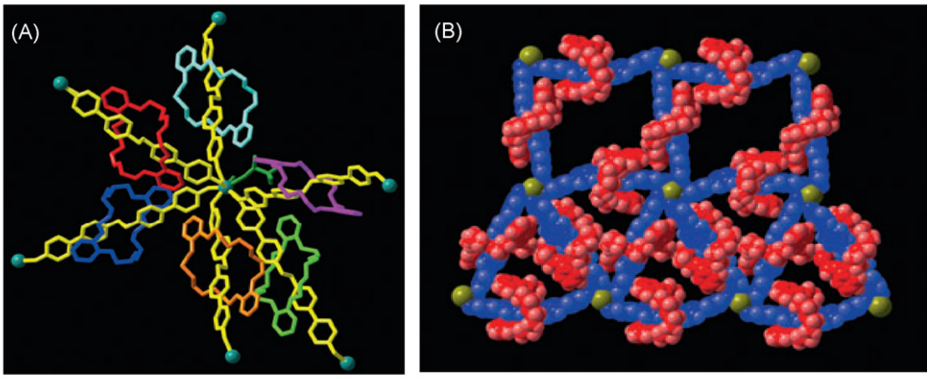
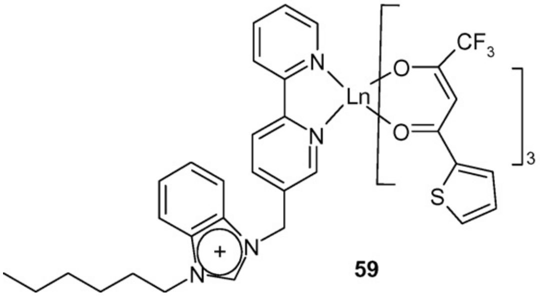
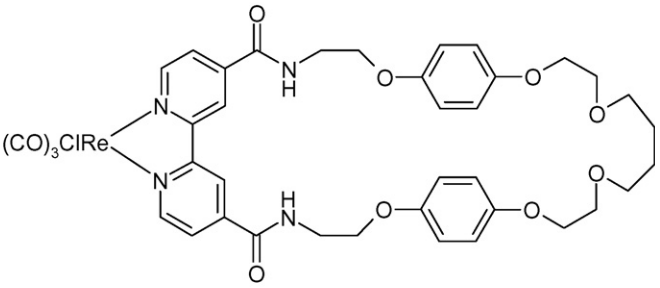


Fig. 4. (A) The crystal structure of **58** after reaction with Sm(III), giving rise to the formation of 6:1 coordination environment around the lanthanide ion. (B) The packing diagram of the resulting polyrotaxane. Published with permission from *Angewandte Chemie*.



59



60

The last example of this short review is **59**, developed in collaboration between Faulkner and Beer, which upon interacting with **60**, gives rise to the formation of [2] pseudorotaxanes between the two molecules, where **59** (Ln = Gd, Nd, Yb) is complexed within the cavity of **60** [109]. The resulting structure was described to be formed through anion templating effects and is, to the best of out knowledge, the only example of such structures which results in the formation of a lanthanide luminescent rotaxane, as upon excitation of the Re-coordination complex, efficient energy transfer was observed to the excited state of the NIR emitting ions Yb(III) and Nd(III), and concomitant emission in the NIR of these ions.

8. Conclusion

This short review has focused on the development of a few and selective examples from the recent literature on the modulation of lanthanide luminescence, either in the visible or the NIR, by both cations and anions and the formation of self-assembly structures which are formed either in such a way that the lanthanide ions directs the formation of the self-assembly, or partakes in it through mediating as an anion acceptor. The examples herein, clearly demonstrate the significant advantages achieved in this field of research in the past few years and that there still exist is an enormous scope for the use of lanthanide ions in various supramolecular function, as recently pointed our in an excellent review by Bünzli et al. [110] entitled "*New Opportunities for Lanthanide Luminescence*". We look forward to follow and participate in the steady grow of this highly topical research area in the years to come.

Acknowledgements

The authors would like to thank the University of Dublin, Trinity College Ireland, Kinerton Ltd. (now Ipsen Ltd.), Enterprise Ireland (EI), Science Foundation Ireland (SFI), Irish Research Council for Science, Engineering and Technology (IRCSET), CSCB and the Wellcome Trust for financial assistance.

References

[1] See special volumes on Photochemistry and Photophysics of Coordination Compounds, V. Balzani, S. Campagna (Eds.), Top. Curr. Chem. 281 (2007).
[2] Special issue on colorimetric and luminescent sensing, J. Mater. Chem. 15 (2005) 2617.
[3] (a) Martínez-Máñez, F. Sancenón, Chem. Rev. 103 (2003) 4419;
(b) C. Suksai, T. Tuntulani, Chem. Soc. Rev. 32 (2003) 192.
[4] (a) A.P. de Silva, B. McCaughan, B.O.F. McKinney, M. Querol, Dalton Trans. 2003 (1902);
(b) J.F. Callan, A.P. de Silva, D.C. Magri, Tetrahedron 36 (2005) 8551;
(c) V. Balzani, Photochem. Photobiol. Sci. 2 (2003) 459;
(d) V. Balzani, A. Credi, M. Venturi, Pure Appl. Chem. 75 (2003) 541;
(e) K. Rurack, Spectrochem. Acta A 57 (2001) 2161;
(f) A.P. de Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, Chem. Rev. 97 (1997) 151.
[5] (a) T. Gunnlaugsson, H.D.P. Ali, M. Glynn, P.E. Kruger, G.M. Hussey, F.M. Pfeffer, C.M.G. dos Santos, J. Tierney, J. Fluoresc. 15 (2005) 287;
(b) R. Parkesh, T.C. Lee, T. Gunnlaugsson, Org. Biomol. Chem. 5 (2007) 310;
(c) T. Gunnlaugsson, P.E. Kruger, P. Jensen, J. Tierney, H.D.P. Ali, G.M. Hussey, J. Org. Chem. 70 (2005) 10875;
(d) T. Gunnlaugsson, B. Bichell, C. Nolan, Tetrahedron Lett. 43 (2002) 4989;
(e) T. Gunnlaugsson, M. Nieuwenhuyzen, R. Ludovic, T. Vera, Tetrahedron Lett. 42 (2001) 4725.
[6] T. Gunnlaugsson, M. Glynn, G.M. Tocci (née Hussey), P.E. Kruger, F.M. Pfeffer, Coord. Chem. Rev. 250 (2006) 3094.
[7] F.M. Raymo, Adv. Mater. 14 (2002) 401.
[8] (a) M. Irie, Chem. Rev. 100 (2000) 1685;
(b) B.L. Feringa, R.A. van Delden, N. Koumura, E.M. Geertsema, Chem. Rev. 100 (2000) 1789.
[9] S. Uchiyama, A.P. de Silva, K. Iwai, J. Chem. Ed. 83 (2006) 720.
[10] (a) J.P. Leonard, T. Gunnlaugsson, J. Fluoresc. 15 (2005) 585;
(b) D. Parker, Chem. Soc. Rev. 33 (2004) 156.
[11] T. Gunnlaugsson, J.P. Leonard, Chem. Commun. (2005) 3114.
[12] (a) J-C.G. Bünzli, Acc. Chem. Res. 39 (2006) 53;
(b) M. Cantuel, F. Gumy, J-C.G. Bünzli, C. Piguet, Dalton Trans. (2006) 2647;

(c) J.-C.G. Bünzli, C. Piguet, Chem. Soc. Rev. 34 (2005) 1048;
(d) D. Imbert, M. Cantuel, J.-C.G. Bünzli, G. Bernardinelli, C. Piguet, J. Am. Chem. Soc. 1251 (2003) 5698;
(e) D. Imbert, M. Cantuel, J.C.G. Bünzli, G. Bernardinelli, C. Piguet, J. Am. Chem. Soc. 125 (2003) 15698.
[13] T. Gunnlaugsson, F. Stomeo, Org. Biomol. Chem. 5 (2007) 1999.
[14] D.L. Caulder, K.N. Raymond, Acc. Chem. Res. 32 (1999) 975.
[15] D. Parker, J.A.G. Williams, Metal Ions in Biological Systems, 40, Marcel Dekker Inc., New York, 2003.
[16] (a) S. Shinoda, H. Miyake, H. Tsukube, Handbook of the Physics and Chemistry of Rare Earths, vol. 35, Elsevier North Holland, 2005;
(b) H. Tsukube, S. Shinoda, Chem. Rev. 102 (2002) 2389.
[17] (a) S. Pandya, J. Yu, D. Parker, Dalton Trans. (2006) 2757;
(b) D. Parker, R.S. Dickins, H. Puschmann, C. Cossland, J.A.K. Howard, Chem. Rev. 102 (2002) 1977.
[18] (a) J.-C.G. Bünzli, J. Alloys Compd 408 (2006) 934;
(b) J-C.G. Bünzli, Metal Ions Biol. Syst. 42 (2004) 39.
[19] G.F. de Sá, O.L. Malta, C. de Mello Donegá, A.M. Simas, R.L. Longo, P.A. Santa-Cruz, E.F. da Silva Jr., Coord. Chem. Rev. 196 (2000) 165.
[20] (a) J. Hamacek, M. Borkovec, C. Piguet, Dalton Trans. (2006) 1473;
(b) C. Piguet, M. Borkovec, J. Hamacek, K. Zeckert, Coord. Chem. Rev. 249 (2005) 705.
[21] M.D. Ward, Coord. Chem. Rev. 251 (2007) 1663.
[22] S. Faulkner, J.L. Matthews, in: Comprehensive Coordination Chemistry, 2nd edition, vol. 9; in: M.D. Ward (Ed.), Application of Coordination Complexes, Elsevier, Amsterdam, 2003.
[23] (a) J.-C.G. Bünzli, in: J.-C.G. Bünzli, G.R. Choppin (Eds.), Lanthanide Probes in Life, Chemical and Earth Sciences, Theory and Practice, Elsevier, New York, 1989;
(b) E. Toth, L. Burai, A.E. Merback, Coord. Chem. Rev. 216 (2001) 363;
(c) S. Aime, M. Botta, M. Fasano, E. Terreno, Chem. Soc. Rev. 27 (1998) 19;
(d) Y. Hass, G. Stein, J. Phys. Chem. 75 (1971) 1093.
[24] J.P. Leonard, C.B. Nolan, F. Stomeo, T. Gunnlaugsson, Top. Curr. Chem. 281 (2007) 1.
[25] A.E. Merbach, É. Tóth, The Chemistry of Contrast Agents in Medical Magnetic Resonance Imaging, Wiley, West Sussex, England, 2001.
[26] (a) I. Hemmilä, V.M. Mukkala, Crit. Rev. Clin. Lab. Sci. 38 (2001) 441;
(b) P.G. Sammes, G. Yahioglu, Nat. Prod. Rep. (1996) 1;
(c) E.F. Gudgin Dickson, A. Pollak, E.P. Diamandis, J. Photochem. Photobiol. B: Biol. 27 (1995) 3;
(d) J. Coates, P.G. Sammes, R.M. West, J. Chem. Soc., Perkin Trans. 2 (1996) 1275.
[27] (a) D. Parker, J.A.G. Williams, J. Chem. Soc., Perkin Tans. 2 (1996) 1581;
(b) T. Gunnlaugsson, D. Mac Donaill, D. Parker, J. Am. Chem. Soc. 123 (2001) 12866;
(c) T. Gunnlaugsson, Tetrahedron Lett. 42 (2001) 8901;
(d) M. Woods, A.D. Sherry, Inorg. Chem. 42 (2003) 4401.
[28] (a) D. Parker, K. Senanayake, J.A.G. Williams, Chem. Commun. (1997) 1777;
(b) D. Parker, K. Senanayake, J.A.G. Williams, J. Chem. Soc., Perkin Trans. 2 (1998) 2129;
(c) D. Parker, J.A.G. Williams, Chem. Commun. (1998) 245l;
(d) T.C. Bazzicalupi, A. Bencini, A. Bianchi, C. Giogi, V. Fusi, A. Masotti, B. Valtancoli, A. Roque, F. Pina, Chem. Commun. (2000) 56.
[29] (a) R.S. Dickins, C.S. Love, H. Puschmann, Chem. Commun. (2001) 2308;
(b) J.I. Bruce, R.S. Dickens, L.J. Govenlock, T. Gunnlaugsson, S. Lopinski, M.P. Lowe, D. Parker, R.D. Peacock, J.J.B. Perry, S. Aime, M. Botta, J. Am. Chem. Soc. 122 (2000) 9674.
[30] B. Alpha, J.M. Lehn, R. Ballardini, V. Balzani, S. Perathoner, N. Sabbatini, Photochem. Photobiol. 52 (1990) 299.
[31] S.J.A. Pope, Polyhedron 26 (2007) 4818.
[32] S. Comby, D. Imbert, A.S. Chauvin, J.-C.G. Bünzli, Chem. Commun. (2007) 732.
[33] Y. Kataoka, Y. Suzuki, D. Paul, H. Miyake, S. Shinoda, H. Tsukube, Dalton Trans. (2007) 2784.
[34] C.P. Montgomery, D. Parker, D.L. Lamarque, Chem. Commun. (2007) 3841.
[35] (a) T.H. Forster, Ann. Phys. 2 (1984) 55;
(b) T.H. Forster, Discuss J. Chem. Phys., Faraday Soc. 27 (1959).
[36] D.L. Dexter, J. Chem. Phys. 21 (1953) 836.
[37] F. Kielar, C.P. Montgomery, E.J. New, D. Parker, R.A. Poole, S.L. Richardson, S.P.A. Stenson, Org. Biomol. Chem. 5 (2007) 2975.
[38] D. Parker, Coord. Chem. Rev. 205 (2000) 109.
[39] R.S. Dickens, D. Parker, A.S. de Sousa, J.A.G. Williams, Chem. Commun. (1996) 697.
[40] A. Beeby, I.M. Clarkson, R.S. Dickens, S. Faulkner, D. Parker, L. Royle, A.S. de Sousa, J.A.G. Williams, M. Woods, J. Chem. Soc., Perkin Trans. 2 (1999) 493.
[41] W.D. Horrocks, D.R. Sudnick, Acc. Chem. Res. 14 (1981) 384.
[42] R.M. Supkowski, W.D. Horrocks, Inorg. Chem. Acta 340 (2002) 44.
[43] A.P. de Silva, H.Q.N. Gunaratne, T.E. Rice, Angew. Chem. Int. Ed. Engl. 35 (1996) 2116.
[44] A.P. de Silva, H.Q.N. Gunaratne, T.E. Rise, S. Stewart, Chem. Commun. (1997) 1891.
[45] (a) T. Gunnlaugsson, D. Parker, Chem. Commun. (1998) 511.
[46] S.J.A. Pope, R.H. Laye, Dalton Trans. (2006) 3108.
[47] (a) K. Hanaoka, K. Kikuchi, H. Kojima, Y. Urano, T. Nagano, Angew. Chem. Int. Ed. 42 (2003) 2996;
(b) K. Hanaoka, K. Kikuchi, H. Kojima, Y. Urano, T. Nagano, J. Am. Chem. Soc. 126 (2004) 12470.
[48] T. Gunnlaugsson, C.P. McCoy, F. Stomeo, Tetrahedron Lett. 45 (2004) 8403.
[49] C.P. McCoy, F. Stomeo, S.E. Plush, T. Gunnlaugsson, Chem. Mater. 18 (2006) 4436.
[50] L. Armelao, G. Bottaro, S. Quici, M. Cavazzini, M.C. Raffo, F. Barigelletti, G. Accorsi, Chem. Commun. (2007) 2911.
[51] T. Gunnlaugsson, J.P. Leonard, Chem. Commun. (2003) 2424.
[52] T. Gunnlaugsson, J.P. Leonard, Dalton Trans. (2005) 3204.
[53] J.B. Coldwell, C.E. Felton, L.P. Harding, R. Moon, S.J.A. Pope, C.R. Rice, Chem. Commun. (2006) 5048.
[54] C. Li, G.-L. Law, W.-T. Wong, Org. Lett. 6 (2004) 4841.
[55] C. Li, W.-T. Wong, Tetrahedron Lett. 45 (2004) 6055.
[56] O. Reany, T. Gunnlaugsson, D. Parker, Chem. Commun. (2000) 473.
[57] O. Reany, T. Gunnlaugsson, D. Parker, J. Chem. Soc., Perkin Trans. 2 (2000) 1819.
[58] (a) T. Gunnlaugsson, J.P. Leonard, K. Sénéchal, A.J. Harte, Commun. Chem. (2004) 782;
(b) T. Gunnlaugsson, J.P. Leonard, K. Sénéchal, A.J. Harte, J. Am. Chem. Soc. 125 (2003) 12062.
[59] S. Quici, G. Marzanni, M. Cavazzini, P.L. Anelli, M. Botta, E. Gianolio, G. Accorsi, N. Armaroli, F. Barigelletti, Inorg. Chem. 41 (2002) 2777.
[60] J. Paris, C. Gamerio, V. Humblet, P.K. Mohapatra, V. Jacques, J.F. Desreux, Inorg. Chem. 45 (2006) 5092.
[61] K. Sénéchal-David, J.P. Leonard, S.E. Plush, T. Gunnlaugsson, Org. Lett. 8 (2006) 2727.
[62] M.S. Tremblay, D. Sames, Chem. Commun. (2006) 4116.
[63] S. Faulkner, S.J.A. Pope, J. Am. Chem. Soc. 125 (2003) 10526.
[64] P.B. Glover, P.R. Ashton, L.J. Childs, A. Rodger, M. Kercher, R.M. Williams, L. DeCola, Z. Pikramenou, J. Am. Chem. Soc. 125 (2003) 9918.
[65] P.D. Beer, F. Szemes, P. Passaniti, M. Maestri, Inorg. Chem. 43 (2004) 3965.
[66] (a) S.I. Klink, H. Keizer, F.C.J.M. van Veggel, Angew. Chem. Int. Ed. 39 (2000) 4319;
(b) S.I. Klink, H. Keizer, H.W. Hofstraat, F.C.J.M. van Veggel, Synth. Met. 127 (2002) 213.
[67] K. Sénéchal-David, S.J.A. Pope, S. Quinn, S. Faulkner, T. Gunnlaugsson, Inorg. Chem. 45 (2006) 10040.
[68] A. Beeby, R.S. Dickins, S. FitzGerald, L.J. Govenlock, D. Parker, J.A.G. Williams, C.L. Maupin, J.P. Riehl, G. Siligardi, Chem. Commun. (2000) 1183.
[69] A. Bodi, K.E. Borbas, J.I. Bruce, Dalton Trans. (2007) 4352.
[70] T. Lazarides, M.A.H. Alamiry, H. Adams, S.J.A. Pope, S. Faulkner, J.A. Weinstein, M.D. Ward, Dalton Trans. (2007) 1484.
[71] M. Gonzalez-Lorenzo, C. Platas-Iglesias, F. Avecilla, S. Faulkner, S.J.A. Pope, A. de Blas, T. Rodriguez-Blas, Inorg. Chem. 44 (2005) 4254.
[72] T.K. Ronson, H. Adams, L.P. Harding, S.J.A. Pope, D. Sykes, S. Faulkner, D. Ward, Dalton Trans. (2007) 1006.
[73] M. Elhabiri, R. Scopelliti, J.C.G. Bunzli, C. Piguet, J. Am. Chem. Soc. 121 (1999) 10747.
[74] S. Floquet, M. Borkovec, G. Bernardinelli, A. Pinto, L.-A. Leuthold, G. Hopfgartner, D. Imbert, J.-C.G. Bünzli, C. Piguet, Chem. Eur. J. 10 (2004) 1091.
[75] J.J. Lessmann, W.D. Horrocks, Inorg. Chem. 39 (2000) 3114.
[76] (a) A.S. Chauvin, S. Comby, B. Song, C.D.B. Vandevyver, J.-C.G. Bünzli, Chem. Eru. J. 14 (2008) 1726;
(b) C.D.B. Vandevyver, A.S. Chauvin, S. Comby, J.-C.G. Bünzli, Chem. Commun. (2007) 1716.
[77] (a) A.P. Bassett, S.W. Magennis, P.B. Glover, D.J. Lewis, N. Spencer, S. Parsons, R.M. Williams, L. DeCola, Z. Pikramenou, J. Am. Chem. Soc. 126 (2004) 9413;
(b) S. Comby, R. Scopelliti, D. Imbert, L. Charbonniére, R. Ziessel, J.-C.G. Bünzli, Inorg. Chem. 45 (2006) 3158;
(c) X.-Y. Chen, Y. Bretonniere, J. Pecaut, D. Imbert, J.-C.G. Bünzli, M. Mazzanti, Inorg. Chem. 46 (2007) 625;
(d) Y. Bretonniere, M. Mazzanti, M. Pecaut, M.M. Olmstead, J. Am. Chem. Soc. 124 (2002) 9012;
(e) H. Hou, Y. Wei, Y. Song, Y. Fan, Y. Zhu, Inorg. Chem. 43 (2004) 1323.
[78] M. Albrecht, O. Osetska, R. Frohlich, J.-C.G. Bünzli, A. Aebischer, F. Gumy, J. Hamacek, J. Am. Chem. Soc. 129 (2007) 14178.
[79] O. Mamula, M. Lama, S.G. Telfer, A. Nakamura, R. Kuroda, H. Stoeckli-Evans, R. Scopelitti, Angew. Chem. Int. Ed. 44 (2005) 2527.
[80] J.P. Leonard, P. Jensen, T. McCabe, J.E. O'Brien, R.D. Peacock, P.E. Kruger, T. Gunnlaugsson, J. Am. Chem. Soc. 129 (2007) 10986.
[81] T. Le Borgne, J.-C. Bénech, S. Floquet, G. Bernardinelli, C. Aliprandini, P. Bettens, C. Piguet, Dalton Trans. (2003) 3856.
[82] (a) S.D. Bonsall, M. Houcheime, D.A. Straus, G. Muller, Chem. Commun. (2007) 3676;
(b) M. Seitz, E.G. Moore, A.J. Ingram, G. Muller, K.N. Raymond, J. Am. Chem. Soc. 129 (2007) 15468;
(c) S. Petoud, G. Muller, E.G. Moore, J. Xu, J. Sokolnicki, J.P. Riehl, U.N. Le, S.M. Cohen, K.N. Raymond, J. Am. Chem. Soc. 129 (2007) 77.
[83] D. Parker, J.A.G. Williams, Chem. Commun. (1998) 245.
[84] Y. Bretonnière, M.J. Cann, D. Parker, R. Slater, Chem. Commun. (2002) 1930.
[85] R.S. Dickins, T. Gunnlaugsson, D. Parker, R.D. Peacock, Chem. Commun. (1998) 1643.
[86] T. Gunnlaugsson, A.J. Harte, J.P. Leonard, M. Nieuwenhuyzen, Supramol. Chem. 15 (2003) 505.
[87] T. Gunnlaugsson, A.J. Harte, J.P. Leonard, M. Nieuwenhuyzen, Chem. Commun. (2002) 2134.
[88] S. Faulkner, B.P. Burton-Pye, T. Khan, L.R. Martin, S.D. Wray, P.J. Skabara, Chem. Commun. (2002) 1668.

[89] S.J.A. Pope, B.P. Burton-Pye, R. Berridge, T. Khan, P.J. Skabara, S. Faulkner, Dalton Trans. (2006) 2907.
[90] C. Li, W.-T. Wong, Chem. Commun. (2002) 2034.
[91] Y. Bretonnière, M.J. Cann, D. Parker, R. Slater, Org. Biomol. Chem. 2 (2004) 1624.
[92] P. Atkinson, Y. Bretonnière, D. Parker, Chem. Commun. (2004) 438.
[93] P. Atkinson, B.S. Murray, D. Parker, Org. Biomol. Chem. 4 (2006) 3166.
[94] J. Yu, D. Parker, R. Pal, R.A. Poole, M.J. Cann, J. Am. Chem. Soc. 128 (2006) 2294.
[95] R.A. Poole, F. Kielar, S.L. Richardson, P.S. Stenson, D. Parker, Chem. Commun. (2006) 4084.
[96] (a) L.O. Palsson, R. Pal, B.S. Murray, D. Parker, A. Beeby, Dalton Trans. (2007) 5726;
(b) R. Pal, D. Parker, Chem. Commun. (2007) 474;
(c) D. Parker, J.H. Yu, Chem. Commun. (2005) 3141.
[97] S.E. Plush, T. Gunnlaugsson, Org. Lett. 9 (2007) 1919.
[98] J.P. Leonard, C.M.G. dos Santos, S.E. Plush, T. McCabe, T. Gunnlaugsson, Chem. Commun. (2007) 129.
[99] J. Massue, S.J. Quinn, T. Gunnlaugsson, J. Am. Chem. Soc. 130 (2008) 6900.
[100] S.J.A. Pope, A.M. Kenwright, V.A. Boote, S. Faulkner, Dalton Trans. (2003) 3780.
[101] A.J. Harte, P. Jensen, S.E. Plush, P.E. Kruger, T. Gunnlaugsson, Inorg. Chem. 45 (2006) 9465.
[102] M.P. Lowe, D. Parker, Chem. Commun. (2000) 707.
[103] J.J. Michels, J. Huskens, D.N. Reinhoudt, J. Am. Chem. Soc. 124 (2002) 2059.
[104] S. Faulkner, B.P. Burton-Pye, Chem. Commun. (2005) 259.
[105] T.A. Miller, J.C. Jeffery, M.D. Ward, H. Adams, S.J.A. Pope, S. Faulkner, Dalton Trans. (2004) 1524.
[106] (a) F. Kennedy, N.M. Shavaleev, T. Koullourou, Z.R. Bell, J.C. Jeffery, S. Faulkner, M.D. Ward, Dalton Trans. (2007) 1492;
(b) T.K. Ronson, T. Lazarides, H. Adams, S.J.A. Pope, D. Sykes, S. Faulkner, S.J. Coles, H.B. Hursthouse, W. Clegg, R.W. Harrington, M.D. Ward, Chem. Eur. J. 12 (2006) 9299.
[107] P. Coppo, M. Duati, V.N. Kozhevnikov, J.W. Hofstraat, L.D. Cola, Angew. Chem. Int. Ed. 44 (2005) 1806.
[108] (a) D.J. Hoffart, S.J. Loeb, Angew. Chem. Int. Ed. 44 (2005) 901;
(b) S.J. Loeb, Chem. Commun. (2005) 1511.
[109] M.R. Sambrook, D. Curiel, E.J. Hayes, P.D. Beer, S.J.A. Pope, S. Faulkner, New J. Chem. 30 (2007) 1133.
[110] J-C.G. Bünzli, S. Comby, A.S. Chauvin, C.D.B. Vandevyver, J. Rare Earth 25 (2007) 257.